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Corrosion: Understanding the Basics (#06691G)

CORROSION

UNDERSTANDING THE BASICS

Edited by
J.R. Davis
Davis & Associates

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Preface

Most people are familiar with corrosion in some form or another. Whether it is a rusty nail in a backyard fence, corroded fenders and/or mufflers on our automobiles, or a perforated underground water pipe, it is safe to say that corrosion is all around us. It is costly to prevent or repair, and it is generally not pleasing to look at. In the industrial workplace, corrosion is certainly one of the most common causes of failure of engineered components and structures. The complexities of corrosion phenomena challenge corrosion scientists, chemists, mechanical, civil, and metallurgical engineers, coating specialists, and maintenance and operating personnel.

In order to better understand corrosion, it is important to first examine the basic concepts that influence the corrosion process; hence, the title of this publication—*Corrosion: Understanding the Basics.* Included in these 12 chapters are practical discussions on the following:

- Thermodynamic and electrochemical principles of corrosion
- Recognition and prevention of various forms of corrosion
- Types of corrosive environments commonly encountered and environmental variables that can increase or decrease corrosion rates
- Corrosion characteristics of metals and alloys and nonmetallic materials
- Methods of corrosion prevention, including design considerations, materials selection, coatings, inhibitors, and cathodic and anodic protection
- Corrosion testing and monitoring
- Techniques for diagnosing corrosion failures

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Although the book is primarily intended for professionals who are not corrosion experts, it should also serve as a quick and useful corrosion-control guide for corrosion engineers.

Assisting in the preparation of this book was Larry Korb from Rockwell International. Larry, who is a Fellow of ASM International and longtime member and former chairman of the ASM Handbook Committee, meticulously reviewed each chapter. I have long been in awe of my friend's exhaustive knowledge of materials and their failure mechanisms (including corrosion), and his keen insight into the editorial process. It is always an honor and a privilege to work with Mr. Korb.

I also wish to acknowledge the contributions of Nalco Chemical Company (Naperville, IL). Many of the photographs illustrating the different modes of corrosion were supplied by Nalco. These originally appeared in two excellent books on failure analysis authored by Nalco engineers Harvey M. Herro (an ASM member) and Robert D. Port. I am indebted to Ms. Connie Szewczyk, a Communications Specialists with Nalco, for supplying these photographs.

Thanks are also extended to Kenneth B. Tator and Alison B. Kaelin from KTA-Tator Inc. (Pittsburgh, PA). Ken supplied an extensive table that reviewed the advantages and limitations of organic coating resins. Alison prepared material on environmental, health, and safety considerations for the coatings industry. Their contributions appear in Chapter 9.

The efforts of the ASM staff are also duly noted. In particular, I would like to thank Scott Henry and Bonnie Sanders from the Publications Department and Eleanor Baldwin and her coworkers from the ASM Library for the help and support throughout the project

Last, I would be remiss in not acknowledging the fact that several chapters in the book were adapted from the ASM Materials Engineering Institute (MEI) course on corrosion that was prepared by Dr. Joe H. Payer from Case Western Reserve University (Cleveland, OH). Chapters 2 and 3, as well as the description of electrochemical test methods in Chapter 11, were based on Dr. Payer's work.

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CHAPTER 1

The Effects and Economic Impact of Corrosion

CORROSION is a natural process. Just like water flows to the lowest level, all natural processes tend toward the lowest possible energy states. Thus, for example, iron and steel have a natural tendency to combine with other chemical elements to return to their lowest energy states. In order to return to lower energy states, iron and steel frequently combine with oxygen and water, both of which are present in most natural environments, to form hydrated iron oxides (rust), similar in chemical composition to the original iron ore. Figure 1 illustrates the corrosion life cycle of a steel product.

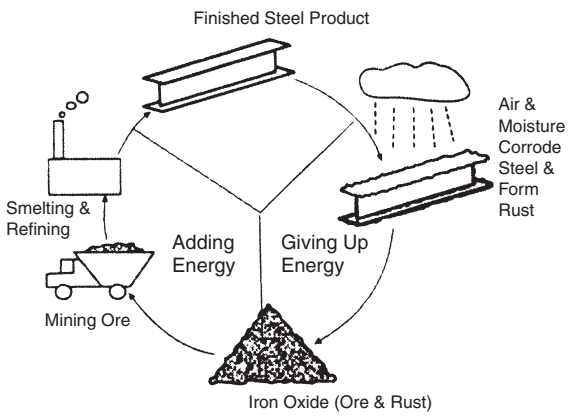


Fig. 1 The corrosion cycle of steel

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The Definition of Corrosion

Corrosion can be defined in many ways. Some definitions are very narrow and deal with a specific form of corrosion, while others are quite broad and cover many forms of deterioration. The word corrode is derived from the Latin *corrodere,* which means "to gnaw to pieces." The general definition of corrode is to eat into or wear away gradually, as if by gnawing. For purposes here, corrosion can be defined as a chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties.

The environment consists of the entire surrounding in contact with the material. The primary factors to describe the environment are the following: (a) physical state—gas, liquid, or solid; (b) chemical composition—constituents and concentrations; and (c) temperature. Other factors can be important in specific cases. Examples of these factors are the relative velocity of a solution (because of flow or agitation) and mechanical loads on the material, including residual stress within the material. The emphasis in this chapter, as well as in other chapters in this book, is on aqueous corrosion, or corrosion in environments where water is present. The deterioration of materials because of a reaction with hot gases, however, is included in the definition of corrosion given here.

To summarize, corrosion is the deterioration of a metal and is caused by the reaction of the metal with the environment. Reference to marine corrosion of a pier piling means that the steel piling corrodes because of its reaction with the marine environment. The environment is air-saturated seawater. The environment can be further described by specifying the chemical analysis of the seawater and the temperature and velocity of the seawater at the piling surface.

When corrosion is discussed, it is important to think of a combination of a material and an environment. The corrosion behavior of a material cannot be described unless the environment in which the material is to be exposed is identified. Similarly, the corrosivity or aggressiveness of an environment cannot be described unless the material that is to be exposed to that environment is identified. In summary, the corrosion behavior of the material depends on the environment to which it is subjected, and the corrosivity of an environment depends on the material exposed to that environment.

It is useful to identify both natural combinations and unnatural combinations in corrosion. Examples of natural or desirable combinations of material and environment include nickel in caustic environments, lead in water, and aluminum in atmospheric exposures. In these environments, the interaction between the metal and the environment does not

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usually result in detrimental or costly corrosion problems. The combination is a natural combination to provide good corrosion service.

Unnatural combinations, on the other hand, are those that result in severe corrosion damage to the metal because of exposure to an undesirable environment. Examples of unnatural combinations include copper in ammonia solutions, stainless steel in chloride-containing environments (e.g., seawater), and lead with wine (acetic acid in wine attacks lead). It has been postulated that the downfall of the Roman Empire can be attributed in part to a corrosion problem, specifically the storage of wine in lead-lined vessels. Lead dissolved in the wine and consumed by the Roman hierarchy resulted in insanity (lead poisoning) and contributed to the subsequent eventual downfall. Another anecdote regarding lead and alcoholic beverages dates back to the era of Benjamin Franklin. One manifestation was the "dry bellyache" with accompanying paralysis, which was mentioned by Franklin in a letter to a friend. This malady was actually caused by the ingestion of lead from corroded lead coil condensers used in making brandy. The problem became so widespread that the Massachusetts legislature passed a law in the late 1700s that outlawed the use of lead in producing alcoholic beverages.

The Effects of Corrosion

The effects of corrosion in our daily lives are both direct, in that corrosion affects the useful service lives of our possessions, and indirect, in that producers and suppliers of goods and services incur corrosion costs, which they pass on to consumers. At home, corrosion is readily recognized on automobile body panels, charcoal grills, outdoor furniture, and metal tools. Preventative maintenance such as painting protects such items from corrosion. A principal reason to replace automobile radiator coolant every 12 to 18 months is to replenish the corrosion inhibitor that controls corrosion of the cooling system. Corrosion protection is built into all major household appliances such as water heaters, furnaces, ranges, washers, and dryers.

Of far more serious consequence is how corrosion affects our lives during travel from home to work or school. The corrosion of steel reinforcing bar (rebar) in concrete can proceed out of sight and suddenly (or seemingly so) result in failure of a section of highway, the collapse of electrical towers, and damage to buildings, parking structures, and bridges, etc., resulting in significant repair costs and endangering public safety. For example, the sudden collapse because of corrosion fatigue of the Silver Bridge over the Ohio River at Point Pleasant, OH in 1967 resulted in the loss of 46 lives and cost millions of dollars.

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Perhaps most dangerous of all is corrosion that occurs in major industrial plants, such as electrical power plants or chemical processing plants. Plant shutdowns can and do occur as a result of corrosion. This is just one of its many direct and indirect consequences. Some consequences are economic, and cause the following:

- Replacement of corroded equipment
- Overdesign to allow for corrosion
- Preventive maintenance, for example, painting
- Shutdown of equipment due to corrosion failure
- Contamination of a product
- Loss of efficiency—such as when overdesign and corrosion products decrease the heat-transfer rate in heat exchangers
- Loss of valuable product, for example, from a container that has corroded through
- Inability to use otherwise desirable materials
- Damage of equipment adjacent to that in which corrosion failure occurs

Still other consequences are social. These can involve the following issues:

- Safety, for example, sudden failure can cause fire, explosion, release of toxic product, and construction collapse
- Health, for example, pollution due to escaping product from corroded equipment or due to a corrosion product itself
- Depletion of natural resources, including metals and the fuels used to manufacture them
- Appearance as when corroded material is unpleasing to the eye

Of course, all the preceding social items have economic aspects also (see the discussion that follows, "Economic Impact of Corrosion"). Clearly, there are many reasons for wanting to avoid corrosion.

The Many Forms of Corrosion

Corrosion occurs in several widely differing forms. Classification is usually based on one of three factors:

- *Nature of the corrodent:* Corrosion can be classified as "wet" or "dry." A liquid or moisture is necessary for the former, and dry corrosion usually involves reaction with high-temperature gases.
- *Mechanism of corrosion:* This involves either electrochemical or direct chemical reactions.

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- *Appearance of the corroded metal:* Corrosion is either uniform and the metal corrodes at the same rate over the entire surface, or it is localized, in which case only small areas are affected.

Classification by appearance, which is particularly useful in failure analysis, is based on identifying forms of corrosion by visual observation with either the naked eye or magnification. The morphology of attack is the basis for classification. Figure 2 illustrates schematically some of the most common forms of corrosion.

Eight forms of wet (or aqueous) corrosion can be identified based on appearance of the corroded metal. These are:

- Uniform or general corrosion
- Pitting corrosion
- Crevice corrosion, including corrosion under tubercles or deposits, filiform corrosion, and poultice corrosion
- Galvanic corrosion
- Erosion-corrosion, including cavitation erosion and fretting corrosion
- Intergranular corrosion, including sensitization and exfoliation
- Dealloying, including dezincification and graphitic corrosion
- Environmentally assisted cracking, including stress-corrosion cracking, corrosion fatigue, and hydrogen damage

In theory, the eight forms of corrosion are clearly distinct; in practice however, there are corrosion cases that fit in more than one category. Other corrosion cases do not appear to fit well in any of the eight categories. Nevertheless, this classification system is quite helpful in the study

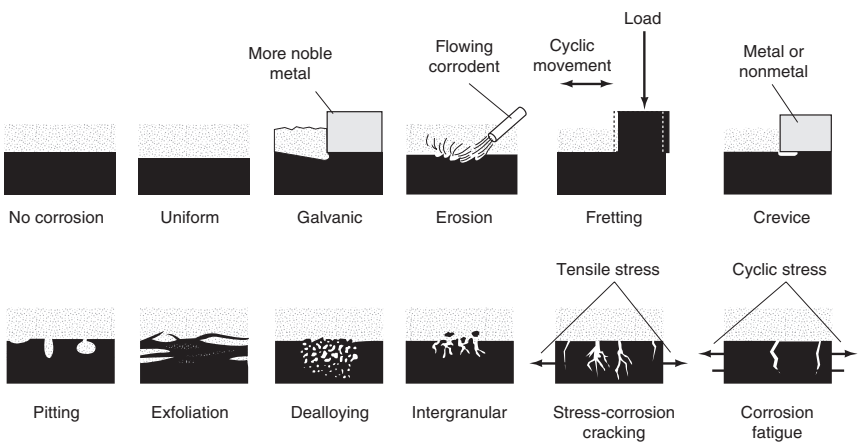


Fig. 2 Schematics of the common forms of corrosion

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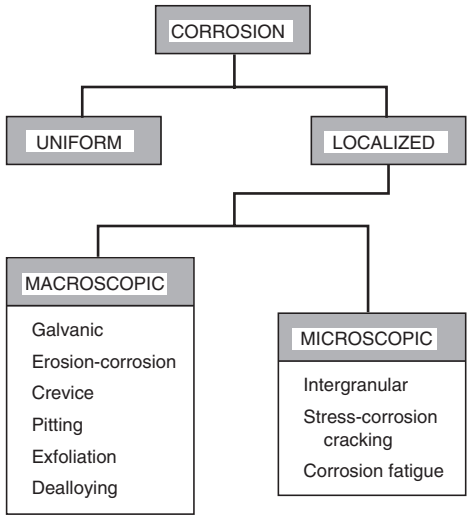


Fig. 3 Macroscopic versus microscopic forms of localized corrosion

of corrosion problems. Detailed information on these eight forms of corrosion can be found in Chapter 4.

Completeness requires further distinction between macroscopically localized corrosion and microscopic local attack. In the latter case, the amount of metal dissolved is minute, and considerable damage can occur before the problem becomes visible to the naked eye. Macroscopic forms of corrosion affect greater areas of corroded metal and are generally observable with the naked eye or can be viewed with the aid of a low-power magnifying device. Figure 3 classifies macroscopic and microscopic forms of localized corrosion.

Methods to Control Corrosion

There are five primary methods of corrosion control:

- Material selection
- Coatings
- Inhibitors
- Cathodic protection
- Design

Each is described briefly here and in more detail in subsequent chapters.

Material Selection

Each metal and alloy has unique and inherent corrosion behavior that can range from the high resistance of noble metals, for example, gold

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and platinum, to the low corrosion resistance of active metals, for example, sodium and magnesium. Furthermore, the corrosion resistance of a metal strongly depends on the environment to which it is exposed, that is, the chemical composition, temperature, velocity, and so forth.

The general relation between the rate of corrosion, the corrosivity of the environment, and the corrosion resistance of a material is:

$$\frac{\text{corrosivity of environment}}{\text{corrosion resistance of metal}} \approx \text{rate of corrosive attack}$$

For a given corrosion resistance of the material, as the corrosivity of the environment increases, the rate of corrosion increases. For a given corrosivity of the environment, as the corrosion resistance of the material increases, the rate of corrosion decreases. Often an acceptable rate of corrosion is fixed and the challenge is to match the corrosion resistance of the material and the corrosivity of the environment to be at or below the specified corrosion rate. Often there are several competing materials that can meet the corrosion requirements, and the material selection process becomes one of determining which of the candidate materials provides the most economical solution for the particular service.

Consideration of corrosion resistance is often as important in the selection process as the mechanical properties of the alloy. A common solution to a corrosion problem is to substitute and alloy with greater corrosion resistance for the alloy that has corroded.

Coatings

Coatings for corrosion protection can be divided into two broad groups—metallic and nonmetallic (organic and inorganic). With either type of coating the intent is the same, that is, to isolate the underlying metal from the corrosive media.

Metallic Coatings. The concept of applying a more noble metal coating on an active metal takes advantage of the greater corrosive resistance of the noble metal. An example of this application is tin-plated steel. Alternatively, a more active metal can be applied, and in this case the coating corrodes preferentially, or sacrificially, to the substrate. An example of this system is galvanized steel, where the sacrificial zinc coating corrodes preferentially and protects the steel.

Organic Coatings. The primary function of organic coatings in corrosion protection is to isolate the metal from the corrosive environment. In addition to forming a barrier layer to stifle corrosion, the organic coating can contain corrosion inhibitors. Many organic coating formulations exist, as do a variety of application processes to choose from for a given product or service condition.

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Inorganic coatings include porcelain enamels, chemical-setting silicate cement linings, glass coatings and linings, and other corrosion-resistant ceramics. Like organic coatings, inorganic coatings for corrosion applications serve as barrier coatings. Some ceramic coatings, such as carbides and silicides, are used for wear-resistant and heat-resistant applications, respectively.

Inhibitors

Just as some chemical species (e.g., salt) promote corrosion, other chemical species inhibit corrosion. Chromates, silicates, and organic amines are common inhibitors. The mechanisms of inhibition can be quite complex. In the case of the organic amines, the inhibitor is adsorbed on anodic and cathodic sites and stifles the corrosion current. Other inhibitors specifically affect either the anodic or cathodic process. Still others promote the formation of protective films on the metal surface.

The use of inhibitors is favored in closed systems where the necessary concentration of inhibitor is more readily maintained. The increased use of cooling towers stimulated the development of new inhibitor/water-treatment packages to control corrosion and biofouling.

Inhibitors can be incorporated in a protective coating or in a primer for the coating. At a defect in the coating, the inhibitor leaches from the coating and controls the corrosion.

Cathodic Protection

Cathodic protection suppresses the corrosion current that causes damage in a corrosion cell and forces the current to flow to the metal structure to be protected. Thus, the corrosion or metal dissolution is prevented. In practice, cathodic protection can be achieved by two application methods, which differ based on the source of the protective current. An impressed-current system uses a power source to force current from inert anodes to the structure to be protected. A sacrificial-anode system uses active metal anodes, for example, zinc or magnesium, which are connected to the structure to provide the cathodic-protection current.

Design

The application of rational design principles can eliminate many corrosion problems and greatly reduce the time and cost associated with corrosion maintenance and repair. Corrosion often occurs in dead spaces or crevices where the corrosive medium becomes more corrosive. These areas can be eliminated or minimized in the design process. Where stress-corrosion cracking is possible, the components can be designed to operate at stress levels below the threshold stress for cracking.

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Where corrosion damage is anticipated, design can provide for maximum interchangeability of critical components and standardization of components. Interchangeability and part standardization reduce the inventory of parts required. Maintenance and repair can be anticipated, and easy access can be provided. Furthermore, for the large items that are critical to the entire operation, such as primary pumps or large fans, redundant equipment is installed to permit maintenance on one unit while the other is operating. These practices are a sampling of rational design principles.

Opportunities in Corrosion Control

The massive costs of corrosion provide many opportunities to users, manufacturers, and suppliers. Opportunities exist to reduce corrosion costs and the risks of failure, and to develop new, expanded markets. Examples of these opportunities and the means to implement a program to capitalize on the opportunities are presented in Table 1.

The costs of corrosion vary considerably from industry to industry; however, substantial savings are achievable in most industries. The first step in any cost-reduction program is to identify and quantify the present costs of corrosion. Based on this analysis and a review of the present status of corrosion control in the industry, priorities can be determined and the most rewarding cost-reduction projects pursued.

Risk of corrosion failure can be lowered in the producer's facility and in its products. Both process and products can be analyzed to identify the areas where corrosion failures can occur. Once identified, the risk of failure can be evaluated from the perspectives of impact on safety, product liability, avoidance of regulation, and loss of goodwill. Where risks

Table 1 Opportunities in corrosion control

Opportunity	Examples	Implementation
Reduce corrosion costs	Lower maintenance and repair costs Extended useful lives of equipment and buildings Reduction of product loss from corrosion damage	Identify all corosion costs by review of total processes, equipment, and buildings Quantify corrosion costs Implement plan to reduce costs
Lower risk of failure	Safety Product liability Avoidance of regulation Loss of goodwill	Review process and products for exposure to risk Evaluate risk and consequences of failure Lower exposure by technology change
Develop new and expanded markets	Coatings Alloys Inhibitors Corrosion monitors	Apply emerging technology Develop competitive advantage by more corrosion-resistant product Transfer existing technology to other industries

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are too great, technological changes can be implemented to reduce the risk. Evaluation also can identify areas where technological advances are required in the industry.

Increased consumer awareness of corrosion provides a competitive advantage for products with improved corrosion resistance. Through the application of existing or emerging technologies to products or services, advances are being made in all methods for corrosion control: material selection, coatings, inhibitors, cathodic protection, and design. Market opportunities are to be found in the transfer of existing technology to other industries.

The Economic Impact of Corrosion

Corrosion of metals costs the U.S. economy almost $300 billion per year at current prices. Approximately one-third of these costs could be reduced by broader application of corrosion-resistant materials and the application of best corrosion-related technical practices. These estimates result from a recent update of findings of the 1978 study *Economic Effects of Metallic Corrosion in the United States.* The study was performed by Battelle Columbus Laboratories and the National Institute of Standards and Technology (NIST) and published in April 1995.

The original work, based upon an elaborate model of more than 130 economic sectors, found that in 1975, metallic corrosion cost the United States $82 billion, or 4.9% of its gross national product (GNP). It was also found that 60% of that cost was unavoidable. The remaining $33 billion (40%) was incurred by failure to use the best practices then known. These were called “avoidable” costs.

Over the last two decades, economic growth and price inflation have increased the GNP more than fourfold. If nothing else had changed, the costs of metallic corrosion would have risen to almost $350 billion annually by 1995, $139 billion of which would have been avoidable. However, 20 years of scientific research and technological change, much of which was initiated because of the 1978 study, have affected these costs.

The Battelle panel updated the earlier results by judgmentally evaluating two decades of corrosion-related changes in scientific knowledge and industrial practices. In the original study, almost 40% of the 1975 metallic corrosion costs were incurred in the production, use, and maintenance of motor vehicles. No other sector accounted for as much as 4% of the total, and most sectors contributed less than 1%. The aircraft sector, for instance, was one of the next largest contributors and accounted for just more than 3%. Pipelines, a sector to which corrosion is a recognized problem, accounted for less than 1% of the total cost.

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The panel found that the automotive sector probably had made the greatest anticorrosion effort of any single industry. Advances have been made in the use of stainless steels, coated metals, and more protective finishes. Moreover, several substitutions of materials made primarily for reasons of weight reduction have also reduced corrosion. Also, the panel estimates that 15% of previously unavoidable corrosion costs can be reclassified as avoidable. The industry is estimated to have eliminated some 35% of avoidable corrosion by improved practices.

In examining the aircraft, pipeline, and shipbuilding sectors, the panel reported that both gains and losses have occurred, most of them tending to offset each other. For instance, in many cases, the use of more expensive materials has reduced the need for corrosion-related repairs or repainting. Overall, it was thought that for the U.S. economy other than in motor vehicle and aircraft applications, total corrosion costs have been reduced by no more than 5% with a further reduction of unavoidable costs by about 2%.

The updated study shows that the total 1995 cost of metallic corrosion was reduced (from what it would have been in 1975 terms) by some 14%, or to 4.2% of the GNP. Avoidable corrosion, which was 40% of the total, is now estimated to be 35% but still accounts for slightly more than $100 billion per year. This figure represents the annual cost to the economy, which can be reduced by broader application of corrosion-resistant materials, improvement in corrosion-prevention practices, and investment in corrosion-related research. Table 2 compares the results of the 1978 and 1995 Battelle/NIST studies.

Factors Influencing Corrosion. Some of the factors that influence corrosion and its costs are shown in Fig. 4. Corrosion costs are reduced by the application of available corrosion technology, which is sup-

Table 2 Cost of metallic corrosion in the United States

	Billions of U.S. dollars	
Industry	**1975**	**1995**
All industries		
Total	82.0	296.0
Avoidable	33.0	104.0
Motor vehicles		
Total	31.4	94.0
Avoidable	23.1	65.0
Aircraft		
Total	3.0	13.0
Avoidable	0.6	3.0
Other industries		
Total	47.6	189.0
Avoidable	9.3	36.0

Source: *Economic Effects of Metallic Corrosion in the United States,* Battelle Columbus Laboratories and the National Institute of Standards and Technology (NIST), 1978, and Battelle estimates

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ported by technology transfer. New and improved corrosion technology results from research and development. The proper application of methods to control corrosion (e.g., coatings, inhibitors, and cathodic protection) reduces the cost of corrosion. The costs of corrosion tend to increase with such factors as deferred maintenance and extended useful lives of buildings and equipment. Increased corrosion costs are often realized when higher-performance specifications and more hostile environments are encountered.

Finally, increased corrosion costs result from government regulations that prohibit the use of time-honored methods of protection because of safety or environmental damage. For example, in an effort to reduce smog, the elimination of lead-based paints on houses and bridges, chromate inhibiting paints on aircraft, and oil-based paints throughout industry has had severe repercussions. Substitute water-based paints have not, in many cases, afforded equivalent corrosion protection.

Cost Elements. Although costs vary in relative significance from industry to industry, several generalized elements combine to make up the total cost of corrosion. Some are readily recognized; others are less recognizable.

In manufacturing, corrosion costs are incurred in the product development cycle in several ways, beginning with the materials, energy, labor, and technical expertise required to produce a product. For example, a product can require painting for corrosion protection. A corrosion-resistant metal can be chosen in place of plain carbon steel, and technical services can be required to design and install cathodic protection on a product. Additional heat treatment can be needed to relieve stresses for protection against stress-corrosion cracking.

Other operating costs are affected by corrosion as well. Corrosion inhibitors, for example, often must be added to water treatment systems.

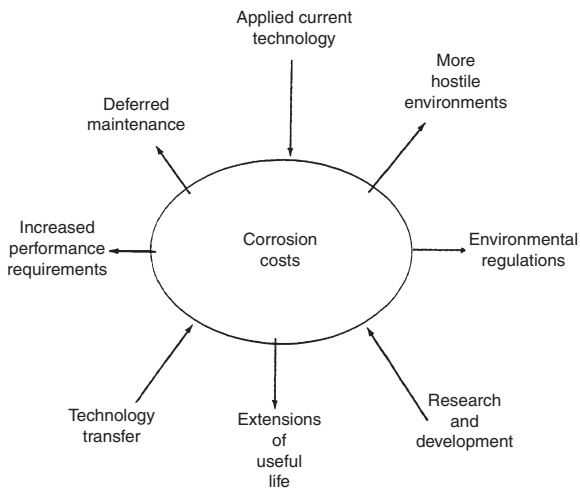


Fig. 4 Factors which increase or decrease the costs of corrosion

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Portions of maintenance and repair costs can be attributed to corrosion, and corrosion specialists are often employed to implement corrosion-control programs.

Capital costs also are incurred because of corrosion. The useful life of manufacturing equipment is decreased by corrosion. For an operation that is expected to run continuously, excess capacity is required to allow for scheduled downtime and corrosion-related maintenance. In other instances, redundant equipment is installed to enable maintenance on one unit while processing continues with another unit.

For the end user or consumer, corrosion costs are incurred for purchases of corrosion prevention and control products, maintenance and repair, and premature replacement.

The original Battelle/NIST study identified ten elements of the cost of corrosion:

- Replacement of equipment or buildings
- Loss of product
- Maintenance and repair
- Excess capacity
- Redundant equipment
- Corrosion control
- Technical support
- Design
- Insurance
- Parts and equipment inventory

Table 3 lists examples under each of these categories.

Replacement, loss of product, and maintenance and repair are fairly straightforward. Excess capacity is a corrosion cost if downtime for a plant scheduled for continuous operation could be reduced were corrosion not a factor. This element accounts for extra plant capacity (capital stock) maintained because of corrosion.

Redundant equipment accounts for additional plant equipment (capital stock) required because of corrosion. Specific critical components such as large fans and pumps are backed up by identical items to allow processing to continue during maintenance for corrosion control.

The costs of corrosion control are straightforward, as are the technical support (engineering, research and development, and testing) costs associated with corrosion. Corrosion costs associated with design are not always as obvious. The last two cost elements, insurance and inventory, can be significant in specific cases.

In addition to these ten categories, other less quantifiable cost factors, such as loss of life or loss of goodwill because of corrosion, can have a major impact. Single, catastrophic failures—for example, a corrosion-

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Table 3 Elements of cost of corrosion

Element of cost	Example
Replacement of equipment or buildings	Corroded pressure vessel
Loss of product	Corrosion leak
	Corrosion contamination of product
	Corrosion during storage
Maintenance and repair	Repair corroded corrugated metal roof
	Weld overlay of chemical reaction tank
	Repair pump handling corrosive slurry—erosion and corrosion
	Scheduled downtime for plant in continuous operation, for example, petroleum refinery
Redundant equipment	Installation of three large fans where two are required during operation
Corrosion control	
Inhibitors	Injection of oil wells
Organic coatings	Coal tar on exterior of underground pipeline
	Paint on wooden furniture
	Topcoat on automobile—aesthetics and corrosion
	Zinc-rich paint on automobile
	Galvanized steel siding
Metallic coatings	Chrome-plated faucets—aesthetics and corrosion
Cathodic protection	Cathodic protection of underground pipelines
Technical support	Corrosion-resistant alloy development
	Materials selection
	Corrosion monitoring and control
Design	
Material of construction for structural integrity	Stainless steel for corrosive applications
	Stainless steel for high-temperature mechanical properties
Material of construction	High alloy to prevent corrosion products contamination, for example, drug industry
Corrosion allowance	Thicker wall for corrosion
Special processing for corrosion resistance	Stress relief, shot peening, special heat treatment (e.g., Al alloys) for corrosion
Insurance	Portion of premiums on policy to protect against loss because of corrosion (to cover charge of writing and administering policy, not protection amount)
Parts and equipment inventory	Pumps kept on hand for maintenance, for example, chemical plant inventory

Source: Ref 1

induced leak in an oil pipeline, with resulting loss of product and environmental contamination—can result in costly damage that is difficult to either assess or repair as well as massive legal penalties as "punative damage."

Sources of Information

Sources of information pertaining to corrosion and corrosion prevention are quite varied and include the following:

- Texts, reference books, and journals
- Videos and home study courses
- Software products
- Computerized databases

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- Metals producers
- Trade associations and technical societies
- Consultants

Titles of several widely used textbooks on corrosion and a comprehensive bibliography relevant to corrosion are provided at the conclusion of this chapter (see the Selected References). Complementing print products are video training courses that are available from ASM International (formerly the American Society for Metals) and NACE International (formerly the National Association of Corrosion Engineers). Reference works that list corrodents in alphabetical order and give information for a variety of metallic and nonmetallic materials are particularly useful. Some provide only qualitative information such as "Resistant," "Unsatisfactory," etc., but others can give a more specific indication of the general corrosion rate. An example of the latter approach is *Corrosion Resistance Tables: Metals, Nonmetals, Coatings, Mortars, Plastics, Elastomers and Linings, and Fabrics* published by Marcel Dekker. In the *Corrosion Data Survey—Metals* and its companion volume, *Corrosion Data Survey—Nonmetals,* published by NACE International, the corrosion rate of a given material is plotted against temperature and corrodent concentration. Electronic versions of these products are also described in Chapter 8.

A number of technical journals on the subject of corrosion exist. Examples include *Corrosion,* and *Materials Performance,* published by NACE International, and *Oxidation of Metals,* published by Plenum Publishing Corp. Journals covering corrosion science and technology can also be found in numerous other metallurgical, surface engineering (coating), chemical, and electrochemical publications. The *Source Journals in Metals & Materials,* available in print or electronic format from Cambridge Scientific Abstracts (Beachwood, OH) lists dozens of journals devoted to corrosion.

Producers of metals and alloys publish considerable product data and educational information, as do trade associations such as the Nickel Development Institute, the Aluminum Association, the Copper Development Association, and the Specialty Steel Industry of North America. Addresses for these and other associations and societies are listed in the appendix to this chapter. Research organizations such as the LaQue Center for Corrosion Technology (Wrightsville Beach, NC) and the Electric Power Research Institute (Palo Alto, CA) also provide extensive corrosion information.

Several technical societies are involved with corrosion work. They serve as a source of technical literature, standards, reports, and software. They also sponsor technical symposia and have technical committees that cover a broad spectrum of corrosion problems. In the United States, the primary society devoted to corrosion is NACE Inter-

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Table 4 NACE International technical committees

Committee	Activity
T-1	Corrosion control in petroleum production
T-2	Energy technology
T-3	Corrosion science and technology
T-5	Corrosion problems in the process industries
T-6	Protective coatings and linings
T-7	Corrosion by waters
T-8	Refining industry corrosion
T-9	Military, aerospace, and electronics equipment corrosion control
T-10	Underground corrosion control
T-11	Corrosion and deterioration of the infrastructure
T-14	Corrosion in the transportation industry

Table 5 ASTM committee G-1 on corrosion of metals

Subcommittee	Activity
G01.02	Terminology
G01.03	Computers in corrosion
G01.04	Atmospheric corrosion
G01.05	Laboratory corrosion tests
G01.06	Stress-corrosion cracking and corrosion fatigue
G01.07	Galvanic corrosion
G01.08	Corrosion of nuclear materials
G01.09	Corrosion in natural waters
G01.10	Corrosion in soils
G01.11	Electrochemical measurements in corrosion testing
G01.12	In-plant corrosion tests
G01.14	Corrosion of reinforcing steel
G01.99.01	Corrosion of implant materials

national. NACE was formed in 1943 with the aim of assisting the public and industry in the use of corrosion prevention and control to reduce the billions of dollars lost each year caused by corrosion. Table 4 lists NACE technical committees. NACE also sponsors a yearly international congress on corrosion.

ASTM (formerly the American Society for Testing and Materials) is also very active in the field of corrosion. The main committee is G-1 on corrosion of metals. Its scope is "the promotion of knowledge, the stimulation of research, the collection of engineering data, and the development of standard test methods, practices, guides, classifications, specifications and terminology relating to corrosion and methods for corrosion-protection of metals." A list of the subcommittees in G-1 is shown in Table 5.

Other societies having interests in corrosion are the American Institute of Mining, Metallurgical, and Petroleum Engineers; the American Petroleum Institute; the Electrochemical Society; the American Institute of Chemical Engineers; the American Welding Society; ASM International; the American Society of Mechanical Engineers; the Society for Protective Coatings (formerly the Steel Structures Painting Council); and SAE International (formerly the Society of Automotive Engineers). Most of these societies have symposia on corrosion at their various meetings.

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Appendix: Addresses of Trade Associations and Technical Societies Involved with Corrosion

Aluminum Association, Inc.
900 19th St., NW
Suite 300
Washington, DC 20006

American Institute of Mining, Metallurgical, and Petroleum Engineers (AIME)
345 E. 47th St., 14th Floor
New York, NY 10017

American Iron and Steel Institute (AISI)
1101 17th St., NW
Suite 1300
Washington, DC 20036-4700

American National Standards Institute (ANSI)
11 W. 42nd St., 13th Floor
New York, NY 10036

American Petroleum Institute (API)
1220 L St., NW
Washington, DC 20005

American Society of Mechanical Engineers (ASME)
345 E. 47th St.
New York, NY 10017

American Welding Society (AWS)
550 N.W. LeJeune Rd.
Miami, FL 33126

ASM International
9639 Kinsman Rd.
Materials Park, OH 44073-0002

ASTM
100 Barr Harbor Dr.
W. Conshohocken, PA 19428-2959

Canadian Institute of Mining, Metallurgy, and Petroleum (CIM)
Xerox Tower
Suite 2110
3400 de Maisonneuve Blvd., W.
Montreal, QC
Canada, H3Z 3B8

Canadian Standards Association (CSA)
178 Rexdale Blvd.
Rexdale, ON
Canada M9W 1R3

Copper Development Association (CDA)
260 Madison Ave.
New York, NY 10016

International Cadmium Association
12110 Sunset Hills Rd.
Suite 110
Reston, VA 22090

International Copper Association Ltd.
260 Madison Ave.
New York, NY 10016

International Lead Zinc Research Organization, Inc. (ILZRO)
2525 Meridian Parkway
P.O. Box 12036
Research Triangle Park, NC 27709

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International Magnesium Association (IMA)
1303 Vincent Place
Suite 1
McLean, VA 22101

International Titanium Association (ITA)
1781 Folsom St.
Suite 100
Boulder, CO 80302-5714

Lead Industries Association, Inc.
295 Madison Ave.
New York, NY 10017

Materials Technology Institute of the Chemical Process Industries, Inc. (MTI)
1570 Fishinger Rd.
Columbus, OH 43221

NACE International
P.O. Box 218340
Houston, TX 77218-8340

National Institute of Standards and Technology (NIST)
Gaithersburg, MD 20899

Nickel Development Institute (NiDI)
214 King St., W.
Suite 510
Toronto, ON Canada M5H 3S6

SAE International
400 Commonwealth Dr.
Warrendale, PA 15096-0001

Society for the Advancement of Materials and Processing Engineering (SAMPE)
P.O. Box 2459
Covina, CA 91722

Specialty Steel Industry of North America (SSINA)
3050 K St., NW
Suite 400
Washington, DC 20007

Steel Founders' Society of America (SFSA)
Cast Metals Federation Building
455 State St.
Des Plaines, IL 60016

The Society for Protective Coatings (SSPC)
40 24th St.
6th Floor
Pittsburgh, PA 15222-4643

The Metallurgical Society (TMS-AIME)
420 Commonwealth Dr.
Warrendale, PA 15086-7514

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CHAPTER 2

Basic Concepts Important to Corrosion

BASIC CONCEPTS important to understanding corrosion that are addressed in this chapter include the following:

- Three possible behaviors of a metal when immersed in a solution
- Four requirements of a corrosion cell
- Important metallurgical factors that influence corrosion behavior
- Inherent tendency of a metal to corrode, that is, reactivity
- Tendency of metals to form corrosion products
- Important solution characteristics with respect to corrosion, including conductivity, acidity/alkalinity, oxidizing power, and solubility
- Determination of corrosion rates and corrosion rate allowances

These principal concepts are referred to throughout this book to assist the reader in understanding corrosion phenomena and methods of controlling corrosion. Information pertaining to important electrochemical and thermodynamic reactions is in Chapter 3.

Behavior of a Metal in an Environment

When a metal is immersed in an environment, the metal can behave in one of three ways. These behaviors are shown schematically in Fig. 1, which represents a metal partially immersed in a corrosive environment.

Immune Behavior. One possibility shown in Fig. 1 is that the metal is immune in an environment. Metals known to display this immunity are called noble metals and include, for example, gold, silver, and platinum. For a combination of metal and environment resulting in immune behavior, there is no reaction of the metal, and there is no corrosion of the metal. If the metal is weighed prior to immersion in the solution and then reweighed after the exposure period, there is no weight loss of the metal. Immune behavior results from the metal being thermodynamically stable in the particular environment; that is, the corrosion reaction does not occur spontaneously.

Active Behavior. Another possible behavior is that the metal corrodes. A metal's behavior is described as active when it corrodes in the solution. When active behavior is observed, the metal dissolves in solution and forms soluble, nonprotective corrosion products. Corrosion or dissolution of the metal continues in this solution because the corrosion products do not prevent subsequent corrosion. Active corrosion is characterized by high weight loss of the metal. If the metal sample is weighed prior to immersion in the solution and then reweighed after the exposure period, a significant weight loss is measured.

Passive Behavior. With the third behavior, the metal corrodes but a state of passive behavior is observed. On immersion of the metal in the solution there is a reaction, and the metal does corrode; however, an insoluble, protective corrosion-product film is formed. This thin (~30Å) protective film, also referred to as a passive film, slows the reaction rate to very low levels. The corrosion resistance when dealing with passive behavior depends on the integrity of the protective film. If the passive film is broken or dissolves, then the metal can revert to active behavior and rapid dissolution can occur. For example, an iron sample immersed in either concentrated (70%) or dilute (water added) nitric acid exhibits no reaction (immune behavior) or passive behavior. However, if the iron is scratched with a glass rod or if the beaker holding the sample/solution is shaken violently so that the sample strikes the sides, a violent reaction occurs. The iron quickly goes into solution and large volumes of nitrogen-bearing gases are released.

Some examples of metals that exhibit passivity are iron, chromium, titanium, nickel, and alloys containing these metals (most notably stain-

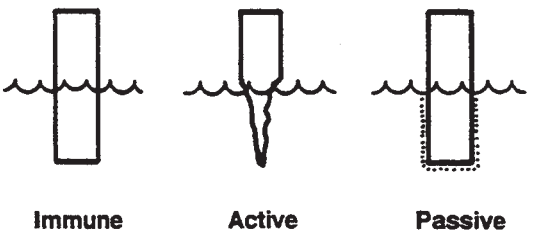


Fig. 1 Three behaviors of metal in an environment

less steels). Passivation is generally associated with oxidizing media. (Discussion on the oxidizing power of a solution follows.)

It is important to realize that a passive film is unlike a coat of paint—though for many practical purposes it can appear to behave as such. This point is of practical significance with respect to the so-called "passivation treatments." These treatments are commonly used for stainless steels. They involve immersing the steel in an oxidizing solution such as nitric acid for approximately half an hour. The prime purpose of such a treatment is not (as is commonly believed) to form a passivation film, but rather to clean the steel—to remove surface inclusions, iron particles, etc., that might act as nucleation sites for attack in future service. In other words, the passivation treatment is only useful in that it creates surface conditions (cleanliness) that can make the stainless steel more amenable to maintaining its passivation.

What is the Desired Corrosive Behavior? From a corrosion-control standpoint, the desired behavior is either immune or passive, while the behavior to be avoided is active. Immune behavior is the most desirable, because corrosion protection does not depend on the stability of protective films. Most engineering alloys, however, are passive in their applications and thus depend on the integrity of the passive film. Where the environment becomes more corrosive, passive metals tend to exhibit localized forms of corrosion, that is, pitting, stress-corrosion cracking, and crevice corrosion. This results because the bulk of the alloy surface remains protected by the passive film, but rapid corrosion occurs in those areas where the film has broken down. Only the most noble metals exhibit immune behavior in a wide variety of corrosive environments. In most cases, it is not practical to use these materials for engineering applications because of their high costs and strength limitations.

While the behavior exhibited by metals is dependent on the corrosive environment to which the metals are exposed, some characteristic behaviors are exhibited. As mentioned above, gold, platinum, and silver typically exhibit noble or immune behavior. Sodium, potassium, and magnesium are active in nearly all aqueous environments. Titanium and tantalum are passive in a wide range of aqueous environments. Aluminum and zinc are very reactive metals and often exhibit active behavior; however, in some important environments they form stable, passive films. The important characteristics of metals and solutions that determine the type of behavior observed are discussed in the following sections of this chapter.

The Four Requirements of a Corrosion Cell

There are four requirements for an electrochemical corrosion cell. These are shown schematically in Fig. 2, where an anode and a cathode

on the metal surface in contact with the solution are indicated. The anode and cathode are connected through the solution by an ionic current path, and they are connected through the metal by an electronic path. An electrochemical reaction involves the transfer of electrons from one species to another, causing direct current flow through the corrosion cell.

The anode is generally where the corrosion occurs. This is the location on the metal surface where metal atoms go into solution as metal ions and weight loss occurs. The direct current going through the corrosion cell enters the solution at the anode. The reactions at the anode are referred to as anodic and are oxidation reactions; that is, electrons are generated.

At the *cathode*, no corrosion occurs and no weight loss occurs. There are, however, reactions occurring that are just as important to the operation of the corrosion cell as the anodic reactions. These reactions are cathodic or reduction reactions; that is, electrons are consumed. The direct current flowing through the corrosion cell enters that metal at the cathode.

The direct current of the corrosion cell moves through the solution by an ionic path. Current flows from the anode to the cathode by the movement of charged ions in the solution. Positively charged ions, or cations, move from the anode to the cathode, and negatively charged ions, or anions, move from the cathode toward the anode. This movement of charged ions in the solution is the vehicle for current flow through this portion of the corrosion cell.

The direct current moves through the metal of the corrosion cell by an electronic path. Electrons generated at the anode by oxidation reactions move to the cathode, where they are consumed by reduction reactions. Current is, by convention, the flow of positively charged particles. Thus, the current (positive charges) flows conceptually from the cathode to the anode.

These four requirements make up the corrosion cell. Metal atoms going into solution at the anode result in corrosion and the generation of electrons at the anode. Current flows from the anode to the cathode by the movement of charged particles. At the cathode, reactions occur that consume electrons, that is, reduction reactions, and the electrons gener-

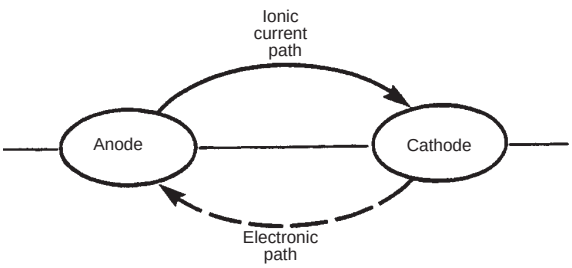


Fig. 2 Four requirements of an electrochemical corrosion cell

ated at the anode are consumed. The electronic path is the path by which electrons move from the anode to the cathode.

The corrosion rate is controlled by the net balance among all of these components of the corrosion cell. The dissolution (oxidation) at the anode can only proceed as quickly as the electrons generated there can be consumed by reduction reactions at the cathode. If the reduction reactions are slowed down, this in turn slows down the dissolution reactions. Resistance in the ionic current path or the electronic current path will slow down the corrosion reaction by limiting the amount of current that can flow through the corrosion cell.

Elimination of any of the four requirements for the corrosion cell stops the corrosion reaction. If the anodes are removed or made inactive, no metal dissolution can occur. An effective control of corrosion is realized by the elimination of the cathodes. If there is no place for the consumption of electrons generated by the corrosion reaction, there is no corrosion reaction. Elimination of the ionic current path also stops corrosion. There is no means for the transfer of electrical charge from the anodes to the cathodes. A practical example of this form of corrosion control is the removal of the electrolyte in a corrosion cell. This can be done by completely drying the metal surface. If there is no moisture on the surface for the formation of an ionic current path, there is no aqueous corrosion. Similarly, elimination of the electronic path between the anode and cathode also eliminates corrosion. If we are dealing with galvanic corrosion, a corrosion reaction driven by two dissimilar metals, the galvanic corrosion can be eliminated by electrically isolating the two metals. There then is no path by which electrons can be transferred from the anode to the cathode, and the two metals do not affect each other.

Metal Characteristics Important to Corrosion

A knowledge of what metals are and how they behave is essential to the understanding of corrosion. In this section, the important characteristics of metals with respect to corrosion are identified. For metals, the metallurgical characteristics, inherent reactivity, and tendency to form insoluble corrosion products all greatly affect their corrosion behavior.

Metallurgical Characteristics

Crystal Structure. Metals are crystallographic in nature; that is, the metal atoms are arranged in an ordered and structured manner throughout the metal crystal. This can be demonstrated by considering each metal atom in the crystal as a sphere. Based on this, models can be built to represent various metal crystal structures. Three such metal crystal

structures are shown in Fig. 3. The atomic packing of atoms in metal crystals with face-centered cubic (fcc), hexagonal close-packed (hcp), and body-centered cubic (bcc) structures are shown. In each structure, the metal atoms have a very well-defined, repeatable, and orderly relationship to one another. The metal crystal can be assembled by putting together layers of planes to build up the overall volume of the crystal. Each plane has the identical arrangement of metal atoms within it.

The surface appearance of a metal crystal on the atomic scale depends on the angle of the planes intercepting that surface. This is shown schematically in Fig. 4. If the surface is directly along the angle of the planes (alpha = 0), then only a single atomic plane is exposed along the surface. As the angle of interception of planes with the surface increases, more and more edges of the planes are exposed. The angles at which the planes intercept the surface affect the reactivity of the metal and its resistance to corrosion because the binding energy of the "end" atoms is less than that of atoms in the plane.

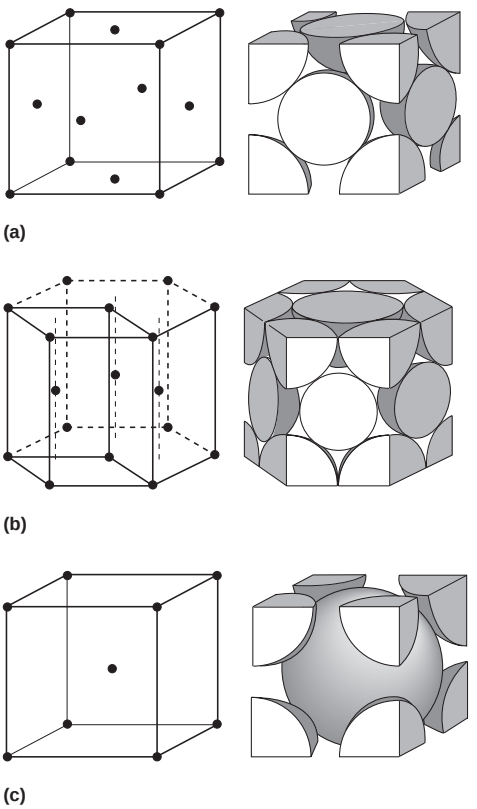


Fig. 3 Unit cells and atom positions for (a) face-centered cubic, (b) hexagonal close-packed, and (c) body-centered cubic unit cells. The positions of the atoms are shown as dots at the left of each pair of drawings, while the atoms themselves are shown close to their true effective size by spheres or portions of spheres at the right of each pair.

Grain Boundaries. Most materials used in service are not single crystals but are in fact made up of many individual crystals or grains. In each grain the metal has planes characteristic of the crystal structure of that metal. The planes from grain to grain are not in the same orientation. This gives rise to grain boundaries between the adjoining crystals. Grain boundaries are shown schematically in Fig. 5. Essentially, the grain boundaries are the area of transition from orientation within one grain to orientation in the neighboring grain. A micrograph of the grain boundaries in a low-carbon steel is shown in Fig. 6.

Grain boundaries are sites of structural discontinuity, and they can also have microstructural and chemical differences with respect to the bulk grains. These discontinuities and differences can affect the corrosion behavior of the metal.

Alloying and Multiphase Structures. While pure metals have many applications, mixtures of several different elements are worked with much more commonly. These intentional mixtures of elements to obtain desirable properties are called *alloys.* Two or more elements mixed together give rise to metals with a wide variety of properties not

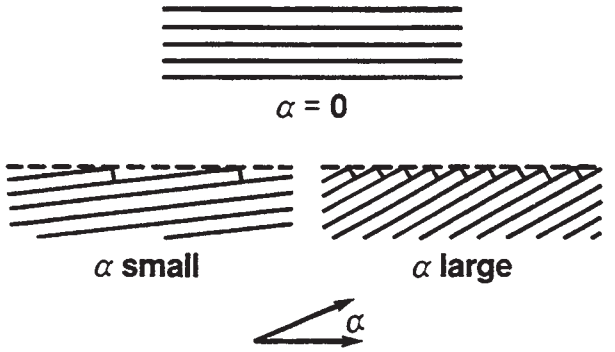


Fig. 4 Crystallographic planes intersecting the surface at different angles

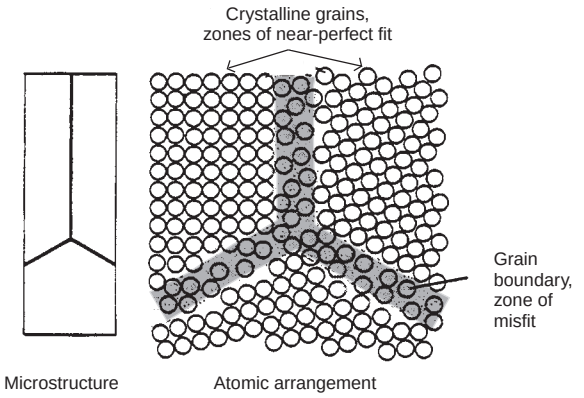


Fig. 5 Schematic diagram of grain boundaries in a metal

available using single elements. The microstructure resulting from the mixture of two elements can vary widely. In some cases the two elements are completely soluble and a homogeneous, single-phase structure is exhibited. Other metals have only limited solubility, and mixtures of these elements result in multiphase materials.

One of the most useful tools for studying the effects of alloying on microstructure is the phase diagram. This is a graph that plots the phase stability relation between various compositions of one metal in another as a function of temperature. In other words, it shows all possible phases of the various possible alloy mixtures and the temperatures at which these phases exist. An excellent introduction to the use and understanding of alloy phase diagrams can be found in *Alloy Phase Diagrams*, Volume 3 of the *ASM Handbook* (see pages 1•1 to 1•29). An example of a phase diagram showing complete solid solubility for the copper-nickel system is shown in Fig. 7. A copper-nickel alloy will be a homogeneous, single phase at any percentage of nickel from pure copper across the diagram to pure nickel. The alloy has grain boundaries in the regions between single crystals of different orientation; however, there is only a single phase of constant composition in all grains. The copper-silver phase diagram with limited solid solubility is shown in Fig. 8. Copper is very sparingly soluble in silver, and silver is very sparingly soluble in copper. This results in two-phase structures being exhibited across nearly the entire range of composition of copper and silver alloys. There is a phase consisting of nearly pure copper and another phase consisting of nearly pure silver. The ratio of amounts of the two phases varies depending on the relative amounts of copper and silver.

The copper-silicon phase diagram shown in Fig. 9 exhibits many different phases with increasing silicon content from pure copper (0% Si)

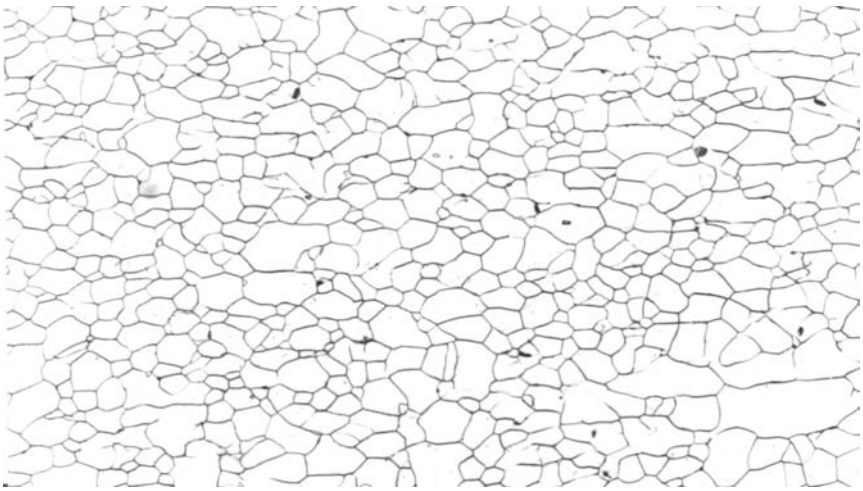


Fig. 6 Ferrite grains and grain boundaries in a low-carbon ferritic sheet steel etched with 2% nital. 300×

to 14 wt% Si. The phases that are present and their relative amounts depend on the composition of the copper-silicon alloy and also on the heat treatment of the alloy.

There are literally thousands of examples of micrographs showing the distribution and morphology of multiple-phase microstructures in the *ASM Handbook* series as well as in other ASM publications. Two notable books are *Metallography and Microstructures,* Vol 9, *ASM Handbook,* which deals with metallographic preparation and microstructural interpretation of industrial alloys, and the *Metals Handbook Desk Edition,* Second Edition. Of particular note in the latter publication is the article "Structure/Property Relationships in Irons and Steels"

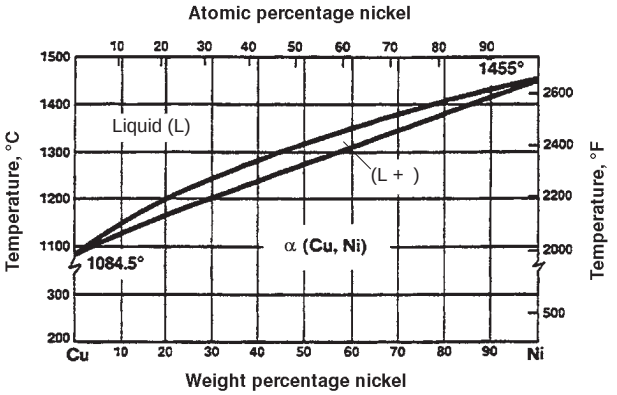


Fig. 7 Copper-nickel phase diagram with complete solid solubility. The diagram consists of two single-phase fields separated by a two- phase field (L + α). The boundary between the liquid field (L) and the two- phase field is called the liquidus; that between the two-phase field and the solid field (α) is the solidus.

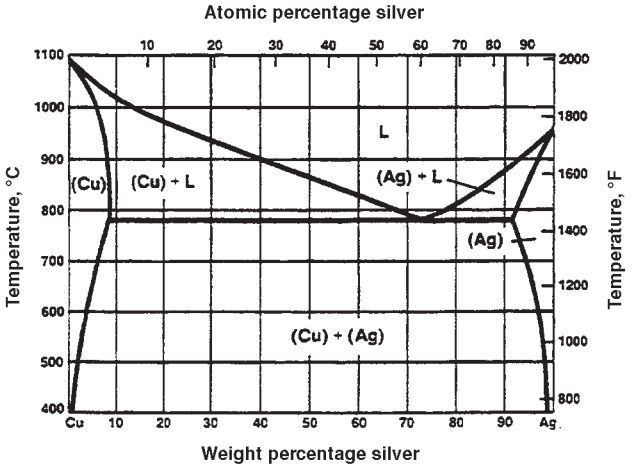


Fig. 8 Copper-silver phase diagram with limited solubility

(pages 153 to 173), which shows many of the various structures possible in iron-base alloys.

Relationship between Microstructure and Corrosion. The important consideration within the context of this corrosion course is that many alloys are not homogeneous, pure materials, but rather are a mixture of multiple phases. Each phase has its characteristic crystallographic structure and chemical composition. When these structures are then exposed to a corrosive environment, it is not surprising that the different phases exhibit different corrosion behaviors. This leads to preferential corrosion of specific constituents of the alloy.

This relationship between microstructure and corrosion behavior is demonstrated in Fig. 10 and 11. Figure 10 shows the microstructure of three different alloys. Alloy 1 is nearly pure A, alloy 2 is A with modest amounts of B, and alloy 3 is a B-rich alloy of A and B. The microstructure of alloy 1 is a single phase of alpha (α), with complete solubility of B within the alpha phase. Alloy 2 has B-additions beyond the solubility limit, and a two-phase structure results. The microstructure is made up of small islands of beta (β) phase distributed throughout a continuous matrix of alpha phase. The microstructure of alloy 3 is a mixture of alpha phase and beta phase.

Figure 11 shows the relationship of the corrosion behavior to the microstructures of the three alloys. In the first scenario, alpha is the more active phase and beta is more noble; that is, the corrosion resistance of alpha is less than the corrosion resistance of beta. A cross section through the alloy surface after exposure to a corrosive environment is represented below the diagram of each microstructure. For the case where alpha is the more active material, a uniform corrosion of alpha is observed for alloy 1. For alloy 2, the beta phase is nearly unattacked and

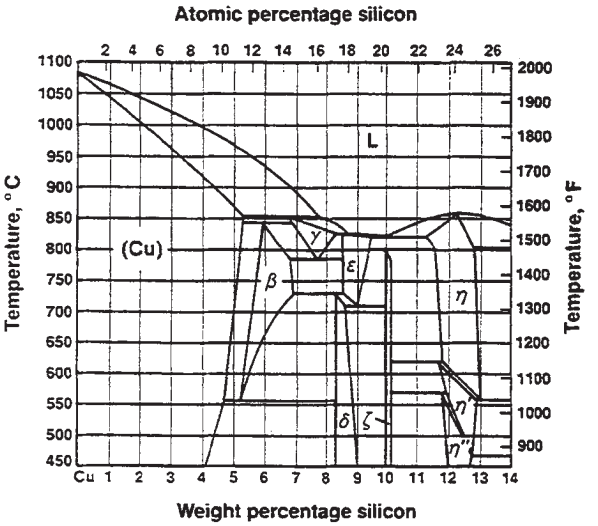


Fig. 9 Copper-silicon phase diagram with multiple solid phases

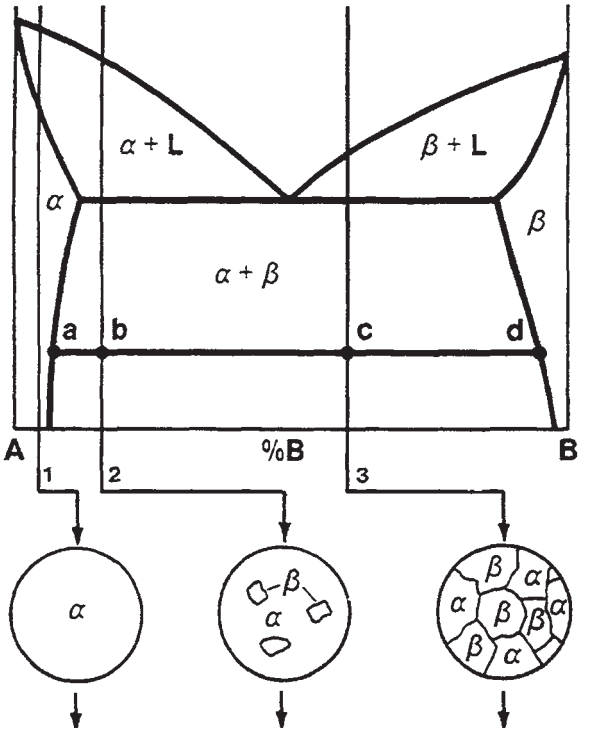


Fig. 10 Relationship of microstructure to the phase diagram

the alpha phase on either side of the beta particle is attacked. For alloy 3, again the alpha phase is attacked and the exposed beta phase is left essentially unattacked.

For the scenario where alpha is noble (more corrosion resistant) and beta is active, the resulting surface profile is shown at the bottom of Fig. 11. In this case the alpha phase is not significantly corroded in alloy 1.

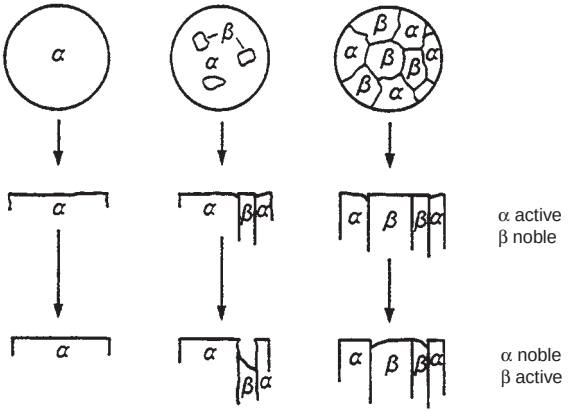


Fig. 11 Relationship of corrosion behavior to microstructure

In alloy 2, the alpha phase remains unattacked, and significant dissolution of the beta phase occurs. Similarly, in alloy 3, the exposed grains of beta phase are attacked while the exposed alpha phase is left unattacked.

This difference in the dissolution behavior of various phases in a multiphase structure provides the basis for optical metallography. In metallographic examinations, the specimen surface is polished to a mirror finish and then exposed to chemical etchants. The chemical solution preferentially attacks particular constituents of the alloy, and thus the microstructure of the alloy is revealed.

Effect of Inclusions and Precipitates. Alloys are intentional mixtures of elements to gain desired properties. The microstructure of an alloy can contain multiple phases, and the distribution and amount of the second phase are controlled to develop desired properties, for example, increased strength or toughness. Other second-phase particles can be undesirable. Examples of undesirable precipitates are oxides and sulfides, which precipitate in the metal from dissolved oxygen and sulfur in the metal-producing process. This results in a distribution of inclusions (small particles of oxide, sulfide, etc.) throughout the alloy.

When these inclusions are exposed at the metal surface to a corrosive environment, they can affect corrosion behavior. The effects of inclusions at the metal surface are shown schematically in Fig. 12. The uppermost figure represents an inclusion exposed at the metal surface prior to corrosion, and the lower diagrams indicate the behavior under different conditions. If the inclusion is active, that is, less corrosion resistant than the matrix, then the inclusion dissolves, leaving a hole or pit in the metal surface. If only portions of the inclusion are active, then the exposed portions are attacked, leaving the other portions intact. If the inclusion is noble (more corrosion resistant than the matrix), then accel-

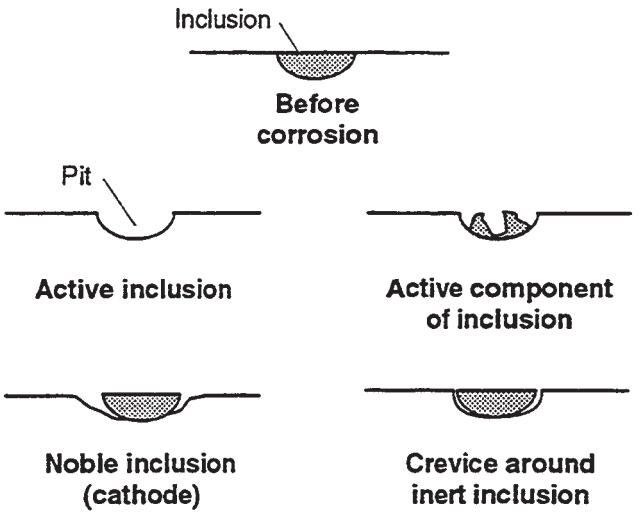


Fig. 12 Effect of an inclusion at the metal surface

erated attack of the matrix adjacent to the noble inclusion can be observed. In other cases where the inclusion is inert to attack, accelerated corrosion adjacent to the inclusion can still occur because of a crevice generated between the inclusion and the matrix.

The presence of precipitates with minor alloying elements and impurities can lead to problems, because phases with widely different electrochemical properties are then present. This can result in local variations in corrosion resistance. Also, the addition of alloying elements to improve the resistance to general, or uniform, corrosion can cause increased susceptibility to localized corrosion processes, such as pitting or intergranular corrosion. The metallurgical factors that can influence localized corrosion of stainless steels are shown in Fig. 13. The precipitation of nitrides or carbides along the grain boundaries of the stainless steel can result in depletion of chromium in regions surrounding the particles, which in turn leads to accelerated corrosion of the chromium-depleted regions. Inclusions represented by a manganese sulfide particle at the surface can result in the initiation of pitting on the surface. Other phases in the stainless steel represented by delta ferrite and alpha prime can cause chemical inhomogeneities and/or structural inhomogeneities, which lead to the initiation of localized corrosion. The effect of mechanical deformation is shown by the generation of active slip steps, which can weaken the protective film on the stainless steel and lead to localized corrosion.

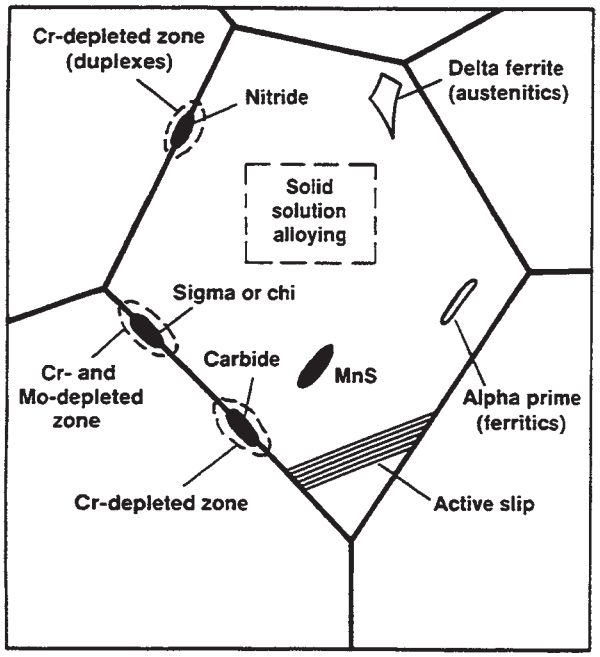


Fig. 13 Schematic of the microstructural variables that can influence the corrosion behavior of stainless steels

Effect of Conductivity. Metals are highly conductive. This is an important feature from the standpoint of corrosion because the metals provide an efficient path to transport electrons from the anode to the cathode. The resistivities of several metals at 20 °C (70 °C) are shown in Table 1. The microohm · cm unit (μΩ · cm) is 10^{-6} ohm · cm (Ω · cm); that is, a cube of material 1 by 1 by 1 cm has a resistance of 10^{-6} Ω from one face to the opposite face. All of these metals have high conductivities with respect to polymers or ceramics. Within the classification of metals, silver, copper, and gold have the highest conductivities. Iron is intermediate among the metals, and lead has one of the lowest conductivities. It should be noted that resistivity and conductivity are inverse relationships; that is, higher resistivities are equivalent to lower conductivities.

Effect of Heat Treatment. Many mechanical properties of materials are improved by heat treatments. Unfortunately, such properties as hardness and strength are often achieved at the expense of corrosion resistance. For example, the hardness and strength of martensitic steels are counterbalanced by a lower corrosion resistance than for the ferritic and austenitic steels. The very high strengths achieved for precipitation-hardened steels are due to the secondary precipitates formed during the solution heat treating and aging process. As discussed above, precipitates with electrochemical properties distinctly different from those of the matrix have a deleterious effect on corrosion.

Effect of Cold Working. Processes such as cold working, in which material is plastically deformed into some desired shape, lead to the formation of elongated and highly deformed grains and a decrease in cor-

Table 1 Electrical resistivities of metals

Metal	Temperature, °C	Temperature, °F	Resistivity, μΩ · cm
Aluminum	20	70	2.828
	100	212	3.86
Brass	20	70	7
Bronze	20	70	18
Cadmium	20	70	7.6
Chromium	28	82	13
Cobalt	20	70	9.8
Copper	20	70	1.724
	100	212	2.28
Gold	20	70	2.44
	100	212	2.97
Iron	20	70	10
	100	212	16.61
Lead	20	70	22
	100	212	27.8
Nickel	20	70	6.141
	100	212	10.327
Platinum	20	70	10
	100	212	14.1
Silver	18	64	1.629
	100	212	2.15
Zinc	0	32	5.76
	92.5	199	8

rosion resistance. Cold working can also introduce residual stresses that make the material susceptible to stress-corrosion cracking. An improvement in corrosion resistance can be achieved by subsequently annealing at temperature at which grain recrystallization can occur. A partial anneal leads to stress relief without a major effect on the overall strength of the material.

Effect of Welding. From the corrosion viewpoint, welding is a particularly troublesome treatment. Because welding involves the local heating of a material, it can lead to phase transformations and the formation of secondary precipitates. It can also induce stress in and around the weld. Such changes can lead to significant local differences in electrochemical properties as well as the onset of such processes as intergranular corrosion. Therefore, the weld filler metal should be as close in electrochemical properties to the base metal as technically feasible, and the weld should be subsequently stress relieved.

Inherent Reactivity

Each metal has its own inherent tendency to corrode. Some metals, such as gold and silver, are very noble and have little tendency to corrode. They can be found in the earth in their natural, metallic state. At the other end of the scale of inherent reactivity are metals such as sodium. Sodium is an extremely active metal and corrodes spontaneously in the presence of water with a violent reaction. Iron is a moderately active metal and corrodes spontaneously in the presence of water. The natural state of iron in the structure of the earth is iron oxide. In order to recover iron from the iron oxide, a considerable amount of energy must be used to decompose the iron oxide and recover the pure iron. The variety of metals available provides a wide range of inherent reactivity, from very noble materials, which do not corrode readily, to extremely active metals, which corrode quite readily.

An alternative way to express the inherent reactivity is to look at the amount of energy required to recover a metal from its oxide. Here, more energy is required for the most active metals; that is, it takes more energy to recover sodium from sodium oxide that it does to recover iron from iron oxide. Similarly, the noble metals have little tendency to form their oxides and are easily recovered from a metal oxide.

The electromotive force (emf) series is a formal ranking of metals with respect to their inherent reactivity. Table 2 is an electromotive force series for many of the metals. The most noble metals are at the top of the emf series and have the highest positive standard electrode potentials. The most active metals are at the bottom of the series and have the most negative standard electrode potentials. The potential for hydrogen is taken as zero by internationally accepted convention. All other standard electrode potentials are referred to this standard hydrogen electrode

(SHE) value. Thus, the potential of gold is +1.50 V with respect to the hydrogen reference potential, and the potential of iron is –0.44 V with respect to the hydrogen reference potential.

The standard electrode potential values are determined for a special set of conditions; that is, the standard potential is for the equilibrium of the pure metal with its own ions at a specified concentration. No other ions are considered in the equilibrium. Thermodynamic calculations yield the standard electrode potential for each metal under these specified conditions.

The emf series is most valuable for indicating the inherent reactivity of metals. Most corrosion applications, however, deal with mixed reactions, that is, not only the reaction of the metal with its own ions but also the reaction of the metal with other species in the solution, such as hydrogen ions or oxygen. In Chapters 3 and 4, various galvanic series for metals are discussed. These galvanic series take into account the other reactions and provide a listing of the inherent reactivity of metals in a specific environment. Nevertheless, the emf series is quite useful.

Metals at the bottom or most negative end of the emf series are active metals. They have less corrosion resistance than metals higher in the series. In order of increasing corrosion resistance, magnesium is the least corrosion resistant, followed by zinc, iron, and copper, with gold being

Table 2 Electromotive force series

Electrode reaction	Standard potential at 25 °C (77 °F), V-SHE
$Au^{3+} + 3e^- \rightarrow Au$	1.50
$Pd^{2+} + 2e^- \rightarrow Pd$	0.987
$Hg^{2+} + 2e^- \rightarrow Hg$	0.854
$Ag^{+} + e^- \rightarrow Ag$	0.800
$Hg_2^{2+} + e^- \rightarrow 2Hg$	0.789
$Cu^{+} + e^- \rightarrow Cu$	0.521
$Cu^{2+} + 2e^- \rightarrow Cu$	0.337
$2H^{+} + 2e^- \rightarrow H_2$	0.000 (Reference)
$Pb^{2+} + 2e^- \rightarrow Pb$	–0.126
$Sn + 2e^- \rightarrow Sn$	–0.136
$Ni^{2+} + 2e^- \rightarrow Ni$	–0.250
$Co^{2+} + 2e^- \rightarrow Co$	–0.277
$Tl^{+} + 2e^- \rightarrow Tl$	–0.336
$In^{3+} + 3e^- \rightarrow In$	–0.342
$Cd^{2+} + 2e^- \rightarrow Cd$	–0.403
$Fe^{2+} + 2e^- \rightarrow Fe$	–0.440
$Ga^{3+} + 3e^- \rightarrow Ga$	–0.53
$Cr^{3+} + 3e^- \rightarrow Cr$	–0.74
$Cr^{2+} + 2e^- \rightarrow Cr$	–0.91
$Zn^{2+} + 2e^- \rightarrow Zn$	–0.763
$Mn^{2+} + 2e^- \rightarrow Mn$	–1.18
$Zr^{4+} + 4e^- \rightarrow Zr$	–1.53
$Ti^{2+} + 2e^- \rightarrow Ti$	–1.63
$Al^{3+} + 3e^- \rightarrow Al$	–1.66
$Hf^{4+} + 4e^- \rightarrow Hf$	–1.70
$U^{3+} + 3e^- \rightarrow U$	–1.80
$Be^{2+} + 2e^- \rightarrow Be$	–1.85
$Mg^{2+} + 2e^- \rightarrow Mg$	–2.37
$Na^{+} + e^- \rightarrow Na$	–2.71
$Ca^{2+} + 2e^- \rightarrow Ca$	–2.87
$K^{+} + e^- \rightarrow K$	–2.93
$Li^{+} + e^- \rightarrow Li$	–3.05

the most corrosion resistant. A metal with a more negative potential in the series will replace from solution the metal ions of a metal more positive in the series. Iron immersed in a solution containing copper ions, for example, a solution of copper sulfate, replaces the copper ions. The iron goes into solution as iron ions, and the copper ions plate out of solution onto metal as metallic copper.

The position of metals in the emf series tells, in general, of the reactivity of the metal with deaerated acids, that is, acids containing no dissolved oxygen. Metals more negative than the hydrogen potential react with deaerated acids. Metals more positive than the hydrogen electrode are not attacked by deaerated acids. This only applies to acids in the absence of oxygen.

The emf series provides an indication of the potential difference between two metals coupled together in a galvanic corrosion cell. If two dissimilar metals are coupled together, the potential difference is a driving force for corrosion reactions. The farther apart the metals are in the emf series, the greater the driving force for corrosion. For example, copper and aluminum form a strong cell with a potential difference of greater than 2 V, while magnesium and aluminum form a weaker cell with a potential difference of less than 1 V. The metal that is more positive in the series is the cathode, and the metal that is more negative in the series is the anode. The anodic member of the galvanic couple is severely corroded. Other considerations for the galvanic-corrosion couple exist, and the emf series should only be used as a general indication. These other considerations are discussed in subsequent chapters.

In summary, the emf series ranks the metals with respect to their tendency to react. The metals at the top of the series are the most corrosion resistant and have the least tendency to be oxidized. An alternative way of expressing this is that the oxidizing power of a solution must be greater in order to corrode a metal higher in the series. It takes a solution with only a low oxidizing potential to corrode the active members of the series, such as sodium, magnesium, and aluminum. A greater oxidizing potential is required to corrode iron and nickel. An even greater oxidizing power of the environment is required to corrode copper, and a very high oxidizing power of the solution is required to corrode platinum and gold. This inherent reactivity of the metals is an important consideration in corrosion.

Formation of Corrosion Products

The term *corrosion products* refers to the substances produced during a corrosion reaction. Corrosion products can be soluble, such as zinc chloride, which is formed when zinc is placed into a dilute hydrochloric acid, or zinc sulfate, which is formed when zinc is placed in

sulfuric acid, or corrosion products can be insoluble compounds, such as iron oxide or hydroxide. The presence of corrosion products is one way corrosion can sometimes be detected (e.g., rust).

The tendency to form insoluble corrosion products is central to corrosion considerations because it is often the insoluble corrosion product films that provide passivity. The insoluble corrosion product film formed on a surface can block the surface from further attack and thus significantly reduce the corrosion rate of a material. The typical compounds of interest are oxides, hydroxides, and sulfates. Lead in sulfuric acid of specific concentrations, for example, forms a protective lead sulfate layer, and the corrosion rate is greatly reduced. Aluminum exposed to air develops a very tenacious and protective aluminum oxide passive film. Referring back to the emf series, aluminum is an extremely reactive metal. However, because of the formation of a very adherent and protective oxide layer, aluminum can be used for many architectural and structural purposes. Iron alloyed with a minimum of 12% Cr spontaneously forms a protective passive film on its surface. This spontaneous passivity for alloys with high chromium concentrations is the basis for an entire series of stainless steel alloys.

The tendency to form an insoluble product is expressed as a solubility product. The solubility product defines the concentration of dissolved metal ions and, for example, hydroxyl ions required for the precipitation of a metal hydroxide. As the metal-ion concentration increases and the hydroxyl-ion concentration increases, the likelihood of formation of an insoluble product increases. Materials such as ferric hydroxide have extremely low solubility products, and it takes only a very small amount of ferric ion in solution to lead to the precipitation of ferric hydroxide.

From the perspective of corrosion control, it is important to understand which products are the most stable and what degree of protection is provided by the solid products. Some insoluble products, such as the aluminum oxide that protects aluminum from corrosion, are very adherent to the metal surface and very dense. Other insoluble products are less dense and can be porous, and therefore provide little or no protection from subsequent corrosion.

Important Solution Characteristics

In the previous section, the important characteristics of metals with respect to corrosion were discussed. In this section, the important characteristics of aqueous solutions are presented. These characteristics include: conductivity of the solution, acidity and alkalinity, oxidizing power, degree of ionization, and solubility in the solution. These characteristics of the solution, in combination with the characteristics of the

metal, will determine the corrosion behavior of a metal/environment combination.

The conductivity of a solution is a measure of its ability to transport current. A high-conductivity solution easily transports current, whereas a solution with low conductivity transports current much less effectively. The conductivity is inversely proportional to resistivity; that is, if conductivity increases, resistivity decreases, and, conversely, if conductivity decreases, resistivity increases.

Various solutions exhibit a wide range of conductivites. Seawater is a highly conductive solution and has a very low resistance to transporting current. Distilled water, on the other hand, is a very low-conductivity solution and has a high resistance to the transport of current. In general, as the concentration of dissolved species in the solution increases, the conductivity increases, and, in general, as the conductivity of the solution increases, the corrosion of metals in that solution increases.

Recall that one of the requirements for a corrosion cell is an ionic conducting path between the anode and cathode. If the resistance of that ionic path is lower, there is less resistance in the corrosion cell, and the corrosion rate can proceed more rapidly. Seawater is much more corrosive than distilled water in part because of its much greater conductivity.

The resistivity and conductivity of a one normal (1*N*) solution of several chemical compounds is presented in Table 3. The compounds are listed with their chemical formulas. The resistivity in ohm · cm and the conductivity in mho · cm are presented. Note that the conductivity values are simply the inverse of the resistivity; that is, to get conductivity, divide 1 by the value of the resistivity. Sodium chloride has a resistivity of 11.6 Ω · cm. This is a very low resistivity for a solution. It can be compared to the resistance of greater than 10^6 Ω for distilled water. Most of the solutions listed in Table 3 are reasonably low-resistance or

Table 3 Resistivity and conductivity of 1 *N* solutions at 20 °C (70 °F)

Compound and formula	Resistivity, Ω · cm	Conductivity, mho · cm
Boric acid, H_3BO_3(a)	70,000	0.000014
Chromic acid, H_2CrO_4	3.18	0.314
Copper sulfate, $CuSO_4$	3.41	0.293
Ferrous chloride, $FeCl_2$	16.5	0.0606
Hydrochloric acid, HCl	3.01	0.3322
Nickel chloride, $NiCl_2$	14.1	0.0709
Nickel sulfate, $NiSO_4$	33.8	0.0295
Potassium chloride, KCl	8.94	0.1119
Potassium cyanide, KCN	8.21	0.1218
Potassium hydroxide, KOH	5.07	0.1972
Sodium chloride, NaCl	11.6	0.0862
Sodium hydroxide, NaOH	5.77	0.1733
Sodium carbonate, Na_2CO_3	19.1	0.0523
Sodium sulfate, Na_2SO_4	16.8	0.0595
Sulfuric acid, H_2SO_4	4.81	0.208
Zinc sulfate, $ZnSO_4$	33.2	0.0301

(a) Concentration is one molar (1*M*) instead of one normal (1 *N*).

high-conductivity solutions. The exception is boric acid, which is a moderately high-resistance medium. Compare the values of sulfuric acid and hydrochloric acid, which are quite low in resistivity, with that of boric acid, which is quite high. All other things being equal, boric acid would be considerably less corrosive than sulfuric or hydrochloric acids at similar concentrations.

The relative acidity or alkalinity of a solution greatly affects its corrosivity for particular metals. Solutions can be described as acidic, neutral, or alkaline based on the relative ratio of hydrogen ions to hydroxyl ions. Figure 14 shows this relationship. Where hydrogen ions and hydroxyl ions are in balance, the solution is neutral. Where hydrogen ions predominate over hydroxyl ions, the solution is acidic, and where the hydroxyl ions predominate over the hydrogen ions, the solution is alkaline. Strongly acidic solutions have a greater number of hydrogen ions, and strongly alkaline solutions have a greater concentration of hydroxyl ions.

The pH defines the acidity or alkalinity of a solution. The pH is defined as $-\log(H^+)$; an increase of one pH unit is equivalent to an order of magnitude, or factor of 10, decrease in the hydrogen ion concentration. Figure 15 shows a pH scale ranging from 1 to 14. A value of pH 7 defines a neutral solution, and low values of pH identify the solution as being acidic. The lower the value, the stronger the acid becomes. High pH values, greater than 7, identify the solution as an alkaline solution, and the higher the pH, the stronger the alkaline environment becomes. Also shown in Figure 15 are some common environments and their typical positions along the pH scale. Hydrochloric, sulfuric, and nitric acids are strong acids and have low pH values even in relatively dilute solutions. Boric, citric, and phosphoric acids are weaker acids and have pH values only slightly acidic. Tap water and seawater typically have neutral pH values. Sodium bicarbonate and ammonium hydroxide are mildly alka-

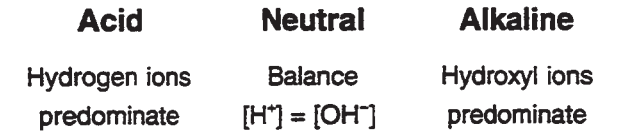


Fig. 14 Range of acidity and alkalinity

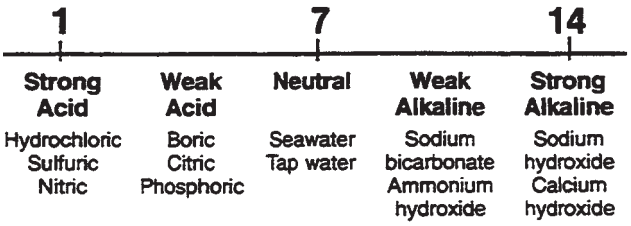


Fig. 15 The pH of several common environments

line solutions and have a pH of approximately 10. Sodium hydroxide is a strongly alkaline solution and has high pH values.

The approximate pH of solutions of acids and bases is shown in Table 4. The strong acids have the lowest values of pH, and the strong bases have the highest values of pH. The pH of an acid becomes lower as the concentration increases; that is, the acid becomes stronger. The pH of a strong base becomes greater as the concentration increases; that is, the solution becomes more highly alkaline.

The effect of acidity or alkalinity of the solution depends very much on the specific metal of interest. For example, nickel is quite resistant to highly alkaline environments, whereas aluminum is severely corroded by strongly alkaline environments. Again, it is important to discuss only the corrosion behavior of a combination of a metal in a specific environment.

The oxidizing power of a solution is a measure of its relative tendency to corrode or oxidize metals. A solution of low oxidizing power corrodes only those metals at the lower (more active) end of the electromotive force series. A solution of strong oxidizing power corrodes all metals on the series except those with the most positive (most noble) values of the emf series. The range of oxidizing power encountered in aqueous environments is from strongly oxidizing to strongly reducing. The oxidizing power is an inherent property of the chemical species.

Increasing oxidizing power means the tendency for the solution to oxidize a metal increases. Figure 16 compares the tendency of a metal to corrode, as expressed by the emf series, with the oxidizing power of the solution, ranging from highly oxidizing at the top to highly reducing at the bottom. Magnesium has the greatest tendency to corrode, and gold

Table 4 Approximate pH of solutions of acids and bases

Solution	Normality, *N*	pH
Acids		
Hydrochloric acid	1	0.1
	0.1	1.1
	0.01	2
Sulfuric acid	1	0.3
	0.1	1.2
	0.01	2.1
Orthophosphoric acid	0.1	1.5
Formic	0.1	2.3
Acetic	1	2.4
	0.1	2.9
	0.01	3.4
Boric acid	0.1	5.2
Bases		
Potassium hydroxide	1	14
Sodium hydroxide	1	14
Sodium and potassium hydroxide	0.1	13
	0.01	12
Trisodium phosphate	0.1	12
Sodium carbonate	0.1	11.6
Ammonium hydroxide	1	11.6
	0.1	11.1
	0.01	10.6
Potassium cyanide	0.1	11

has the least tendency to corrode. Concentrated nitric acid is a highly oxidizing environment, aerated (containing oxygen) acid is mildly oxidizing, and deaerated (no oxygen) acid is a relative reducing environment. The oxidizing power of a deaerated acid is sufficient to corrode both magnesium and iron but is insufficient to corrode copper or gold. An aerated acid, that is, one containing dissolved oxygen, has sufficient oxidizing power to corrode magnesium, iron, and copper. An aerated acid is still insufficient to corrode gold. Concentrated nitric acid has a highly oxidizing power and corrodes gold, copper, iron, and magnesium.

The addition of oxygen dissolved in a solution increases its oxidizing power. Other chemical species, however, also increase the oxidizing power. Ferric ions and cupric ions greatly increase the oxidizing power of the solution. As mentioned previously, concentrated nitric acid is a strongly oxidizing environment. Deaerated hydrochloric acid is an example of a highly reducing environment.

Dissociation or Ionization. The corrosivity of an environment is strongly dependent upon the degree of ionization of chemical species in the solution. Ionization or dissociation is the separation of the chemical into ionic species, examples of which include the following: sodium chloride, $NaCl \rightarrow Na^+ + Cl^-$; sulfuric acid $H_2SO_4 \rightarrow H^+ + HSO_4^-$ and $HSO_4^- \rightarrow H^+ + SO_4^-$; and sodium hydroxide, $NaOH \rightarrow Na^+ + OH^-$. Sodium chloride (NaCl) dissolved in water ionizes to form a sodium ion (Na^+) and a chloride ion (Cl^-). Sulfuric acid can ionize to form a hydrogen ion plus a negatively charged species and can further dissociate to form a second hydrogen ion plus a sulfate ion. Sodium hydroxide ionizes to form a sodium ion and a hydroxyl ion. The degree of ionization or the number of sodium chloride molecules that break up into sodium ions and chloride ions depends on the particular compound and its concentration.

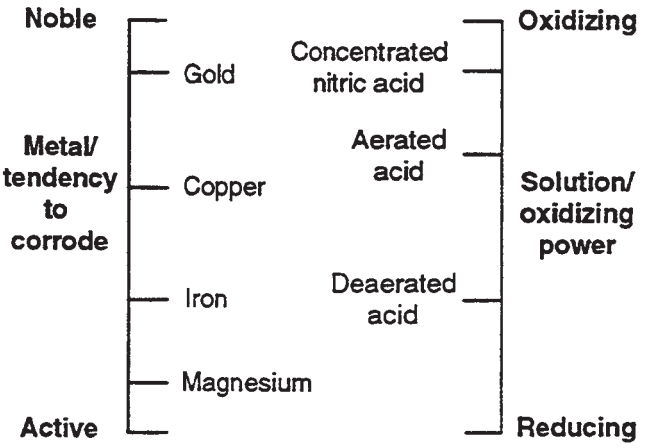


Fig. 16 Relationship between the tendency of a metal to corrode and the oxidizing power of a solution

The degree of ionization of several chemicals is shown in Table 5. Complete ionization is represented by a degree of ionization equal to 1.0. Values close to 1.0 for the degree of ionization indicate that the compound forms many ions, and very low values indicate that the compound forms only a few ions. Hydrochloric acid and potassium hydroxide have high degrees of ionization, and these compounds dissociate to a large degree, forming ions in solution. Boric acid and ammonium hydroxide have low degrees of ionization and form fewer ions in solution. This accounts for hydrochloric acid and potassium hydroxide being a strong acid and a strong base, respectively.

These compounds also produce a large number of hydrogen ions (hydrochloric acid) and hydroxyl ions (potassium hydroxide) in solution. Boric acid and ammonium hydrogen, on the other hand, are a weak acid and a weak base, respectively, because there are only a few hydrogen ions and hydroxyl ions in their solutions.

The chemicals that are acids generate hydrogen ions when they dissociate. The chemicals that are bases produce hydroxyl ions when they dissociate. Salts are chemicals that produce neither hydrogen ions nor hydroxyl ions when they dissociate. Hydrochloric acid produces a large number of hydrogen ions. Potassium hydroxide produces a large number of hydroxyl ions, and sodium chloride produces only sodium ions and chloride ions, that is, neither hydrogen ions nor hydroxyl ions.

Solubility is a measure of the quantity of an ion or gas in a solution. There is a saturation limit, or upper limit, on solubility for species in a given solution. For example, if one starts with a solution containing no oxygen and bubbles oxygen through that solution, the oxygen dissolved in the solution begins to increase. The dissolved oxygen concentration continues to increase until the saturation limit is reached. At the saturation limit, the addition of more oxygen simply bubbles through the solution

Table 5 Degree of ionization of acids, bases, and salts at 25 °C (77 °F)

Solution	Degree of ionization	
Acids		**[H^+]**
Hydrochloric acid, 1 *N*	0.784	0.784 *N*
Hydrochloric acid, 0.5 *N*	0.876	0.438 *N*
Sulfuric acid, 1 *N*	0.510	0.510 *N*
Hydrofluoric acid, 1 *N*	0.070	0.070 *N*
Boric acid, (primary ionization), 0.1 *M*	0.0001	0.00001 *N*
Hydrocyanic acid, 0.1 *M*	0.0001	0.00001 *N*
Phosphoric acid, (secondary ionization), 0.5 *N*	0.170	0.085 *N*
Bases		**[OH^-]**
Potassium hydroxide, 1 *N*	0.77	0.77 *N*
Sodium hydroxide, 1 *N*	0.73	0.73 *N*
Ammonium hydroxide, 1 *N*	0.004	0.004 *N*
Salts		**[Metal ion]**
Such as KCl, 0.1 *N*	0.86	0.86 *N*
Such as K_2SO_4, Na_2AO_4, 0.1 *N*	0.72	0.072 *N*
Such as $CuSO_4$, $NiSO_4$, 0.1 *N*	0.45	0.045 *N*

without increasing the amount dissolved. Similarly, solids dissolve in a solution and continue to increase in concentration until their saturation limit is reached. Beyond the saturation limit, solid deposits form in a solution and precipitate from solution. Some of the solids that form can provide a protective film (passive film) and reduce the corrosion rate of the metal.

Complexing agents can combine with ions in solution and increase the apparent solubility of those ions. This is done by tying up a number of those ions in the form of soluble complexes. A result of the presence of complexing agents in a solution can be the prevention of the formation of a protective film. An example of a complexing agent is ammonia with copper. The presence of ammonia species in the solution greatly increases the solubility of copper ions and consequently increases the corrosion rate of copper. The formation of protective, insoluble products on the copper surface is retarded by the complexing species.

From a corrosion perspective, the solubility of oxygen in a solution is one of the most significant effects. Figure 17 shows the effect of increasing oxygen concentration on the corrosion rate of iron in water. At any given temperature, the corrosion rate of iron increases with increasing oxygen concentration. This figure also shows the increase in the corrosion rate of iron with increasing temperature at any given oxygen concentration. Table 6 provides corrosion rates for various metals

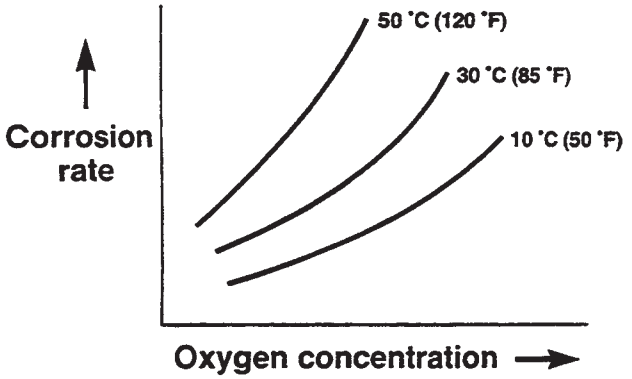


Fig. 17 The effect of oxygen concentration on the corrosion rate of iron

Table 6 Comparison of corrosion rates (in mm/yr) in oxygen-free (hydrogen-saturated) and oxygen-saturated solutions

Metal	Acid	Corrosion rate	
		Hydrogen saturated(a)	Oxygen saturated
Mild steel	6% H_2SO_4	40	500
Lead	4% HCl	35	325
Copper	4% HCl	25	2150
Tin	6% H_2SO_4	9	1090
Nickel	4% HCl	9	675
Monel	2% H_2SO_4	2	140

(a) No oxygen

Table 7 Oxygen solubility in water

Temperature		Oxygen solubility	
°C	°F	Grams per kg water	Parts per million
0	32	0.069	69
20	70	0.043	43
40	105	0.031	31
60	140	0.027	27
80	140	0.014	14
100	212	0.00	<1

in solutions with no oxygen (hydrogen-saturated) and in solutions saturated with oxygen. For all of the metals listed, the addition of oxygen to the solution significantly increases the corrosion rate. The presence of oxygen in a solution provides an additional reduction process, that is, an additional reaction to consume electrons. As stated earlier in this chapter, iron atoms going into solution leave electrons at the anodic sites, and the corrosion reaction can only go on as quickly as these electrons can be consumed in a cathodic reaction. Thus, the addition of oxygen allows more electrons to be consumed by an additional reduction reaction, and the corrosion rate of many metals increases.

The oxygen solubility in water as a function of temperature is shown in Table 7. The oxygen solubility decreases as temperature increases from 0 °C (32 °F) through 100 °C (212 °F). At the boiling point, all oxygen is stripped from the water, and the solubility essentially becomes zero. The corrosion rate of an oxygen-saturated solution based on oxygen solubility would be predicted to decrease with increasing temperature. This effect is often offset by increasing reaction kinetics as temperature increases; however, the corrosion rate drops rapidly at the boiling point because of a discontinuous drop in oxygen concentration.

Corrosion Rate Expressions and Allowances

Corrosion Rate Expressions. The term *corrosion rate* refers to the effect of general (or uniform) corrosion on a metal (or nonmetal) per unit of time. The type of corrosion rate expression used depends on the technical system and on the type of corrosion effect. Thus, corrosion rate can be expressed as (a) the mass of metal turned into corrosion products per unit area of surface per unit of time (weight loss), or (b) an increase in corrosion depth per unit time (penetration rate). The corrosion effect, which refers to a change in any part of the corrosion system (metal/environment combination), can vary with time and might not be the same at all points of the corroding surface. Reports of corrosion rates, therefore, should be accompanied by information on the type, time dependency, and location of the corrosion effect.

Weight-loss tests are the most common of all corrosion-test measurements for determining corrosion rates. A clean coupon is measured, weighed, exposed to the corrodent for a known time, removed, cleaned to remove corrosion products, and reweighed. The rate of metal removal due to corrosion is then calculated from:

$$R = KW/ATd$$

where R is the corrosion rate, K is a constant, W is weight loss in g to the nearest mg (corrected for any loss during cleaning), A is the area to the nearest 0.01 cm^2, T is time of exposure in hours to the nearest 0.01 h, and d is the density in g/cm^3.

Many different units are used to express the corrosion rate, R. Using the preceding units for W, A, T, and d, the corrosion rate can be calculated in a variety of units with the appropriate value of K:

Corrosion rate units desired (mpy)	Constant (K) in corrosion rate equation
Mils per year (mpy)	3.45×10^6
Inches per year (in./yr)	3.45×10^3
Inches per month (ipm)	2.87×10^2
Millimeters per year (mm/yr)	8.76×10^4
Micrometers per year (μm/yr)	8.76×10^7
Picometers per second (pm/s)	2.78×10^6
Grams per square meter per hour ($g/m^2/h$)	$1.00 \times 10^4 \times d$(a)
Milligrams per square decimeter per day (mdd)	$2.40 \times 10^6 \times d$(a)
Micrograms per square meter per second ($\mu g/m^2/s$)	$2.78 \times 10^6 \times d$(a)

(a) Density is not needed to calculate the corrosion rate in these units. The density in the constant K cancels out the density in the corrosion rate equation.

If desired, these constants can also be used to convert corrosion rates from one set of units to another. To convert corrosion rate in units, X, to a rate in units, Y, multiply by K_Y/K_X. For example, if R is 15 mpy, the rate in pm/s would be calculated from the following:

$$15\left(\frac{2.78\times10^6}{3.45\times10^6}\right) = 12.1 \text{ pm/s}$$

In the United States, the most widely used expression for quantitatively defining the rate of corrosion in mils per year (abbreviated mpy or mils/yr) and calculated from:

$$\text{Mils per year} = 534W/dAT$$

where W is the weight loss in mg; d is the density, g/cm^3; A is the specimen area, $in.^2$; and T is the exposure time, h. Throughout this book, metals and nonmetals are compared on the basis of their corrosion resistance measured in mpy and the appropriate metric equivalent.

Relationships among some of the units commonly used for corrosion rates are given in Table 8.

When to Use Metals and Alloys in Certain Corrosion Rates. As discussed in later chapters, different metals and alloys have varying corrosion rates depending, of course, on specific environments and environmental variables. Table 9 lists some general guidelines, which can serve as a starting point when trying to determine maximum corrosion rates for specific working conditions for cases of general (uniform) corrosion.

Corrosion Allowance. By knowing the expected general corrosion rate and the anticipated plant or service life of a part, the designer can calculate the extra wall thickness required for corrosion resistance of the process equipment being designed. After determining a wall thickness that meets mechanical requirements, such as pressure and weight of equipment, an extra thickness called a *corrosion allowance* is added to the wall thickness to compensate for the metal expected to be lost over the life of the equipment. Then, because the penetration depth can vary, a corrosion allowance is assigned a safety factor of 2.

As an example, suppose a tank wall required a 5 mm ($\frac{3}{16}$ in.) wall thickness for mechanical considerations. The designer has determined that the corrosion rate will be 15 mpy (0.4 mm/yr) and the expected life of the equipment will be 10 yr. The total corrosion allowance is the corrosion rate per year (0.4 mm, or 0.015 in.) × 10 yr = 4 mm (0.15 in.). The corrosion allowance is doubled to 0.3 in. (8 mm) as a safety consideration.

Table 8 Relationships among some units commonly used for corrosion rates

d is metal density in grams per cubic centimeter (g/cm^3).

	Factor for conversion to					
Unit	**mdd**	**$g/m^2/d$**	**μm/yr**	**mm/yr**	**mils/yr**	**in./yr**
Milligrams per square decimeter per day (mdd)	1	0.1	36.5/*d*	0.0365/*d*	1.144/*d*	0.00144/*d*
Grams per square meter per day ($g/m^2/d$)	10	1	365/*d*	0.365/*d*	14.4/*d*	0.0144/*d*
Microns per year (μm/yr)	0.0274*d*	0.00274*d*	1	0.001	0.0394	0.0000394
Millimeters per year (mm/yr)	27.4*d*	2.74*d*	1,000	1	39.4	0.0394
Mils per year (mils/yr)	0.696*d*	0.0696*d*	25.4	0.0254	1	0.001
Inches per year (in./yr)	696*d*	69.6*d*	25,400	25.4	1,000	1

Table 9 Characteristics and uses of corrosion rates

Penetration rate, mpy	**Characteristics and uses**
1 max	Very low corrosion; recommended for services where product contamination is a problem, e.g., food industry equipment
10 max	Low corrosion; recommended for thin-walled process equipment
20 max	Fairly low corrosion; can be considered the normal maximum allowed in chemical equipment
50 max	High corrosion; seldom tolerated except in thick-walled equipment where product contamination is controlled
Rates > 50	Excessive corrosion; very seldom tolerated and only then in very thick-walled equipment where massive product contamination is not a problem

The final wall thickness would be 0.3 + 0.1875 = 0.4875 in. (8 + 5 = 13 mm). The designer would then specify a ½ in. (13 mm) wall thickness as the closest standard plate available. Additional information on corrosion allowance calculations can be found in Chapter 7.

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CHAPTER 3

Principles of Aqueous Corrosion

CORROSION OF METALS in aqueous environments is electrochemical in nature involving two or more electrochemical reactions taking place on the metal surface. As a result, some of the elements of the metal or alloy change from a metallic state into a non-metallic state. The products of corrosion can be dissolved species or solid corrosion products; in either case, the energy of the system is lowered as the metal converts to a lower-energy form. Rusting of steel is the best known example of conversion of a metal (iron) into a nonmetallic corrosion product (rust). The change in the energy of the system is the driving force for the corrosion process, which behaves according to the laws of thermo-dynamics.

The thermodynamics of aqueous corrosion is the subject of the first half of this Chapter. Important concepts described include the following:

- Corrosion reactions and free-energy change
- The relationship between free energy and electrochemical potential
- The effect of ionic concentration on electrode potential
- The corrosion behavior of a metal based on its potential-pH diagram

As indicated above, corrosion is an electrochemical process. Electrochemical processes require anodes and cathodes in electrical contact and an ionic conduction path through an electrolyte (see, for example, Fig. 2 in Chapter 2). The electrochemical process includes electron flow between the anodic and cathodic areas; the rate of this flow corresponds to the rates of the oxidation and reduction reactions that occur at the surfaces.

Understanding the kinetics of corrosion and the factors that control the rates of corrosion reactions requires examination of the concepts of polarization behavior and identification of the various forms of polarization in an electrochemical cell. As described in the second half of this chapter (see the section "The Kinetics of Aqueous Corrosion"), these concepts include anodic and cathodic reactions, the mixed-potential theory, and the exchange currents.

The Thermodynamics of Aqueous Corrosion

Thermodynamics is a powerful science that defines which reactions are possible and whether a particular reaction will occur. It provides a sound basis for the understanding of corrosion phenomena and is central to the study of corrosion processes. This section identifies the important concepts of thermodynamics relevant to corrosion and discusses applications of those concepts.

Thermodynamics describes equilibria as a function of the elements and compounds present and the environmental conditions, such as pressure, temperature, and chemical composition. Thermodynamics is used to determine whether corrosion can occur and to predict the stable corrosion products that will form.

Thermodynamic concepts are referenced throughout this book to explain observed corrosion behavior. For example, copper will not corrode in a strong hydrochloric acid (HCl) solution if oxygen is not present; if oxygen is dissolved in the HCl, however, copper corrodes at a rapid rate. This behavior is readily explained using thermodynamic concepts.

Corrosion Reactions and Free-Energy Change

A law of nature is that the most stable state for a set of reactants is that state which has the lowest free energy. Consequently, a metal in contact with a solution moves toward the lowest free-energy state. When the system arrives at this state, there is no further change. This final, unique, lowest-energy state is called *equilibrium*. At equilibrium, the system is stable, and there is no driving force for any change from that state.

This concept can be demonstrated by considering the corrosion of iron in water. When iron is immersed in water, the corrosion reaction of interest is the reaction between iron atoms in the metal and the corrosion products of the iron that is, ferrous ions (Fe^{2+}) in solution. This reaction can be expressed as the following:

$$\text{Ferrous ion in solution} \xleftrightarrow{\text{Reacts}} \text{Iron atom in metal}$$

or

$$Fe^{2+} + 2e^{-} \leftrightarrow Fe$$

The reaction shows the equilibrium between dissolved ferrous ions in solution and metallic iron. The reaction can move either from left to right or from right to left. The first type of reaction results in ferrous ions combining with electrons to form new iron atoms at the metal surface. This is equivalent to a metal plating process. The reaction from right to left involves the removal of an iron atom from the metal surface with the formation of a new ferrous ion (Fe^{2+}) in solution. Two electrons are left at the iron surface for each iron atom that becomes a ferrous ion. This type of reaction is equivalent to corrosion and results in metal loss.

When at equilibrium, the reaction proceeds at the same rate in both directions, and there is no net change in ferrous ion concentration or weight loss of the iron. If the free energy of the system is lowered by a decrease in the ferrous ion concentration, then there is a greater driving force for the reaction to proceed from left to right, with a net reduction in ferrous ion concentration. As the reaction proceeds, the driving force is lowered, and the system moves toward its equilibrium state.

If, on the other hand, the system would have a lower free energy by increasing the concentration of ferrous ions in solution, there would be a driving force for the reaction to proceed from right to left. As this occurs, iron atoms at the metal surface react to form ferrous ions in solution. This reaction of iron atoms increases the ferrous ions in solution. Also, the driving force for further reaction would be decreased, and the system would move toward its equilibrium.

As stated previously, if the system is at equilibrium, there is no driving force for a net reaction from either left to right or right to left, and the ferrous ion concentration remains constant. This latter case is the specific concentration that results in equilibrium.

This phenomenon can be illustrated with the use of free-energy diagrams. Three diagrams are shown in Fig. 1; each represents one of the cases described above. On the diagrams, the free-energy change is identified as ΔG. The free energy of a ferrous ion in solution is represented

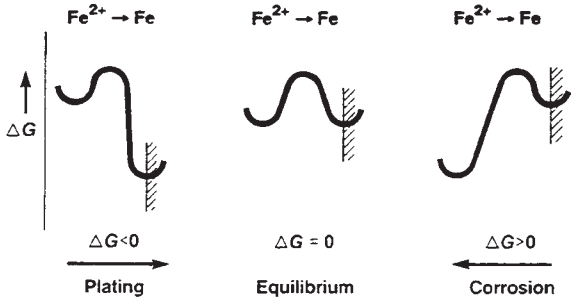


Fig. 1 Free-energy diagrams for reactions of ferrous ions and iron atoms

by the bottom of the trough under the Fe^{2+} symbol, and the free energy of an iron atom in the metal surface is shown by the bottom of the trough beneath the Fe symbol. In all cases, the reaction of a ferrous ion in solution to become an iron atom on the metal surface is considered. The net free-energy change for the reaction is shown by comparing the relative levels of the bottom of each trough. For the diagram on the left of Fig. 1, the trough for the ferrous ion in solution is more positive than the trough for the iron atom. This reaction proceeding from left to right results in a net decrease in free energy; that is ΔG is less than zero. For this case, the system could lower its free energy by the reaction of ferrous ions to form metal atoms on the surface; the plating process will occur. The reaction will proceed from left to right.

For the case shown in the diagram on the right of Fig. 1, the trough for the ferrous ion is more negative than the trough for the iron atom. The reaction of ferrous ions to form metal atoms will result in an increase in free energy; that is, ΔG is positive. This reaction as written will not proceed, because it involves an increase in free energy; rather, the reaction proceeds in the reverse direction. Iron atoms go into solution as ferrous ions, thus reducing the free energy of the system.

The diagram in the center of Fig. 1 represents the equilibrium condition. In this case, the trough for the ferrous ion is at the same level as the trough for the iron atom. Under these conditions, there is no change in free energy for the reaction from either right to left or left to right; that is, ΔG is equal to zero. For this case, there is no driving force for either the plating process or the corrosion process, and the system remains at the equilibrium state. The ferrous ion concentration in solution remains constant, and there is no corrosion of the iron in this solution. An iron sample exposed under these conditions would have the same weight after any length of exposure as it had on being immersed in the solution.

Another behavioral characteristic is that any system will move toward equilibrium. The system will react in a manner to offset any driving force for reactions, and equilibrium is eventually obtained when there is no net driving force, or $\Delta G = 0$, for the reaction in either direction. For the diagram on the left of Fig. 1, the ferrous ion concentration is greater than the equilibrium concentration. Because of this, there is a net driving force to consume some of those ferrous ions and to deposit metal atoms on the surface, thus reducing the ferrous ion concentration in solution. For the diagram on the right of Fig. 1, the ferrous ion concentration is lower than the equilibrium concentration. Because of this, there is a driving force for the production of ferrous ions by the removal of metal atoms from the surface and an increase in ferrous ion concentration, thus moving toward the equilibrium concentration.

To summarize, a metal in a solution has a characteristic free-energy change with respect to metal atoms at the surface of the metal and metal ions in solution, which is determined by such factors as the composition

of the metal, the chemical composition of the solution, temperature, and pressure. A law of nature is that systems react to minimize their free energy. The reactions between metal atoms at the metal surface and metal ions in solution proceeds to lower the free energy of the system. The reaction removes metal ions from solution and increases the metal atoms at the surface (metal plating) or proceeds to remove metal atoms from the surface and produces metal ions in solution (corrosion). The direction of the reaction depends on the relative change in free energy. When there is no difference in free energies between the metal atoms and the metal ions in solution, the system is at equilibrium and no further net reaction occurs.

The preceding discussion focuses on the equilibrium behavior of ferrous ions and iron. A general relationship for any metal ion in solution and the corresponding metal atom on the surface is:

$$M^{n+} + ne^- \leftrightarrow M$$

This general electrode reaction refers to the reaction of ions of the metal (M) with electrons to produce uncharged metal atoms of M on the metal surface. The charge of the metal ion and the number of electrons involved in the reaction are identified by *n* and is called "valence." The value of *n* is a characteristic of the particular metal. Electrode reactions for several metals with their corresponding values of *n* are presented in Table 1. The characteristic value for gold is 3+ and the characteristic value for iron and zinc is 2+. The characteristic value for aluminum is 3+. Some metals have alternative valences, and multiple values of *n* are listed, for example, *n* values of 1+ or 2+ for copper.

Free Energy and Electrochemical Potential

The relationship between free energy (ΔG) and electrochemical (or cell) potential (E) is described by the equation:

$$\Delta G = -nFE$$

where *n* is the number of electrons in the reaction and *F* is Faraday's constant. The free-energy change of the reaction is equal to the negative of the product of the number of the electrons in the reaction times a constant value (Faraday's constant) times the electrode potential. Large negative free-energy changes give rise to large positive potential differences, and large positive free-energy changes give rise to large negative potential differences. These terms are equivalent in that they both describe the magnitude of the driving force for a reaction to occur. Furthermore, at equilibrium, where there is no driving force for the reaction, both the free-energy change (ΔG) and the driving force in terms of potential (E)

Table 1 Electrode reactions of several metals and their ions

Metal	Electrode reaction(a)
Aluminum	$Al^{3+} + 3e^- \leftrightarrow Al$
Beryllium	$Be^{2+} + 2e^- \leftrightarrow Be$
Cadmium	$Cd^{2+} + 2e^- \leftrightarrow Cd$
Calcium	$Ca^{2+} + 2e^- \leftrightarrow Ca$
Chromium	$Cr^{3+} + 3e^- \leftrightarrow Cr$
	$Cr^{2+} + 2e^- \leftrightarrow Cr$
Cobalt	$Co^{2+} + 2e^- \leftrightarrow Co$
Copper	$Cu^{+} + e^- \leftrightarrow Cu$
	$Cu^{2+} + 2e^- \leftrightarrow Cu$
Gallium	$Ga^{3+} + 3e^- \leftrightarrow Ga$
Gold	$Au^{3+} + 3e^- \leftrightarrow Au$
Hafnium	$Hf^{4+} + 4e^- \leftrightarrow Hf$
Hydrogen	$2H^{+} + 2e^- \leftrightarrow H_2$
Indium	$In^{3+} + 3e^- \leftrightarrow In$
Iron	$Fe^{2+} + 2e^- \leftrightarrow Fe$
Lead	$Pb^{2+} + 2e^- \leftrightarrow Pb$
Lithium	$Li^{+} + e^- \leftrightarrow Li$
Magnesium	$Mg^{2+} + 2e^- \leftrightarrow Mg$
Manganese	$Mn^{2+} + 2e^- \leftrightarrow Mn$
Mercury	$Hg^{2+} + 2e^- \leftrightarrow 2Hg$
	$Hg_2^{2+} + 2e^- \leftrightarrow 2Hg$
Nickel	$Ni^{2+} + 2e^- \leftrightarrow Ni$
Palladium	$Pd^{2+} + 2e^- \leftrightarrow Pd$
Potassium	$K^{+} + e^- \leftrightarrow K$
Silver	$Ag^{+} + e^- \leftrightarrow Ag$
Sodium	$Na^{+} + e^- \leftrightarrow Na$
Thallium	$Tl^{+} + e^- \leftrightarrow Tl$
Tin	$Sn^{2+} + 2e^- \leftrightarrow Sn$
Titanium	$Tl^{2+} + 2e^- \leftrightarrow Ti$
Uranium	$U^{3+} + 3e^- \leftrightarrow U$
Zinc	$Zn^{2+} + 2e^- \leftrightarrow Zn$
Zirconium	$Zr^{4+} + 4e^- \leftrightarrow Z\rho$

(a) Note the characteristic value for n, i.e., the number of electrons

are equal to zero. In order to maintain the signs appropriate to those conventions, two procedures are followed:

- All reactions are written to consume electrons, e.g., for the reaction of ferrous ions plus electrons to produce uncharged metal atoms expressed as $Fe^{2+} + 2e^- \rightarrow Fe$.
- The relationship $\Delta G = -nFE$ is used.

Using these two procedures ensures that consistent values for potential and the proper sign for the driving force for a reaction are realized.

The relationships among free energy and potential and the significance to the direction in which a reaction will proceed are shown in Table 2. For the reaction of metal ions plus electrons to produce metal atoms at the surface, the values of ΔG and E determine whether the reaction is at equilibrium or proceeds spontaneously from left to right or from right to left. When the driving force for the reaction, expressed either as ΔG or E, is equal to zero, the system is at equilibrium, and there is no further net reaction. When the free-energy change is less than zero or when the difference in electrode potential is greater than zero, the reaction proceeds spontaneously from left to right; that is, the system re-

Table 2 Relationships among free energy, potential, and the direction in which the reaction ($M^{n+} + ne^- \leftrightarrow M$) will proceed

ΔG	E	Spontaneous net reaction
0	0	Equilibrium; no net reaction
<0 (negative)	>0 (positive)	Spontaneous reaction; left to right; plating
>0 (positive)	<0 (negative)	Spontaneous reaction; right to left; corrosion

acts with the consumption of metal ions and the production of metal atoms at the surface. When the free-energy change for the reaction is greater than zero or the difference in electrode potential is less than zero, the reaction proceeds spontaneously from right to left; that is, the reaction proceeds to remove metal atoms from the surface and produces metal ions in solution.

This relationship between free-energy and the thermodynamics of electrochemical potential is central to the study of corrosion. Through the measurement and control of electrode potential, the free energy can be measured and controlled. A consequence of this is that an instrument that allows the change and control of potential to desired values is essentially a free-energy pump. The direction of reaction and the thermodynamically stable species can be controlled by the control of electrode potential.

Tendency for Metals to Corrode

Each metal has a characteristic, inherent tendency to corrode or to react in an aqueous environment to produce metal ions. This inherent reactivity can be described in terms of either free-energy, ΔG, or electrochemical potential, E. The inherent reactivity of a metal can be expressed by the magnitude of the free-energy change on the metal going to a metal corrosion product. Table 3 presents the free-energy change for the reactions of four common metals to form their hydroxides. The first reaction is for magnesium reacting with water and oxygen to form a solid corrosion product, that is, magnesium hydroxide. The second reaction is for iron reacting with water and oxygen to form ferrous hydroxide, and the third is for copper reacting with water and oxygen to form cuprous hydroxide.

The free-energy change, ΔG, measured in joules, is presented for each of these reactions. A negative value for the free-energy change indicates that the metal will react spontaneously to form the corrosion

Table 3 Inherent reactivity of four metals expressed as the magnitude of free-energy change for a given corrosion reaction

Metal	Corrosion reaction	ΔG, kJ
Magnesium	$Mg + H_2O(l) + \frac{1}{2}O_2(g) \leftrightarrow Mg(OH)_2(s)$	–597
Iron	$Fe + H_2O(l) + \frac{1}{2}O_2(g) \leftrightarrow Fe(OH)_2(s)$	–249
Copper	$Cu + H_2O(l) + \frac{1}{2}O_2(g) \leftrightarrow Cu(OH)_2(s)$	–120
Gold	$Au + \frac{3}{2}H_2O(l) + \frac{3}{4}O_2(g) \leftrightarrow Au(OH)_3(s)$	+66

product. It is important to note again that while thermodynamics indicates that a reaction will occur, it does not provide any information as to the rate of reactions. A positive free-energy change means that the reaction of the metal is not spontaneous and will not occur. The more negative the value of ΔG, the greater the inherent reactivity of the metal. A comparison of the free-energy change values for each reaction in Table 3 indicates that magnesium is the most reactive metal, followed by iron and copper. The positive value for the free-energy change of gold, whose corrosion reaction is also shown in Table 3, indicates that gold will not spontaneously react in the presence of water and oxygen. Gold is referred to as being noble or immune from attack under these conditions whereas magnesium, iron, and copper are active and will corrode.

Effect of Ionic Concentration on Electrode Potential

Understanding the effect of ion concentration on electrode potential is facilitated by reference to the reaction $Fe^{2+} + 2e^- \rightarrow Fe$, which shows that ferrous ions (Fe^{2+}) plus two electrons ($2e^-$) can be reduced to metallic iron (Fe). The Nernst equation, which is useful for determining the effect of ionic concentration on the electrode potential for such a reaction, is expressed as the following:

$$E = E^0 - \frac{RT}{nF} \ln \frac{(\text{red})}{(\text{ox})} \qquad \text{(Eq 1)}$$

where E is the electrode potential, E^0 is the standard electrode potential, R is the gas constant, T is the absolute temperature (in degrees Kelvin), n is the number of electrons involved in the reaction, F is the Faraday constant, and (red) and (ox) are the concentrations of reduced and oxidized species, respectively. The standard electrode potential is determined for the special condition of all elements in the reaction in a pure state and all ions at 1 M concentration. Electrode potential increases or decreases from the value of the standard electrode potential based on the ratio of concentration of the reduced species, in this case iron, and the concentration of the oxidized species, in this case the ferrous ion.

For the ferrous ion reduction to iron reaction expressed as:

$$E = -0.440 - \frac{0.059}{2} \log \frac{\text{Fe}}{\text{Fe}^{2+}} \qquad \text{(Eq 2)}$$

the standard electrode potential is –0.440 V with respect to the standard hydrogen electrode (SHE). At 25 °C (75 °F), the value for the constant 2.3 times RT divided by F is 0.059. The 2.3 factor converts the natural log (ln) to log base 10 (log). The value for n in this equation is 2. The activity or concentration of a pure solid phase, for example, iron, is equal to 1.

The final equation for the electrode potential as a function of concentration can be expressed as the following:

$$E = -0.440 + 0.030 \log Fe^{2+} \quad \text{(Eq 3)}$$

This equation indicates that an order of magnitude, or factor of 10, increase in the ferrous ion concentration increases the electrode potential by 0.030 V. Conversely, a decrease in the ferrous ion concentration by a factor of 10 decreases the electrode potential by 0.030 V.

The effect of concentration on the equilibrium electrode potential of two reactions is shown in Table 4. The ferrous ion reduction reaction is considered first. The standard electrode potential value is determined when pure iron is in equilibrium with ferrous ions at a 1 *M* concentration (unit activity). This is the value of –0.440 V-SHE. If the ferrous ion concentration is decreased by a factor of 1000, or three orders of magnitude, the resulting ferrous ion concentration is 10^{-3}, and the electrode potential is decreased to –0.530 V-SHE. For an additional decrease in concentration by three orders of magnitude to 10^{-6}, the corresponding electrode potential is –0.620 V-SHE, and for a concentration of 10^{-9} *M* ferrous ion concentration, the electrode potential is equal to –0.710 V-SHE. These values are calculated from Eq 1, 2, and 3.

Similar calculations for the ferric ion reduction to ferrous ions yields the values shown at the bottom of Table 4. The reduction reaction involves the reaction of a ferric ion plus one electron being reduced to a

Table 4 Effect of concentration on equilibrium electrode potential

Ferrous ion reduction

Ferrous ion + 2 electrons → iron

$Fe^{2+} + 2e^- \rightarrow Fe$

$$E = -0.440 - \frac{0.059}{2} \log\left(\frac{1}{Fe^{2+}}\right)$$

Ferrous ion, molar	*E*, V-SHE
1	–0.440
10^{-3}	–0.530
10^{-6}	–0.620
10^{-9}	–0.710

Ferric ion reduction

Ferric ion + 1 electron → ferrous ion

$Fe^{3+} + e^- \rightarrow Fe^{2+}$

$$E = 0.771 - 0.059 \log\left(\frac{Fe^{2+}}{Fe^{3+}}\right)$$

Ferrous ion, molar	Ferric ion, molar	*E*, V-SHE
1	1	+0.771
10^{-6}	10^{-12}	+0.417
10^{-6}	10^{-3}	+0.948

ferrous ion. The standard electrode potential for this reaction is determined for ferrous ions at 1 *M* concentration and ferric ions at 1 *M* concentration. The standard electrode potential for the ferric ion reduction is +0.771 V-SHE. For a ferrous ion concentration of 10^{-6} *M* and a ferric ion concentration of 10^{-12} *M*, the electrode potential is +0.417 V-SHE. For a ferrous ion concentration of 10^{-6} *M* and a ferric ion concentration of 10^{-3} *M*, the potential is +0.948 V-SHE. It is apparent that the equilibrium electrode potential for a reaction is quite sensitive to the concentration of the ions involved in the reaction.

The equilibrium electrode potential is the value at which the oxidized and reduced species in the reaction are at equilibrium, and the potential at which both can be present and stable at the stated concentrations. This is demonstrated in Fig. 2. For the reaction of ferrous ions being reduced to iron, the standard electrode potential is –0.44 V-SHE. This is for a concentration of ferrous ions equal to 1 *M*. The significance of this value is that at –0.44 V-SHE, the iron and ferrous ions of 1 *M* concentration (unit activity) coexist or are at equilibrium. That is to say, with time there will be no net change in the weight of iron immersed in the solution, and there will be no net change in the concentration of ferrous ions in the solution. At a potential more positive than –0.44 V-SHE, the oxidized species or ferrous ion is stable. At a potential more negative than –0.44 V-SHE, the reduced species is stable, that is, iron.

The equilibrium electrode potential defines the boundary between the stable oxidized species and the stable reduced species. At a potential value on the boundary, the oxidized species and reduced species are both stable and can coexist. At a potential more positive than the boundary value, the oxidized species is stable and the reduced species reacts to form more of the oxidized species. At a potential more negative than the boundary value, the reduced species is stable and any oxidized species present reacts to form more reduced species.

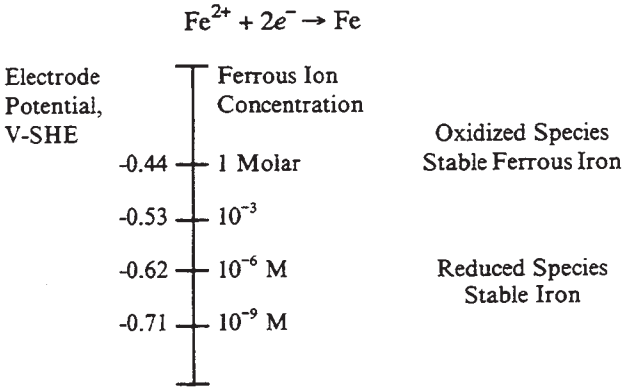


Fig. 2 Effect of concentrations on the boundary between a stable oxidized species (ferrous ions) and a stable reduced species (iron)

The values calculated for the equilibrium electrode potential at various ferrous ion concentrations are given in Table 4 and are plotted on the electrode potential axis in Fig. 2. As the ferrous ion concentration decreases, the equilibrium electrode potential decreases. The effect of this is that the boundary between the oxidized species (ferrous ion) and the reduced species (iron) moves to more negative electrode potentials.

The following behavior is predicted by these calculations. A pure iron rod put into an aqueous environment at –0.71 V-SHE can corrode until the ferrous ion concentration increases to 10^{-9} *M*. At this point, the iron and ferrous ion concentration are at equilibrium, and no further net reaction will occur. If the potential of the iron is then made more positive, for example, –0.53 V-SHE, the iron can again corrode and the ferrous ion concentration can increase to 10^{-3} *M*. A new equilibrium is established, and the iron is at equilibrium with no net reaction occurring. Now, however, the iron is in contact with a solution whose ferrous ion concentration is equal to 10^{-3} *M*.

In summary, the calculation of electrode potential based on thermodynamic data and the Nernst equation (Eq 1) is most useful in determination of the boundaries between stable oxidized species and stable reduced species. The equilibrium electrode potential values are a function of the temperature and concentration of oxidized species and reduced species. The Nernst equation provides a sound thermodynamic basis on which the effect of concentration can be determined.

Electromotive Force Series

As described in Chapter 2, the electromotive force (emf) series ranks metals with respect to their inherent reactivity. The metals are placed on the series in the descending order of standard electrode potentials. The metals with the most positive values are placed at the top of the series, and the values of electrode potential descend through zero and to larger negative values. The values for standard electrode potential are determined using the Nernst equation for a metal in contact with a solution of its own ions at a 1 *M* concentration. The values determined under these specific conditions are used to generate the electromotive force series.

The standard electrode potential for hydrogen ion reduction to hydrogen gas is defined as the 0.0 reference state by international convention. All other electrode potentials are calculated with respect to this reference state. The standard electrode potentials for the emf series in Table 5 range from 1.5 V versus V-SHE for the reaction of gold ions to gold to a large negative value of –2.37 V-SHE for the reaction of magnesium ions with magnesium. This wide range of potential values indicates a wide range in inherent tendencies to corrode. The more noble metals are at the more positive values. The more active metals, those prone to corrosion, are at the more negative values.

Table 5 Standard electrode potential for selected metals at 25 °C (75 °F)

Electrode reaction	Standard potential, V-SHE
$Au^{3+} + 3e^- \leftrightarrow Au$	1.50
$Ag^+ + e^- \leftrightarrow Ag$	0.800
$Cu^{2+} + 2e^- \leftrightarrow Cu$	0.337
$2H^+ + 2e^- \leftrightarrow H_2$	0.000 (Reference)
$Pb^{2+} + 2e^- \leftrightarrow Pb$	–0.126
$Sn^{2+} + 2e^- \leftrightarrow Sn$	–0.136
$Ni^{2+} + 2e^- \leftrightarrow Ni$	–0.250
$Cd^{2+} + 2e^- \leftrightarrow Cd$	–0.403
$Fe^{2+} + 2e^- \leftrightarrow Fe$	–0.440
$Zn^{2+} + 2e^- \leftrightarrow Zn$	–0.763
$Al^{3+} + 3e^- \leftrightarrow Al$	–1.66
$Mg^{2+} + 2e^- \leftrightarrow Mg$	–2.37

A more comprehensive listing of electrode potentials can be found in the table of the electromotive force series in Chapter 2.

For any given metal, the standard electrode potential represents the potential at which the metal is at equilibrium with its own ions at a 1 *M* concentration. At a potential more positive than this value, the metal ion is stable and the metal would react spontaneously to form more metal ions. At potentials more negative than the standard electrode potential, the metal is stable, and no corrosion is predicted. It is important to note that the emf series is for these special circumstances and would not be used by itself to predict the likelihood of corrosion in a practical case.

Galvanic Series

The galvanic series is a ranking of metals from the most noble to the most active in a specific environment. Table 6 presents a galvanic series of several commercial metals and alloys in seawater. As in the emf series, the most noble, or cathodic, metals are listed at the top of the series. The ranking proceeds downward to the most active, or anodic, metals.

The general positions of metals on the galvanic series and the emf series are similar. Gold and silver are at the most noble end of the series, and magnesium and zinc are at the most active end. However, there are several important shifts of metals in the galvanic series. The principal reason for a shift in the position of a metal or alloy is that some metals and alloys develop stable protective corrosion product films as they react with an aqueous environment. When such a film forms, an alloy is referred to as being in the passive condition. Stainless steels and titanium are two examples of this class of material. The relative position in the galvanic series varies greatly depending on whether the metal is in the active (corroding) or passive (protected) condition. Note in Table 6 the large shift in position for an 18-8 stainless steel (a widely used corrosion-resistant, austenitic 18-8 alloy) in the active condition to a much more noble position in the passive condition.

The galvanic series is quite useful in determining the likelihood of detrimental corrosion effects when dissimilar metals are coupled. The

Table 6 Galvanic series of selected commercial metals and alloys in seawater

Noble or cathodic end of series
Platinum
Gold
Graphite
Titanium
Silver
Chlorimet 3 (62Ni-18Cr-18Mo)
Hastelloy C (62Ni-17Cr-15Mo)
18-8Mo stainless steel (passive)
18-8 stainless steel (passive)
Chromium stainless steel 11-30% Cr (passive)
Inconel (passive) (80Ni-13Cr-7Fe)
Nickel (passive)
Silver solder
Monel (70Ni-30Cu)
Cupronickels (60-90Cu, 40-10Ni)
Bronzes (Cu-Sn)
Copper
Brasses (Cu-Zn)
Chlorimet 2 (66Ni-32Mo-1Fe)
Hastelloy B (60Ni-30Mo-6Fe-1Mn)
Inconel (active)
Nickel (active)
Tin
Lead
Lead-tin solders
18-8Mo stainless steel (active)
18-8 stainless steel (active)
Ni-Resist (high-nickel cast iron)
Chromium stainless steel, 13% Cr (active)
Cast iron
Steel or iron
Aluminum alloy 2024
Cadmium
Aluminum alloy 1100
Zinc
Magnesium and magnesium alloys
Active or anodic end of series

farther apart two metals are on the galvanic series, the more likely that detrimental galvanic corrosion will occur. When two metals are in electrical contact, the metal at the more noble position in the series becomes the cathode of an electrochemical cell, and the metal in the more active position (lower in the series) becomes the anode and thus corrodes more rapidly. For example, a galvanic couple between platinum and magnesium is disastrous. The more noble platinum greatly accelerates the corrosion of the very active magnesium. Graphite coupled to steel significantly increases the corrosion rate of steel in seawater. When two metals are closer together in the galvanic series, the detrimental galvanic effect is lessened.

Several cautions must be recognized when applying the galvanic series. The galvanic series is a ranking of materials for a specific environment under a specific set of conditions. Application of a particular series to a different set of conditions or to a different environment is dangerous and can lead to erroneous predictions. The most common galvanic series is for metals and alloys in nonflowing seawater. Such a ranking system must never be used for predicting corrosion behavior in,

for example, a strongly acidic environment. More detailed information on the galvanic series, including its inherent limitations, can be found in Chapter 4 (in the description of galvanic corrosion).

Standard Electrode Potentials for Other Reactions

The emf series presents standard electrode potentials for metals in equilibrium with their own ions. Many practical cases involve additional reactions that are of interest in an operating corrosion cell (see Table 7). Most notable of these reactions are the electrode potentials for the oxygen reduction reactions. Oxygen reacting with hydrogen ions in solution plus electrons can produce water. The standard electrode potential for this reaction is +1.229 V-SHE. An alternative presentation for the reduction of oxygen in alkaline solutions is the reaction of oxygen plus water plus electrons to produce hydroxyl ions. The standard electrode potential for this reaction is +0.401 V-SHE.

These electrode potential values along with those presented in the emf series are useful in determining the maximum cell voltage in a corrosion cell made up of two different reactions. The more positive member of the cell is the cathode, and the reaction proceeds in the direction that consumes electrons. The more negative member of the cell is the anode, and the reaction proceeds in the oxidation direction, or the direction that produces electrons.

Using values of the standard electrode potentials and the Nernst equation (Eq 1) to determine the effect of ionic concentration on electrode potentials, the electrode potentials for the reactions of interest can be determined. Such determination provides a powerful tool for predicting the likelihood of corrosion and calculating the driving force for the corrosion reactions, that is, the potential difference between the anode and the cathode.

Potential-pH Diagrams: General Aspects

One of the most important steps in the science of electrochemical corrosion was the development of diagrams showing thermodynamic conditions as a function of electrode potential (E) and concentration of hydrogen ions, that is, pH. These potential-pH diagrams present a map of the regions of stability of a metal and its corrosion products in aqueous environments. The diagrams identify conditions under which (a) the

Table 7 Additional standard electrode potentials

Electrode reaction	Standard potential at 25 °C (75 °F), V-SHE
$O_2 + 4H^+ + 4e^- \leftrightarrow 2H_2O$	+1.229
$Fe^{3+} + e^- \leftrightarrow Fe^{2+}$	+0.771
$O_2 + 2H_2O + 4e^- \leftrightarrow 4OH^-$	+0.401
$Cu^{2+} + e^- \leftrightarrow Cu^+$	+0.153

metal is stable and will not corrode, (b) soluble reaction products are formed and corrosion will occur, and (c) insoluble reaction products are formed and passivity will occur. The diagrams are generated from thermodynamic calculations; they are not determined experimentally by conducting corrosion tests.

Potential-pH diagrams are calculated primarily for pure metals in pure water at 25 °C (75 °F). Advances and extensions of the diagrams have been made to include other ionic species and temperatures. These diagrams are also called Pourbaix diagrams in honor of Marcel Pourbaix, a Belgian scientist credited with the development and wide use of these diagrams.

Before a discussion of the behavior of specific metals is presented, the format of a potential-pH diagram is described. Figure 3 shows the potential-pH diagram for water with no metal involved. The horizontal axis identifies the pH of the solution. The solutions range from acid conditions at the left (pH 0 to 7) to alkaline solutions at the right (pH 7 to 14). In the middle of the diagram are relatively neutral solutions (pH 5 to 9). The vertical axis is used to plot the oxidizing power (electrode potential) of the solution. These values range from strongly reducing solutions with large negative potentials, for example, –1.2 V-SHE, to strongly oxidizing solutions with large positive potentials, for example, +1.2 V-SHE.

The two diagonal lines, identified as (a) and (b), define the region of stability of water as a function of potential and pH. For any value of potential and pH above line (b), water is thermodynamically unstable with respect to the evolution of oxygen. At any conditions of potential and pH below line (a), water is thermodynamically unstable with respect to the generation of hydrogen gas. For potential and pH conditions between lines (a) and (b), water is thermodynamically stable.

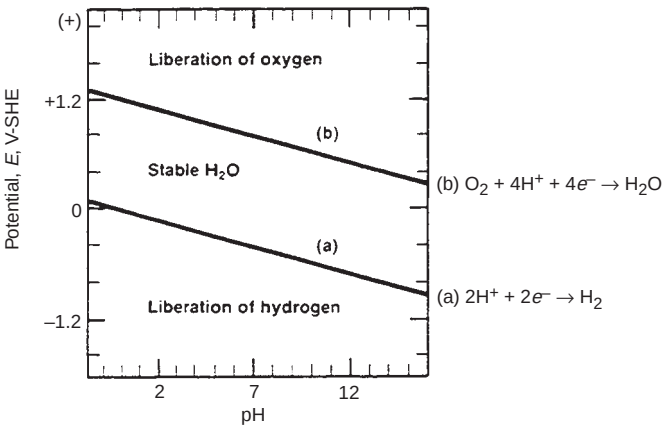


Fig. 3 Potential-pH diagram for water

Line (a) represents the equilibrium for the reaction of hydrogen ions to evolve hydrogen gas:

$$2H^+ + 2e^- \rightarrow H_2$$

Using the Nernst equation, the equation for this line is as follows:

$$E = 0.00 - 0.059\ pH$$

The potential at pH 0 is 0.0, and the potential decreases by 0.059 V for each unit increase of pH. At any potential and pH below this line, the hydrogen ion in water will react with electrons to evolve hydrogen gas.

Line (b) represents the equilibrium of oxygen plus hydrogen ions and electrons to form water:

$$O_2 + 4H^+ + 4e^- \rightarrow H_2O$$

Based on the Nernst equation, the equation for this equilibrium is as follows:

$$E = 1.229 - 0.059\ pH$$

The potential is +1.229 V-SHE at pH 0 and decreases by 0.059 V for every unit increase in pH. Above line (b) the oxidized species are stable, and water under those conditions reacts spontaneously to produce oxygen and hydrogen ions.

The diagram shown in Fig. 3 describes the thermodynamic stability of water and predicts what will occur on a metal surface in contact with water at the full range of potentials and pHs covered by the diagram. If a metal electrode is at a potential and pH below line (a), the water is in an unstable region, and with time, bubbles will evolve on the metal surface. Analysis of these bubbles would show that the gas evolved on the electrode under such conditions is hydrogen. Similarly, for any metal electrode potential-pH condition above line (b), gas evolution will again be observed. Analysis of the gas bubbles under these conditions would show that the evolved gas is oxygen. For any potential-pH condition between lines (a) and (b), water is thermodynamically stable, and no gas evolution would be observed.

In dealing with the stability of metals in aqueous solutions, the thermodynamic stability of water is central to discussion of corrosion. Because of this, and to give points of reference, the lines (a) and (b) are included (although not always labeled) on most of the potential-pH diagrams shown in the remainder of this Chapter.

The potential-pH diagram can be divided into four regions that describe the general categories of aqueous solutions. As shown in Fig. 4,

the diagram can be divided vertically at pH 7. Solutions to the left are acidic, and those to the right are alkaline. The diagram can be further divided along a diagonal line. The upper region is oxidizing, the lower region is reducing. Based on this classification, solutions with potentials and pHs in the upper left of the diagram are characterized as being oxidizing and acidic, and those in the upper right are characterized as oxidizing and alkaline. Those to the lower left are reducing and acidic, and those to the lower right are reducing and alkaline. It is important to note that these are relative descriptions used to compare aqueous solutions with one another.

Even though the thermodynamic calculations are based on pure water, potential-pH diagrams can be related to many practical situations with more complex solutions. Figure 5 presents typical pH values for some common solutions, ranging from highly acidic environments, such as battery acid and lemon juice, through mildly acidic solutions, such as boric acid. The figure also shows the neutral solutions, such as milk, through mildly alkaline solutions, such as sodium bicarbonate and borax, and the more highly alkaline solutions, such as sodium hydroxide. The approximate locations of several common environments on the potential-pH diagrams are shown in Fig. 6. Nitric acid (HNO_3) is a strongly oxidizing acid, and solutions of HNO_3 have potential-pH values

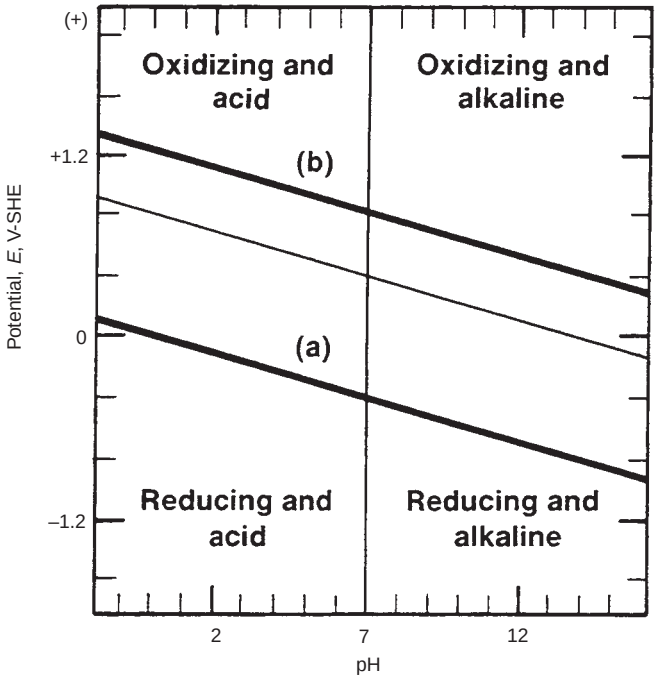


Fig. 4 General categories of aqueous solutions. The diagonal line between lines (a) and (b) separates the oxidizing and reducing regions of the diagram.

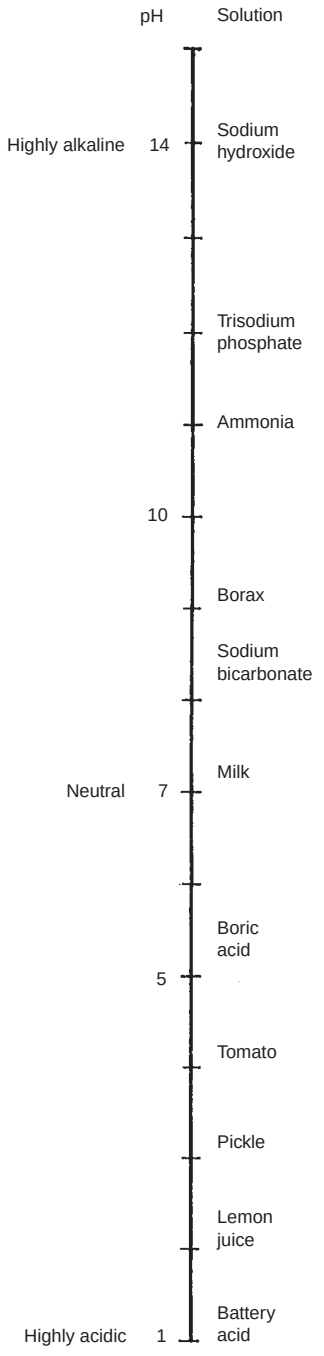


Fig. 5 Range of pH values for some common solutions

in the upper left portion of the diagram. Hydrochloric acid is a strongly reducing acid, and its solutions have potential-pH values at the lower left region of the diagram. Oxygen dissolved in HCl increases the oxidizing power and shifts the potential-pH to somewhat more positive values.

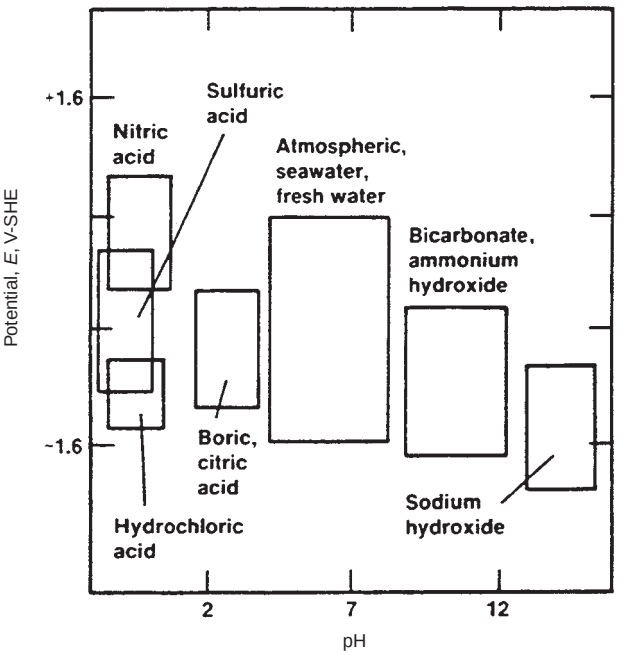


Fig. 6 Approximate locations of several common environments on a potential-pH diagram

Sulfuric acid (H_2SO_4) is a strong acid, yielding low pHs. The oxidizing power of H_2SO_4 solutions range from mildly reducing to moderately oxidizing. Boric and citric acids represent weak acids and are located to the right of the stronger acids on the diagram. Seawater, fresh water, and atmospheric exposures result in nominally neutral conditions and moderately oxidizing conditions.

Bicarbonate and ammonium hydroxide solutions (NH_4OH) are mildly alkaline and are located just to the right of center in the diagram. Sodium hydroxide (NaOH) forms strongly alkaline environments, and these solutions are located to the extreme right of the diagram.

The general behavior of metals in a variety of solutions can often be more easily understood when related to potential-pH diagrams on this basis. The environment determines the general location on the potential-pH diagram. The unique diagram predicts the behavior of a metal in that potential-pH region.

Potential-pH Diagrams for Specific Metals

The following paragraphs describe the corrosion (potential-pH) behavior of iron, gold, copper, zinc, aluminum, and titanium. Potential-pH diagrams for some 90 pure elements are available in the *Atlas of Electrochemical Equilibria in Aqueous Solution* by M. Pourbaix, published by

NACE International (see the Selected References at the conclusion of this Chapter).

The potential-pH diagram for iron is shown in Fig. 7. The diagram is a map of the regions of immune, passive, and corrosion behavior for iron as a function of potential and pH. Four distinct regions are shown. The region at the bottom of the diagram represents the conditions where iron is immune and no corrosion occurs. Under these conditions, iron is thermodynamically stable. This region covers reducing conditions (negative potentials) across the entire pH range, from acid to alkaline. For any potential-pH combination in this region, iron is stable and does not corrode.

The two narrow-banded, cross-hatched areas represent regions where iron corrodes. In both the region to the left (oxidizing and acidic) and the small region to the extreme right (reducing and highly alkaline), iron reacts to form soluble products, and corrosion continues. The shaded area represents a region of passivity for iron. Under oxidizing conditions in neutral to alkaline solutions, iron reacts to form insoluble products and further corrosion reaction is blocked by a protective film. An assumption of the potential- pH diagram is that any insoluble product will be protective. In practice, this is not always the case, and caution must be exercised when using these diagrams for practical applications. For example, the insoluble product on titanium yields a stable passive film. On iron, however, the insoluble products are often porous and not protective in many environments.

Potential-pH diagrams allow presentation of a large amount of information in a compact and efficient format. For instance, a single diagram (Fig. 7) describes the general corrosion behavior of iron. Iron is a relatively active metal and corrodes under reducing, moderately oxidizing, and strongly oxidizing conditions in strong acids. In weak acids, iron

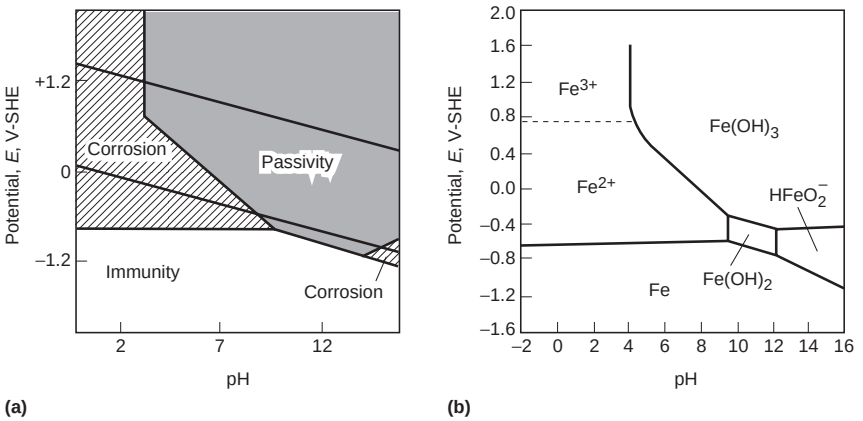


Fig. 7 Simplified potential-pH diagrams for iron at 25 °C (75 °F) showing (a) areas of immunity (no corrosion), passivity, and corrosion, and (b) reaction/corrosion products produced

again corrodes under reducing and moderately oxidizing conditions; however, iron can become passive if the oxidizing conditions are increased to a high enough level. Under neutral and mildly alkaline conditions, iron does not corrode, because it either is immune under strongly reducing conditions or is in a passive state for more oxidizing conditions. In strong alkaline environments, iron is free from corrosion except for the small region of potentials and pHs where a soluble, alkaline, corrosion product forms.

This general behavior relates fairly well to what is observed in several common environments (Fig. 6). Iron is attacked by strong acids, such as HCl and HNO_3. In neutral and mildly alkaline environments, iron is either immune from attack or is protected from corrosion by the formation of passive films. In highly concentrated NaOH solutions, iron exhibits severe corrosion, which is again in agreement with the small region of corrosion predicted by the potential-pH diagram for iron.

The specific reactions represented by the lines on the potential-pH diagram for iron are discussed in more detail in the section on construction of these diagrams. The thermodynamically stable species in the immune region is metallic iron. The thermodynamically stable species in the acid corrosion regions are ferrous ions (Fe^{2+}) and ferric ions (Fe^{3+}). Both ferric and ferrous ions are soluble. The thermodynamically stable species for the alkaline corrosion region is hypoferrite ion ($HFeO^{2-}$). In the passive range, the insoluble corrosion products that are thermodynamically stable are oxides or hydroxides of iron, for example Fe_3O_4 and Fe_2O_3.

***E*-pH of Gold.** The potential-pH diagrams for gold and iron are shown in Fig. 8. The diagram of iron is repeated in each of these comparisons as a frame of reference showing the relative locations of the regions of stability. It is readily apparent that gold is a much more noble metal than iron. The evidence for this is the wide region of immunity of gold,

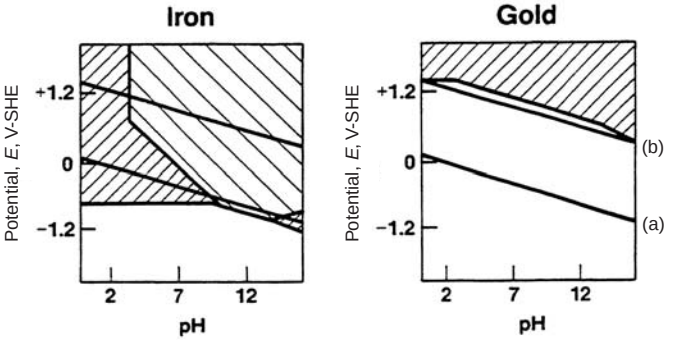


Fig. 8 Potential-pH diagrams for iron and gold. The broad-banded, cross hatched area in the iron *E*-pH diagram represents a region of passivity. The narrow-banded cross-hatched areas represent where iron and gold will corrode.

extending to the most oxidizing conditions and beyond line (b) on the diagram, which represents oxygen evolution. Gold is thermodynamically stable and will not corrode under a wide range of conditions, from highly acid to highly alkaline and from reducing to strongly oxidizing. The corrosion region for gold extends from highly acid to highly alkaline only at extremely high oxidizing conditions.

This is consistent with the observed behavior of gold. Gold is a noble metal and immune from attack, Gold occurs naturally in the surface of the earth in the metallic state. To corrode or dissolve gold requires use of highly oxidizing solutions, such as aqua regia, which is a mixture of concentrated HNO_3 (providing a strongly oxidizing environment), and H_2SO_4 and HCl (to break down surface films.) Iron will corrode readily under a wide range of potential-pH conditions (predominantly acid), while gold is generally immune to corrosion.

***E*-pH of Copper.** The potential-pH diagrams for iron and copper are shown in Fig. 9. Copper is a moderately noble metal, with its region of immunity extending above line (a), which represents the line for evolution of hydrogen gas. Copper will corrode under mildly acidic and strongly acidic conditions when the oxidizing power of the environment is moderate to high. Copper will also corrode in strongly alkaline conditions under moderately to highly oxidizing potentials. Copper is resistant to corrosion under neutral to mildly alkaline conditions, because it is immune under reducing conditions and develops protective films (and thus becomes passive) under more oxidizing conditions.

Copper is more corrosion resistant than iron under reducing and moderately oxidizing conditions. In a strong acid, iron will corrode in either the deaerated or aerated condition. In contrast, copper is immune from attack under highly reducing, strongly acidic conditions but will corrode under moderately oxidizing, strongly acidic conditions. These conditions are indicated by the arrows on each diagram in Fig. 9. This is consistent with observed behavior. Copper will not corrode in strong HCl acid in the absence of dissolved oxygen or other oxidizing species but will corrode readily in the presence of dissolved oxygen. The addi-

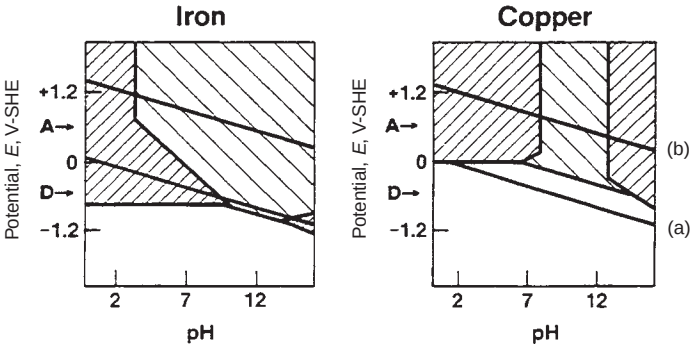


Fig. 9 Potential-pH diagrams for iron and copper. A, aerated; D, deaerated

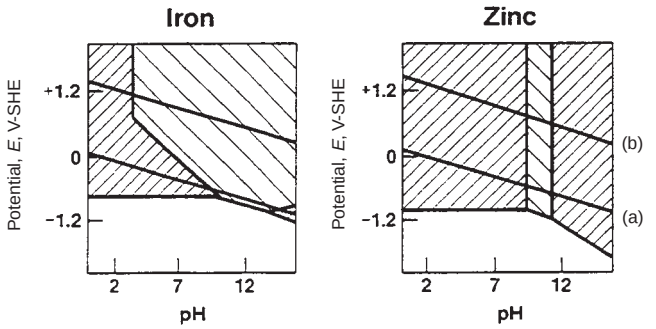


Fig. 10 Potential-pH diagrams for iron and zinc

tion of oxygen to the corrosive environment is sufficient to increase the oxidizing condition and to shift copper from a potential-pH in the immune region to a potential-pH in a corrosion region.

***E*-pH of Zinc.** The potential-pH diagrams for iron and zinc are shown in Fig. 10. Zinc is a more active metal than iron. This is indicated by the immune region for zinc being displaced to significantly lower levels than that for iron. Zinc will exhibit active corrosion under acidic conditions ranging from reducing through highly oxidizing and in strongly acidic up through neutral environments. Zinc also sustains attack and forms soluble corrosion products under strongly alkaline conditions. Zinc resists corrosion in mildly alkaline conditions due to the formation of passive films.

This is consistent with the observed corrosion behavior of zinc. Zinc, an active metal, is used extensively for sacrificial cathodic protection of iron and for exposed surfaces in atmospheric corrosion, where it develops a passive film. Zinc is not used for structural purposes under strongly acidic or strongly alkaline conditions.

***E*-pH of Aluminum.** The potential-pH diagrams for iron and aluminum are shown in Fig. 11. Aluminum is more active than iron or zinc; its immune region is at the lower extremes of the diagram. Aluminum corrodes

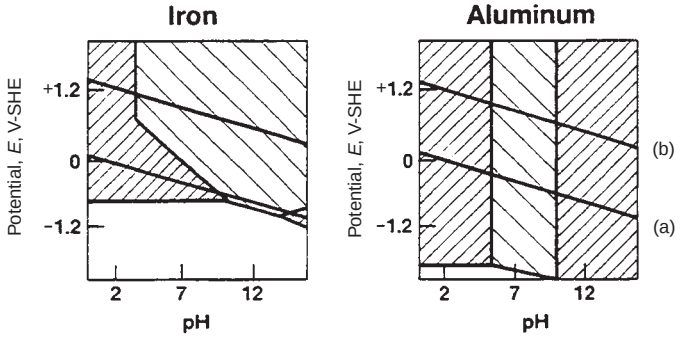


Fig. 11 Potential-pH diagrams for iron and aluminum

in mildly and strongly acidic and in mildly and strongly alkaline environments. The insoluble corrosion products are stable under neutral conditions and a wide range of oxidizing conditions. This passive range over neutral conditions is responsible for the wide use of aluminum and aluminum alloys for structural purposes. When these alloys are being used, strongly alkaline or strongly acidic conditions must be avoided.

***E*-pH of Titanium.** The potential-pH diagrams for iron and titanium are shown in Fig. 12. Titanium is an extremely active metal, and its immune region is nearly off the bottom of the potential-pH diagram. The excellent corrosion resistance of titanium and titanium alloys in a wide range of solutions can be attributed to the tenacious, passive film that forms on them. The passive region extends over the entire range of pH, from highly acidic to highly alkaline, under moderately reducing to highly oxidizing conditions.

Titanium does have a corrosion region under reducing and highly acidic conditions, as shown at the lower left region of the diagram. Titanium will corrode under these conditions, as demonstrated by the attack it undergoes in warm deaerated hydrochloric acid. This environment is highly acidic and strongly reducing and results in the breakdown of the protective film that forms on titanium, followed by significant corrosion.

Comparison of *E*-pH Diagrams for Metals. The potential-pH diagrams for several metals in water at 25 °C (75 °F) are shown in Fig. 13. Metals exhibit a wide range of corrosion behaviors, extending from the noble alloys—such as gold, iridium, and platinum—to extremely active metals—for example, beryllium, zinc, and aluminum. Some of the active metals can be used in many corrosion applications because of the formation of insoluble corrosion products and the development of protective passive films. It is important to realize, however, that it is the integrity of these protective films that is being relied on for the corrosion resistance of these materials. A much more reliable practice is the application of immune metals, where corrosion resistance is imparted by thermodynamic stability.

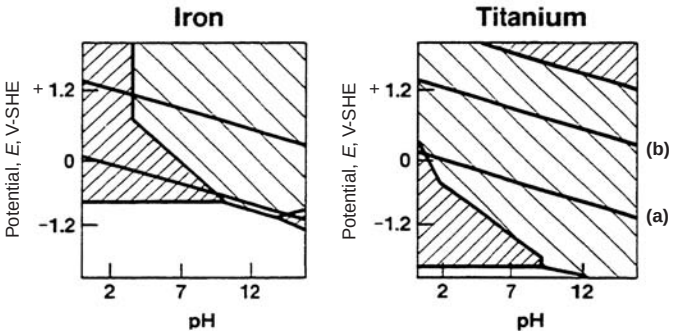


Fig. 12 Potential-pH diagrams for iron and titanium

The behavior of several of these metals in specific environments can be compared by first identifying a specific environment, labeled A to H in Table 8. Environment A represents a strongly acidic (pH 0) and strongly reducing (0 V-SHE) condition. The location of environment A on the potential-pH axis is indicated on the diagram in the upper right of Table 8, along with locations of the other environments. The corrosion behavior of various metals can be determined in each of the environments by comparing the environment location with the predictions of the potential-pH diagrams presented in Fig. 13. Taking aluminum as an example, corrosion is predicted in environments A, B, and C, and passivity is predicted in environments D and E. Corrosion is also predicted in environments F, G, and H.

Similar comparisons and tabulations can be made for titanium, copper, iron, zinc, and gold. The comparison of the corrosion behavior of a

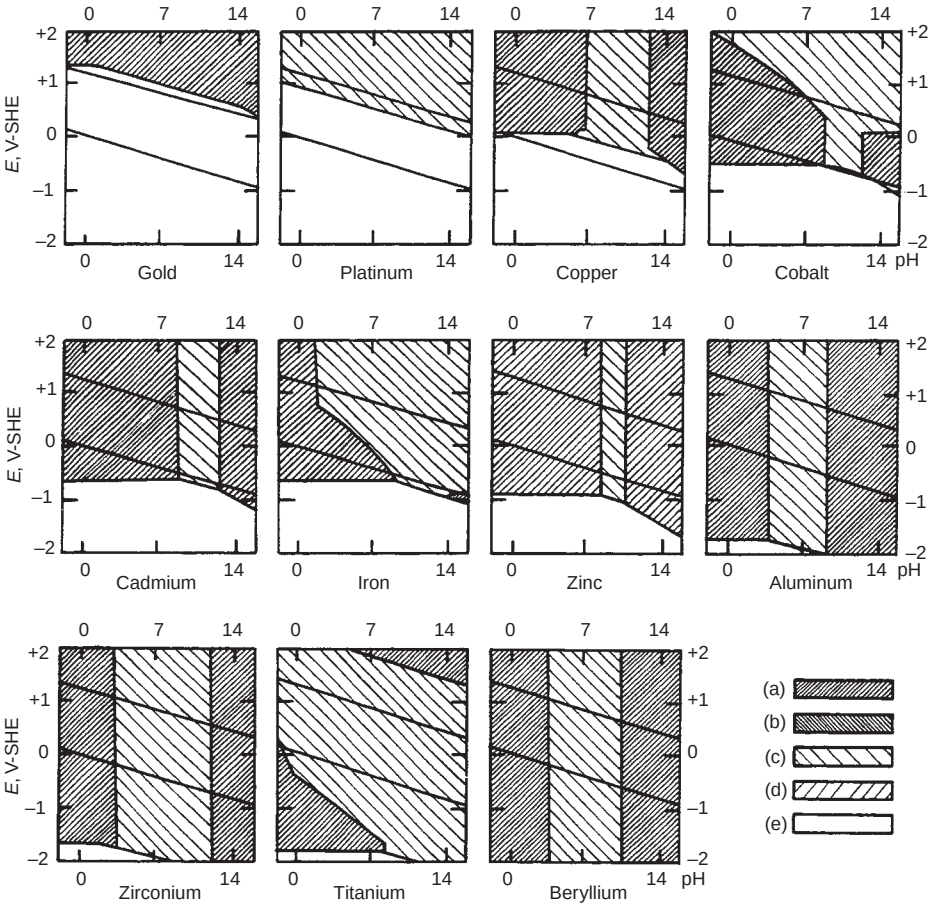
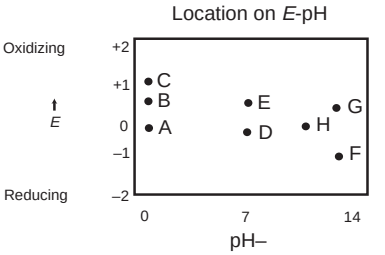


Fig. 13 Potential-pH diagrams for several metals in water at 25 °C (75 °F). (a) Corrosion by dissolution. (b) Corrosion by gasification. (c) Passivation by oxide or hydroxide layer. (d) Passivation by hydroxide layer. (e) Immunity

Table 8 Corrosion behavior of metals in a variety of environments based on potential-pH diagrams

Environment	pH, conditions	*E*, V-SHE
A → strong acid	0, strongly reducing	0
B → strong acid	0, mildly oxidizing	0.5
C → strong acid	0, strongly oxidizing	1.0
D → neutral	7, reducing	–0.3
E → neutral	7, oxidizing	0.5
F → strong alkaline	14, strongly reducing	–0.8
G → strong alkaline	14, strongly oxidizing	–0.2
H → mild alkaline	10, mildly oxidizing	0



Environment	pH	*E*, V-SHE	Corrosion behavior(a)					
			Al	Ti	Cu	Fe	Zn	Au
A	0	0	C	P	I	C	C	I
B	0	+0.5	C	P	C	C	C	I
C	0	+1.0	C	P	C	C	C	I
D	7	–0.3	P	P	I	C	C	I
E	7	+0.5	P	P	P	P	C	I
F	14	–0.8	C	P	I	C	C	I
G	14	+0.2	C	P	C	P	C	I
H	10	0	C	P	P	P	P	I

(a) C, corrosive; P, passive; I, immune

material in any given environment can be readily determined by reading across Table 8 and identifying regions of corrosion, passivity, or immunity.

Strategies for Corrosion Control from E-pH Diagrams

The potential-pH diagram for iron in water at 25 °C (75 °F) can be used to rationalize methods of corrosion control. The starting position for the analysis will be iron in a mildly oxidizing acid condition; that is, $E = –0.2$ V-SHE and pH = 4. This potential-pH location is indicated by the cross in Fig. 14, a condition representative of iron in a mildly oxidizing, weak acid. Under this condition, iron is predicted to corrode with formation of soluble ferrous ions. Corrosion can be controlled by employing several options, indicated by the arrows and letters in Fig. 14. If the pH of the environment is increased to neutralize the acid and to move into the slightly alkaline region, the iron is moved from a region of corrosion by the formation of soluble products to a region of passivity through the formation of insoluble products. This method of corrosion control is a form of water treatment or change in environment and is indicated by path A.

The corrosion of iron can also be controlled by making the conditions more reducing. This is done by changing the potential of the steel surface from mildly oxidizing to a more negative potential. At the more reducing potential, iron is in an immune region and is thermodynamically stable. This control method is cathodic protection and involves the application of a protective current that shifts the potential of the steel surface to more negative values, as indicated by path B in Fig. 14.

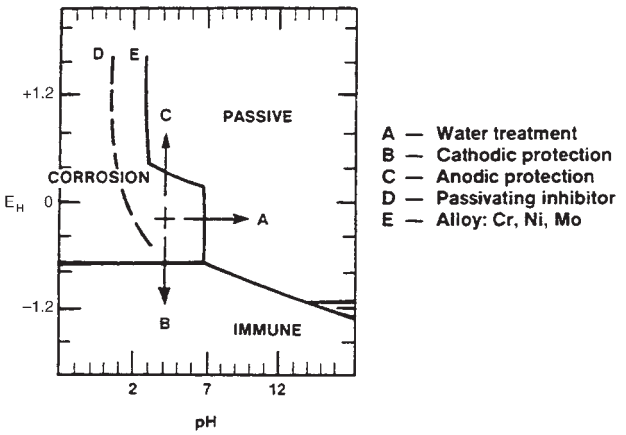


Fig. 14 Methods of corrosion control for iron related to the potential-pH diagram

Another method for controlling the corrosion of iron under this environment would be to increase the oxidizing conditions. This method of protection, that is, anodic protection, requires the movement of the steel electrode potential from a region of corrosion resulting from soluble ion formation into a region of more oxidizing conditions where passivity results from the formation of insoluble corrosion products. This method of control is represented by path C in Fig. 14.

It is important to understand the difference between anodic protection (path C) and cathodic protection (path B). In cathodic protection, the steel is moved into a region of immunity where iron is the thermodynamically stable phase. In anodic protection, the iron is moved into a region where passivity is favored. If the protective nature of the insoluble products is distributed such that they do not provide complete coverage or if the anodic protection is incomplete, then corrosion can in fact be made much more severe. Both of these methods of corrosion protection are described in Chapter 10.

The corrosion protection methods indicated by methods D and E in Fig. 14 involve increasing and extending the potential-pH range over which passive behavior is observed. This can be accomplished by the addition of a passivating chemical species, such as chromate ions, to the environment, promoting the formation of insoluble products on the surface (path D). Alternatively, the region of passivity can be extended by adding constituents to the iron that promote the formation of insoluble films. This alloying option for iron includes the addition of chromium (Cr), nickel (Ni), and molybdenum (Mo). Iron alloyed with more than 12% Cr, plus Ni and Mo, has spontaneous passivity over a wide range of environments. These alloys constitute entire families of austenitic stainless steels and nickel alloys.

This general approach to the application of potential-pH diagrams for determining and identifying corrosion control strategies can be quite

useful. Each control method can be evaluated based on the initial potential-pH condition for the metal and environment.

Limitations of E-pH Diagrams

The preceding discussion emphasizes the utility and wide application of potential-pH diagrams. However, their limitations must also be understood. Potential-pH diagrams are the result of thermodynamic calculations and do not provide any kinetic data or information as to reaction rates. The thermodynamically stable state and species are identified based on the lowest free-energy state for the reactions considered. There are two dangers. The first danger that the thermodynamically stable species will not be achieved due to kinetic considerations. The second danger is that operative reactions might not be considered due to oversight or the lack of complete knowledge of the constituents in a complex environment.

The potential-pH diagrams are based on the reaction of pure metal with the constituents of water. This approach neglects all the possibly important effects of other ions in solution, for example, chloride, nitrate, reduced sulfur species, and beneficial species such as chromate ions. The diagrams presented in this Chapter are calculated for 25 °C (75 °F). Changes in temperature can greatly affect the regions of passivity and shift the regions of immunity. The treatment of potential-pH diagrams has dealt specifically with calculations for pure metal, while most engineering applications deal with alloys or mixtures of metals. The treatment assumes that all insoluble products result in passivity. In practice, this is not the case. Many insoluble products are porous or loosely attached to the metal surface and provide limited protection against further corrosion. For example, oxides on titanium are quite protective, whereas oxides on iron can be either protective or nonprotective, depending on the specific conditions.

Yet another limitation is that use of potential-pH diagrams generally involves the prediction of behavior at a given potential and pH. As the corrosion reaction proceeds, it is likely that the potential and pH will change from their initial values. The trajectory of potential-pH variance is not readily determined without employing additional information.

Although these limitations are substantial, the use and benefit of potential-pH diagrams in the understanding and control of corrosion cannot be disputed. Extensions of the treatment presented in this Chapter have provided for considerable progress in overcoming several of the limitations previously noted. One of the drawbacks to many of these extensions, however, is that the major benefit of the potential-pH diagrams is often sacrificed. That is, the ultimate simplicity and convenience of presentation of a large amount of information in a compact

and efficient form are compromised when other considerations are added to the analysis.

The Kinetics of Aqueous Corrosion

As described in the first half of this Chapter, thermodynamics has been widely applied to corrosion studies for many years. Use of thermodynamic calculations permits prediction of conditions under which a metal is stable and corrosion will not occur.

Thermodynamics does not predict, however, how fast the corrosion reaction will occur. To understand the kinetics or rate of corrosion, examination of a number of electrochemical principles for example, mixed-potential behavior, polarization behavior, and the concept of exchange currents, for example, is required.

Electrochemical Reactions

The characteristics of an electrochemical reaction are that oxidation (or the generation of electrons) and reduction (or consumption of electrons) both occur, and there is an electron transfer from the anode to the cathode. The characteristics of an electrochemical reaction are illustrated by considering the behavior of iron in hydrochloric acid. Iron reacts vigorously with HCl; hydrogen is evolved and the iron gradually goes completely into solution. The reaction is:

$$Fe + 2HCl \rightarrow FeCl_2 + H_2 \qquad \text{(Eq 4)}$$

The solid iron gradually disappears and a gas is evolved. This can be seen with the naked eye. The solution in the above reaction is ionized and contains positively and negatively charged ions. The HCl contains hydrogen ions (H^+) and chloride ions (Cl^-). One drop of acid contains millions of each of these ions. Likewise, ferrous chloride in solution can be considered as iron ions (Fe^{2+}) and chloride ions (Cl^-). Therefore, Eq 4 can be written as the following:

$$Fe + 2H^+ + 2Cl^- \rightarrow Fe^{2+} + 2Cl^- + H_2 \qquad \text{(Eq 5)}$$

The iron converted to an iron with two positive charges. By definition, the iron is said to have been oxidized (loss of electrons). On the other hand, the hydrogen ions have each gained an electron. By definition, they have been reduced. The overall reaction can be considered as two separate ones:

$$\text{Oxidation: } Fe \rightarrow Fe^{2+} + 2e^- \qquad \text{(Eq 6)}$$

Reduction: $2H^+ + 2e^- \rightarrow H_2$ (Eq 7)

Equations 6 and 7 both take place on the surface of the metal. The areas where oxidation occurs are defined as anodes, and those where reduction takes place are defined as cathodes. An electrical potential exists between the anode and cathode areas. The electrons produced in Eq 6 flow through the metal to the cathode areas to take part in the reaction of Eq 7. Hydrogen ions in the vicinity of the anode areas are not needed there, and they flow (under the influence of the potential difference) to the cathode to sustain the reduction reaction. A complete electrical circuit exists, and a current flows from anode to cathode. The faster the solid is converted to iron ions (i.e., the greater the corrosion), the larger is the current flowing in this corrosion cell.

The mechanism for the preceding case is shown schematically in Fig. 15. Many such corrosion cells occur on a corroding metal surface. Anode and cathode sites can switch roles so that uniform corrosion can occur. Equations 6 and 7 must occur at the same rate to conserve the electrical neutrality of the metal. If Eq 6 stops, then so must Eq 7, and vice versa.

The corrosion reactions of other metals and corrodents are similar. In all cases of electrochemical corrosion, the anodic reaction consists of oxidation of the solid metal, M, to its ions in solution as follows:

$$M \rightarrow M^{n+} + ne^-$$

When an alloy corrodes, several anodic reactions can take place simultaneously. For example, the anodic reactions for an aluminum-copper alloy might be the following:

$$Al \rightarrow Al^{3+} + 3e^-$$
$$Cu \rightarrow Cu^{2+} + 2e^-$$
$$Mg \rightarrow Mg^{2+} + 2e^-$$

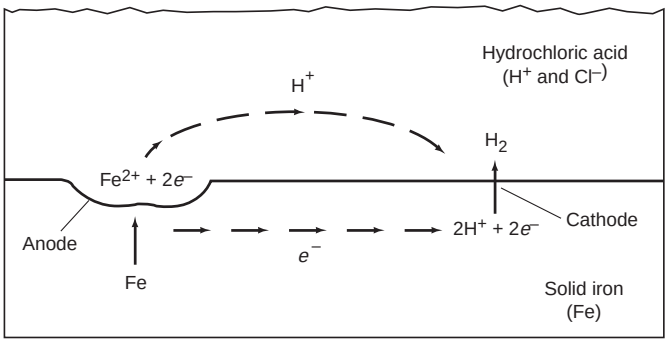


Fig. 15 Corrosion of iron in hydrochloric acid

Therefore, the possible anodic reactions in a system are relatively easy to predict.

With cathodic reactions, there are more possibilities. Various types of reduction can occur, including the following, for example:

Hydrogen evolution in acid solutions:

$$2H^+ + 2e^- \rightarrow H_2$$

Oxygen reduction in acid solutions:

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$$

Oxygen reduction in neutral or alkaline solutions:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$$

Metal-ion reduction:

$$M^{3+} + e^- \rightarrow M^{2+}$$

Metal plating:

$$M^+ + e^- \rightarrow M$$

Hydrogen evolution and oxygen reduction are the most common cathodic reactions. Different cathodic reactions can occur simultaneously on a corroding metal surface.

In summary, corrosion in the electrochemical sense occurs by solid metal being oxidized to positively charged metal ions in solution. This occurs at areas called anodes. The resulting excess of electrons passes through the metal to surface areas called cathodes where electrons are removed by a reduction reaction. The corrodent must contain a species that can be reduced at the cathode and ions capable of completing the electrical circuit between anode and cathode areas (i.e., the corrodent must be an electrolyte). A current flows through the solution from anode to cathode areas. As described subsequently, the driving force in the reaction is the electrical-potential difference that causes current flow between the anode and cathode.

Mixed-Potential Theory

Mixed-potential theory provides a solid basis for the treatment of the rates of electrochemical reactions. The concepts of mixed-potential theory can be used to describe and explain many of the material and environmental effects of observed in corrosion phenomena. The theory

particularly delineates the importance of the reduction reactions in an electrochemical process as well as the anodic and dissolution process.

Two basic premises underlie mixed-potential theory. First, the anodic current in an electrochemical cell must equal the cathodic current. This is a requirement of the conservation of electrical charge. The number of electrons generated by the total of all oxidation reactions must be exactly equal to the number of electrons consumed by the total of all reduction reactions. Second, for the purpose of examination and definition of the electrochemical cell, the anodic (oxidation) and cathodic (reduction) reactions can be defined, written, and treated independently. As shown in Fig. 15, the anodic reactions account for the generation of electrons, and the cathodic reactions account for the consumption of electrons. Conceptually, these can be dealt with separately. For an operating corrosion cell, then, the reactions are coupled through the principle of conservation of electrical charge. The application of mixed-potential theory to corrosion phenomena is discussed in succeeding paragraphs. More detail is available in several of the selected references listed at the conclusion of this Chapter.

The free-energy change for the oxidation of iron to ferrous ions is shown schematically in Fig. 16. As the free-energy wells are drawn in Fig. 16, the system can lower its free energy, ΔG, by the oxidation of an iron atom at the metal surface to form a dissolved metal ion in solution. The net decrease in free energy is indicated by ΔG oxidation. The free energy of the reaction is related to the electrochemical potential through the Nernst equation (Eq 1). The net free-energy change, ΔG oxidation, is equivalent to an electrochemical overpotential (η_{anodic}). The reaction in Fig. 16 shows a spontaneous reaction of iron to corrode (oxidize) with a net decrease in free energy or a positive overpotential.

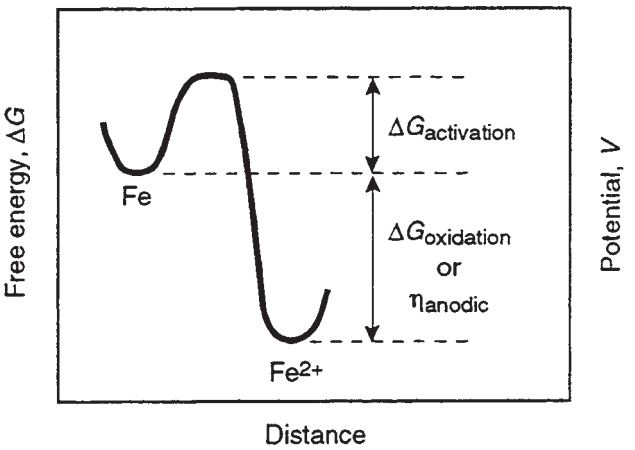


Fig. 16 Free energy and electrochemical potential for an activation-controlled reaction. Reaction rate increases exponentially with driving force.

The driving force for this corrosion reaction is the free-energy change or the overpotential. The rate of the reaction can be expressed as a current or the number of electrons generated per unit time. The rate of the reaction (current) increases exponentially with the driving force (overpotential):

$$\text{Current} = A\exp\left(\frac{-\Delta G}{RT}\right)$$

$$\text{Current} = A\exp\left(\frac{n\text{F}\eta}{RT}\right)$$

where A is a constant, ΔG is the free-energy change, R is the gas constant, T is temperature, n is the number of electrons generated per ion, F is Faraday's constant, and η is overpotential (ΔE).

The overpotential is equivalent to ΔE or $E–E_0$, where E is the potential of the metal surface and E_0 is the equilibrium potential for the reaction. An equivalent expression for this relationship is that the overpotential is proportional to the log of the current, that is, $\eta \propto \log i$. This relationship indicates that a unit increase in the driving force, that is, the overpotential, results in an order of magnitude increase in the reaction rate, that is, current.

An electrochemical reaction that behaves as described in the preceding paragraph is referred to as being under the control of *activation polarization*. Activation polarization simply means that the driving force for the reaction (overpotential) is proportional to the log of the reaction rate (current). The relationships for anodic and cathodic processes under activation polarization are as follows:

$$\eta_a = \alpha_a + \beta_a \log i \,(\text{anodic})$$

$$\eta_c = \alpha_c + \beta_c \log i \,(\text{cathodic})$$

Anodic overpotential (η_a) equals a constant α_a plus a constant β_a times the logarithm of the current. The cathodic overpotential (η_c) is equal to a constant α_c minus a constant β_c times the logarithm of the cathodic current. The constants α and β are referred to as the anodic and cathodic Tafel constants, respectively. Over the potential range where these equations describe the relationships between potential and current, reaction is under activation control.

Mixed-potential theory deals with the anodic and the cathodic reactions independently. The reactions then are coupled by the rule that the total of all anodic currents (i_a) and the total of all cathodic currents (i_c) are equal. Where activation control governs the reaction rate, there is an exponential relationship between potential and current.

Types of Polarization

As stated in the preceding sections, the driving force for the corrosion reaction is the potential difference between the anode and the cathode in the corrosion cell, and the reaction rate is equal to the current that flows through the cell. The total resistance throughout the corrosion cell is the total of the resistance associated with the anode plus the resistance of the ionic path plus the resistance associated with the cathode plus the resistance of the electronic path. As with Ohm's law, that is, $E = iR$, for a simple electrical circuit, the potential, current, and resistance in a corrosion cell are related. For a given potential difference between the anode and the cathode, the current or corrosion rate will increase as the resistance throughout the cell decreases or, conversely, the corrosion rate will decrease as the resistance throughout the cell increases. Various types of *polarization* describe the resistance elements throughout the corrosion cell. Three forms of polarization are discussed in this section: activation polarization, concentration polarization, and ohmic polarization.

Activation polarization is defined by the relationships given in the previous section describing electrochemical reactions. Figure 17 graphically illustrates the relationship for the anodic reaction, which is the oxidation of iron atoms to soluble, ferrous ions. The potential is plotted on the vertical axis, with more positive or oxidizing potentials at the top. The reaction rate or log of the anodic current is plotted on the horizontal axis, with increasing currents to the right. The activation polarization curve for this anodic reaction is a straight line extending from the lower left to the upper right. The slope of the line is given by the anodic Tafel slope, β_a. Figure 17 shows that a unit increase in the overpotential, E, results in an order of magnitude increase in the reaction rate. As the oxidizing potential becomes more positive, the rate of the corrosion or oxidation of iron increases, that is, the anodic overpotential increases.

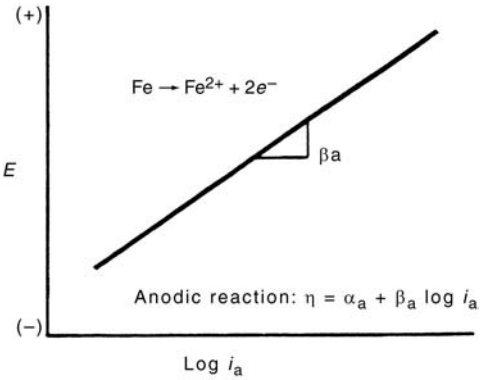


Fig. 17 Activation polarization curve for the anodic reaction of iron and ferrous ions

Ferrous ions are generated more rapidly, and more electrons are left at the metal surface.

The activation polarization curve for the cathodic reaction of hydrogen ions to form hydrogen gas is shown in Fig. 18. The axes are the same as described for Fig. 17. The cathodic or reduction reaction is a straight line extending from the upper left to the lower right. The slope of the line is the cathodic Tafel slope, β_c. The reduction reaction increases as the oxidizing conditions become more reducing or the overpotential becomes more negative. As the potential becomes more reducing by a unit value, the rate of the reduction reaction increases by an order of magnitude. As the conditions become more reducing, hydrogen ions and electrons are consumed more rapidly at the metal surface and more hydrogen gas is generated. It is important to note that the anodic current, i_a, is the rate of generation of electrons and that cathodic current, i_c, is the rate of consumption of electrons. In an operating electrochemical cell, oxidation current leaves the metal surface at the anode, and a cathodic current enters the metal surfaces at the cathode.

The anodic reaction of Fig. 17 and the cathodic reaction of Fig. 18 are combined on a single diagram in Fig. 19—an activation polarization diagram for the anodic and cathodic reactions. The requirements of mixed-potential theory are met at only a single point, that is, the point where the anodic and cathodic reaction curves cross. This is the only location at which the anodic reaction rate equals the cathodic reaction rate. The potential of this intersection is identified as E_{corr}, and the current at this intersection is defined as i_{corr}. The potential intersection is referred to by several terms, including the corrosion potential, the free corroding potential, and the open-circuit potential. The current intersection is referred to as the corrosion current. At potentials more positive or more oxidizing than the corrosion potential, the anodic current is greater than the cathodic current, and more electrons are generated than

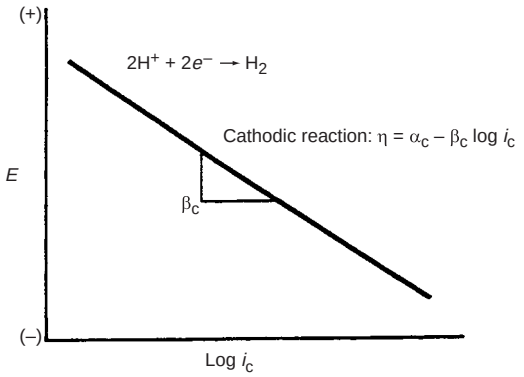


Fig. 18 Activation polarization curve for the cathodic reaction of hydrogen ions and hydrogen gas

are consumed. At potentials more negative or more reducing than the corrosion potential, the cathodic current is greater than the anodic current, and more electrons are consumed than are generated. A steady state of no net consumption or generation of electrons is achieved only at the corrosion potential. Neither of these cases (i.e., potentials more oxidizing or more reducing than the corrosion potential) results in a steady state. In order to maintain a system away from the corrosion potential (E_{corr}), current must be supplied from an external source or other reactions.

The slopes β_a and β_c are determined by the properties of both the metal surface and the electrolyte. There are three forms of activation polarization control: mixed control, cathodic control, and anodic control (Fig. 20). The type of control essentially results from the slope values of the anodic and cathodic curves. Under mixed control, the corrosion rate is equally sensitive to shifts in the anodic or oxidation reaction and the cathodic or reduction reaction. Under cathodic control, the slope of the reduction curve is greater than the slope of the oxidation curve. This re-

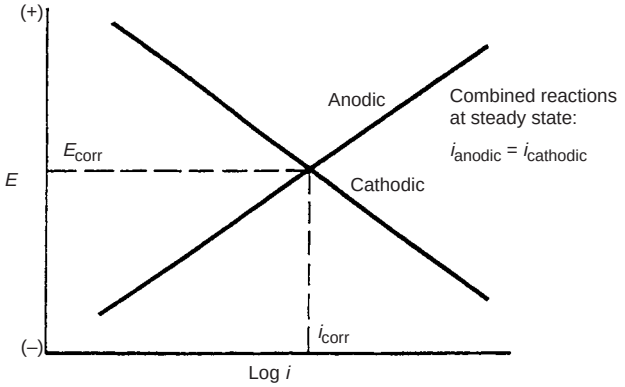


Fig. 19 Combined diagram of an anodic reaction and a cathodic reaction with activation polarization.

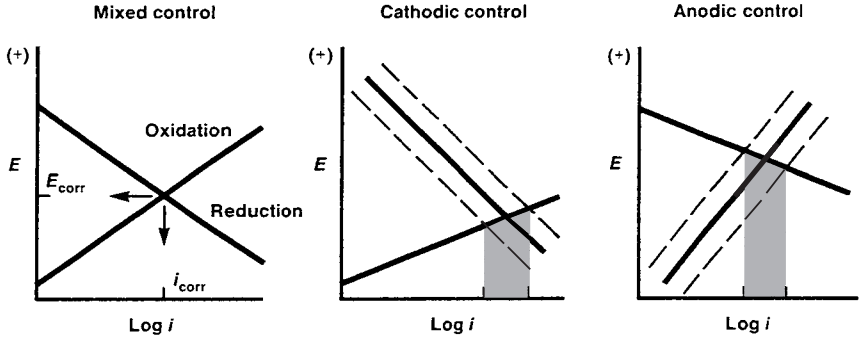


Fig. 20 Schematic diagrams of the three forms of activation polarization control

sults in the corrosion reaction being more sensitive to changes in the reduction reaction kinetics than to changes in the oxidation reaction kinetics. Under anodic control, the slope of the oxidation reaction is greater than the slope of the reduction reaction curve. This results in the corrosion rate being more sensitive to changes in the anodic reaction kinetics than to changes in the cathodic reaction kinetics.

It is useful to note that form of control which is operative under a given set of circumstances. This knowledge allows one to focus on control of the most sensitive portion of the corrosion cell; that is, corrosion control can be focused on either the anodic or the cathodic reaction, whichever will have the most effect on lowering the corrosion rate. In practice, systems employing all three types of activation control are used.

Concentration polarization results from mass transfer or diffusion-limited effects at the reacting metal surface. The effect of concentration polarization on the shape of the cathodic polarization curve for a reduction reaction is shown in Fig. 21. At lower currents, the cathodic reaction is controlled by activation polarization, and a straightline sloping from the upper left to the lower right results. The slope of this curve is $-\beta_c$, the cathodic Tafel slope. In this region, as the potential becomes more negative or more reducing, the rate of the reaction increases. As the potential continues to become more reducing, the overpotential of the reduction reaction increases, as does the driving force for the reduction reaction. There is, thus, a greater driving force for reduction, and the rate continues to increase. As the cathodic overpotential becomes even greater (i.e., the potential becomes even more negative), a point is reached at which increasing the driving force no longer increases the rate of reaction. This is the region of concentration polarization.

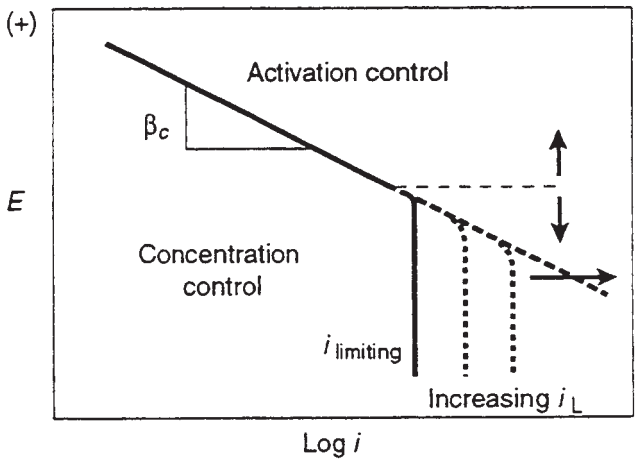


Fig. 21 Onset of concentration polarization at more reducing potentials for a cathodic reduction reaction

The dashed horizontal line on Fig. 21 indicates the separation between the potential region where the reaction is under activation control (above the dashed line) and the potential region where the reduction reaction is under concentration control (below the dashed line). The region of activation control is described by the straight, sloped line, and the concentration control region is described by the vertical line. In the region of concentration control, there is more than sufficient driving force for the reaction to occur as reactants arrive at the electrode surface.

Therefore, the reaction rate is no longer dependent on the potential (driving force) but rather becomes dependent on either the rate at which reactants species arrive at the electrode or the rate at which products of the reaction can be removed from the vicinity of the electrode surface. The reaction rate is controlled by the mass transfer of reactant and products of the reaction, and this mass transport is essentially independent of potential. A curved portion of the reduction reaction kinetics curve is shown near the horizontal line. In this region, both the activation-dependent kinetics and concentration-control kinetics affect the potential versus log current behavior. In the linear regions of the curve, the kinetics are dominated either by activation control or by concentration control.

The magnitude of the reduction current in the region of concentration control, that is, the value of current where the vertical segment of the curve intersects the log current axis, is defined as the limiting current (i_L), which can be determined by the following:

$$i_L = \left(\frac{DnF}{\delta}\right) c$$

where D is the diffusion coefficient for the ionic species being reduced at the electrode surface, n is the number of electrons consumed by the reduction reaction, F is Faraday's constant, δ is the thickness of the diffusion layer of the electrolyte near the electrode surface, and c is the concentration of the species being reduced. This relationship describes the limiting current for the reduction kinetics, where the rate of reaction is controlled by the arrival of the species being reduced at the electrode surface. For example, in the hydrogen evolution reaction this reaction will predict the reaction rate when the arrival of hydrogen ions from the solution to the metal surface controls the reaction rate.

The effect of increasing the magnitude of the limiting current is shown by the dashed lines in Fig. 21. As the increasing limiting current moves the vertical segment of the line farther to the right to higher current values, more of the linear portion controlled by activation control is observed. Referring to the equation above, the factors that can result in increasing limiting current are identified. The limiting current under concentration control will increase when the diffusion coefficient of the

species being reduced (D) increases, when the concentration of the species being reduced (c) is increased, and when the thickness of the diffusion layer (δ) is decreased.

The preceding discussion has focused on the concentration-control portion of the reaction rates for a reduction reaction. Concentration control also can be observed for oxidation or anodic reactions. For such reactions, concentration polarization is delineated where the anodic polarization curve on a diagram of potential versus log current deviates from a straight, diagonal line with a slope equal to the anodic Tafel slope and approaches a vertical line that is independent of potential.

Ohmic Polarization. The third form of polarization in an electrochemical cell is ohmic polarization, which results from pure resistance elements along the current path in the cell. Ohmic resistance is also referred to as iR effects. Ohmic polarization is observed either in the region of ionic conductivity, where current is transported by the movement of ions through the electrolyte from the anode to the cathode, or in the electronic conductivity region, where current is transported through the metallic path from the cathode to the anode. Because metals have relatively low resistivity or high conductivity, ohmic polarization along the electronic path is not generally significant. Exceptions to this include cases where the current travels long distances between the cathode and anode along the metallic path. Ohmic polarization effects are not uncommon in the electrolyte, because many electrolytes have significant resistances to the ionic current flow.

The effect of ohmic polarization on the corrosion current in an electrochemical corrosion cell is shown in Fig. 22. Three cases are shown, with the resistance of the solution increasing from a value of R_1 (where resistance is essentially 0) to R_3 (a high resistance value). The resulting current through the corrosion cell for each of these resistances is indicated by i_1, i_2, and i_3. When the conductivity of the solution is quite high, corresponding to essentially no resistance in the electrolyte, the cathodic reduction curve and the anodic oxidation curve intersect at i_1. In this case, the potentials of the anode and cathode are polarized to the same value. As the resistance of the solution increases, the potential of the anode and the cathode are no longer equal. A potential drop (iR) in the solution results from the passage of current (i) through the resistive solution (R). The resulting effect is that some of the potential difference between the anode and cathode is taken up by the potential drop through the solution and is, therefore, unavailable to drive the activation-controlled reactions. As the resistance of the solution increases from R_1 to R_2 to R_3, the magnitude of the potential drop of ohmic polarization in the cell increases, with a resulting decrease in the corrosion current of the cell from i_1 to i_2 to i_3. Note that in all cases the anodic current equals the cathodic current.

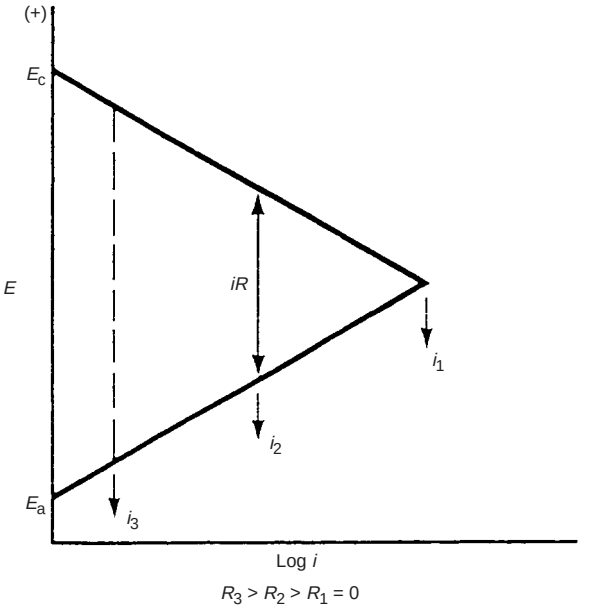


Fig. 22 Effect of ohmic polarization on the current in a corrosion cell

The effect of ohmic polarization on the corrosion rate can be illustrated by the behavior of galvanic couples comprised of copper electrically coupled to steel in different waters. The driving force for the corrosion reaction is the potential difference between the copper cathode and the steel anode. In seawater, which has high conductivity, there is very little resistance to current flow, and a high corrosion rate (equivalent to i_1) is observed. Tap water has a much lower conductivity than seawater, and the resulting corrosion rate is also significantly lower (equivalent to i_2). Distilled water has even less conductivity than tap water, and the resulting corrosion rate is still lower for the galvanic couple (equivalent to i_3). Thus, an effective way to reduce the corrosion current in a corrosion cell is to increase the resistance to ionic current flow through the cell.

Applications of Mixed-Potential Theory Diagrams

The basis for mixed-potential theory diagrams and the various forms of polarization that can be observed and described using these diagrams were described in the preceding sections. These diagrams can be most useful for predicting and explaining observed corrosion behavior. Examples of the application of mixed-potential theory are presented here.

Corrosion of Zinc in Deaerated Acid. Figure 23 describes the corrosion behavior of zinc, an active metal, in a strong (pH 0) deaerated acid. In this system, two half-cell reactions are coupled in an electrochemical corrosion cell; thus, the principles of the mixed-potential theory will be obeyed. The system will be polarized to a potential where

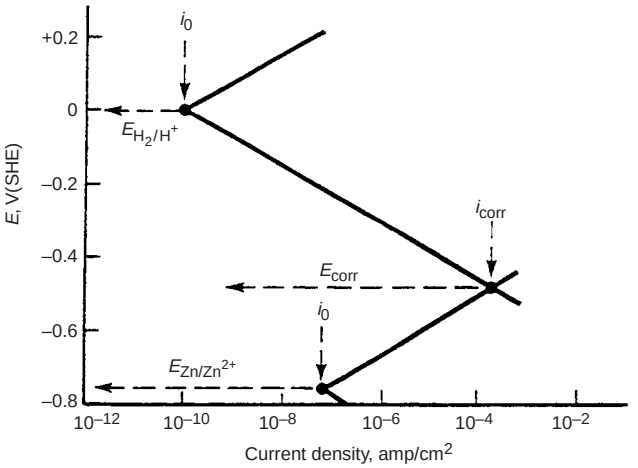


Fig. 23 Mixed-potential theory diagram for the corrosion of zinc in a deaerated acid

the sum of the currents from the cathodic reduction reactions equals the sum of the currents from the anodic oxidation reactions. The open-circuit potential and current densities (i_0) for each half-cell reaction are shown in Fig. 23. The corrosion potential, E_{corr}, and the corrosion current, i_{corr}, for the coupled reactions in the corrosion cell are also indicated. When zinc is immersed in a strong acid, the corrosion potential is approximately –0.5 V-SHE, and the corrosion current is approximately 10^{-4} A/cm^2. The oxidation current at the anodic results almost completely from the oxidation of zinc atoms and the formation of zinc ions in solution, with the release of electrons at the metal surface. The reduction reaction current is almost completely the result of the reduction of hydrogen ions from solution and the formation of hydrogen gas, with the consumption of electrons at the metal surface. At the corrosion potential, zinc ions are being produced and hydrogen ions are being consumed at a rate equivalent to the corrosion current. The mixed-potential theory diagrams for the two half-cell reactions can, thus, be used to predict the resulting corrosion behavior of zinc in a deaerated acid. Unless an external current is impressed upon the system, the system will remain at the steady-state condition, where the sum of the anodic currents equals the sum of the cathodic currents.

Effect of pH on Corrosion of Active Metals. The effect of increasing the acidity of the solution on the corrosion rate of an active metal is shown in Fig. 24. As the acidity is increased (lower pH), the hydrogen ion concentration in solution increases where the reduction reaction is due to the reduction of hydrogen ions and evolution of hydrogen gas, increasing the concentration of hydrogen ions in solution has the effect of increasing the cathodic reduction rate at every potential. The effect is shown in Fig. 24 by shifting the reduction curve to the right from $E_c(1)$

to $E_c(2)$. As the reduction kinetics are increased, the intersection with the anodic dissolution curve also shifts to higher current values. The corrosion rate for the higher-pH solution (lower hydrogen ion concentration) is i_1, and the corrosion rate in the lower-pH solution (higher hydrogen ion concentration) is i_2. Therefore, for the corrosion of an active metal in a deaerated acid, the corrosion rate of the metal is predicted to increase as the strength of the acid increases.

Active-Passive Behavior. Anodic polarization curves for an active metal and an active-passive metal are shown in Fig. 25 (the basic concepts associated with passive behavior are described in Chapter 2). The anodic dissolution rate of an active metal increases as the potential becomes more oxidizing. A linear increase is observed until the onset of concentration polarization. The behavior of the active-passive metal is similar at the start; that is, as the potential increases, a linear increase is observed. However, as the potential continues to become more oxidizing, a sharp drop to a much lower corrosion current is observed. This sharp decrease in current corresponds to the attainment of a potential range in which an insoluble corrosion product forms, significantly lowering the rate at which the metal corrodes. Within this passive range, the small corrosion current is independent of potential, as indicated by the vertical line at higher potential for the active-passive metal. A polarization curve typical of the active-passive behavior of stainless steels is shown in Fig. 26.

The effect of increasing the rate of cathodic reaction on the corrosion behavior of an active-passive metal is shown in Fig. 27. For the

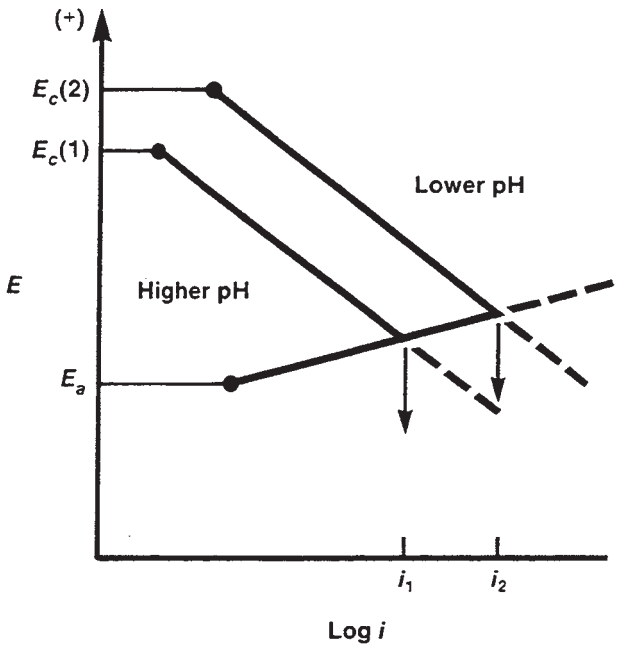


Fig. 24 Effect of lower pH (greater acidity) on the corrosion rate of an active metal

initial conditions, the corrosion potential and corrosion current are indicated by $E_{corr}(1)$ and $i_{corr}(1)$, respectively. The reduction kinetics curve intersect the oxidation kinetics curve in the active region, and a relatively high corrosion rate is predicted. When the rate of cathodic reaction is increased, as shown by a shift of the cathodic reduction curve to

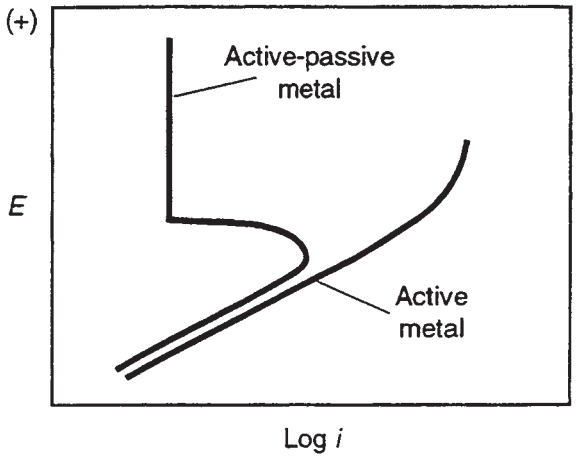


Fig. 25 Anodic polarization curves for an active metal and an active-passive metal

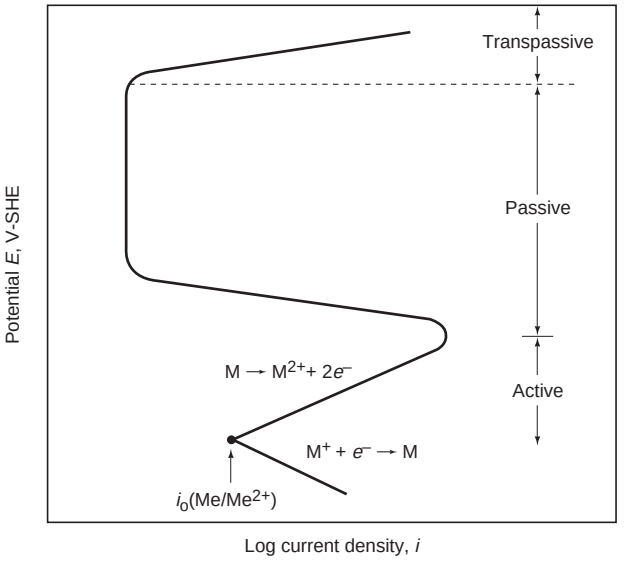


Fig. 26 Schematic polarization curve for a metal (e.g., stainless steel) that displays an active-passive transition. At relatively low potential values, within the active region, the behavior is linear, as it is for normal metals. With increasing potential, the current density suddenly decreases to a very low value, which remains independent of potential. This is termed the passive region. Finally, at even higher potential values, the current density again increases with potential in the transpassive region.

the right, the intersection is moved to values of $E_{corr}(2)$ and $i_{corr}(2)$. The net effect of increasing the rate of cathodic reaction is to significantly decrease the corrosion current in the cell and to shift the corrosion potential to a more positive (more oxidizing) value. Comparison of Fig. 24 and 27 shows that increasing the cathodic reaction rates for an active metal increases the corrosion rate; for an active-passive metal, on the

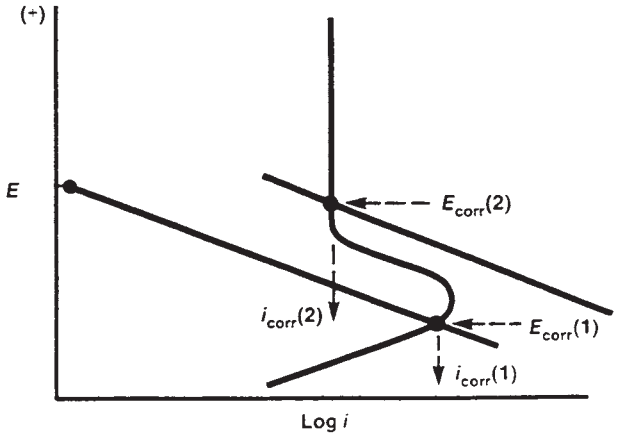


Fig. 27 Effect of increasing the rate of cathodic reaction on the corrosion behavior of an active-passive metal

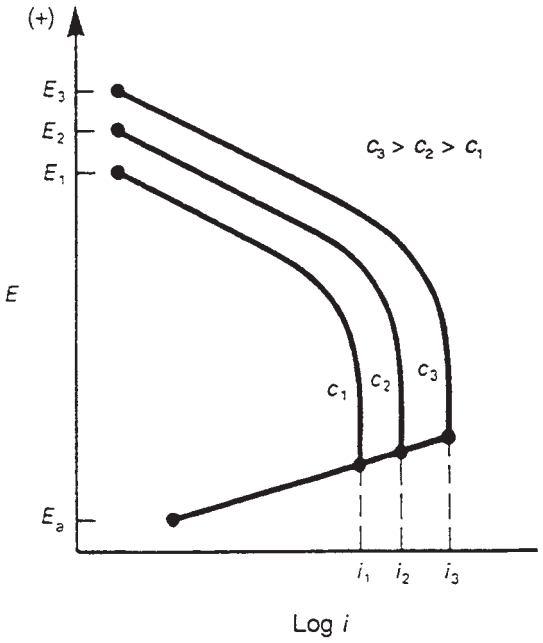


Fig. 28 Effect of increasing the concentration of reducible species on the cathodic polarization curve and the corrosion rate of an active metal

other hand, increasing the cathodic reaction rate can significantly decrease the corrosion rate. As with the active metal, for the active-passive metal, the steady-state condition is the point at which the cathodic reaction curve intersects the anodic behavior curve.

Effect of Increasing the Concentration of Reducible Species. Figure 28 illustrates the effect of increasing the concentration of reducible species on the cathodic polarization curve and the corrosion rate of an active metal. As the concentration of reducible species increases from c_1 to c_2 to c_3, the cathodic reduction current increases in both the activation-controlled and concentration-polarization-controlled portions of the curve. The net effect is to shift the entire curve to the right. The intersection of the cathodic polarization curve and the anodic polarization curve moves to the right from i_1 to i_2 to i_3 as the concentration of reducible species increases. In each of these cases, the concentration polarization portion of the curve, that is, the limiting current value, intersects the anodic polarization curve. The prediction of the mixed-potential theory diagram is that the corrosion rate of the active metal will increase as the concentration of reducible species is increased.

Effect of Increasing Solution Velocity. Figure 29 shows the effect of increasing the velocity of the solution for a corroding system under cathodic control. In this instance, the corrosion rate is being controlled by the intersection of the limiting current under concentration control with the anodic polarization curve of the active metal. The effect of increasing the velocity of the solution is to decrease the thickness of the

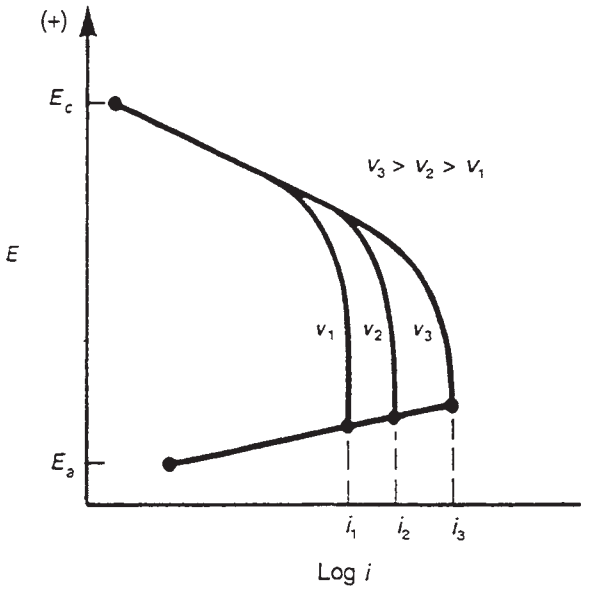


Fig. 29 Effect of increasing the velocity of the solution for a corroding system under cathodic concentration control

diffusion layer adjacent to the electrode surface. As shown in the section on concentration polarization, decreasing the thickness of the diffusion layer increases the value of the limiting current and shifts it farther to the right on the diagram. The portion of the cathodic polarization curve described by activation control is not affected by increasing velocity. The net effect of increasing velocity is to increase the corrosion rate of an active metal under these conditions of concentration control for the reduction reaction.

Effect of Inhibitors. Mixed-potential theory diagrams have been used to identify the mechanism of inhibition in corrosion reactions. The effect of an anodic inhibitor and a mixed inhibitor on the anodic and cathodic polarization curves and the corrosion rate of iron in H_2SO_4 is shown in Fig. 30 for the inhibition of corrosion of iron in H_2SO_4. The addition of anodic inhibitor significantly reduced the value of the anodic current at any potential; there was little effect on the cathodic polarization curve. The net effect was to shift the anodic polarization curve to the left, with a corresponding decrease in corrosion current from i_1 to i_2 and a corresponding increase in (more positive) corrosion potential from E_1 to E_2. This inhibitor is referred to as anodic inhibitor because its major influence on the corrosion reaction results from its decrease in the anodic reaction kinetics.

The mixed inhibitor significantly reduced both the cathodic reaction kinetics and the anodic reaction kinetics, and both the cathodic and anodic curves were shifted to lower current values (to the left in Fig. 30). The net effect in this instance was to significantly reduce the corrosion

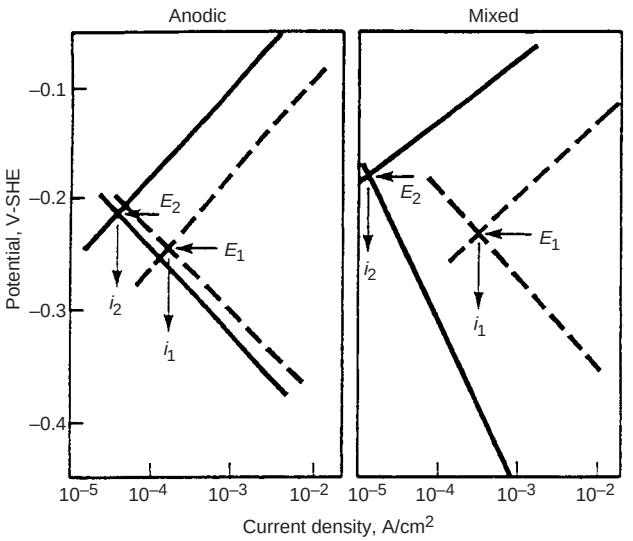


Fig. 30 Effect of an anodic inhibitor and a mixed inhibitor on the anodic and cathodic polarization curves and corrosion rate of iron in sulfuric acid. Dashed lines, before addition of inhibitor; solid lines, after addition of inhibitor

current from i_1 to i_2 and to increase the corrosion potential from E_1 to E_2.

It should be apparent from Fig. 30 that simply measuring the effects of an inhibitor on corrosion potential does not provide a definitive picture of inhibitor behavior. The figure also shows the benefit of determination of anodic and cathodic polarization curves as a function of inhibitor type and concentration. Useful insight as to the mechanism of inhibition can be gained.

Exchange Currents

The concept of exchange current is important in mixed-potential theory. The magnitude of the exchange current for a given half-cell reaction can greatly affect the resulting corrosion rate observed in an operating corrosion cell. The exchange current is defined as the steady-state value of current for a given half-cell reaction. This is demonstrated in Fig. 31 for the equilibrium or steady-state free-energy condition for the hydrogen evolution reaction. The electrochemical reaction for the reduction of hydrogen ions and evolution of hydrogen gas is shown. The reaction proceeding from left to right results in the evolution of hydrogen gas and is a reduction reaction. The reaction proceeding from right to left results in the generation of hydrogen ions and is an oxidation reaction. When the free energy of the hydrogen ions is equal to the free energy of hydrogen gas, the system is at steady state or equilibrium. At this condition, the rate at which hydrogen ions are consumed to generate hydrogen gas is equal to the rate at which hydrogen gas is consumed to generate hydrogen ions. The forward and reverse reactions occur at equal rates. The magnitude of the current where the forward and reverse reactions are equal is defined as the *exchange current.*

The magnitude of the exchange current depends on the properties of the electrode surface upon which the reaction occurs. This is demonstrated

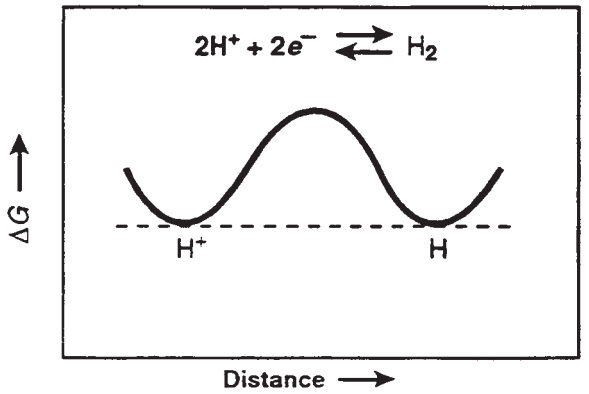


Fig. 31 Equilibrium or steady-state free-energy condition for hydrogen evolution

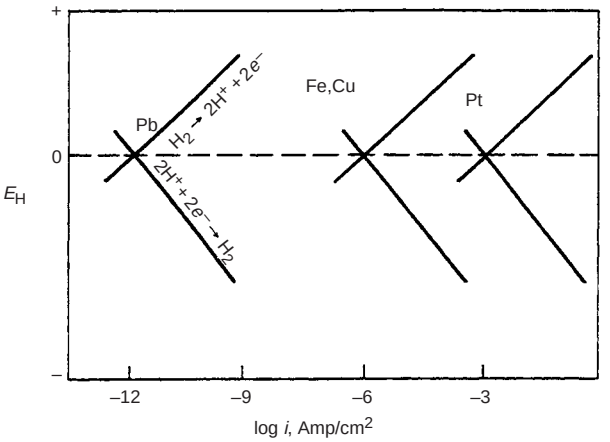


Fig. 32 Exchange-current densities for hydrogen evolution of lead, iron, copper, and platinum

for the hydrogen evolution reaction in Fig. 32, which shows mixed-potential theory diagrams for the oxidation and reduction reactions of hydrogen evolution on lead, iron, copper, and platinum. The anodic reaction is the consumption of hydrogen gas with the production of hydrogen ions, and the reduction reaction is the consumption of hydrogen ions with the production of hydrogen gas. The steady-state value is described by the intersection of these curves. For lead, the curves intersect at an exchange-current value of 10^{-12} A/cm^2. For iron and copper, the exchange current is 10^{-6} A/cm^2. For platinum, the exchange current is 10^{-3} A/cm^2. For these metals, the exchange current for hydrogen evolution varies over a range of nine orders of magnitude. Lead is the least efficient cathodic surface, and the hydrogen evolution reaction proceeds relatively slowly; platinum is the most efficient cathodic surface, and the hydrogen evolution reaction occurs much more rapidly. Each half-cell reaction has its characteristic exchange current on the particular electrode surface. Referring to Fig. 23, the exchange current for hydrogen evolution on zinc is seen to be approximately 10^{-10} A/cm^2, and the exchange current for the zinc to zinc ion reaction is seen to be approximately 10^{-7} A/cm^2. These values are indicated by i_0 for each reaction in Fig. 23.

The magnitude of the exchange current can significantly affect the corrosion rate. The effect of the exchange current for the hydrogen evolution reaction on mercury, zinc, and platinum on the corrosion rate of an active metal is shown in Fig. 33. Platinum is the most efficient cathodic surface for this reaction, followed by zinc and then mercury. On the platinum surface, the hydrogen evolution reaction proceeds much more rapidly, and the cathodic polarization curve is shifted far to the right. On mercury, the hydrogen evolution reaction occurs relatively slowly, and the curve is shifted to the left. The corrosion rate of the active metal cou-

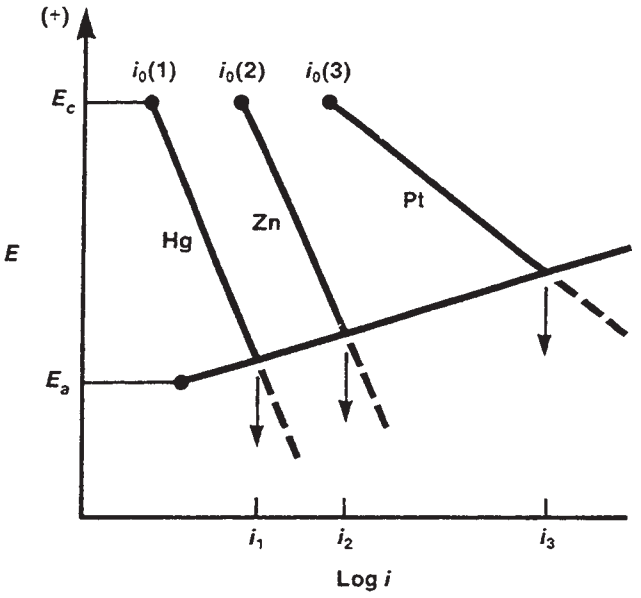


Fig. 33 Effect of increasing the efficiency of cathodic reaction surfaces on the corrosion rate of an active metal

pled with hydrogen evolution on a mercury, zinc, or platinum surface is indicated by i_1, i_2, and i_3, respectively. The corrosion rate in the presence of a highly efficient cathodic surface such as platinum can be many orders of magnitude greater than for a relatively sluggish cathodic surface such as mercury.

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CHAPTER 4

Forms of Corrosion: Recognition and Prevention

CORROSION PROBLEMS can be divided into eight categories based on the appearance of the corrosion damage or the mechanism of attack:

- Uniform or general corrosion
- Pitting corrosion
- Crevice corrosion, including corrosion under tubercles or deposits, filiform corrosion, and poultice corrosion
- Galvanic corrosion
- Erosion-corrosion, including cavitation erosion and fretting corrosion
- Intergranular corrosion, including sensitization and exfoliation
- Dealloying
- Environmentally assisted cracking, including stress-corrosion cracking (SCC), corrosion fatigue, and hydrogen damage (including hydrogen embrittlement, hydrogen-induced blistering, high-temperature hydrogen attack, and hydride formation)

Although these forms are presented in the context of aqueous corrosion, many of them are also operative at high temperature. For example, high-temperature corrosion by oxidation or sulfidation can take the form of uniform attack, pitting, or dealloying. Molten metal or molten

salt environments can produce uniform corrosion, dealloying, or intergranular attack.

While the corrosion classification scheme listed above is convenient, it should be emphasized that it is arbitrary and by no means perfect. Many corrosion problems are due to more than one form of corrosion acting simultaneously. For example, pitting corrosion may be caused by crevice corrosion, deposit corrosion, cavitation, or fretting corrosion. Additionally, in some metal systems where dealloying may occur, this form of corrosion may be a precursor to stress-corrosion cracking. Similarly, deep pits can act as stress raisers and serve as nucleation sites for corrosion fatigue failures.

Some forms of corrosion such as stray-current corrosion and deposition corrosion are extremely difficult to classify. Stray-current corrosion is different from natural corrosion because it is caused by an extremely induced electrical current and is basically independent of some of the environmental factors that influence other forms of corrosion. Deposition corrosion is a combination of pitting and galvanic corrosion that can occur in a liquid environment when ions of more cathodic metal (e.g., copper) are plated out of solution onto a more anodic metal surface (e.g., aluminum).

Despite its shortcomings, the classification of corrosion forms based on physical appearance or attack mechanism allows a large and complex technology to be broken down into more usable and understandable pieces. This classification system is particularly useful for failure analysis, guiding investigators in the determination of contributing factors and of methods for controlling the specific form of corrosion.

Uniform Corrosion

General Description. Uniform or general corrosion, as the name implies, results in a fairly uniform penetration (or thinning) over the entire exposed metal surface. The general attack results from local corrosion-cell action; that is, multiple anodes and cathodes are operating on the metal surface at any given time. The location of the anodic and cathodic areas continues to move about on the surface, resulting in uniform corrosion.

Uniform corrosion represents the greatest destruction of metal on a tonnage basis. This form of corrosion however, is not of too great concern from a technical standpoint because the life of equipment can be accurately estimated on the basis of comparatively simple immersion tests. These tests allow weight (mass) loss to be monitored, and the reduction of thickness as a function of time can be calculated. Corrosion rate expressions and allowances for general corrosion are described in Chapter 2.

Uniform corrosion often results from atmospheric exposure (especially polluted industrial environments); exposure in fresh, brackish, and salt waters; or exposure in soils and chemicals. Corrosion in these environments is discussed in Chapter 5.

Metals Affected. All metals are affected by uniform corrosion, although passive materials, such as stainless steels or nickel-chromium alloys are normally subjected to localized forms of attack. The rusting of steel (Fig. 1), the green patina formation on copper, and the tarnishing of silver are typical examples of uniform corrosion. In some metals, such as steel, uniform corrosion produces a somewhat rough surface by removing a substantial amount of metal, which either dissolves in the environment or reacts with it to produce a loosely adherent, porous coating of corrosion products. In such reactions as in the tarnishing of silver in air, the oxidation of aluminum in air, or attack on lead in sulfate-containing environments, thin, tightly adherent protective films are produced, and the metal surface remains smooth.

Prevention. Uniform corrosion can be prevented or reduced by proper materials selection, the use of coatings or inhibitors, or cathodic or anodic protection. These corrosion prevention methods can be used individually or in combination. Uniform corrosion is often treated by building a corrosion allowance into the structure. If the corrosion rate is



Fig. 1 Uniform corrosion (rusting) of a weathering steel highway bridge girder

100 μm/year, then the addition of 500 μm to the thickness of metal will provide 5 years of operation. The measure of uniform corrosion rate required for determination of the corrosion allowance is estimated from prior conditions in similar service, data presented in the corrosion literature, and experimental data determined from coupon exposures. More detailed information on prevention of uniform corrosion can be found in Chapters 7 to 10. Corrosion allowances are also discussed in Chapter 2.

Pitting Corrosion

General Description. Pitting is a highly localized form of corrosion that produces sharply defined holes. These holes may be small or large in diameter, but in most cases, they are relatively small. Pits may be isolated from each other on the surface or so close together that they resemble a roughened surface. Variations in the cross-sectional shape of pits are shown in Fig. 2.

Every engineering metal or alloy is susceptible to pitting. Pitting occurs when one area of a metal becomes anodic with respect to the rest of the surface or when highly localized changes in the corrodent in contact with the metal, as in crevices, cause accelerated localized attack.

Difficulty of Detection. Pitting is one of the most insidious forms of corrosion. It can cause failure by perforation while producing only a small weight loss on the metal. Also, pits are generally small and often remain undetected. A small number of isolated pits on a generally uncorroded surface are easily overlooked. A large number of very small pits on a generally uncorroded surface may not be detected by simple visual examination, or their potential for damage may be underestimated.

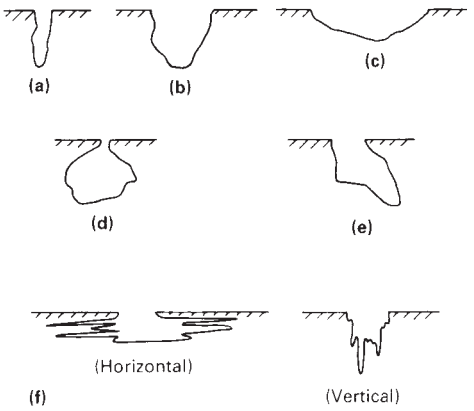


Fig. 2 Variations in the cross-sectional shape of pits. (a) Narrow and deep. (b) Elliptical. (c) Wide and shallow. (d) Subsurface. (e) Undercutting. (f) Shapes determined by microstructural orientation. Source: ASTM G 46

When pits are accompanied by slight or moderate general corrosion, the corrosion products often mask them.

Pitting is sometimes difficult to detect in laboratory tests and in service because there may be a period of months or years, depending on the metal and the corrodent, before the pits initiate and develop to a readily visible size. Delayed pitting sometimes occurs after an unpredictable period of time in service, when some change in the environment causes local destruction of a passive film. When this occurs on stainless steels, for example, there is a substantial increase in solution potential of the active area, and pitting progresses rapidly.

Stages of Pitting. Immediately after a pit has initiated, the local environment and any surface films on the pit-initiation site are unstable, and the pit may become inactive after just a few minutes if convection currents sweep away the locally high concentration of hydrogen ions, chloride ions, or other ions that initiated the local attack. Accordingly, the continued development of pits is favored in a stagnant solution.

When a pit has reached a stable stage, barring drastic changes in the environment, it penetrates the metal at an ever-increasing rate by an autocatalytic process. In the pitting of a metal by an aerated sodium chloride solution, rapid dissolution occurs within the pit, while reduction of oxygen takes place on adjacent surfaces. This process is self-propagating. The rapid dissolution of metal within the pit produces an excess of positive charges in this area, causing migration of chloride ions into the pit (Fig. 3).

Thus, in the pit there is a high concentration of metal chlorides (M^+Cl^-) and as a result of hydrolysis, a high concentration of hydrogen ions. Both hydrogen and chloride ions stimulate the dissolution of most metals and alloys, and the entire process accelerates with time. Because the solubility of oxygen is virtually zero in concentrated solutions, no reduction of oxygen occurs within a pit. Cathodic reduction of oxygen on the surface areas adjacent to pits tends to suppress corrosion on these surface areas. Thus, isolated pits cathodically protect the surrounding metal surface.

Because the dense, concentrated solution within a pit is necessary for its continuing development, pits are most stable when growing in the direction of gravity. Also, the active anions are more easily retained on the upper surfaces of a piece of metal immersed in or covered by a liquid.

Some causes of pitting are local inhomogeneity on the metal surface, local loss of passivity, mechanical or chemical rupture of a protective oxide coating, galvanic corrosion from a relatively distant cathode, the formation of a metal ion or oxygen concentration cell under a solid deposit (crevice corrosion), and the presence of biological organisms.

The rate of pitting is related to the aggressiveness of the corrodent at the site of pitting and the electrical conductivity of the solution containing the corrodent. For a given metal, certain specific ions increase the

probability of attack from pitting and accelerate that attack once initiated. Pitting is usually associated with metal-environment combinations in which the general corrosion rate is relatively low. For a given combination, the rate of penetration into the metal by pitting can be 10 to 100 times that by general corrosion.

With carbon and low-alloy steels in relatively mild corrodents, pits are often generally distributed over the surface and change locations as they propagate. If they blend together, the individual pits become virtually indistinguishable, and the final effect is a roughened surface but a generally uniform reduction in cross section. If the initial pits on carbon steel do not combine in this way, the result is rapid penetration of the metal at the sites of the pits and little general corrosion.

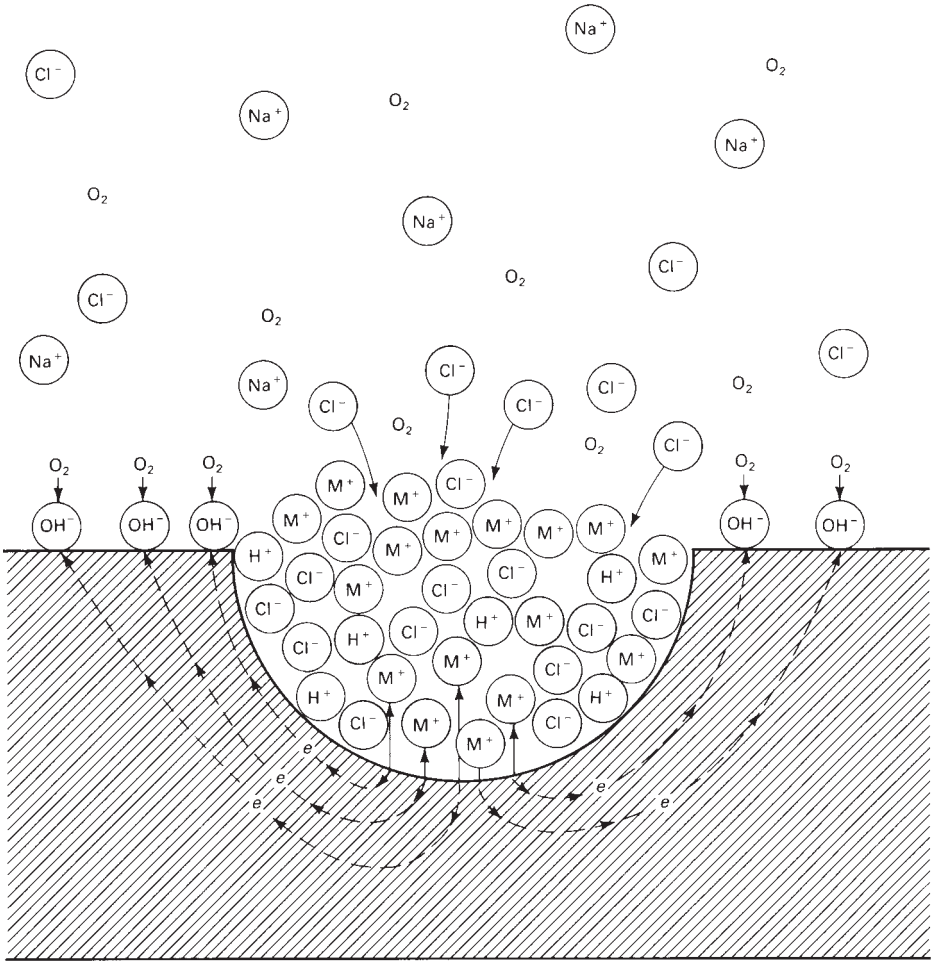


Fig. 3 Autocatalytic processes occurring in a corrosion pit. The metal, M, is being pitted by an aerated sodium chloride (NaCl) solution. Rapid dissolution occurs within the pit, while oxygen reduction takes place on the adjacent surfaces. A more detailed explanation of this self-sustaining process is given in Ref 1.

The most common causes of pitting in steels are surface deposits that set up local concentration cells and dissolved halides that produce local anodes by rupture of the protective oxide film. Anodic corrosion inhibitors, such as chromates, can cause rapid pitting if present in concentrations below a minimum value that depends on the metal-environment combination, temperature, and other factors. Pitting also occurs at mechanical ruptures in protective organic coatings if the external environment is aggressive or if a galvanic cell is active.

With corrosion-resistant alloys, such as stainless steels, the most common cause of pitting corrosion is highly localized destruction of passivity by contact with moisture that contains halide ions, particularly chlorides. Figure 4 shows deep pits that formed in a type 316 stainless steel centrifuge head from a calcium chloride ($CaCl_2$) solution. Chloride-induced pitting of stainless steels usually results in undercutting (see Fig. 2e), producing enlarged subsurface cavities or caverns. Undercutting also occurs when most metals are exposed to highly acidic conditions (Fig. 5).

Pitting of Various Metals. Pitting occurs in most commonly used metals and alloys. Iron buried in the soil corrodes with the formation of shallow pits, but carbon steels in contact with hydrochloric acid or stainless steels immersed in seawater characteristically corrode with the formation of deep pits (Fig. 4 and 6). Aluminum tends to pit in waters containing chloride ions (for example, at stagnant areas), and aluminum brasses are subject to pitting in polluted waters.

Despite their good resistance to general corrosion, stainless steels are more susceptible to pitting than many other metals. High-alloy stainless steels containing chromium, nickel, and molybdenum are also more resistant to pitting but are not immune under all service conditions.

Pitting failures of corrosion-resistant alloys, such as Hastelloy C, Hastelloy G, and Incoloy 825, are relatively uncommon in solutions that do not contain halides, although any mechanism that permits the establishment of an electrolytic cell in which a small anode is in contact with a large cathodic area offers the opportunity for pitting attack.

Prevention. Typical approaches to alleviating or minimizing pitting corrosion include the following:

- Reduce the aggressiveness of the environment, for example, chloride ions concentration, temperature, acidity, and oxidizing agents
- Upgrade the materials of construction, for example, use molybdenum-containing (4 to 6% Mo) stainless steels, molybdenum + tungsten nickel-base alloys, overalloy welds, and use corrosion-resistant alloy linings
- Modify the design of the system, for example, avoid crevices and the formation of deposits, circulate/stir to eliminate stagnant solutions, and ensure proper drainage

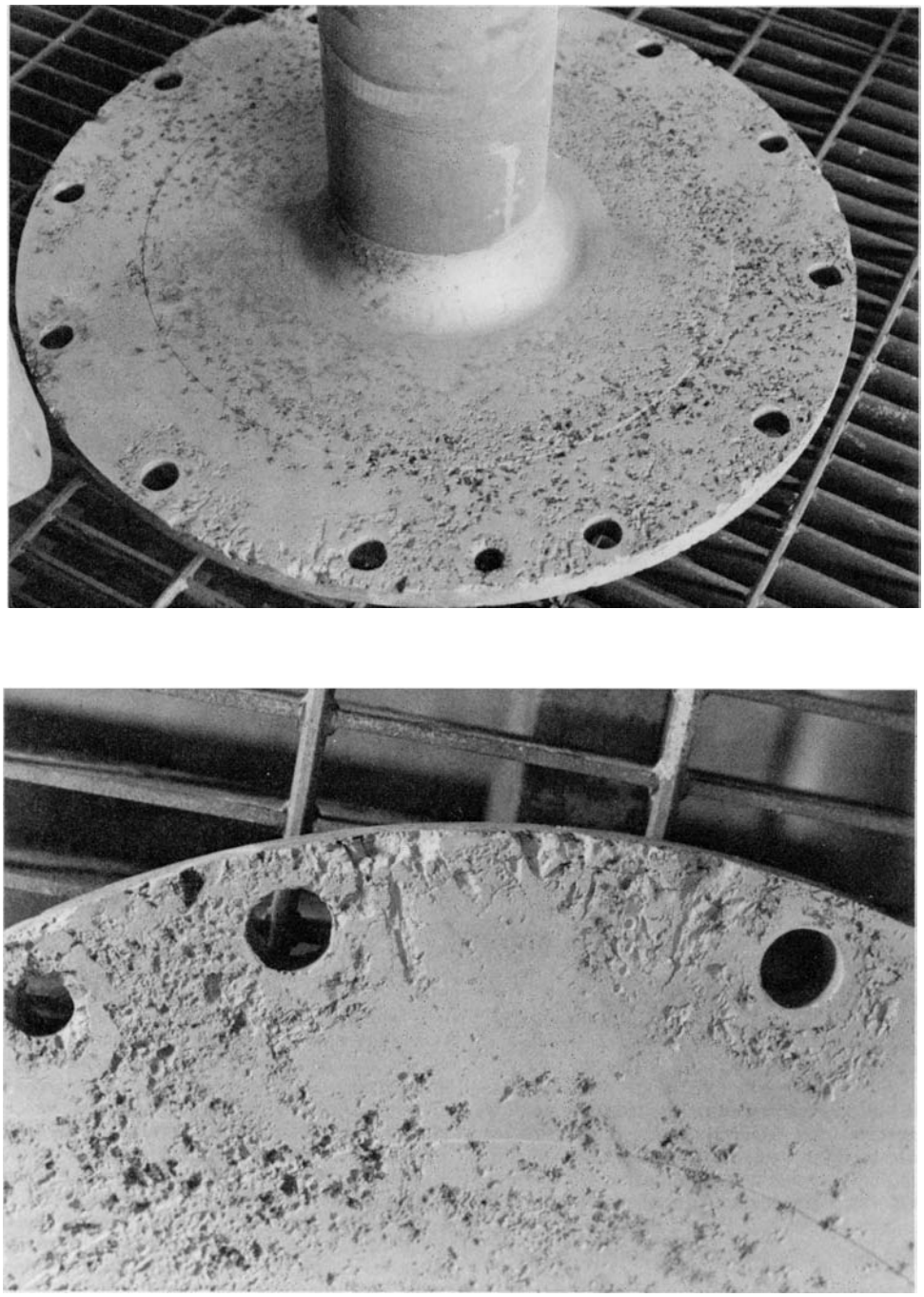
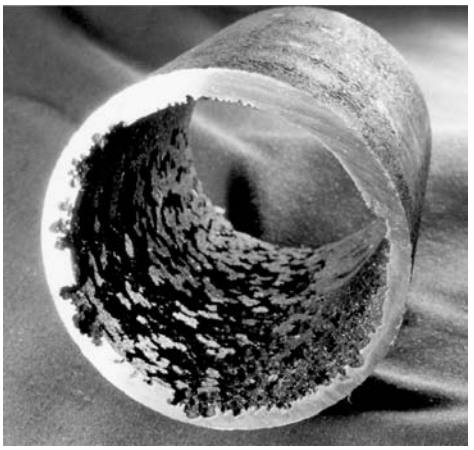


Fig. 4 Two views of deep pits in a type 316 stainless steel centrifuge head due to exposure to $CaCl_2$ solution



(a)



(b)

Fig. 5 (a) Pitting of a carbon steel pipe exposed to a strong mineral acid. (b) Close-up view shows the narrow pit mouths and the pronounced undercutting. Source: Nalco Chemical Company

Crevice Corrosion

General Description. Crevice corrosion is a form of localized attack that occurs at narrow openings or spaces (gaps) between metal-to-metal or nonmetal-to-metal components. This type of attack results from a concentration cell formed between the electrolyte within the crevice, which is oxygen starved, and the electrolyte outside the crevice, where oxygen is more plentiful. The material within the crevice acts as the anode, and the exterior material becomes the cathode.

Crevices may be produced by design or accident. Crevices caused by design occur at gaskets, flanges, rubber O-rings, washers, bolt holes, rolled tube ends, threaded joints, riveted seams, overlapping screen

wires, lap joints, beneath coatings (filiform corrosion) or insulation (poultice corrosion), and anywhere close-fitting surfaces are present. Occluded regions are also formed under tubercles (tuberculation), deposits (deposit corrosion), and below accumulations or biological materials (biologically influenced corrosion). Similarly, unintentional crevices such as cracks, seams, and other metallurgical defects could serve as sites for corrosion.

Resistance to crevice corrosion can vary from one alloy-environment system to another. Although crevice corrosion affects both active and passive metals, the attack is often more severe for passive alloys, particularly those in the stainless steel group. Breakdown of the passive film within a restricted geometry leads to rapid metal loss and penetration of the metal in that area.

Numerous interrelated metallurgical, geometrical, and environmental factors, as well as electrochemical reactions, affect both crevice initiation and propagation. A number of these factors are indicated in Table 1.

Crevice Corrosion Propagation. The propagation of crevice corrosion is thought to involve the dissolution of metal and the maintenance of a high degree of acidity within the crevice solution by hydrolysis of the dissolved metal ions (Ref 1). The crevice corrosion propagation process is illustrated schematically in Fig. 7 for stainless steel corroding in a

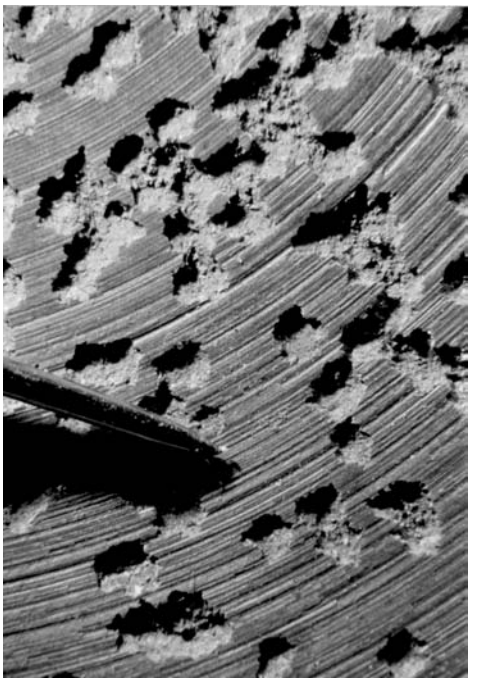


Fig. 6 Deep pits on a carbon steel check valve that was inadvertently exposed to hydrochloric acid during a plant upset. Note how pits intersect to form areas of jagged metal loss. A steel probe tip is also shown in the photo. Source: Nalco Chemical Company

neutral aerated sodium chloride solution. The anodic metal dissolution reaction within the crevice, $M \rightarrow M^{n+} + ne^-$, is balanced by the cathodic reaction on the adjacent surface, $O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$. The increased concentration of M^+ within the crevice results in the influx of chloride ions (Cl^-) to maintain neutrality. The metal chloride formed, M^+Cl^-, is hydrolyzed by water to the hydroxide and free acid as:

$$M^+Cl^- + H_2O \rightarrow MOH + H^+Cl^-$$

The acid produced by the hydrolysis reaction keeps the pH to values below 2 (Ref 2), while the pH of the solution outside the crevice remains neutral (pH 7). In simple terms, the electrolyte present within an actively corroding crevice can be regarded as concentrated hydrochloric acid containing metal chlorides dissolved at concentrations near saturation.

Examples of Crevice Corrosion. Figure 8 shows crevice corrosion of a type 304 stainless steel fastener removed from a seawater jetty after 8 years. Although the washer shows severe deterioration, the function

Table 1 Factors that can affect the crevice corrosion resistance of various alloys

Factor	Type
Geometrical	Type of crevice
	Metal-to-metal
	Nonmetal to metal
	Crevice gap (tightness)
	Crevice depth
	Exterior-to-interior surface area ratio
Environmental	Bulk solution
	O_2 content
	pH
	Chloride level
	Temperature
	Agitation
	Mass transport, migration
	Diffusion and convection
	Crevice solution: hydrolysis equilibria
	Biological influences
Electrochemical reactions	Metal dissolution
	O_2 reduction
	H_2 evolution
Metallurgical	Alloy composition
	Major elements
	Minor elements
	Impurities

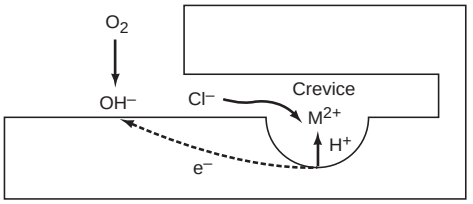


Fig. 7 A schematic of the crevice corrosion propagation mechanism

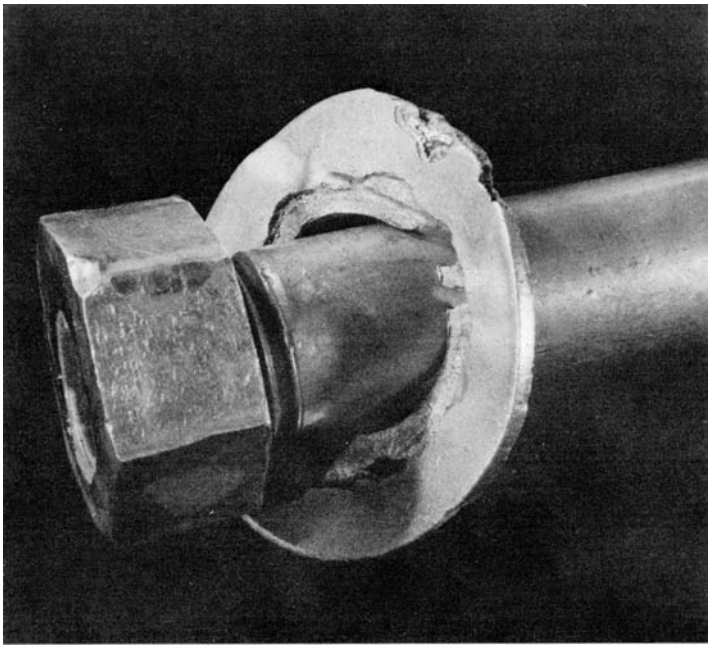


Fig. 8 Crevice corrosion at a metal-to-metal crevice site formed between components of type 304 stainless steel fastener in seawater

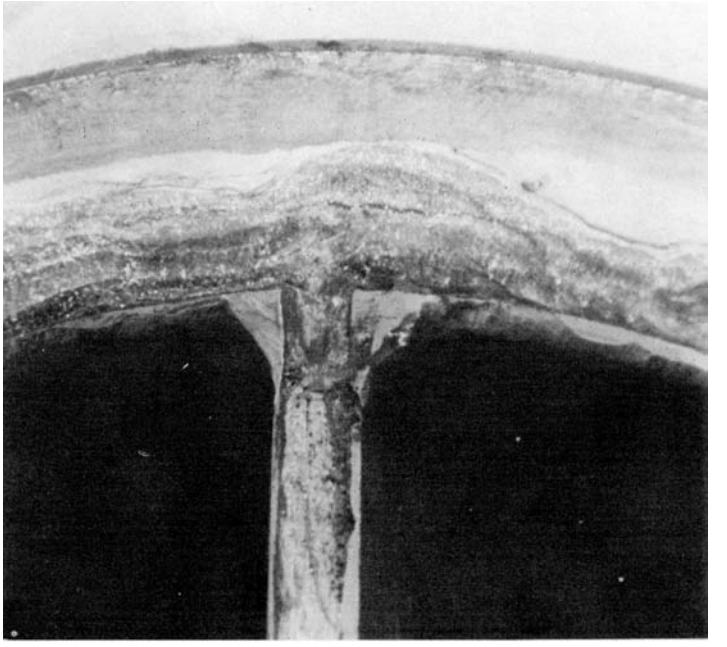
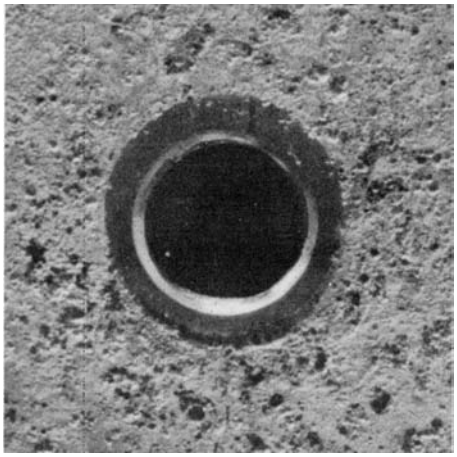


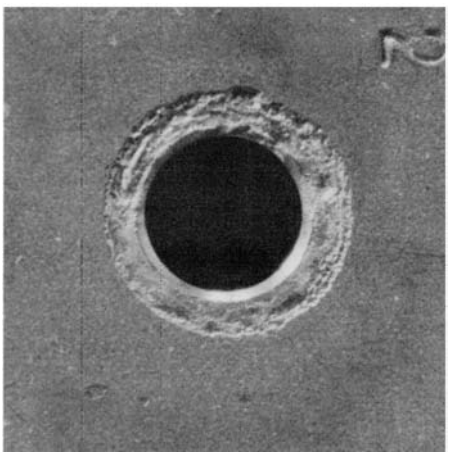
Fig. 9 Crevice corrosion at nonmetal gasket site on an alloy 825 seawater heat exchanger

of the fastener was not diminished. On the other hand, Fig. 9 shows crevice corrosion beneath the water-box gasket of an alloy 825 (44Ni-22Cr-3Mo-2Cu) seawater heat exchanger that allowed sufficient leakage to warrant shutdown and replacement after only 6 months.

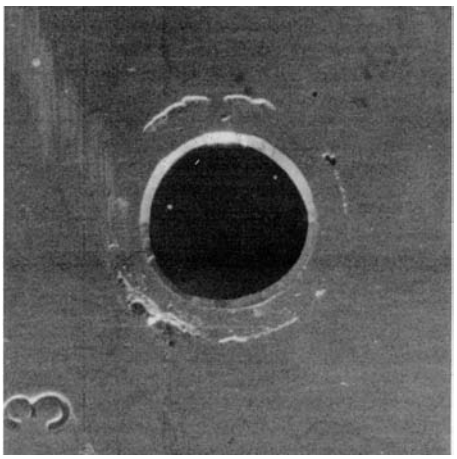
In cases in which the bulk environment is particularly aggressive, general corrosion may preclude localized corrosion at a crevice site. Figure 10 compares the behavior of type 304 and type 316 stainless steels exposed in different zones of a model sulfur dioxide (SO_2) scrubber. In the aggressive acid condensate zone, type 304 incurred severe general corrosion of the exposed surfaces, while the more resistant type 316 suffered attack beneath a polytetrafluoroethylene (PTFE) insulating spacer. In the higher pH environment of the limestone slurry zone, type 304 was resistant to general corrosion but was susceptible to crev-



(a)



(b)



(c)

Fig. 10 Variation in stainless steel corrosion resistance in model SO_2 scrubber environments. (a) Type 304 in acid condensate. (b) Type 316 in acid condensate. (c) Type 304 in limestone slurry zone

ice corrosion. Other alloy systems, such as aluminum and titanium, may also be susceptible to crevice corrosion. For aluminum, the occurrence of crevice corrosion would depend on the passivity of the particular alloy. In most cases, general corrosion would likely preclude crevice corrosion. Titanium alloys are typically quite resistant but may be susceptible to crevice corrosion in elevated temperature, chloride-containing acidic environments.

Although the occurrence of crevice corrosion in cast irons and carbon steels is not frequent, the presence of chlorides and/or crevices or other shielding areas presents conditions that can be favorable to crevice attack. Rust often accumulates at crevice mouths, and darker oxides are present within the crevices. Figure 11 shows a cast-iron valve block that exhibited crevice corrosion beneath rubber O-rings.

In seawater, localized corrosion of copper and its alloys at crevices is different from that of stainless-type materials because the attack occurs outside of the crevice rather than within. In general, the degree of crevice- related attack increases. Figure 12 compares the crevice corrosion behavior for several different materials exposed to ambient-temperature seawater for various periods. In each case, a nonmetallic washer created the crevice. The more classical form of crevice corrosion (that is, beneath the crevice former) is shown for type 904L stainless steel (20Cr-25Ni-4.5Mo-1.5Cu) after only 30 days of exposure (Fig. 12a). For 70Cu-30Ni, corrosion occurred just outside of the crevice mouth and was found to be quite shallow after 6 months (Fig. 12b). In contrast, crevice-related corrosion of alloy 400 (70Ni-30Cu) was more severe after only 45 days (Fig. 12c). In some cases, corrosion may occur within as well as outside of the crevice.

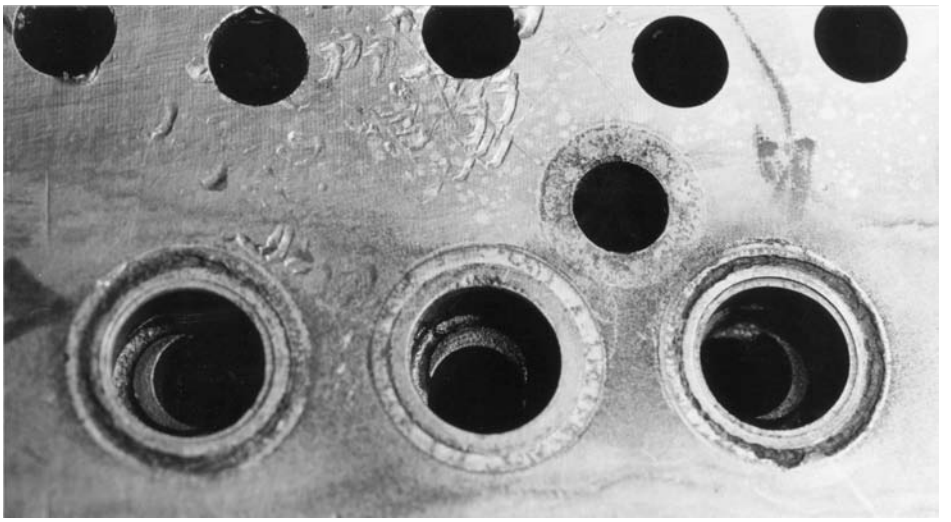
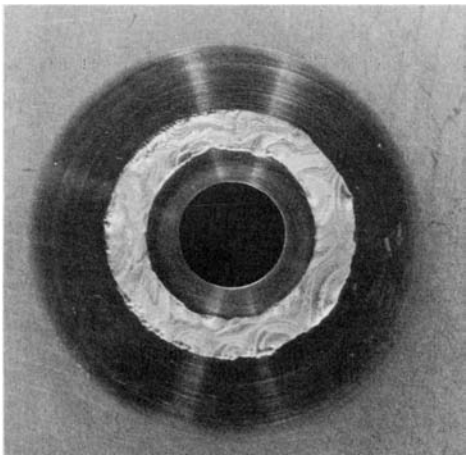
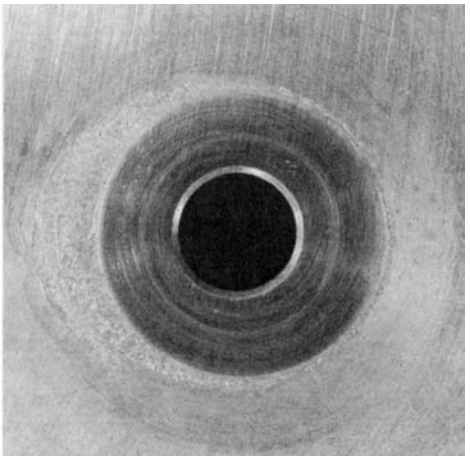


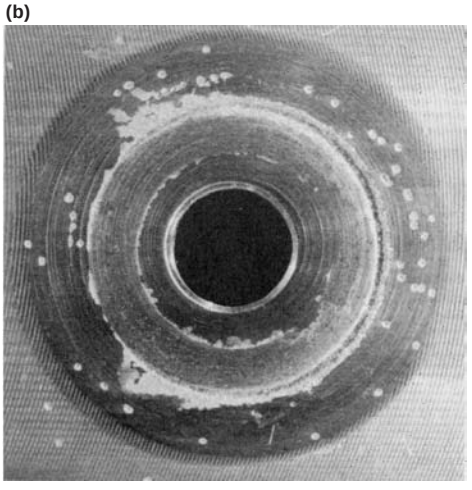
Fig. 11 Closeup of annular regions below rubber O-rings on a cast-iron valve block. Note how damage varies from hole to hole, probably due to variation in the crevice geometry. Source: Nalco Chemical Company



(a)



(b)



(c)

Fig. 12 Crevice-related corrosion for different alloys in natural seawater. (a) Alloy 904L (20Cr-25Ni-4.5Mo-1.5Cu) after 30 days. (b) 70Cu-30Ni after 180 days. (c) Alloy 400 (70Ni-30Cu) after 45 days

Prevention. Many of the factors listed in Table 1 must be considered if crevice corrosion is to be eliminated or minimized. Wherever possible, crevices should be eliminated at the design stage (guidelines and illustrations are presented in Chapter 7). When unavoidable, they should be kept as open and shallow as possible to allow continued entry of the bulk environment.

As with pitting corrosion, a common way to protect against crevice corrosion is to select more corrosion-resistant materials (e.g., molybdenum-containing, more highly alloyed stainless steels and nickel-base alloys). Weld overlays can also be employed.

The influence of gasket material on nonmetal-to-stainless steel crevice formation should also be considered. Natural and synthetic elastomer-type gaskets are less likely to promote crevice corrosion than polytetrafluoroethylene (PTFE) gaskets (with or without glass fiber) and para-aramid fiber + nitrile binder-type gaskets. While carbon and graphite-containing gaskets promote crevice, PTFE and para-aramid + nitrile promote even greater attack.

Cleanliness is an important factor, particularly when conditions promote deposition on metal surfaces. Regular cleaning involving mechanical methods is commonly employed. Filters can also be employed to remove materials that can deposit on the metal surface. It is very important to try to avoid using hydrochloric acid to clean stainless steel systems. Chloride will concentrate in preexisting crevices during cleaning and may not be removed subsequently.

Tuberculation (Ref 3)

General Description. Tuberculation, which is a specific type of crevice corrosion often encountered in cooling water systems, is defined as "the formation of localized corrosion products scattered over the surface in the form of knoblike mounds called tubercles." Tubercles can choke pipes, leading to diminished flow and increased pumping costs (Fig. 13). Tubercles form on steel and cast iron when surfaces are exposed to oxygenated waters. Soft waters with high bicarbonate alkalinity stimulate tubercle formation, as do high concentrations of sulfate, chloride, and other aggressive anions (Ref 3). The formation of tubercles by biological organisms acting in conjunction with electrochemical corrosion also occurs in many aqueous environments. Sulfate-reducing and acid-producing bacteria associated with biological organisms accelerate crevice attack. It should be noted, however, that tubercles frequently form without the presence of any biological organisms, and the following discussion does not take into account biological effects. Chapter 5 describes the influence of biological organisms and biofilms on corrosion.

Features and Growth Characteristics. Tubercles are much more than amorphous lumps of corrosion product and deposit. As shown in Fig. 14(a), they are highly structured and consist of five distinct layers (Ref 4):

- Outer crust (primarily red, brown, and orange corrosion products (i.e., rust)
- Inner shell (magnetite)
- Core material (ferrous hydroxide)
- Fluid-filled cavity (containing Fe^{2+}, Cl^{-}, and SO_4^{2+})
- Corroded floor, which is almost always a dish-shaped depression that is much wider than it is deep (Fig. 15). Average corrosion rates are usually 0.5 mm/year (20 mils/year) or less.

Typical reactions occurring within these five layers are shown in Fig. 14(b). As rust accumulates, oxygen migration is reduced through the corrosion product layer. Regions below the rust layer become oxygen depleted. An oxygen concentration cell then develops. Corrosion naturally becomes concentrated into small regions beneath the rust, and volcanolike structures, or tubercles, are generated.

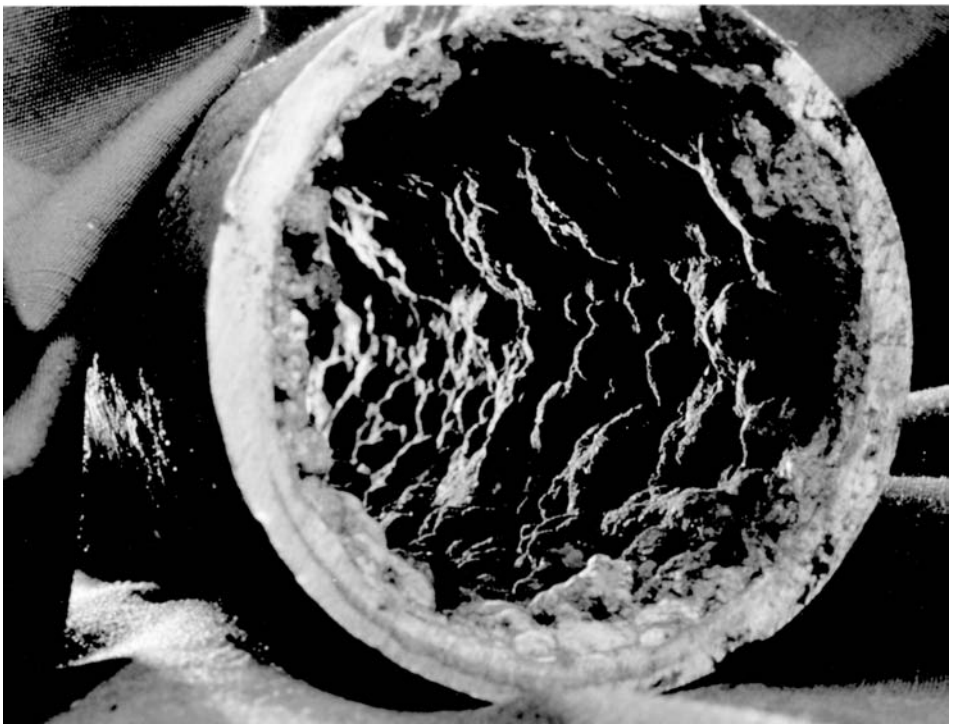


Fig. 13 Heavily tuberculated 75 mm (3 in.) outer diameter steel mill water supply line. Source: Nalco Chemical Company

The unique features of tubercles can better be appreciated by examining the series of photos in Fig. 16 and 17 that show a tuberculated 1010 carbon steel baffle plate from a test water box in a utility cooling system. After a two-week period to monitor corrosion and fouling, small, hollow incipient tubercles dotted the surface of the plate (Fig. 16a). Each tubercle capped a depression (pit) no deeper than 0.13 mm (0.005 in.) (Fig. 16b). This indicated local average corrosion rates were as high as 3.3 mm/year (130 mils/year). Each tubercle exhibited small clam-shell marks or growth rings (Fig. 17a). Each ring was formed by fracture at the tubercle base during growth. Ejected internal contents rapidly deposited

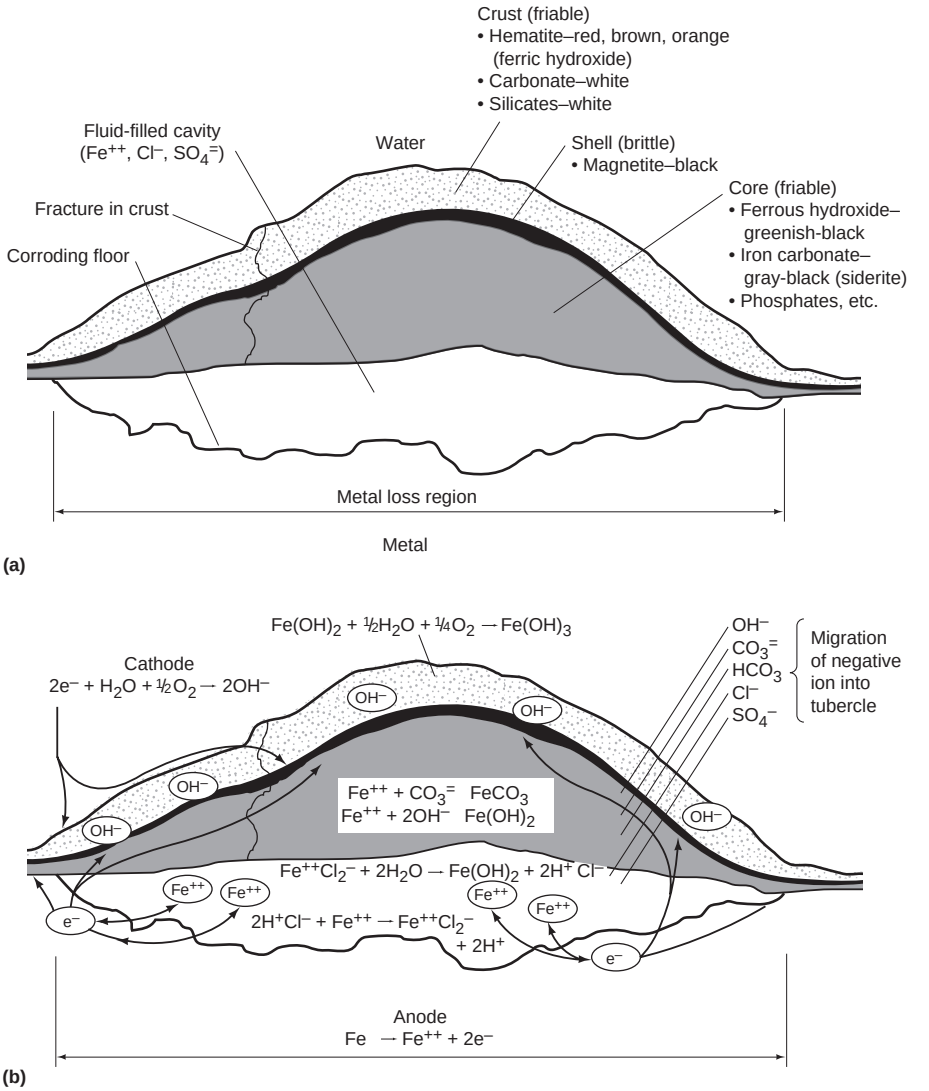


Fig. 14 Schematics of tubercles formed on iron or steel in oxygenated waters. (a) Structural features and associated compounds. (b) Corrosion reactions within the tubercle. Source: Ref 4

when contacting oxygenating water. Tubercles were hollow (Fig. 17b), and the surfaces below the cap contained concentrations exceeding 10% of chloride and sulfate, producing severe localized acidic conditions.

Prevention. Tuberculation can be prevented or minimized by the following:

- Using inhibitors
- Altering system operation (e.g., controlling water flow and temperature conditions)
- Coating the carbon steel or cast iron components with epoxy or other field-applied or factory-applied organic coatings
- Using more corrosion-resistant materials such as stainless (not sensitized), brasses, copper-nickels, titanium, or aluminum. None of these materials will form tubercles in oxygenated water. However, each of these alloys may suffer other problems that would preclude their use in a specific environment.

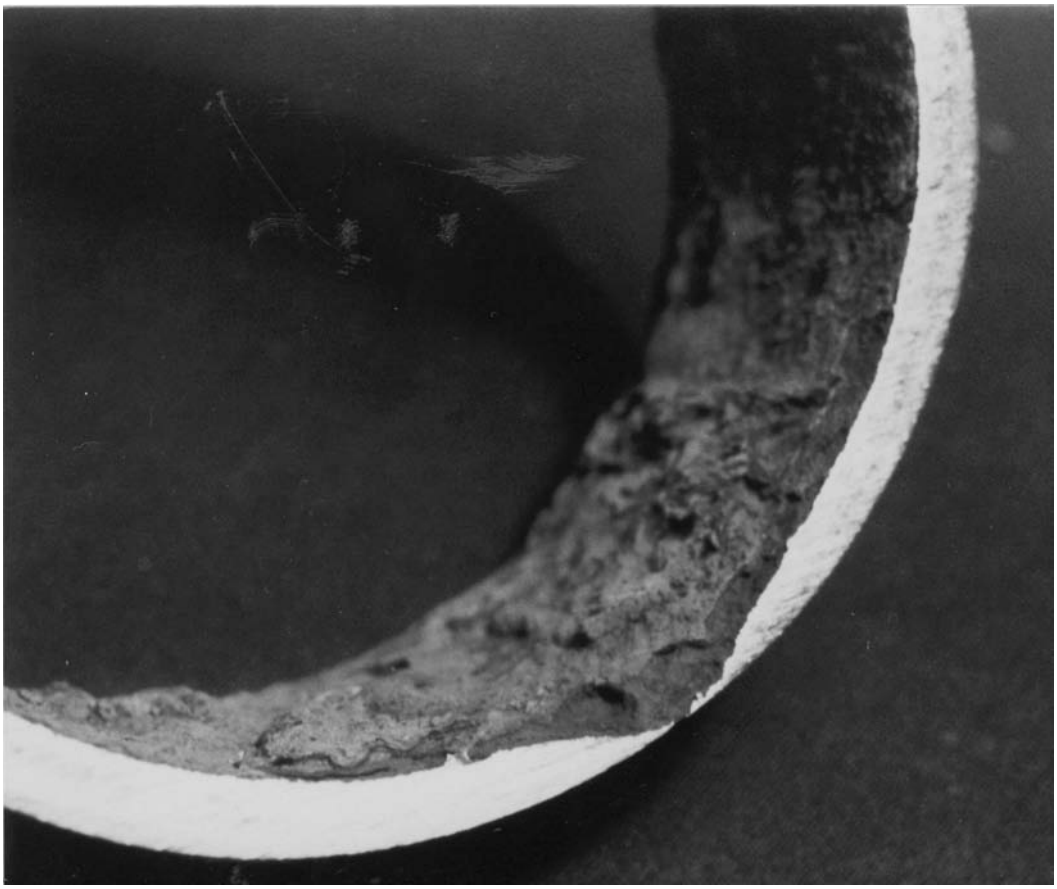


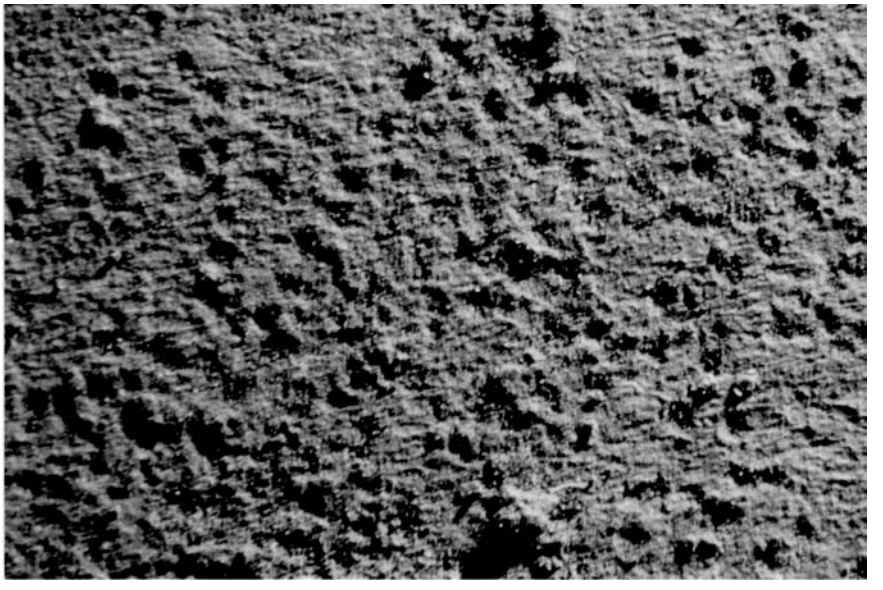
Fig. 15 Perforation at a dish-shaped depression on the internal surface of a large-diameter steel pipe. A large tubercle capped the depression but was dislodged during tube sectioning. Source: Nalco Chemical Company

Deposit Corrosion

General Description. Deposit corrosion refers to crevice corrosion occurring under naturally occurring nonman-made deposits. It has also been referred to as "underdeposit corrosion" in the literature (Ref 3).



(a)



(b)

Fig. 16 Tuberculation of a steel baffle plate. (a) Numerous incipient tubercles formed in 2 weeks. (b) Tubercles removed to show pitlike depressions beneath each mound. Source: Nalco Chemical Company

Deposits include water-borne precipitates (e.g., carbonates, silicates, and phosphates in cooling water systems), transported particulate, corrosion products (e.g., manganese-rich deposits or iron oxides), biological materials, and a variety of contaminants such as grease, oil, process chemicals, silt, sand, and road debris (e.g., salt, mud, and water deposited

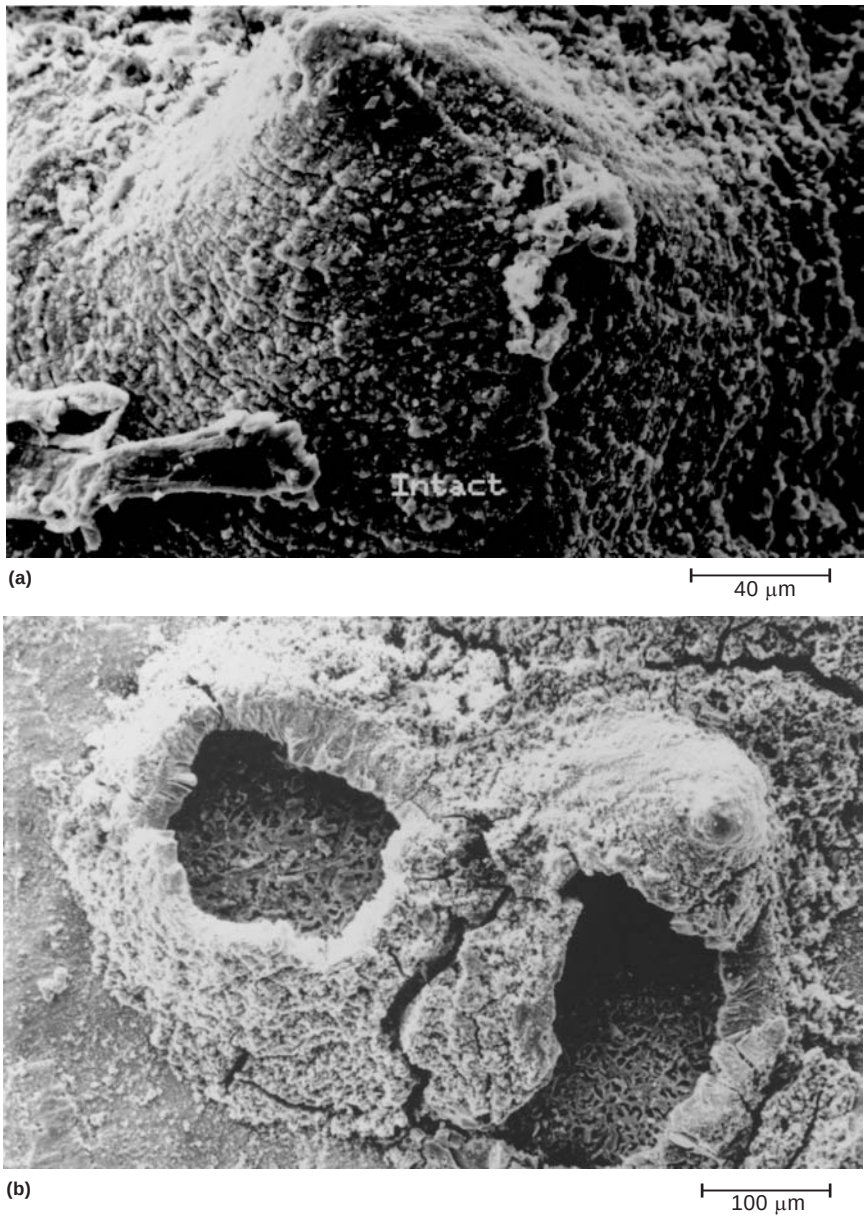


Fig. 17 Scanning electron micrographs of the tubercles shown in Fig. 16. (a) Clam-shell growth steps formed by successive fractures of the tubercle base. (b) Tubercles broken open to reveal hollow interiors. Source: Nalco Chemical Company

on the underside of automobile fenders). Associated corrosion is fundamentally related to whether deposits are innately aggressive (e.g., deposits containing corrosive substances such as sulfur-containing and chlorine-containing species) or simply serve as an occluding medium beneath which concentration cells develop. Severe wastage from pitting or general corrosion can occur under these deposits. Deposits that are heavily stratified can also clog pipelines (Fig. 18). Figure 19 shows deposits containing organic acids formed by oxidation of rolling mill oils. Up to 40% by weight of the lumps shown in Fig. 19 are iron oxides, hydroxides, and organic-acid iron salts.

Metals Affected. Unlike tuberculation, which is associated with only cast irons and steels, deposit corrosion affects a wide variety of metals and is of particular concern with passive alloys such as stainless steels, aluminum, nickel, and titanium. Figure 20 shows how the concentration of aggressive ions beneath deposits can produce severe localized corrosion on stainless steels. Materials selection should be based on careful testing in the specific service environment anticipated.

Prevention. Deposit-related corrosion may be minimized by the following:

- Regular cleaning to remove deposits



Fig. 18 Thick calcium carbonate deposits on a condenser tube and a copper transfer pipe. Heavily stratified deposits reflect changes in water chemistry, heat transfer, and flow. Corrosion may be slight beneath heavy accumulations of fairly pure calcium carbonate because such layers can inhibit some forms of corrosion. However, calcium carbonates are often intermixed with silt, metal oxides, and other precipitates, leading to severe deposit attack. Source: Nalco Chemical Company

- Design changes. Deposition caused by settling of suspended particulate may be reduced by increasing flow. Dead legs, stagnant areas, and other low-flow regions should be eliminated if possible.
- Water treatments, such as removing suspended solids, the use of biodispersants and biocides in biofouled systems, and the judicious use of inhibitors
- Cathodic protection

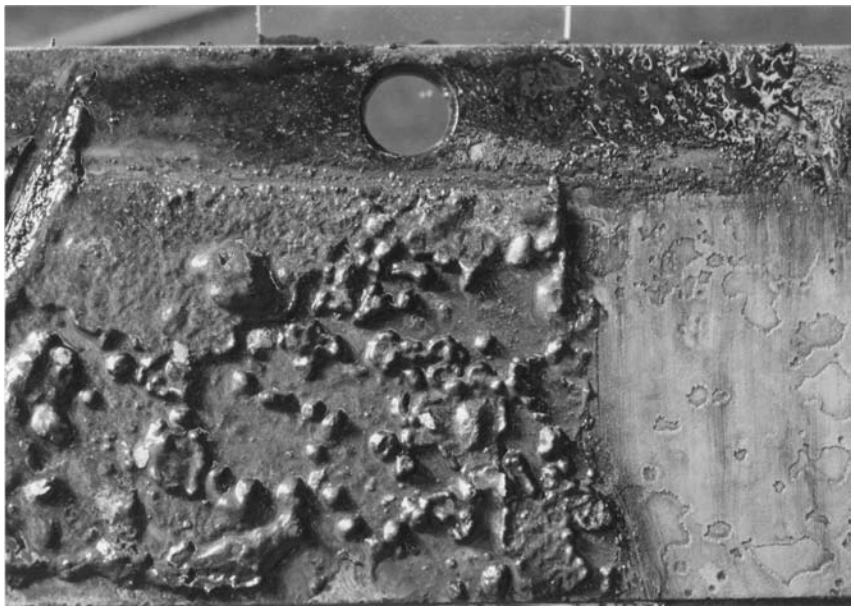


Fig. 19 Carbon steel coupon removed from a rolling mill cooling tank. Note the thick greasy deposits resulting from rolling oils. Removal of the deposits shows the corrosion beneath (see right side of figure). Source: Nalco Chemical Company

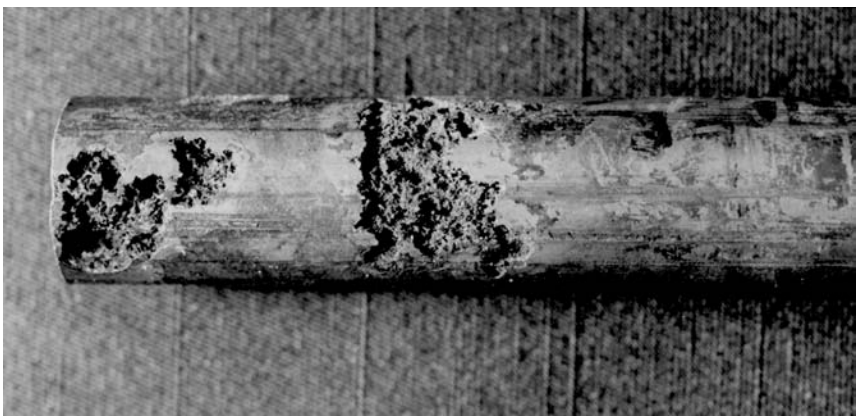


Fig. 20 Severe localized corrosion on a type 316 stainless steel heat exchanger tube. Attack occurred beneath deposits, which were removed to show wastage. Source: Nalco Chemical Company

- Protective coatings such as water-impermeable phenolic resins, epoxies, and other organic compounds, sacrificial coatings (e.g., zinc thermal spray coatings), and electroplated coatings

Filiform Corrosion

General Description. Filiform corrosion is a special case of concentration-cell corrosion that occurs on metallic surfaces coated with a thin organic film that is typically 0.1 mm (4 mils) thick. The pattern of attack is characterized by the appearance of fine filaments emanating from one or more sources in semirandom directions. The source of initiation is usually a defect or scratch in the coating. The filaments are fine tunnels composed of corrosion products underneath the bulged and cracked coating. Filiforms are visible at an arm's length as small blemishes. Upon closer examination, they appear as fine striations shaped like tentacles or cobweblike traces (Fig. 21). A filiform has an active head and a filamentous tail (Fig. 22).

Filiform attack occurs when the relative humidity is typically between 65 and 90% in most cases. The average width of a filament varies between 0.05 to 3 mm (2 to 120 mils). Filament width depends on the

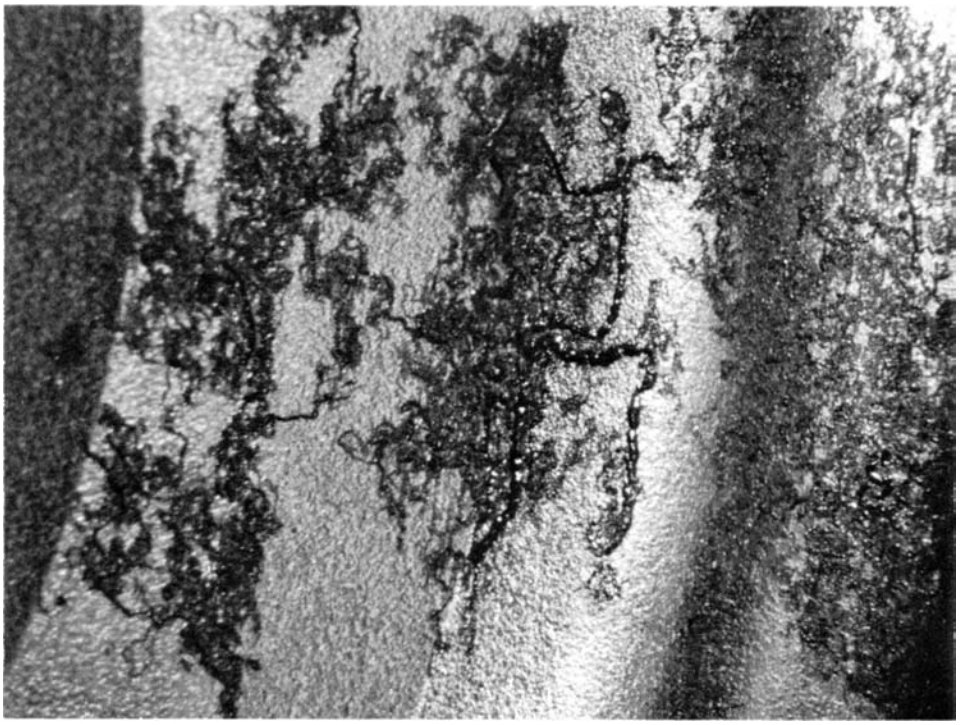
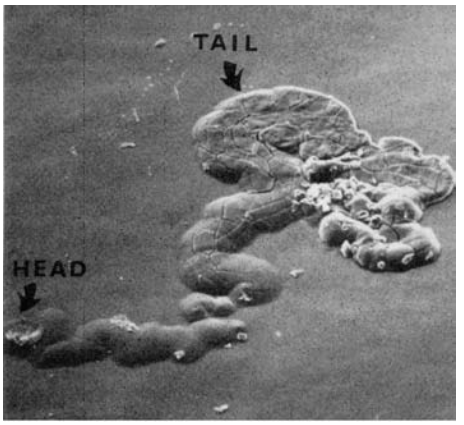
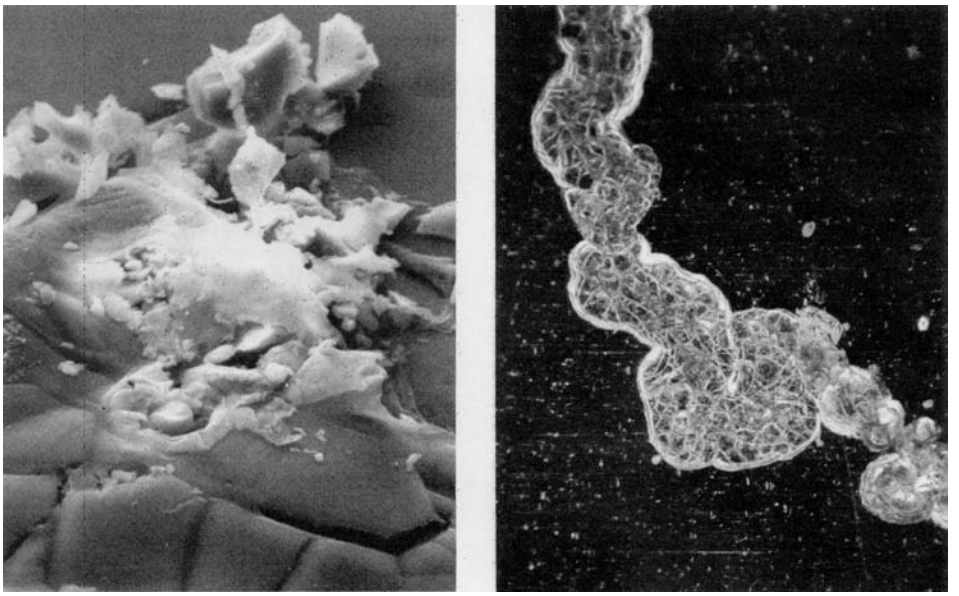


Fig. 21 A lacquered steel can lid exhibiting filiform corrosion showing both large and small filaments partially oriented in the rolling direction of the steel sheet. Without this 10× magnification by a light microscope, the filiforms look like fine striations or minute tentacles.

coating, the ambient relative humidity, and the corrosive environment. Typical filament height is about 20 μm (0.8 mil). The filament growth rate can also vary widely, with rates observed as low as 0.01 mm/day (0.4 mil/day) and up to a maximum rate of 0.85 mm/day (35 mils/day). The depth of attack in the filiform tunnels can be as deep as 15 μm (0.6 mil). The fluid in the leading head of a filiform is typically acidic, with a



(a)



(b) (c)

Fig. 22 Filiform corrosion of PVC-coated aluminum foil. (a) Advancing head and cracked tail section of a filiform cell. Scanning electron microscopy (SEM), 80×. (b) The gelatinous corrosion products of aluminum oozing out of the porous end tail section of a filiform cell. SEM. 830×. (c) Tail region of a filiform cell. Tail appears iridescent due to internal reflection. Light microscopy, 60×

pH from 1 to 4. In all cases, oxygen or air and water were needed to sustain filiform corrosion.

Metals Affected. Filiform corrosion routinely occurs on coated steel cans, coated tin-plated steel, aluminum foil-laminated packaging, painted aluminum, painted magnesium, and other lacquered metallic items placed in areas subjected to high humidity. Growth rates for filiform corrosion on various coated metals are listed in Table 2.

Prevention. Prevention of filiform corrosion can be accomplished by the following:

- Reduction of relative humidity to below 60% by the use of drying fans, dehumidifiers, or the addition of desiccants in packaging applications
- Use of zinc (galvanizing) and zinc primers on steels
- Use of zinc chromate primers, chromic acid anodizing, and chromate or chromate-phosphate conversion coatings on aluminum
- Use of multiple-coat paint systems
- Use of less active metal substrates (e.g., copper, stainless steel, or titanium)

Table 2 Filiform corrosion growth rates on various coated metals

Coating	Initiating environment	Typical rate		Relative humidity, %	Filament width	
		mm/day	mils/day		mm	mils
Steels						
Varnish	NaCl	0.33–0.53	13–21	65–85	0.1–0.3	4–12
	Acetic acid	0.5	20	86	0.15	6
Copol	NaCl	0.03	1.2	60–94	…	…
Lacquer	Acetic acid	0.85	33.5	…	0.1–0.5	4–20
Linseed oil	NaCl	0.04–0.08	1.6–3.1	…	0.05–0.1	2–4
Alkyds	NaCl	0.50	20	80	0.1–0.5	4–20
	Acetic acid	0.1	4	85	…	…
Alkyd urea	$FeCl_2$	0.26–0.43	10–17	80	0.25	10
Epoxy urea	$NaCl/FeCl_2$	0.01–0.46	0.4–18	80	0.25	10
Epoxy	Acetic acid	0.16	6.3	85	…	…
Acrylic	NaCl	0.19–0.86	7.5–34	80	0.25	10
	Acetic acid	0.1	4	85	…	…
Polyurethane	NaCl	0.16–0.50	6.3–20	90	0.1–0.3	4–12
	Acetic acid	0.9	3.5	85	…	…
Polyester	Acetic acid	0.08	3.1	85	…	…
Aluminum alloys						
Alkyds	HCl vapor	0.1	4	85	0.5–1.0	20–40
Acrylic	HCl vapor	0.1	4	85	0.5–1.0	20–40
Polyurethane	HCl vapor	0.1	4	75–85	0.5–1.0	20–40
Polyester	HCl vapor	0.2	4	85	0.5–1.0	20–40
Epoxy	HCl vapor	0.09	3.5	85	0.5–1.0	20–40
Magnesium						
Alkyds	HCl vapor	0.2	8	75	…	…
Acrylic	HCl vapor	0.3	12	75	…	…
Polyurethane	HCl vapor	0.3	12	75	…	…
Polyester	HCl vapor	0.2	8	75	…	…
Epoxy	HCl vapor	0.3	12	75	…	…

Poultice Corrosion (Ref 5)

General Description. Poultice corrosion is a special case of localized corrosion due to differential aeration, which usually takes the form of pitting when an absorptive material such as paper, wood, asbestos, sacking, or cloth is in contact with a metal surface that becomes wetted periodically. No action occurs while the entire assembly is wet, but during the drying period, adjacent wet and dry areas develop. Near the edges of the wet zones, differential aeration develops, which leads to pitting, as in the case of crevice corrosion.

Prevention. Poultice corrosion is prevented by avoiding the contact of absorptive materials with a metal surface, by painting the surface that will contact such materials, or by designing to prevent such materials from becoming wet in service.

Galvanic Corrosion

General Description

Galvanic corrosion occurs when a metal or alloy is electrically coupled to another metal or conducting nonmetal in the same electrolyte. The three essential components are the following:

- Materials possessing different surface potential
- A common electrolyte
- A common electrical path

A mixed metal system in a common electrolyte that is electrically isolated will not experience galvanic corrosion, regardless of the proximity of the metals or their relative potential or size.

During galvanic coupling, corrosion of the less corrosion-resistant metal increases, and the surface becomes anodic, while corrosion of the more corrosion-resistant metal decreases, and the surface becomes cathodic. The driving force for corrosion or current flow is the potential developed between the dissimilar metals. The extent of accelerated corrosion resulting from galvanic coupling is affected by the following factors:

- The potential difference between the metals or alloys
- The nature of the environment
- The polarization behavior of the metals or alloys
- The geometric relationship of the component metals or alloys

The differences in potential between dissimilar metals or alloys cause electron flow between them when they are electrically coupled in a

conductive solution. The direction of flow and, therefore, the galvanic behavior depend on which metal or alloy is more active. Thus, the more active metal or alloy becomes anodic, and the more noble metal or alloy becomes cathodic in the couple. The driving force for galvanic corrosion is the difference in potential between the component metals or alloys.

Galvanic Series

When all that is necessary to know is which of the materials in a system are possible candidates for galvanically accelerated corrosion and which will be unaffected or protected, information obtained from a galvanic series in the appropriate medium is useful. A galvanic series is a list of freely corroding potentials of the materials of interest in the environment of interest, arranged in order of potential. A galvanic series is easy to use and is often all that is required to answer a simple galvanic corrosion question. The material with the most negative, or anodic, corrosion potential has a tendency to suffer accelerated corrosion when electrically connected to a material with a more positive, or cathodic (noble), potential. The disadvantages of using a galvanic series include the following:

- No information is available on the rate of corrosion.
- Active-passive metals may display two widely differing potentials.
- Small changes in the electrolyte can cause significant changes in the potentials.
- Potentials may be time dependent.

Creating a galvanic series is a matter of measuring the corrosion potentials of various materials of interest in the electrolyte of interest against a reference electrode half cell, such as saturated calomel. Preparation of a valid galvanic series for specific materials in a particular service environment must account for all the factors that affect the potential of these materials in that environment. These factors include material composition, heat treatment, surface preparation (mill scale, coatings surface finish, and so on), surface oxides occurring in air, environmental composition (trace contaminants, dissolved gases, and so on), temperature, and flow rate. Exposure time is also important, particularly for materials that form corrosion product layers. All of the precautions and warnings regarding the generation and use of a galvanic series are given in ASTM standard G 82 “Standard Guide for Development and Use of a Galvanic Series for Predicting Galvanic Corrosion Performance.”

The galvanic series for metals in seawater at room temperature is presented in Fig. 23. While this galvanic series is quite useful, its use for corrosion applications in other environments or at other temperatures is

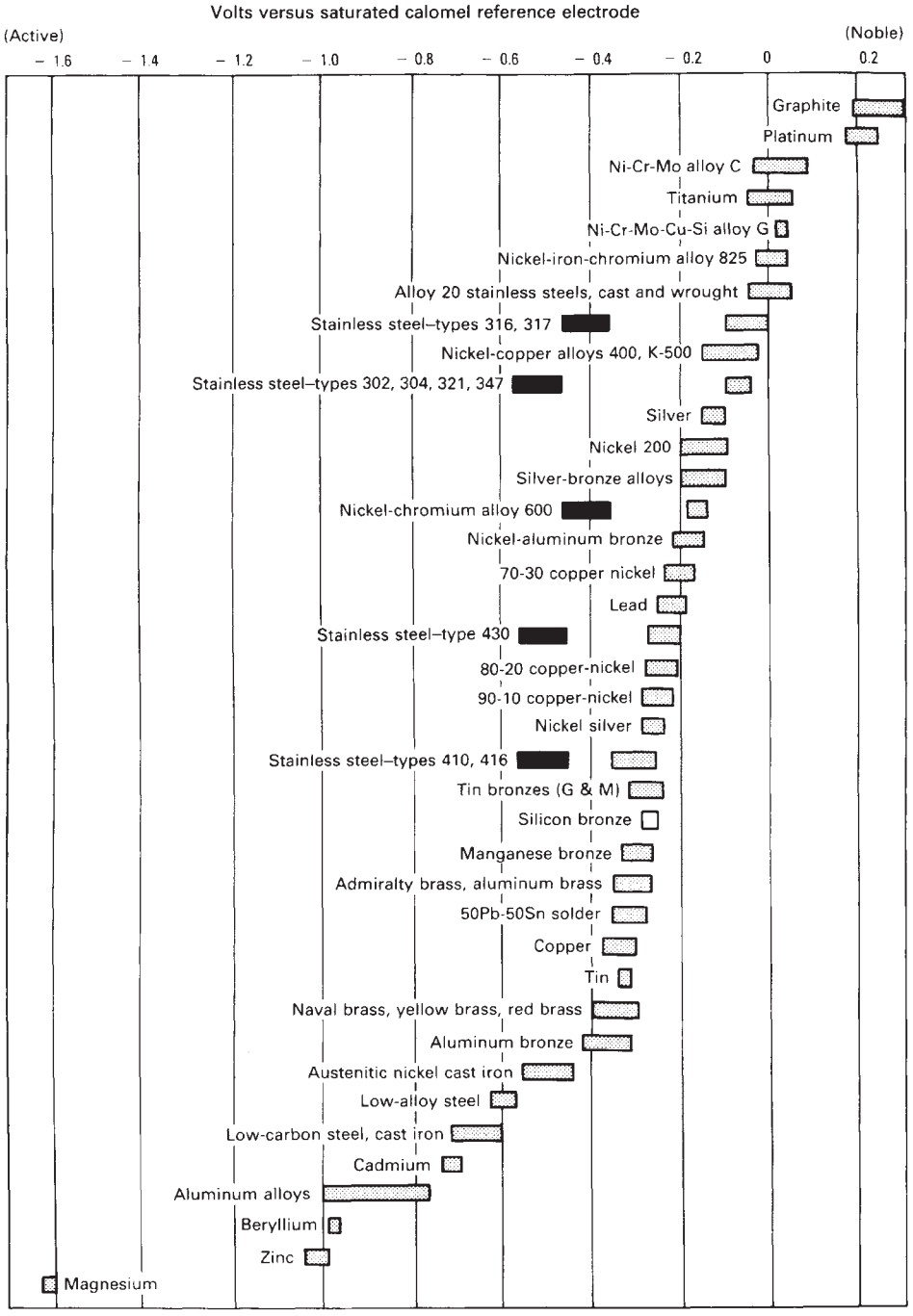


Fig. 23 Galvanic series for seawater. Dark boxes indicate active behavior of active-passive alloys.

inappropriate and dangerous. A galvanic series in the appropriate environment is required. Generally, the more corrosion-resistant metals, such as platinum, titanium, and silver, have the most positive potentials in seawater and are located near the upper end of the series. The more electronegative metals, such as magnesium, zinc, and aluminum, are located at the lower end of the series.

When electrically coupled in a common solution, the more negative (more active) metal will be the anode of the galvanic corrosion cell, and its corrosion rate will increase. The more positive (more noble) metal will be the cathode, and its corrosion rate will decrease. Active-passive metals, such as stainless steels, can exhibit either of two widely different potentials. In the active condition, these metals have a more negative potential, and in the passive state, they have a more positive potential. In a galvanic series, these active-passive metals will be listed at two levels: one more negative for the active state and the other more positive for the passive state.

Example 1: How the Galvanic Series Can Mislead (Ref 6). Figure 24 shows the potential of nickel-200, type 304 stainless steel, and a 70-30 copper-nickel alloy measured separately (i.e., not in a coupled system) against a saturated calomel reference electrode. The metals were immersed in seawater for more than 15 months. The nickel and cupronickel were relatively constant during the test. Type 304 stainless steel, on the other hand, changed its potential from above the other metals to between them, and then below, and between again. The reason for this behavior was that the stainless steel changed from a passive condition to an active one, whereby localized corrosion occurred, and then changed back to a passive condition. Therefore, alloys such as type 304 can occupy two positions in a galvanic series (refer to Fig. 23).

This behavior illustrates why a simple galvanic series provides limited—and sometimes incorrect—material selection and design information. Slight variations in service conditions or in the metals themselves can cause significant changes in the relative positions of the metals in the galvanic series.

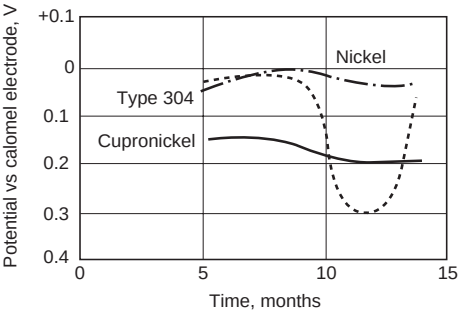


Fig. 24 Potential of metals immersed in seawater for more than 15 months. Source: Ref 6

Polarization

The potential generated by a galvanic cell consisting of dissimilar metals often changes with time. This potential causes a flow of current and corrosion to occur at the anodic area—the amount of corrosion being directly proportional to the current flow. As corrosion progresses, reaction products or corrosion products may accumulate at either the anode, the cathode, or both. This accumulation reduces the rate at which corrosion proceeds.

The potential of the anode drifts toward that of the cathode and vise versa. The change in potentials is called polarization—anodic polarization at the anode and cathodic polarization at the cathode. Polarization is defined as the displacement of electrode potential resulting from the effects of current flow.

In most corrosion reactions, cathodic polarization is more predominant. Because the degree of cathodic polarization and its effectiveness varies with metals and alloys, something about their polarization characteristics must be known before the extent or degree of galvanic corrosion for a given couple can be predicted. For example, titanium is very noble and demonstrates excellent resistance to seawater, yet when less noble metals are coupled to titanium, galvanic corrosion usually is accelerated much less than would be anticipated, if at all. The reason for this is that titanium polarizes readily and quickly in seawater, thereby significantly reducing corrosion rate.

Factors Influencing Galvanic Corrosion Behavior

Factors such as anode-to-cathode area ratios, distance between electrically connected materials, and geometric shapes also affect galvanic-corrosion behavior.

Area effects in galvanic corrosion involve the ratio of the surface area of the more noble to the more active member(s). When the surface area of the more noble metal or alloy is large in comparison to the more active member, an unfavorable area ratio exists for the prevailing situation in which a couple is under cathodic control. The anodic current density on the more active metal or alloy is extremely large; therefore, the resulting polarization leads to more pronounced galvanic corrosion. The opposite area ratio—large active member surface, smaller noble member surface—produces only slightly accelerated galvanic effects because of the predominant polarization of the more noble material.

Effect of Distance. Dissimilar metals in a galvanic couple that are in close physical proximity usually suffer greater galvanic effects than those that are farther apart. The distance effect is dependent on solution conductivity because the path of current flow is the primary consideration. Thus, if dissimilar pipes are butt welded with the electrolyte flowing

through them, the most severe corrosion will occur adjacent to the weld on the anodic member.

Effect of Geometry. The geometry of the circuit also enters into the effect to the extent that current will not readily flow around corners. This is simply an extension of the principle described previously, in which the current takes the path of least resistance.

Situations That Promote Galvanic Attack

Galvanic corrosion of the anodic member(s) of a couple may take the form of either general or localized corrosion, depending on the configuration of the couple, the nature of the films induced, and the nature of the metals or alloys involved.

Dissimilar metals commonly are combined in engineering designs by mechanical or other means, for example, in heating or cooling coils in vessels, heat exchangers, or machinery. Such combinations often lead to galvanic corrosion. Examples are shown in Fig. 25 to 27.

Nonmetallic Conductors. Less frequently recognized is the influence of nonmetallic conductors as cathodes in galvanic couples. Carbon brick in vessels is strongly cathodic to the common structural metals and alloys. Impervious graphite, especially in heat-exchanger applications, is cathodic to the less noble metals and alloys. Carbon-filled polymers can act as noble metals in a galvanic couple. Graphite-epoxy structures in aerospace applications must be adequately insulated from aluminum to prevent galvanic corrosion.

Another example is the behavior of conductive films, such as mill scale (magnetite, Fe_3O_4) or iron sulfides on steel, or of lead sulfate on lead. Such films can be cathodic to the base metal exposed at breaks or pores in the scale or even to such extraneous items as valves or pumps in

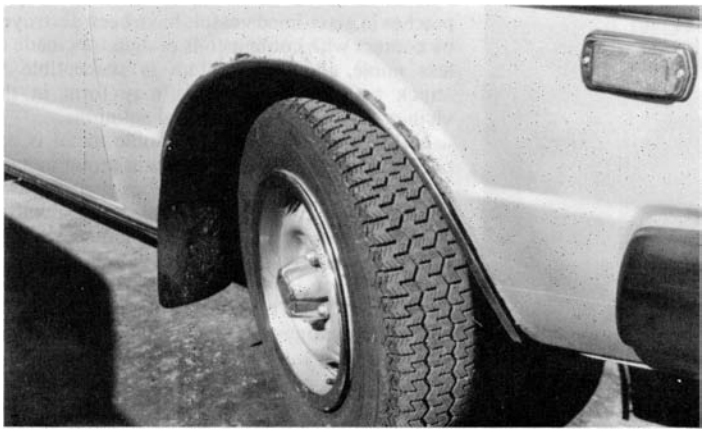


Fig. 25 Galvanic corrosion of painted steel auto body panel in contact with stainless steel wheel opening molding

a piping system. As described in the following example, passive surface films can contribute to galvanic corrosion problems.

Example 2: Galvanic Corrosion Occurring at the Same-Metal Couple (Ref 7). A well water copper piping system failed because of pitting corrosion. The water had a pH of 7.0 to 7.7, and pitting was caused by dissolved carbon dioxide. During failure analysis, researchers noticed that corrosion attack also occurred where a new replacement

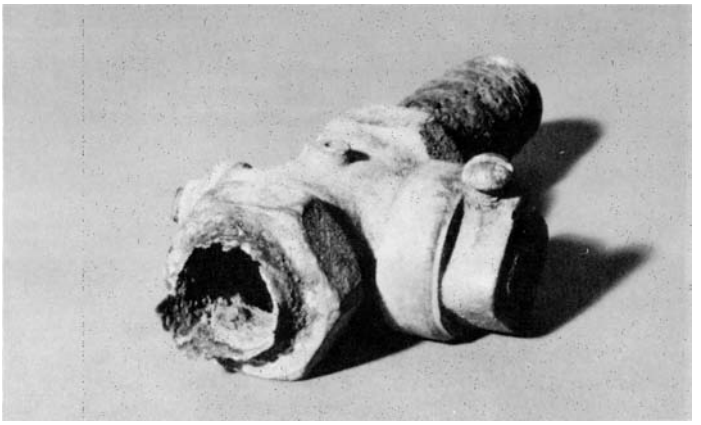


Fig. 26 Galvanic corrosion of steel pipe at brass fitting in humid marine atmosphere



Fig. 27 Failure of the aluminum inner ring of an extruder (for plastics) cooling system due to galvanic corrosion. Note the severe deterioration adjacent to nozzle holes where brass nozzles had been inserted. Source: Nalco Chemical Company

copper pipe section was joined into a copper pipe section that was in service for several years. The two pieces of copper were of the same designation, C11000, which is electrolytic tough pitch (ETP) copper (99.95Cu-0.04O). The replacement pipe was only in service for about 2 months before significant galvanic corrosion occurred. The old section had a passive film and a noble electrochemical potential. The new section had an active potential surface not yet protected by an oxide film.

Corrective Measures. This galvanic corrosion can be corrected by the following method:

- Thoroughly cleaning the system so the old metal has the same potential as the new section
- Electrically isolating the new section from the old section with a rubber tube and securing the tube to the metal piping with hose clamps until the new section has developed a passive film. After 2 months, the new metal can be soldered to the old metal with insignificant galvanic corrosion occurring.
- Injecting a chemical (inhibitor) into the water system to accelerate the formation of a passive film on the new metal
- Selecting an alternative material of construction for replacement piping that would be noble to the old metal piping. A candidate would be 90-10 copper-nickel alloy (C70600).

Laboratory Tests. Laboratory electrochemical polarization studies were carried out on a piece of new copper pipe, the old copper pipe, and a 90Cu-10Ni sample. The testing indicated that the electrochemical potential for the new copper specimen was –0.137 V versus a saturated calomel reference electrode. The 2-year-old scaled copper specimen was –0.070 V, and the new 90Cu-10Ni specimen was –0.061 V.

Final Recommendations. The length of the replacement pipe would be approximately 6 ft (1.8 m), while the old piping would be several hundred feet. Although galvanically more noble, the surface area of the cathode (90Cu-10Ni) would be sufficiently small compared to the surface area of the anode (old copper piping) so that galvanic corrosion would be minimized.

Metallic Coatings. Two types of metallic coatings are used in engineering design: noble metal coatings and sacrificial metal coatings. Noble metal coatings are used as barrier coatings over a more reactive metal. Galvanic corrosion of the substrate can occur at pores, damage sites, and edges in the noble metal coating. Sacrificial metal coatings provide cathodic protection of the more noble base metal, as in the case of galvanized steel or alclad aluminum.

Cathodic Protection. Magnesium, zinc, and aluminum galvanic (sacrificial) anodes are used in a wide range of cathodic protection applications. The galvanic couple of the more active metal and a more noble

structure (usually steel, but sometimes aluminum, as in underground piping) provides galvanic (cathodic) protection, while accelerated corrosion of the sacrificial metal (anode) occurs. Chapter 10 contains information on the principles and applications of this method of corrosion prevention and the selection of anode materials.

Metal Ion Deposition. Ions of a more noble metal may be reduced on the surface of a more active metal—for example, copper on aluminum or steel, or silver on copper. This process is also known as cementation, especially with regard to aluminum alloys. The resulting metallic deposit provides cathodic sites for further galvanic corrosion of the more active metal.

Prevention of Galvanic Corrosion

A number of procedures or practices can be used to combat or minimize galvanic corrosion. Sometimes a single practice is sufficient, but a combination of several of the following may be required:

- Select combinations of metals as close together as possible in the galvanic series suitable for the particular application or service environment.
- Avoid combinations in which the area of the less noble material is relatively small. It is good practice to use the more noble metals for fasteners or other parts in equipment built largely of less corrosion-resistant materials if dissimilar metals must be used.
- Insulate dissimilar metals wherever practicable; if possible, insulate them completely. A common error in this regard concerns bolted joints such as two flanges, for example, a pipe to a valve, where the pipe might be steel or lead and the valve a different material. Polymeric washers under the bolt heads and nuts are assumed to insulate the two parts, yet the shank of the bolt touches the flanges. This problem is solved by placing plastic tubes over the bolt shanks, plus the washers, so that the bolts are isolated completely from the flanges. Figure 28 shows proper insulation for a bolted joint. If complete insulation cannot be achieved, a material such as paint or a plastic coating at joints (to increase the resistance of the circuit) will help.
- Apply coatings with caution. When painting, for example, do not paint the less noble material without also coating the more noble material; otherwise, greatly accelerated attack may be concentrated at imperfections in coatings on the less noble metal. Keep such coatings in good repair. If only one surface can be painted, the more noble surface should be chosen to reduce or eliminate the cathode area.
- In cases where the metals cannot be painted and are connected by a conductor external to the liquid, the electrical resistance of the liquid

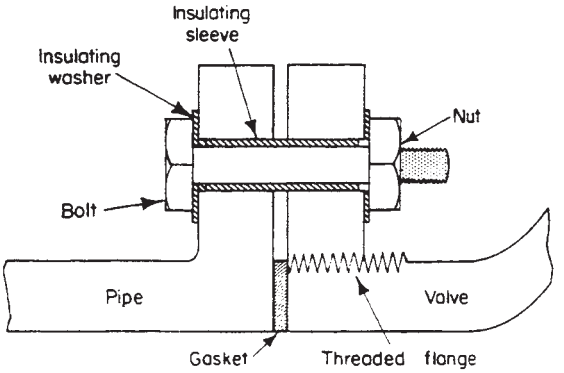


Fig. 28 Proper insulation of a bolted joint

path may be increased by keeping the metals as far apart as possible. This is not practical in most cases.

- If practical, add chemical inhibitors to the corrosion solution according to the nature of the solution to be inhibited. This reduces the corrosiveness of the environment.
- Avoid joining materials well apart in the galvanic series by threaded connections because the threads will probably deteriorate excessively. As shown in Fig. 28, much of the effective wall thickness of the metal is cut away during the threading operation. In addition, spilled liquid or condensed moisture can collect and remain in the thread grooves. Brazed joints are preferred, using a brazing alloy more noble than at least one of the metals to be joined. Welded joints using welds of the same alloy are even better.
- Employ cathodic protection measures. Magnesium, zinc, and aluminum galvanic (sacrificial) anodes are used in a wide range of cathodic protection applications. The galvanic couple of the more active metals and a more noble structure provides galvanic (cathodic) protection, while accelerated corrosion of the sacrificial metal (anode) occurs. Galvanized steel is composed of a thin layer of zinc on a steel substrate. The active zinc provides cathodic protection to exposed steel surfaces through beneficial galvanic action.

Erosion-Corrosion

General Description

Erosion-corrosion is the acceleration or increase in the rate of deterioration or attack on a metal because of mechanical wear or abrasive contributions in combination with corrosion. The combination of wear or

abrasion and corrosion results in more severe attack than would be realized with either mechanical or chemical corrosive action alone. Metal is removed from the surface as dissolved ions, as particles of solid corrosion products, or as elemental metal. The spectrum of erosion-corrosion ranges from primarily erosive attack, such as sandblasting, filing, or grinding of a metal surface, to primarily corrosion failures where the contribution of mechanical action is quite small. This section focuses on those instances where there is a fairly well-defined contribution from both mechanical and corrosive factors. Erosion-corrosion resulting from the relative movement between a corrosive fluid and the metal surface is discussed first, followed by a discussion of two special forms of erosion-corrosion, namely, cavitation and fretting corrosion.

Erosion-corrosion is characterized in appearance by grooves, waves, rounded holes, and/or horseshoe-shaped grooves. Examples are shown in Fig. 29 and 30. Analysis of these marks can help determine the direction of flow. Affected areas are usually free of deposits and corrosion products, although corrosion products can sometimes be found if erosion-corrosion occurs intermittently, and/or the liquid flow rate is relatively low.

Most metals are susceptible to erosion-corrosion under specific conditions. Metals that depend on a relatively thick protective coating of corrosion product for corrosion resistance are frequently subject to erosion-corrosion. This is due to the poor adhesion of these coatings relative to the thin films formed by the classical passive metals, such as stainless steels and titanium. Both stainless steels and titanium are relatively immune to erosion-corrosion in many environments. Metals that are soft and readily damaged or worn mechanically, such as copper and lead, are quite susceptible to erosion-corrosion. Even the noble or precious metals, such as silver, gold, and platinum, are subject to erosion-corrosion. Figure 31 shows a schematic of erosion-corrosion of a



Fig. 29 Erosion-corrosion of a cast stainless steel pump impeller after exposure to hot concentrated sulfuric acid with some solids present. Note the grooves, gullies, waves, and valleys common to erosion-corrosion damage.

condenser tube wall. The direction of flow and the resulting attack where the protective film on the tube has broken down are indicated.

All types of corrosive media generally can cause erosion-corrosion, including gases, aqueous solutions, organic systems, and liquid metals. For example, hot gases may oxidize a metal and then a high velocity blow off an otherwise protective scale. Solids in suspension in liquids (slurries) are particularly destructive from the standpoint of erosion-corrosion.

Virtually anything that is exposed to a moving liquid is subject to erosion-corrosion. Examples include piping systems, particularly at bends, elbows, or wherever there is a change in flow direction or increase in turbulence; pumps; valves; centrifuges; tubular heat exchangers; impellers; and turbine blades.



Fig. 30 Horseshoe-shaped depressions on the internal surface of a brass heat exchanger tube caused by erosion-corrosion. Source: Nalco Chemical Company

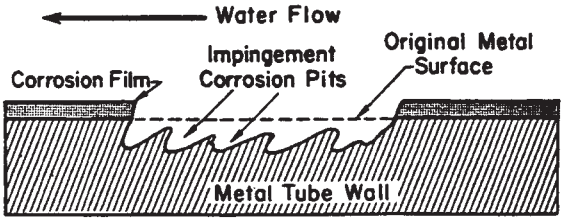


Fig. 31 Schematic of erosion-corrosion of a condenser tube

Critical Factors Influencing Erosion-Corrosion

Erosion-corrosion is a fairly complex failure mode influenced by both metal characteristics and environmental factors. Although some of these factors are interrelated, they are discussed separately insofar as possible.

Surface Films. The nature and properties of the protective "films" that form on some metals and alloys are very important from the standpoint of resistance to erosion-corrosion. The ability of these films to protect the metal depends on the speed or ease with which they form when originally exposed to the environment, their resistance to mechanical damage or wear, and their rate of reformation when destroyed or damaged. A hard, dense, adherent, and continuous film provides better protection than one that is easily removed by mechanical means or that "wears off." A brittle film that cracks or spalls under stress is not protective. The nature of the protective film that forms on a given metal depends on the specific environment to which it is exposed; this in turn, determines its resistance to erosion-corrosion by that fluid.

Stainless steels depend heavily on a protective film (passivity) for their good resistance to corrosion. Consequently, these materials are vulnerable to erosion-corrosion. Figure 32 shows rapid attack due to erosion-corrosion of type 316 (18Cr-12Ni) stainless steel by a sulfuric acid/ferrous sulfate slurry moving at high velocity. The rate of deterioration is about 110 mm/year 4500 mils/year) at 55 °C (130 °F). This material showed no weight loss and was completely passive under stagnant conditions, as shown by the data point on the abscissa at approximately 60 °C (140 °F).

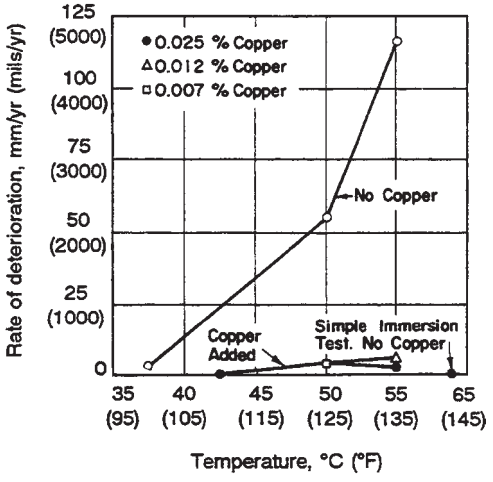


Fig. 32 Effect of temperature and copper ion addition on erosion-corrosion of type 316 stainless steel. The velocity of the sulfuric acid slurry was 12 m/s (39 ft/s)

Lead depends on the formation of a lead sulfate/lead oxide protective surface film for long life in sulfuric acid environments; in many cases, more than 20 years of service may be obtained. Lead gains weight when exposed to sulfuric acid because of the surface coating or corrosion product formed (except in strong acid wherein the lead sulfate is soluble and not protective). However, lead valves failed in less than 1 week, and lead bends were rapidly attacked in a plant handling a 3% sulfuric acid solution at 90 °C (194 °F). As a result of these failures, erosion-corrosion tests were made; the results are plotted in Fig. 33. Under static conditions, the lead exhibited no deterioration (slight gain in weight), as shown by the points on the abscissa. Under high-velocity conditions, erosion-corrosion attack increased with temperature, as shown by the curve.

Although rapidly attacked in solutions with a concentration of about 93% or higher, where lead sulfate is soluble, the protectiveness of the coating on lead can vary in dilute concentrations. Figure 34 shows that erosion-corrosion increases up to about 25% acid and then decreases.

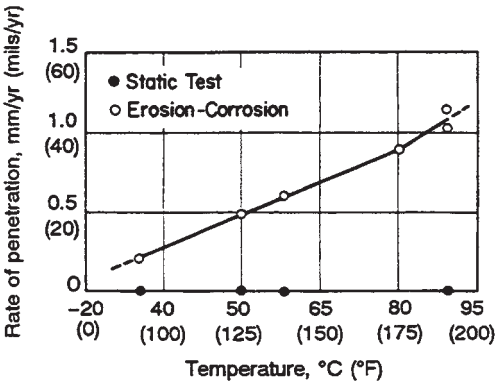


Fig. 33 Effect of temperature and velocity on attack of lead. The velocity of the 10% sulfuric acid was 12 m/s (39 ft/s)

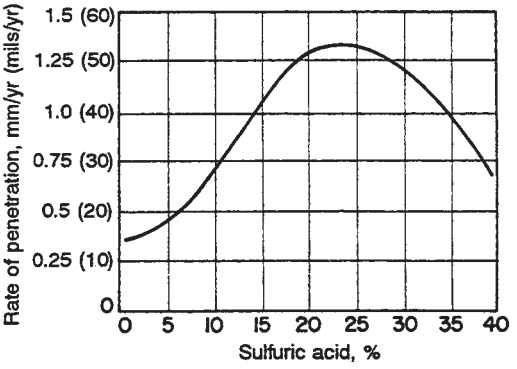


Fig. 34 Erosion-corrosion of lead as a function of sulfuric acid concentration. Velocity, 12 m/s (39 ft/s); temperature, 95 °C (203 °F)

Apparently, the rate of formation of the lead sulfate coating and/or its stability is not sufficient to decrease attack until concentrations greater than 25% are reached. The nature of the coating undoubtedly changes with acid concentration. Contaminants in sulfuric acid may result in soft and loose sulfates on lead, as is discussed later.

Variations in the amount of attack on steel by water with different pH values and at different velocities can be attributed to the nature and composition of the surface scales formed. The scale on specimens exhibiting high rates of deterioration is porous, has poor adhesion, an is not protective. Below pH 5, the corrosion product film is increasingly more soluble because the pH is reduced (more acidic), and high rates of attack are observed as the protective oxide scale breaks down. In regions of low attack (higher pH and lower velocity), the scale formed on the steel is nonporous and has strong adhesion. This protective barrier film is stable and results in low corrosion rates.

The behavior of steel and low-alloy steel tubes handling oils at high temperatures in petroleum refineries depends somewhat on the sulfide films formed. When the film "erodes away," erosion-corrosion and rapid attack occur. For example, a normally tenacious sulfide film becomes porous and nonprotective when cyanides are present in these organic systems.

Tests on copper and brass in sodium chloride solutions with and without oxygen showed that copper was attacked more than brass in oxygen-saturated solutions. The copper was covered with a black and yellow-brown film, copper chloride ($CuCl_2$). The brass was covered with a dark gray film, cupric oxide (CuO). The better resistance of the brass to attack was attributed to the greater stability or protectiveness of the dark gray film. Difficulty was encountered in obtaining reproducible results until a controlled alkali cleaning and drying procedure for the specimens was adopted. This indicates that surface films formed on copper and brass, because of atmospheric exposure, abrading, or other reasons, can have a definite effect on erosion-corrosion performance under some conditions.

Titanium is a reactive metal but is resistant to erosion-corrosion in many environments because of the stability of the titanium dioxide (TiO_2) film formed. It shows excellent resistance to seawater and chloride solutions and also to nitric acid. This corrosion resistance can be destroyed by erosion and wear. Strongly reducing conditions, such as deaerated hydrochloric acid, are damaging to titanium.

Velocity. Because erosion-corrosion involves movement between a metal and its environment, the velocity of the environment plays an important role. Velocity often strongly influences the mechanism of the corrosion reaction. High velocities and environments containing solids in suspension result in a corrosion mechanism that is more mechanical in nature. Figures 32 and 33 show large increases in attack because of

velocity. Table 3 shows the effect of velocity on a variety of metals and alloys exposed to seawater. These data show that the effect of velocity may be nil or extremely great.

Increases in velocity generally result in increased attack, particularly if substantial rates of flow are involved. The effect may be nil or increase slowly until a critical velocity is reached, and then the attack may increase at a rapid rate. Figure 35 shows the "breakaway" or critical velocity effect. Table 3 lists several examples that exhibit little effect when the velocity is increased from 0.3 to 1.2 m/s (1 to 4 ft/s), but which undergo destructive attack at 8.2 m/s (27 ft/s). This high velocity is below the critical value for other materials listed at the bottom of Table 3.

Erosion-corrosion can occur on metals and alloys that are completely resistant to a particular environment at low velocities. For example, hardened straight-chromium stainless steel valve seats and plugs give excellent service in most steam applications, but grooving or so-called "wire drawing" occurs in high-pressure steam reducing or throttling valves.

Table 3 Erosion-corrosion rates of metals by seawater moving at different velocities

	Typical corrosion rates, mg/dm^2/day		
Material	**0.3 m/s (1 ft/s)(a)**	**1.2 m/s (4 ft/s)(b)**	**8.2 m/s (27 ft/s)(c)**
Carbon steel	34	72	254
Cast iron	45	…	270
Silicon bronze	1	2	343
Admiralty brass	2	20	170
Hydraulic bronze	4	1	339
G bronze	7	2	280
Aluminum bronze (10% Al)	5	…	236
Aluminum brass	2	…	199
90-10 Cu-Ni (0.8% Fe)	5	…	99
70-30 Cu-Ni (0.5% Fe)	2	…	199
70-30 Cu-Ni (0.5% Fe)	<1	<1	39
Monel	<1	<1	4
Stainless steel (Type 316)	1	0	<1
Hastelloy C	<1	…	3
Titanium	0	…	0

(a) Immersed in tidal current at a velocity of 0.3 m/s (1 ft/s). (b) Immersed in seawater flume at a velocity of 1.2 m/s (4 ft/s). (c) Attached to immersed rotating disk at a velocity of 8.2 m/s (27 ft/s)

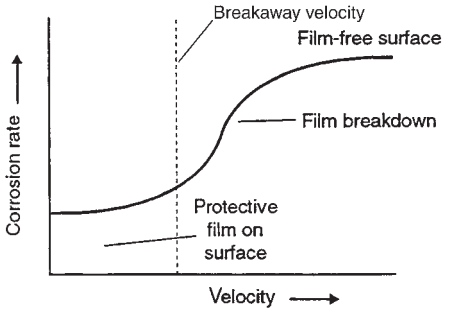


Fig. 35 Schematic of the critical velocity effect for erosion-corrosion

Increased velocity may increase or reduce attack, depending on its effect of the corrosion mechanism involved. It may increase attack on steel by increasing the supply of oxygen, carbon dioxide, or hydrogen sulfide in contact with the metal surface. Velocity may also increase diffusion or transfer of ions by reducing the thickness of the stagnant film at the surface.

Velocity can decrease attack and increase the effectiveness of inhibitors by supplying the chemical to the metal surface at a higher rate. It has been shown that less sodium nitrite inhibitor was needed at high velocity to protect steel in tap water. Similar mechanisms have been postulated for other types of inhibitors. It should be noted that the effective use of inhibitors to decrease erosion-corrosion depends, in many cases, on the nature and type of films formed on the metal as a result of the reaction between the metal and the inhibitor.

Higher velocities may also decrease attack in some cases by preventing the deposition of silt or dirt that would cause concentration-cell corrosion. On the other hand, solids in suspension moving at high velocity may have a scouring effect and thus destroy surface protection. Many stainless steels have strong tendency to pit in seawater and other chlorides. However, some of these materials are used successfully in seawater, provided that the water is kept moving at a substantial velocity. This motion prevents the formation of deposits and concentration cells that cause pitting.

Impingement. Impingement attack has been defined as localized erosion-corrosion caused by turbulence or impinging flow. This type of corrosion occurs in pumps, valves, orifices, on heat exchanger tubes, and at elbows and tees in tubes or pipelines. It occurs as deep, clean, horseshoe-shaped pits with the deep, or undercut, end pointing in the direction of flow. Impingement-corrosion attack can also occur as the result of partial blockage of a tube. A stone, a piece of wood, or some other object can cause the main flow to deflect against the wall of the tube, thereby creating turbulence and increasing fluid velocity. The impinging stream can rapidly perforate tube walls. Water that carries sand, silt, or mud will have an additional severely erosive effect on tubes.

Steam erosion is another form of impingement corrosion. It occurs when high-velocity wet steam contacts a metal surface. The resulting attack usually produces a roughened surface showing a large number of small cones with the points facing in the direction of flow.

Influence of Galvanic Corrosion. Galvanic, or two-metal corrosion, corrosion can influence erosion-corrosion when dissimilar metals are in contact in a flowing system. The galvanic effect may be nil under static conditions but may be greatly increased when movement is present. Figure 36 shows that attack on type 316 by itself was nil in high-velocity sulfuric acid, but increased to very high values when this alloy was in contact with lead. The passive film was destroyed by the

combined effects of galvanic corrosion and erosion-corrosion. Couples of lead and type 316 showed no corrosion under static conditions.

Velocity changes can produce surprising galvanic effects. In seawater at low velocity, the corrosion of steel is not appreciably affected by coupling with stainless steel, copper, nickel, or titanium. At high velocities, the attack on steel is much less when coupled to stainless steel and titanium than when coupled to copper or nickel. This is attributed to the more effective cathodic polarization of stainless steel and titanium at high velocities.

Nature of Metal or Alloy. The chemical composition, corrosion resistance, hardness, and metallurgical history of metals and alloys can play important roles in the performance of these materials under erosion-corrosion conditions. The composition of most alloys determines to some extent their general corrosion resistance. If a reactive metal or an alloy composed of active elements is under consideration, its corrosion resistance is due chiefly to its ability to form and maintain a protective film—for example, aluminum and the stainless steels.

The more noble metals possess good inherent corrosion resistance. In general, a material with better inherent resistance would be expected to show better performance when all other factors are equal. For example, an 80Ni-20Cr alloy should be superior to an 80Fe-20Cr alloy because nickel has better inherent corrosion resistance than iron. For the same reason, a nickel-copper alloy should be (and is) better than an alloy of zinc and copper.

The addition of a third (or fourth) element to an alloy often increases its resistance to erosion-corrosion. For example, the addition of iron to a copper-nickel alloy produces a marked increase in resistance to erosion-

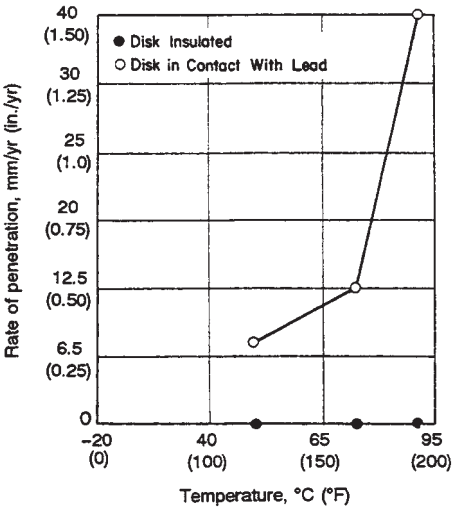


Fig. 36 Effect of contact with lead on erosion-corrosion of type 316 stainless steel. The velocity of the 10% sulfuric acid solution was 12 m/s (39 ft/s)

corrosion by seawater, as shown in Table 3. The addition of molybdenum to 18Cr-8Ni stainless steel (type 304) to make type 316 (18Cr-12Ni-2Mo) makes it more resistant to corrosion and erosion-corrosion. In both of these cases, the additional element produces a more stable protective film. Aluminum brasses show better erosion-corrosion resistance than straight (copper-zinc) brass.

Reports on the resistance of steel and iron-chromium alloys to acid mine waters under erosion-corrosion conditions showed a straight-line increase in resistance with increasing chromium up to 13%. At this content and above, no attack occurred. Low-alloy chromium steels showed better erosion-corrosion resistance than straight carbon steels in high-temperature boiler feedwater. Chromium-plated steel and a leaded bronze were not suitable. Type 3 Ni-Resist, a cast iron containing 30% nickel (Ni) and 3% chromium (Cr), showed practically no attack by seawater after 60 days under erosion-corrosion conditions, whereas ordinary cast iron was badly deteriorated. Table 3 shows the effect of various material compositions on erosion-corrosion by seawater.

Soft metals such as lead are, in a general way, more susceptible than the hard metals to erosion-corrosion because they are more subject to mechanical wear. Hardness is a fairly good criterion for predicting resistance to straight erosion or abrasion but it is not necessarily a good criterion for predicting resistance to erosion-corrosion. There are many methods for hardening metals and alloys. Perhaps the only method that comes close to producing good erosion-corrosion resistance is solid-solution hardening. This method involves adding an element to a given metal to produce a solid solution that is corrosion resistant and is inherently harder than the original metal. It cannot be softened by heat treatment or further hardened by heat treatment.

Heat Treatment Effects. Hardening by heat treatment results in changes in microstructure and usually in heterogeneity. Quite often this decreases corrosion resistance because local anodic and cathodic areas are more readily formed. This makes a material more susceptible to erosion-corrosion. For example, the precipitation-hardening stainless steels would not be expected to perform as well as type 304 stainless steel under erosion-corrosion conditions, because the latter forms a more stable protective (passive) film.

An example of poor performance by a high-hardness material is presented in the comparison of type 316 and type 329 stainless steels, the latter of which is hardenable by heat treatment. Both types of stainless steels show no measurable corrosion in a sulfuric acid slurry under static conditions, even when the type 329 is age hardened to 450 HB (Brinell hardness scale). Under the erosion-corrosion conditions in a centrifuge test, however, the hard type 329 steel deteriorates more than 10 times faster than the soft (150 HB) type 316. Both materials possess good “passive” resistance in the static condition, but the type 316 steel has a more stable

film and maintains passivity more successfully when exposed to the more severe erosion-corrosion conditions in the centrifuge test.

The nature of the carbide structure in carbon steel may have an important bearing on its resistance to erosion-corrosion. In some oil well and sulfuric acid applications involving flow, so-called "ringworm corrosion" occurs. Carbon steel with a normal pearlitic structure is not attacked significantly, but the same steel containing spheroidized pearlite is badly corroded.

Cast iron sometimes shows better performance than steel under erosion-corrosion conditions, particularly in hot, strong sulfuric acid. The iron in the cast iron is corroded, but the remaining "graphitized" layer, consisting of the original graphite network and corrosion products, forms a protective layer.

Prevention of Erosion-Corrosion

Five methods are used to prevent or minimize damage due to erosion-corrosion. In order of their extent of use, they are use of materials with better resistance to erosion-corrosion, design, alteration of the environment, coatings, and cathodic protection. The reasons for using better materials that give better performance are obvious. This method usually represents an economical solution to most erosion-corrosion problems.

Design is an important corrosion-control method in that the life of presently used or less costly materials can be extended considerably or the attack practically eliminated. Design here involves change in shape or geometry, and not in selection of material. Erosion-corrosion damage can be reduced by implementing the following design recommendations:

- Increase the pipe diameter to decrease velocity not only from the mechanical standpoint but also to ensure lamellar flow.
- Increase the diameter and/or streamline bends to reduce impingement effects.
- Increase the thickness of material in vulnerable areas. In one instance of severe erosion-corrosion of lead, maintenance costs were reduced to a satisfactory level by using a sweeping bend and doubling the thickness of the pipe.
- Streamline the design of other equipment, such as inlets and outlets, to remove obstructions for the same reasons.
- Insert readily replaceable impingement plates or baffles.
- Direct inlet pipes toward the center of a tank instead of near its wall.
- Design tubes to extend several centimeters beyond the tube sheet at the inlet end. In one case, tubing life was practically doubled by increasing the length by 10 cm (4 in.). The protruding tube ends were attacked, but operation was not affected.

- Insert ferrules or short lengths of flared tubing in the inlet ends. These could be made of the same material as the tubes or of materials with better resistance. Nonmetallic ferrules are available and are used in condensers. The end of the ferrule should be "feathered" to blend the flow. If this is not done, erosion-corrosion occurs on the tube just beyond the end of the ferrule because of the "step" present. Galvanic corrosion must be considered when using metallic inserts. Tubing life in a vertical evaporator was doubled by turning the evaporator upside down when the inlet or bottom ends of the tubes became thin. The outlet ends, which were not appreciably attacked, became inlet ends.
- Design equipment so that parts are readily replaceable. For instance, tube bundles that are readily removed and replaced by spares can be repaired at leisure. Buckets and conveyor flights that are easily installed on centrifugals and other conveying equipment reduce costs. Use of pumps with interchangeable parts of different alloys helps to reduce costs when an unsatisfactory alloy is originally selected. When shutdown of equipment is serious from a production standpoint, it is often desirable to design a standby or alternate unit.

Good design implies proper construction and workmanship. In one case, some of the blades of a steam turbine were out of line, and the protruding blades suffered severe erosion-corrosion damage from water droplets in the stream. Misalignment from one pipe section to the next can cause erosion-corrosion in both flanged and welded joints.

Environment. Alteration of the environment, such as deaeration and the addition of inhibitors, is effective and is sometimes used to minimize erosion-corrosion damage. In many cases, however, this method is not economical. Settling and/or filtration to remove solids is very helpful. Whenever possible, the temperature of the environment should be reduced. This has been done in many cases without appreciably affecting the particular process. Temperature is a serious problem in erosion- corrosion, as it is in all types of corrosion.

Coatings. Applied coatings of various types that produce an effective barrier between the metal and its environment can be used, but this method is not always feasible for solving most erosion-corrosion problems. Hardfacings, or weld overlays, are sometimes helpful, provided that the facing has good corrosion resistance. Repair or buildup of attacked areas by welding is often feasible.

Cathodic protection has been used to reduce erosion-corrosion attack, but it has not found widespread application. Cathodic protection systems for preventing erosion-corrosion must be properly designed and maintained to be effective. Corrosion can be intensified if the polarity of the cathodic protection system is inadvertently reversed.

Cavitation

General Description. Cavitation is a form of erosion-corrosion that is caused by the formation and collapse of vapor bubbles in a liquid against a metal surface. Cavitation occurs in hydraulic turbines, on pump impellers, on ship propellers, and on many surfaces in contact with high-velocity liquids subject to changes in pressure.

Mechanism (Ref 8). Figure 37 is a simplified representation of the cavitation process. Figure 37(a) shows a vessel containing a liquid. The vessel is closed by an airtight plunger. When the plunger is withdrawn (Fig. 37b), a partial vacuum is created above the liquid, causing vapor bubbles to form and grow within the liquid. In essence, the liquid boils without a temperature increase. If the plunger is then driven toward the surface of the liquid (Fig. 37c), the pressure in the liquid increases, and the bubbles condense and collapse (implode). In a cavitating liquid, these three steps occur in a matter of milliseconds. As shown in Fig. 37(d), implosion of a vapor bubble creates a microscopic "torpedo" of water that is ejected from the collapsing bubble at velocities that may range from 100 to 500 m/s (330 to 1650 ft/s). When the torpedo impacts the metal surface, it dislodges protective surface films and/or locally deforms the metal itself. Thus, fresh surfaces are exposed to corrosion and the reformation of protective films, which is followed by more cavitation, and so on. Damage occurs when the cycle is allowed to repeat over and over again.

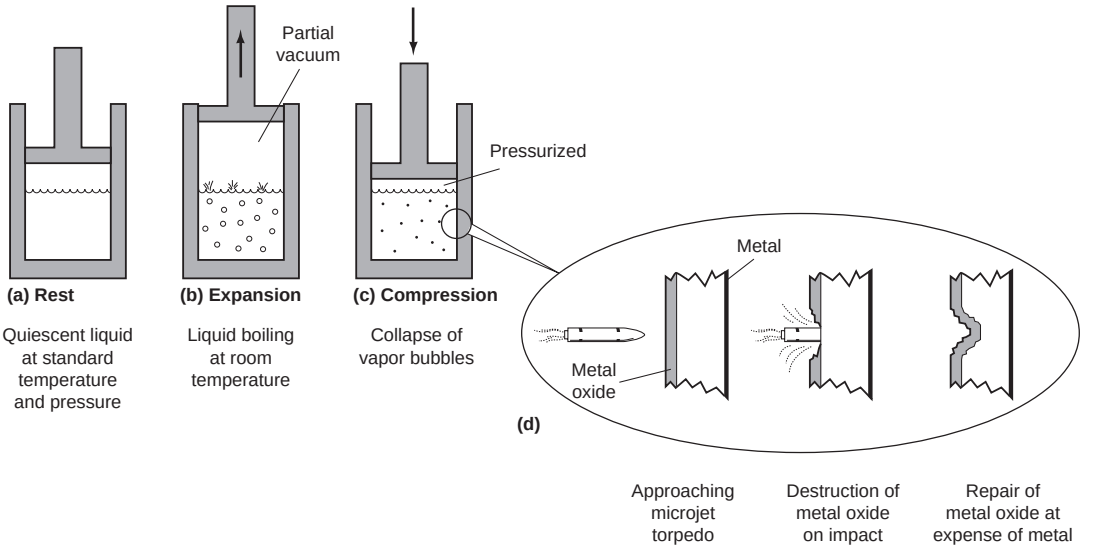


Fig. 37 Schematic representation of cavitation showing a cross section through a vessel and plunger enclosing a fluid. (a) Plunger stationary, liquid at standard temperature and pressure. (b) Plunger withdrawn, liquid boils at room temperature. (c) Plunger advanced, bubbles collapse. (d) Disintegration of protective corrosion product by impacting microjet "torpedo." Source: Ref 8

The appearance of cavitation is similar to pitting except that surfaces in the pits are usually much rougher. The affected region is free of deposits and accumulated corrosion products if cavitation has been recent. Typically, affected surfaces are highly localized to specific regions, although, if cavitation is severe and widespread, the area affected may be extensive (Fig. 38). On symmetrical components having repeated elements (e.g., impellers) the pattern of damage may repeat itself at identical locations on each element as shown in Fig. 39.

Prevention. Cavitation can be controlled or minimized by the following:

- Improving design to minimize hydrodynamic pressure differences
- Employing stronger (harder) and more corrosion-resistant materials. Figure 40 compares the cavitation resistance of a number of metals and alloys. Cobalt-based Stellite alloys are frequently employed for applications requiring resistance to cavitation. Cobalt-containing stainless steels have also proved effective. Hardfacing alloys are also frequently employed.
- Specifying a smooth finish on all critical metal surfaces
- Coating with resilient materials such as rubber or some plastics. However, such materials are subject to disbondment at the metal/elastomer interface at high cavitation intensities, even if the exposure is brief.

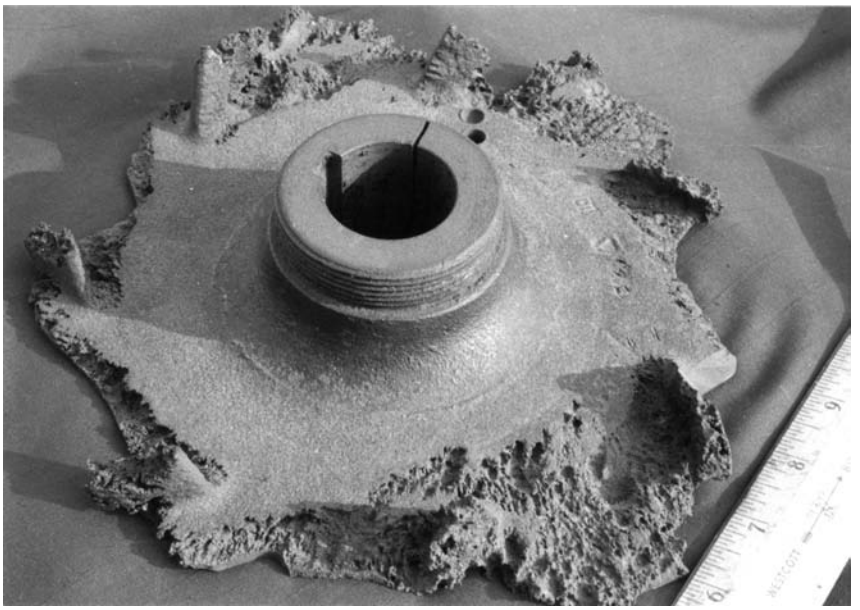


Fig. 38 A cast steel feedwater-pump impeller severely damaged by cavitation. Note how damage is confined to the outer edges of the impeller where vane speed was maximum. Source: Nalco Chemical Company



Fig. 39 Cavitation damage repeated on successive vanes of a bronze impeller. Source: Nalco Chemical Company

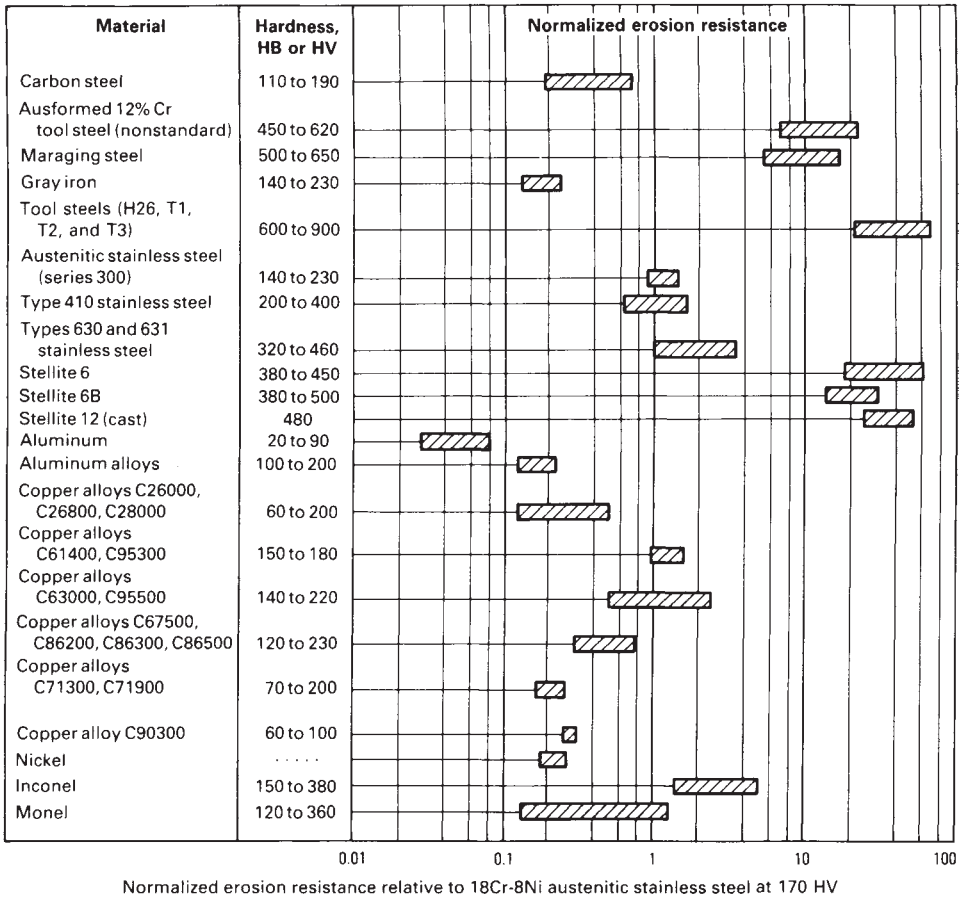


Fig. 40 Classification of 22 alloys or alloy groups according to their normalized cavitation erosion resistances relative to 18Cr-8Ni austenitic stainless steel having a hardness of 170 HV

Fretting Corrosion

General Description. Fretting corrosion is a combined wear and corrosion process in which material is removed from contacting surfaces when motion between the surfaces is restricted to very small amplitude oscillations (often, the relative movement is barely discernible). Usually, the condition exists in machine components that are considered fixed and not expected to wear. Pressed-on wheels can often fret at the shaft/wheel hole interface.

Oxidation is the most common element in the fretting process. In oxidizing systems, fine metal particles removed by adhesive wear are oxidized and trapped between the fretting surfaces (Fig. 41). The oxides act like an abrasive (such as lapping rouge) and increase the rate of material removal. This type of fretting in ferrous alloys is easily recognized by the red material oozing from between the contacting surfaces.

Fretting damage can be very serious and catastrophic. For example, in gas turbines, the blades are often anchored in dovetail slots in the hub. Vibrations in the blade system can cause fretting in the blade roots and loosening. The loose blades then rattle around and break out because of fatigue or impact wear. A piece of blade moving into the gas flow through the turbine can cause severe damage, destroying rows of blades and causing engine failure. Another fretting problem that has injury potential is the loosening of wheels or flywheels from shafts or axles. Railroad car wheels, for example, are shrink fitted onto their axles. If the wheel loosens from running vibrations and comes off during operation of the train, it can cause derailment and has the potential to become a loose rolling missile capable of penetrating nearby buildings. Other mechanical parts susceptible to fretting damage include couplings, riveted and pin joints, surgical implants, rolling contact bearings, and bridge bearings.

Recognizing Fretting Corrosion. Fretting corrosion takes the form of local surface dislocations and deep pits. These occur in regions where slight relative movements have occurred between mating, highly loaded surfaces. The pits can sometimes provide stress raisers for the

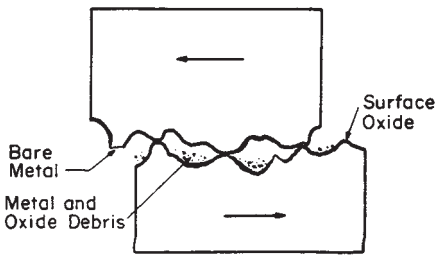


Fig. 41 Schematic of the fretting process.

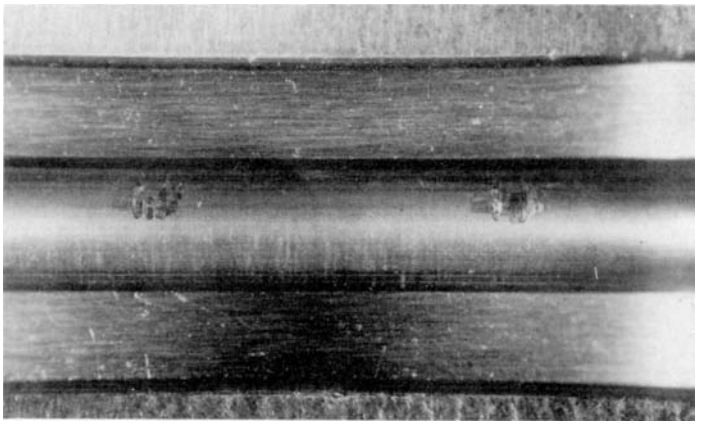


Fig. 42 Fretting corrosion of the bearing race of a helicopter drive train over-running clutch. This problem was caused by vibration (and rubbing) of the ball in the inner and outer races of bearings that support the rotor shaft. Note the two areas on the left- and right-hand sides of the figure exhibiting fretting damage.

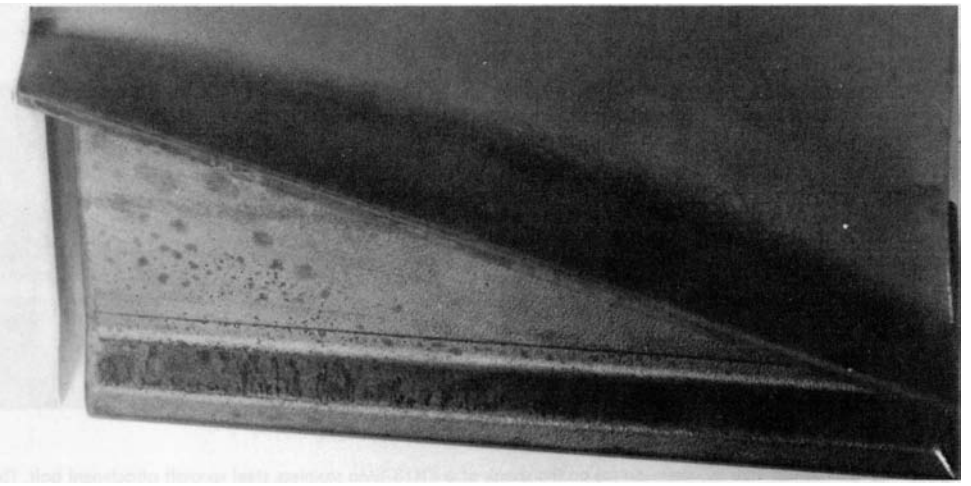


Fig. 43 Fretting corrosion on the root surface of an aircraft power plant compressor blade. Fatigue cracks can initiate as a result of this fretting pitting damage.

initiation of corrosion fatigue. Examples of fretting corrosion of aircraft components are shown in Fig. 42 and 43.

Prevention. Fretting corrosion can be controlled by the following

- Lubricating (e.g., low-viscosity oils) the faying surfaces
- Restricting the degree of movement
- Selecting materials and combinations that are less susceptible to fretting corrosion (Table 4)

Table 4 Resistance to fretting corrosion of various material couples under dry conditions

Couple	Resistance to fretting
Steel on steel	Low
Nickel on steel	Low
Aluminum on steel	Low
Antimony plate on steel	Low
Tin on steel	Low
Aluminum on aluminum	Low
Zinc-plated steel on aluminum	Low
Iron-plated steel on aluminum	Low
Cadmium on steel	Medium
Zinc on steel	Medium
Copper alloys on steel	Medium
Zinc on aluminum	Medium
Copper plate on aluminum	Medium
Nickel plate on aluminum	Medium
Iron plate on aluminum	Medium
Silver plate on aluminum	Medium
Lead on steel	High
Silver plate on steel	High
Silver plate on aluminum plate	High
Steel with conversion coating on steel	High

Intergranular Corrosion

General Description

Intergranular corrosion is defined as the selective dissolution of grain boundaries, or closely adjacent regions, without appreciable attack of the grains themselves. This dissolution is caused by potential differences between the grain-boundary region and any precipitates, intermetallic phases, or impurities that form at the grain boundaries. The actual mechanism differs with each alloy system.

Precipitates that form as a result of the exposure of metals at elevated temperatures (for example, during production, fabrication, and welding) often nucleate and grow preferentially at grain boundaries. If these precipitates are rich in alloying elements that are essential for corrosion resistance, the regions adjacent to the grain boundary are depleted of these elements. The metal is thus sensitized and is susceptible to intergranular attack in a corrosive environment. For example, in austenitic stainless steels such as AISI type 304, the cause of intergranular attack is the precipitation of chromium-rich carbides ($(Cr, Fe)_{23}C_6$) at grain boundaries. These chromium-rich precipitates are surrounded by metal that is depleted in chromium; therefore, they are more rapidly attacked at these zones than on undepleted metal surfaces.

Impurities that segregate at grain boundaries may promote galvanic action in a corrosive environment by serving as anodic or cathodic sites. Therefore, this would affect the rate of the dissolution of the alloy matrix in the vicinity of the grain boundary. An example of this is found in aluminum alloys that contain intermetallic compounds, such as Mg_5Al_8

and $CuAl_2$, at the grain boundaries. During exposures to chloride solutions, the galvanic couples formed between these precipitates and the alloy matrix can lead to severe intergranular attack. Susceptibility to intergranular attack depends on the corrosive solution and on the extent of intergranular precipitation, which is a function of alloy composition, fabrication, and heat treatment parameters.

Intergranular Corrosion of Austenitic Stainless Steels

General Description. At temperatures above about 1035 °C (1900 °F), chromium carbides are completely dissolved in austenitic stainless steels. However, when these steels are slowly cooled from these high temperatures or reheated into the range of 425 to 815 °C (800 to 1500 °F), chromium carbides are precipitated at the grain boundaries. These carbides contain more chromium than the matrix does.

The precipitation of the carbides depletes the matrix of chromium adjacent to the grain boundary. The diffusion rate of chromium in austenite is slow at the precipitation temperatures; therefore, the depleted zone persists, and the alloy is sensitized to intergranular corrosion. This sensitization occurs because the depleted zones have higher corrosion rates than the matrix in many environments. Figure 44 illustrates how the chromium content influences the corrosion rate of iron-chromium alloys in boiling 50% sulfuric acid (H_2SO_4) containing ferric sulfate ($Fe_2(SO_4)_3$). In all cases, the alloys are in the passive state. The wide differences in the corrosion rate are the result of the differences in the chromium content.

If the austenitic stainless steels are cooled rapidly to below about 425 °C (800 °F), the carbides do not precipitate, and the steels are immune to intergranular corrosion. Reheating the alloys to 425 to 815 °C (800 to 1500 °F), as for stress relief, will cause carbide precipitation and sensitivity to intergranular corrosion. The maximum rate of carbide precipitation occurs at about 675 °C (1250 °F). Because this is a common temperature for the stress relief of carbon and low-alloy steels, care must be exercised in selecting stainless steels to be used in dissimilar-metal joints that are to be stress relieved.

Effects of Welding. Welding is the common cause of the sensitization of stainless steels to intergranular corrosion. Although the cooling rates in the weld itself and the base metal immediately adjacent to it are sufficiently high to avoid carbide precipitation, the weld thermal cycle will bring part of the heat-affected zone (HAZ) into the precipitation range. Carbides will precipitate, and a zone somewhat removed from the weld will become susceptible to intergranular corrosion (Fig. 45). Welding does not always sensitize austenitic stainless steels. In thin sections, the thermal cycle may be such that no part of the HAZ is at sensitizing temperatures long enough to cause carbide precipitation. Once

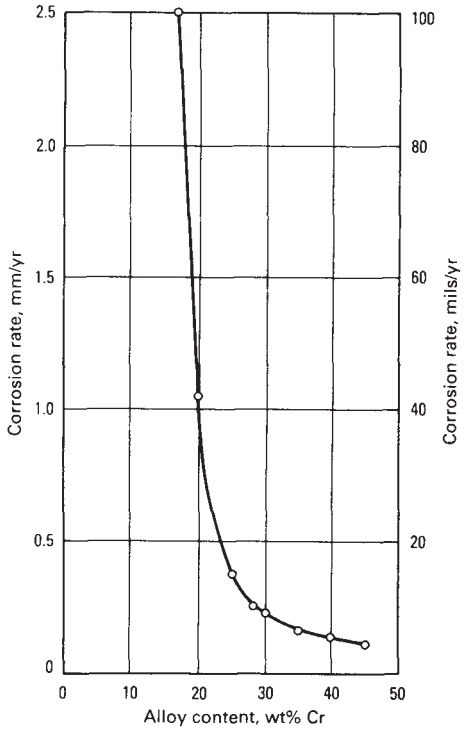


Fig. 44 The effect of chromium content on the corrosion behavior of iron-chromium alloys in boiling 50% H_2SO_4 with $Fe_2(SO_4)_3$.

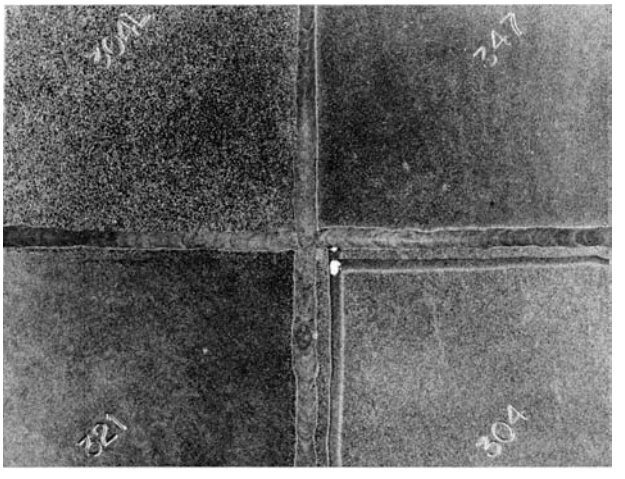


Fig. 45 Intergranular corrosion of sensitized HAZ grain boundaries and methods for its prevention. The four different panels were joined by welding and then exposed to a hot solution of nitric-hydrofluoric acid (HNO_3-HF). Weld decay, such as that shown in the type 304 steel (bottom right), is prevented by reduction of the carbon content (type 304L, top left) or by stabilization with titanium (type 321, bottom left) or niobium (type 347, top right).

the precipitation has occurred, it can be removed by reheating the alloy to above 1035 °C (1895 °F) and cooling it rapidly.

Prevention. Susceptibility to intergranular corrosion in austenitic stainless steels can be avoided by controlling their carbon contents or by adding elements whose carbides are more stable than those of chromium. For most austenitic stainless steels, restricting their carbon contents to 0.03% or less will prevent sensitization during welding and most heat treatment. This method is not effective for eliminating sensitization that would result from long-term service exposure at 425 to 815 °C (800 to 1500 °F).

Titanium and niobium form more stable carbides than chromium and are added to stainless steels to form these stable carbides, which remove carbon from solid solution and prevent precipitation of chromium carbides. The most common of these stabilized grades are types 321 and 347. Type 321 contains a minimum of titanium equal to $5 \times (C + N)\%$, and type 347, a minimum of niobium equal to $8 \times C\%$. Nitrogen must be considered when titanium is used as a stabilizer, not because the precipitation of chromium nitride is a problem in austenitic steels, but because titanium nitride is very stable. Titanium will combine with any available nitrogen; therefore, this reaction must be considered when determining the total amount of titanium required to combine with the carbon.

The stabilized grades are more resistant to sensitization by long-term exposure at 425 to 815 °C (800 to 1500 °F) than the low-carbon grades are, and the stabilized grades are the preferred materials when service involves exposure at these temperatures. For maximum resistance to intergranular corrosion, these grades are given a stabilizing heat treatment at about 900 °C (1650 °F). The purpose of treatment is to remove carbon from solution at temperatures where titanium carbides are stable but chromium carbides are not. Such treatments prevent the formation of chromium carbide when the steel is exposed to lower temperatures.

Figure 45 illustrates how both carbon control and stabilization can eliminate intergranular corrosion in as-welded austenitic stainless steels. It also shows that the sensitized zone in these steels is somewhat removed from the weld metal.

Knife-Line Attack. Stabilized austenitic stainless steels may become susceptible to a localized form of intergranular corrosion known as knife-line attack or knife-line corrosion. During welding, the base metal immediately adjacent to the fusion line is heated to temperatures high enough to dissolve the stabilizing carbides, but the cooling rate is rapid enough to prevent carbide precipitation. Subsequent welding passes reheat this narrow area into the temperature range in which both the stabilizing carbide and the chromium carbide can precipitate. The

precipitation of chromium carbide leaves the narrow band adjacent to the fusion line susceptible to intergranular corrosion.

Knife-line attack can be avoided by the proper choice of welding variables and by the use of stabilizing heat treatments.

Testing. The common methods of testing austenitic stainless steels for susceptibility to intergranular corrosion are described in ASTM A 262 "Standard Practices for Detecting Susceptibility to Intergranular Attack in Austenitic Steels." Practice A is a screening test that uses an electrolytic oxalic acid etch combined with metallographic examination. The other practices (B through E) involve exposing the material (possibly after a sensitizing treatment) to boiling solutions of 65% nitric acid (HNO_3), acidified ferric sulfate ($Fe_2(SO_4)_3$) solution, nitric-hydrofluoric acid (HNO_3-HF) solution, or acidified cupric sulfate ($CuSO_4$) solution, depending on the specific alloy and its application. Similar ASTM tests have been developed for other higher-alloyed austenitic stainless steels, ferritic stainless steels, high nickel-based alloys, and aluminum alloys (Table 5).

Intergranular Corrosion of Other Alloy Systems

Ferritic Stainless Steels and Nickel-Base Alloys. Some ferritic stainless steels (e.g., types 430 and 446) are susceptible to intergranular corrosion, as are the following nickel alloys: Inconel alloys 600 and 601, Incoloy 800, despite the presence of titanium, Incoloy 800H, Nickel 200, and Hastelloy alloys B and C. Intergranular corrosion in these alloys is avoided by one or a combination of the following:

- Keeping the alloy in the solution heat-treated condition at all times.
- Limiting interstitial elements, primarily carbon and nitrogen, to the lowest practical levels.
- Adding carbide-stabilizing elements, such as titanium, niobium, and titanium, along with a stabilizing heat treatment where necessary.

Aluminum Alloys. Intergranular corrosion in aluminum alloys is caused by potential differences between the grain-boundary region and the adjacent grain bodies. The location of the anodic path varies with the different alloy systems. In 2*xxx* series alloys, it is a narrow band on either side of the grain boundary that is depleted in copper; in 5*xxx* alloys, it is the anodic constituent $MgAl_3$, when that constituent forms a continuous path along a grain boundary; in copper-free 7*xxx* series alloys, it is generally considered to be the anodic zinc- and magnesium-bearing constituents on the grain boundary; and in the copper-bearing 7*xxx* series alloys, it is the copper-depleted bands along the grain

boundaries. The 6*xxx* series alloys generally resist this type of corrosion, although slight intergranular attack has been observed in highly aggressive environments. The 1*xxx* and 3*xxx* series are immune to intergranular corrosion.

Other alloy systems such as copper, magnesium, lead, and zinc are also susceptible to intergranular corrosion under very specific conditions. However, very few case histories have been reported in the literature.

Table 5 Appropriate evaluation tests and acceptance criteria for wrought alloys

UNS number	Alloy name	Applicable tests (ASTM standards)	Sensitizing treatment	Exposure time, h	Criteria for passing, appearance, or maximum allowable corrosion rate, mm/month (mils/month)
S43000	Type 430	Ferric sulfate (A 763-X)	None	24	1.14 (45)
S44600	Type 446	Ferric sulfate (A 763-X)	None	72	0.25 (10)
S44625	26-1	Ferric sulfate (A 763-X)	None	120	0.05 (2) and no significant grain dropping
S44626	26-1S	Cupric sulfate (A 763-Y)	None	120	No significant grain dropping
S44700	29-4	Ferric sulfate (A 763-X)	None	120	No significant grain dropping
S44800	29-4-2	Ferric sulfate (A 763-X)	None	120	No significant grain dropping
S30400	Type 304	Oxalic acid (A 262-A)	None	…	(a)
		Ferric sulfate (A 262-B)		120	0.1 (4)
S30403	Type 304L	Oxalic acid (A 262-A)	1 h at 675 °C (1250 °F)	…	(a)
		Nitric acid (A 262-C)		240	0.05 (2)
S30908	Type 309S	Nitric acid (A 262-C)	None	240	0.025 (1)
S31600	Type 316	Oxalic acid (A 262-A)	None	…	(a)
		Ferric sulfate (A 262-B)		120	0.1 (4)
S31603	Type 316L	Oxalic acid (A 262-A)	1 h at 675 °C (1250 °F)	…	(a)
		Ferric sulfate (A 262-B)		120	0.1 (4)
S31700	Type 317	Oxalic acid (A 262-A)	None	…	(a)
		Ferric sulfate (A 262-B)		120	0.1 (4)
S31703	Type 317L	Oxalic acid (A 262-A)	1 h at 675 °C (1250 °F)	…	(a)
		Ferric sulfate (A 262-B)		120	0.1 (4)
S32100	Type 321	Nitric acid (A 262-C)	1 h at 675 °C (1250 °F)	240	0.05 (2)
S34700	Type 347	Nitric acid (A 262-C)	1 h at 675 °C (1250 °F)	240	0.05 (2)
N08020	20Cb-3	Ferric sulfate (G 28-A)	1 h at 675 °C (1250 °F)	120	0.05 (2)
N08904	904L	Ferric sulfate (G 28-A)	None	120	0.05 (2)
N08825	Incoloy 825	Nitric acid (A 262-C)	1 h at 675 °C (1250 °F)	240	0.075 (3)
N06007	Hastelloy G	Ferric sulfate (G 28-A)	None	120	0.043 (1.7) sheet, plate, and bar; 0.05 (2) pipe and tubing
N06985	Hastelloy G-3	Ferric sulfate (G 28-4)	None	120	0.043 (1.7) sheet, plate, and bar; 0.05 (2) pipe and tubing
N06625	Inconel 625	Ferric sulfate (G 28-A)	None	120	0.075 (3)
N06690	Inconel 690	Nitric acid (A 262-C)	1 h at 540 °C (1000 °F)	240	0.025 (1)
N10276	Hastelloy C-276	Ferric sulfate (G 28-A)	None	24	1 (40)
N06455	Hastelloy C-4	Ferric sulfate (G 28-A)	None	24	0.43 (17)
N06110	Allcorr	Ferric sulfate (G 28-B)	None	24	0.64 (25)
N10001	Hastelloy B	20% Hydrochloric acid	None	24	0.075 (3) sheet, plate, and bar; 0.1 (4) pipe and tubing
N10665	Hastelloy B-2	20% Hydrochloric acid	None	24	0.05 (2) sheet, plate, and bar; 0.086 (3.4) pipe and tubing
A95005-A95657	Aluminum Association 5*xxx* alloys	Concentrated nitric acid (G 67)	None	24	(b)
A92001-A92618, A97001-A97475	Aluminum Association 2*xxx* and 7*xxx* alloys	Sodium chloride + hydrogen peroxide (G 110)	None	24	(c)

(a) See A 262, practice A. (b) See G 67, section 4.1. (c) See G 110

Exfoliation

General Description. Exfoliation is a form of localized corrosion that primarily affects aluminum alloys in industrial or marine environments. Corrosion proceeds laterally from initiation sites on the surface and generally proceeds intergranually along planes parallel to the surface. The corrosion products that form in the grain boundaries force metal away from the underlying base material, resulting in a layered or flakelike appearance (Fig. 46).

Prevention Through Proper Alloy/Temper Selection. The commercial-purity (1*xxx*) and aluminum-manganese (3*xxx*) alloys are quite resistant to exfoliation corrosion in all tempers. Exfoliation has been encountered in some highly cold-worked aluminum-magnesium (5*xxx*) materials such as 5456-H321 boat hull plates. These developed a highly elongated grain structure and selective grain boundary precipitation. This exfoliation problem led to the establishment of special boat hull plate tempers, H116 and H117, for alloys 5083, 5086, and 5456, which have high resistance to exfoliation corrosion.

In the heat treatable aluminum-copper-magnesium (2*xxx*) and aluminum-zinc-magnesium-copper (7*xxx*) alloys, exfoliation corrosion has usually been confined to relatively thin sections of highly worked products with an elongated grain structure. In 2124-T351 plate, for example,

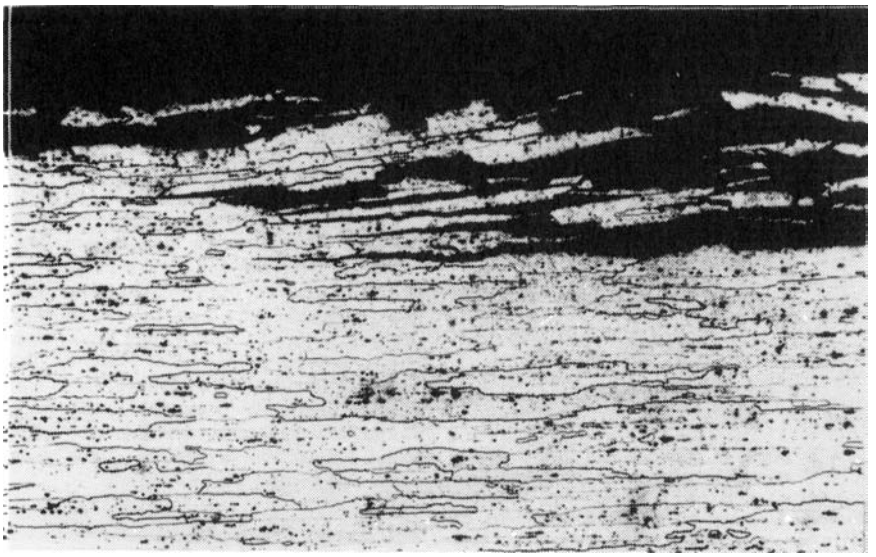


Fig. 46 Exfoliation corrosion in an alloy 7178-T651 plate exposed to a seacoast environment. Cross section of the plate shows how exfoliation develops by corrosion along boundaries of thin, elongated grains. As corrosion proceeds along multiple narrow paths parallel to the surface, the insoluble products that are formed occupy a larger volume than the metal consumed in producing them. These voluminous corrosion products exert a wedging action, which develops lateral tensile forces. This results in the splitting, flaking, or delamination of uncorroded layers of metal.

13 mm (0.5 in.) plate was quite susceptible in laboratory and atmospheric tests, while 50 mm (2 in.) and 100 mm (4 in.) plate, with less directional structures, did not exfoliate. In extrusions, the surface is often quite resistant to exfoliation because of its recrystallized grain structure. Subsurface grains are unrecrystallized, elongate, and vulnerable to exfoliation. In aluminum-zinc-magnesium alloys containing copper, such as 7075, resistance to exfoliation can be improved markedly by overaging. This is designated by the temper designations of T7*xxx* for wrought products. (e.g., 7075-T7351). While a 5 to 10% loss in strength occurs, improved resistance to exfoliation is provided. In copper-free or low-copper 7*xxx* alloys, exfoliation corrosion resistance can be controlled by overaging or by recrystallizing heat treatments and can also be controlled to some extent by changes in alloying elements. In aluminum-copper-magnesium (2*xxx*) alloys, artificial aging to the T6 or T8 condition provides improved resistance.

Dealloying Corrosion

Dealloying, also referred to as selective leaching or parting corrosion, is a corrosion process in which the more active metal is selectively removed from an alloy, leaving behind a porous weak deposit of the more noble metal. Specific categories of dealloying often carry the name of the dissolved element. For example, the preferential leaching of zinc from brass is called dezincification. If aluminum is removed, the process is called dealuminification, and so forth. In the case of gray iron, dealloying is called graphitic corrosion.

In the dealloying process, typically one of two mechanisms occurs: alloy dissolution and replating of the cathodic element or selective dissolution of an anodic alloy constituent. In either case, the metal is left spongy and porous and loses much of its strength, hardness, and ductility.

Table 6 lists some of the alloy-environment combinations for which dealloying has been reported. Descriptions of the most common types of dealloying, dezincification and graphitic corrosion, follow.

Dezincification

General Description. Copper-zinc alloys containing more than 15% zinc are susceptible to dezincification. In the dezincification of brass, selective removal of zinc leaves a relatively porous and weak layer of copper and copper oxide. Corrosion of a similar nature continues beneath the primary corrosion layer, resulting in gradual replacement of sound brass by weak, porous copper. Unless arrested, dealloying even-

tually penetrates the metal, weakening it structurally and allowing liquids or gases to leak through the porous mass in the remaining structure.

Dezincification is the usual form of corrosion for uninhibited brasses in prolonged contact with waters high in oxygen and carbon dioxide (CO_2). It is frequently encountered with quiescent or slowly moving solutions. Slightly acidic water, low in salt content and at room temperature, is likely to produce uniform attack, but neutral or alkaline water, high in salt content and above room temperature, often produces plug-type attack.

Identification. The two major forms of dezincification are layer-type and plug-type dealloying. In layer-type dezincification, the majority of the component surface is converted to corrosion product to a roughly uniform depth (Fig. 47 and 48). Plug-type dezincification produces small pockets or plugs of almost pure copper (Fig. 49 and 50).

Layer-type dezincification is easy to recognize visually. The original component shape and dimensions are usually preserved but the metal changes from the gold yellow of zinc brass to the red of elemental copper at the dezincified surface (Fig. 47).

Plug-type dezincification is common on horizontal pipe/tube sections. Attack is usually confined to areas beneath deposits lying along pipe bottoms (see Fig. 49). Plugs are sometimes blown out of the pipe wall due to internal pressure and produce holes. More often, fluids weep through the porous plugs, causing additional corrosion problems.

Prevention through Alloy Selection. Brasses with copper contents of 85% or more resist dezincification. Dezincification of brasses with

Table 6 Combinations of alloys and environments subject to dealloying and elements preferentially removed

Alloy	Environment	Element removed
Brasses	Many waters, especially under stagnant conditions	Zinc (dezincification)
Gray iron	Soils, many waters	Iron (graphic corrosion)
Aluminum bronzes	Hydrofluoric acid, acids containing chloride ions	Aluminum (dealuminification)
Silicon bronzes	High-temperature steam and acidic species	Silicon (desiliconification)
Tin bronzes	Hot brine or steam	Tin (destannification)
Copper nickels	High heat flux and low water velocity (in refinery condenser tubes)	Nickel (denickelification)
Copper-gold single crystals	Ferric chloride	Copper
Monels	Hydrofluoric and other acids	Copper in some acids, and nickel in others
Gold alloys with copper or silver	Sulfide solutions, human saliva	Copper, silver
Tungsten carbide-cobalt	Deionized water	Cobalt
High-nickel alloys	Molten salts	Chromium, iron, molybdenum, and tungsten
Medium- and high-carbon steels	Oxidizing atmospheres, hydrogen at high temperatures	Carbon (decarburization)
Iron-chromium alloys	High-temperature oxidizing atmospheres	Chromium, which forms a protective film
Nickel-molybdenum alloys	Oxygen at high temperature	Molybdenum



Fig. 47 Layer-type dezincification of a brass pump component. The dark (red) outer layers are uniformly corroded regions surrounding the uncorroded metal (original yellow) of the brass. Source: Nalco Chemical Company

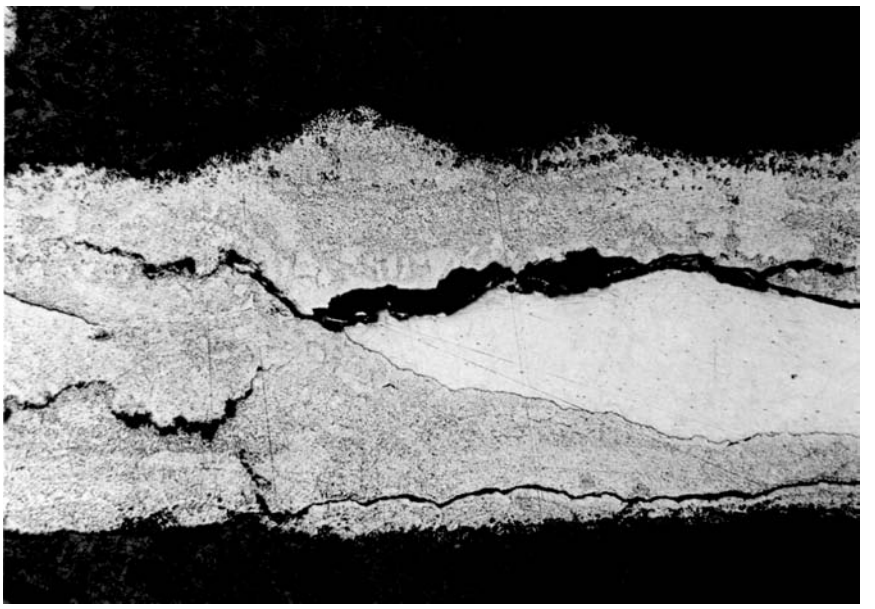


Fig. 48 Layer-type dezincification of a thin brass sheet. The 0.48 mm (0.019 in.) sheet is shown in cross section. The dezincified layers converge toward the edge (left side) of the sheet. Note the porosity of the dezincified metal. Source: Nalco Chemical Company

two-phase structures is generally more severe, particularly if the second phase is continuous. It usually occurs in two stages: the high-zinc β phase, followed by the lower-zinc α phase.

Tin tends to inhibit dealloying, especially in cast alloys. Alloys C46400 (naval brass) and C67500 (manganese bronze), which are α-β



Fig. 49 A large plug of dezincified metal beneath a deposit on a brass pipe. Source: Nalco Chemical Company

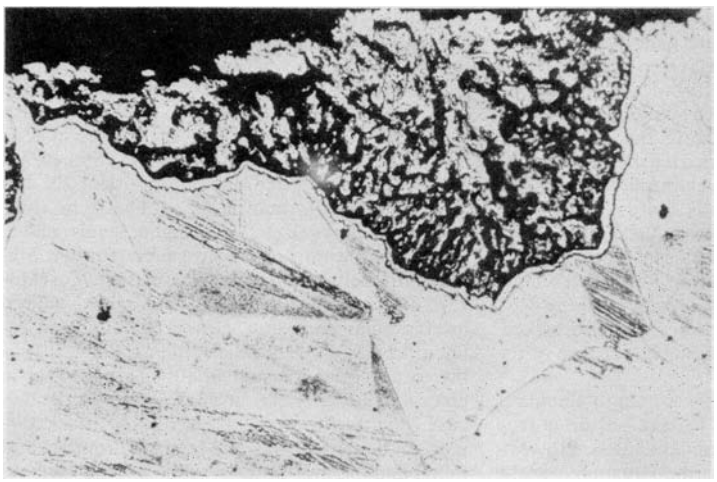


Fig. 50 Plug-type dezincification in an α-brass (70Cu-30Zn) exposed for 79 days in 1 *N* NaCl at room temperature. Note porous structure within the plug. The dark line surrounding the plug is an etching artifact. 160×

brasses containing about 1% Sn, are widely used for naval equipment and have reasonably good resistance to dezincification. Addition of a small amount of phosphorus, arsenic, or antimony to admiralty metal (an all-α 71Cu-28Zn-1Sn brass) inhibits dezincification. Inhibitors are not entirely effective in preventing dezincification of the α-β brasses because they do not prevent dezincification of the β phase.

Where dezincification is a problem, red brass, commercial bronze, inhibited admiralty metal, and inhibited aluminum brass can be successfully used. In some cases, the economic penalty of avoiding dealloying by selecting a low-zinc alloy may be unacceptable. Low-zinc alloy tubing requires fittings that are available only as sand castings, but fittings for higher-zinc tube can be die cast or forged much more economically. Where selection of a low-zinc alloy is unacceptable, inhibited yellow brasses are generally preferred.

Graphitic Corrosion

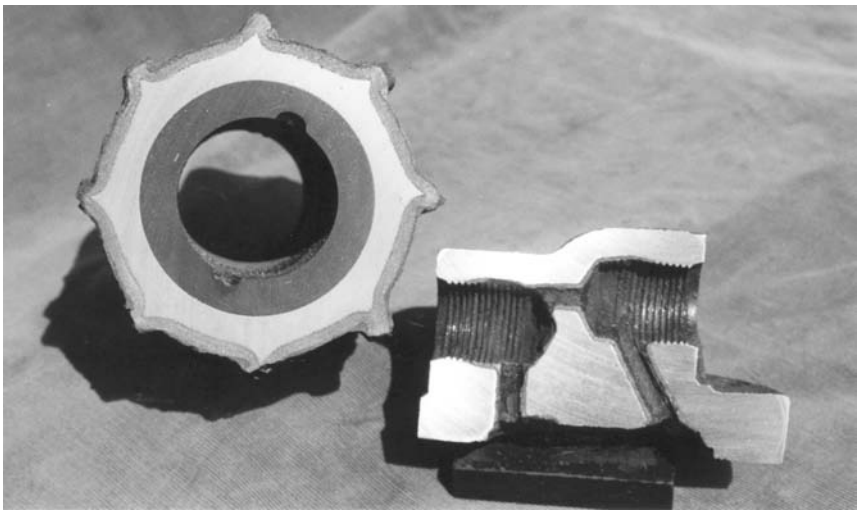
General Description. Graphitic corrosion is a form of dealloying unique to cast irons. It is observed in gray cast irons in relatively mild environments in which selective leaching of iron leaves a graphite network. Selective leaching of the iron takes place because the graphite is cathodic to iron, and the gray iron structure establishes an excellent galvanic cell. This form of corrosion generally occurs only when corrosion rates are low. If the metal corrodes more rapidly, the entire surface, including the graphite, is removed, and more or less uniform corrosion occurs. Graphitic corrosion can cause significant problems because, although no dimensional changes occur, the cast iron loses its strength and metallic properties. Thus, without detection, potentially dangerous situations may develop in pressure-containing applications.

Environments Promoting Graphitic Corrosion (Ref 9). Experience has demonstrated that graphitic corrosion is favored by relatively mild environments such as soft waters, waters having a slightly acidic pH, waters containing low levels (as little as 1 ppm) of hydrogen sulfide, and brackish and other high-conductivity waters. It should not be inferred from this that gray or nodular cast irons are immune to more aggressive environments but, rather, that graphitic corrosion is less likely in them. In more aggressive environments, corrosion may indeed occur but may be manifested as general metal loss rather than as graphitic corrosion. Moist soils, especially those containing sulfates, will frequently produce graphitic corrosion of unprotected gray and nodular cast iron. Stray currents have also been identified as causes of graphitic corrosion in subterranean pipelines.

Identification (Ref 10). Cast iron is converted to a soft mixture of iron oxides and graphite. Pieces of corrosion product smudge hands and

can be used to mark paper, just as if the corroded material were lead in a pencil.

Attack is often uniform, with all exposed surfaces corroded to roughly the same depth (Fig. 51). If localized deposits are present, especially those containing sulfate and chloride or other acidic species, corrosion may be confined to pockets. When attack is severe or prolonged, the entire component is converted to corrosion product. Surface contour



(a)



(b)

Fig. 51 Examples of graphitic corrosion of gray cast-iron parts. (a) Cross sections cut through graphitically corroded regions will readily show bright, intact metal surrounded by a soft, dark, corroded area. (b) Graphitically corroded valve butterfly. Original surface contours are preserved. Edges, which were completely converted to brittle product, have broken. Source: Nalco Chemical Company

and appearance are often preserved. Attack is usually not apparent until surfaces are probed or stressed.

Prevention. Attack by graphitic corrosion is reduced by the following:

- Alloy substitution. Ductile cast iron is less prone to serious graphitic corrosion than gray irons, although it is not immune. White cast iron, which is essentially free of graphite, is immune to graphitic corrosion. Corrosion-resistant cast irons containing chromium, nickel, and silicon are also immune to graphitic corrosion.
- Raising water pH to neutral or slightly alkaline levels to decrease attack, especially if relatively high concentrations of aggressive anions such as chloride and sulfate are present.
- Use of inhibitors
- Avoidance of stagnant water conditions

Stress-Corrosion Cracking

General Description. Stress-corrosion cracking (SCC) is a cracking phenomenon that occurs in susceptible alloys and is caused by the conjoint action of a surface tensile stress and the presence of a specific corrosive environment. For SCC to occur on an engineering structure, three conditions must be met simultaneously, namely, a specific crack-promoting environment must be present, the metallurgy of the material must be susceptible to SCC, and the tensile stresses must be above some threshold value. Stresses required to cause SCC are small, usually below the macroscopic yield stress. The stresses can be exter-

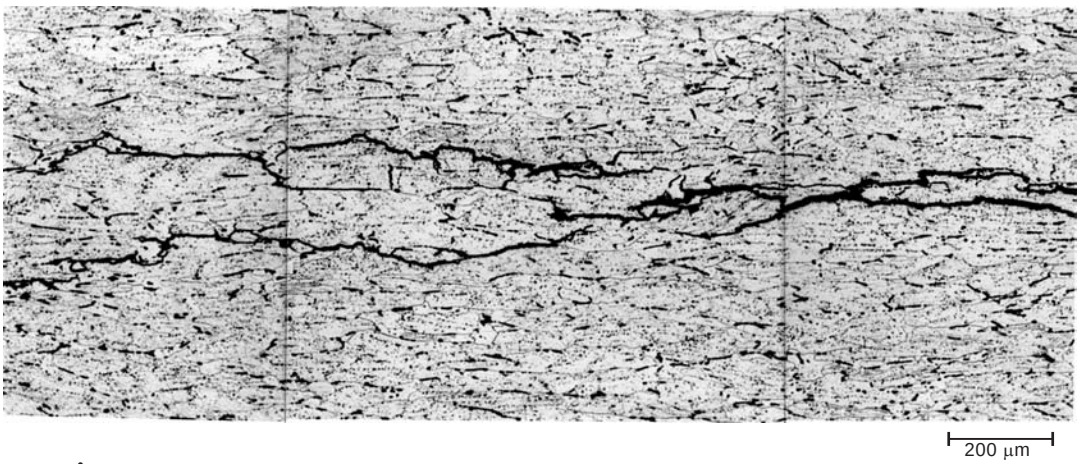


Fig. 52 Intergranular stress corrosion crack produced in 7050-T651 following exposure to 90 °C (195 °F), 90% relative humidity air. Specimens were etched in 10% NaOH at 70 °C (160 °F) for 20 s, nitric acid rinse.

nally applied, but residual stresses often cause SCC failures. This cracking phenomenon is of particular importance to users of potentially susceptible structural alloys because SCC occurs under service conditions that can result, often with no warning, in catastrophic failure.

Stress-corrosion cracks often undergo extensive branching and proceed in a general direction perpendicular to the stresses contributing to their initiation and propagation. Figure 52 shows intergranular SCC in a specimen of high-strength aluminum alloy 7050 that occurred following exposure to 90 °C (195 °F), 90% relative humidity air. Figure 53 shows an SCC failure of a titanium alloy pressure vessel used to contain uninhibited nitrogen tetroxide (N_2O_4) under pressure. The penetration of multiple stress-corrosion cracks from the internal surface of the tank is visible. A group of these cracks eventually grew to such a depth that the remaining wall thickness was unable to support the pressure, and mechanical failure occurred. Figure 54 shows a type 304 stainless steel heat exchanger tube that failed after exposure to chlorides. The cracks were highly branched and transgranular. As these figures indicate, in some metals, cracking propagates intergranularly; in others, transgranularly. In certain metals, such as high-nickel alloy, iron-chromium alloys, and brasses, either type of cracking can occur, depending on the metal-environment combination.

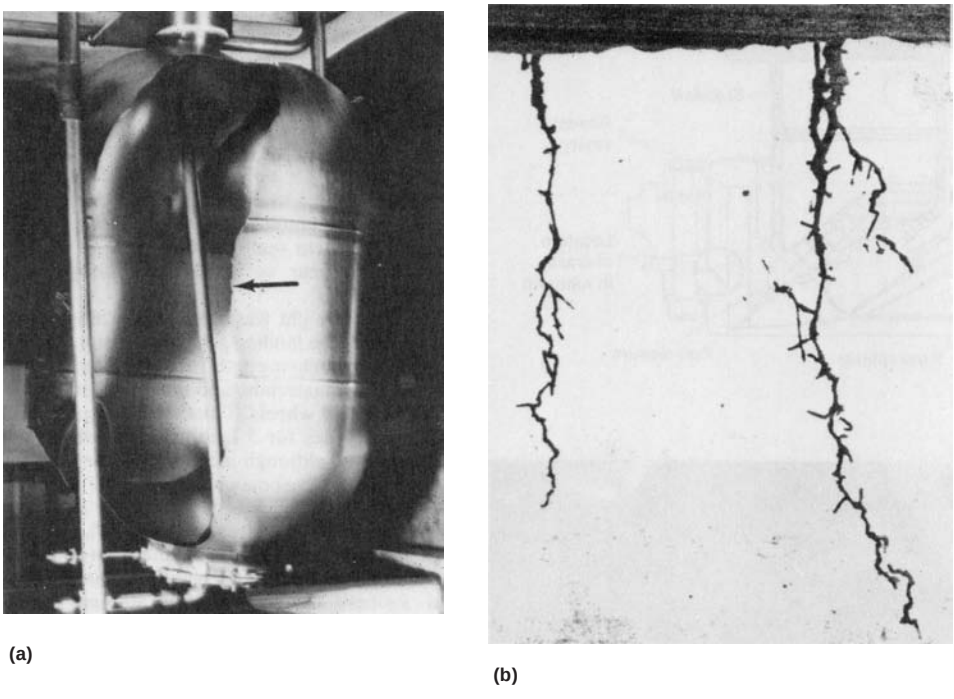
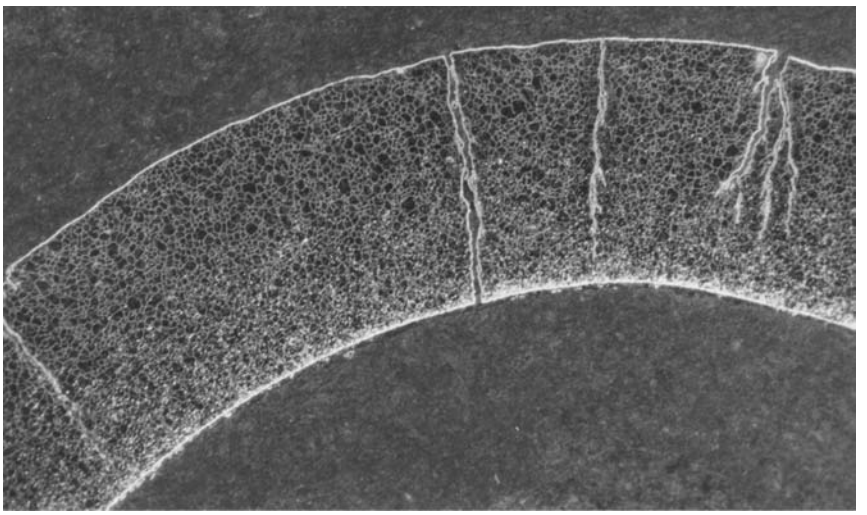


Fig. 53 Stress-corrosion failure of an Apollo Ti-6Al-4V RCS pressure vessel due to nitrogen tetroxide. (a) Failed vessel after exposure to pressurized N_2O_4 for 34 h. (b) Cross section through typical stress-corrosion cracks. 250×

Materials Factors Influencing SCC Behavior. The alloy composition and microstructure have a great effect on the susceptibility of a material to SCC in a particular environment. The bulk alloy composition may affect the formation and stability of a protective film on the surface. The alloy composition includes the nominal composition, the presence of constituents, and the presence and composition of impurities or trace elements. The metallurgical condition, which affects the susceptibility to SCC, includes the strength level, the presence of



(a)



(b)

Fig. 54 Stress-corrosion failure of a type 304 stainless steel heat exchanger tube from carbon dioxide compressor intercooler after exposure to a pressurized chloride-containing (200 ppm) environment at 120 °C (250 °F) (a) Cracks on the external surface. (b) Cracks originating on the external surface. Note the branching of the cracks. 33×. Source: Nalco Chemical Company

phases in the matrix and at the grain boundaries, the composition of the phases, the grain size and orientation of the phases, the grain size and orientation, grain-boundary segregation, and residual stresses.

An example of strong influence of alloy composition and microstructure on the susceptibility to SCC is given by austenitic stainless steels, where chromium and molybdenum promote the formation of passive films on the surface. Trace elements such as carbon at concentrations greater than 0.03 wt%, may cause sensitization by forming chromium carbides at the grain boundaries and depleting zones around the carbides of chromium, thereby rendering the steel susceptible to intergranular SCC (IGSCC). Austenitic stainless steels will fail transgranularly in high-temperature chloride solutions.

Similarly, the susceptibility of aluminum alloys to SCC strongly depends on the microstructure, which can be modified by heat treatment. The 7000 series aluminum alloys are precipitation-hardening alloys, and the peak-aged microstructure (T6) is the most susceptible to SCC. Overaging to the T76 or T73 condition usually reduces or eliminates the susceptibility to cracking. Peak aging of this alloy results in a fine distribution of coherent precipitates, which give strength to the alloy. However, the heat treatment also results in the formation of large incoherent precipitates at the grain boundaries and the depletion of solute in the region adjacent to the grain boundaries.

Environmental Factors Influencing SCC Behavior. Stress-corrosion cracking of susceptible alloys is environment specific. NACE International and the Materials Technology Institute of the Chemical Process Industries and others have published tables of corrodents known to cause SCC of various metals and alloy systems. Table 7 lists these data in condensed form and covers the SCC environments of major importance to materials engineers. This table, as well as those published in the literature, should be used only as a guide for screening candidate materials for further in-depth investigation, testing, and evaluation.

Stress-corrosion cracking is not a certainty in the listed environments under all conditions. Metals and alloys that are indicated as being susceptible can give good service under specific conditions (Table 7):

- Anhydrous ammonia will cause SCC in carbon steels, but rarely at temperatures below 0 °C (32 °F) and only when such impurities as air or oxygen are present; addition of a minimum of 0.2% H_2O will inhibit SCC.
- Aqueous fluorides and hydrofluoric acid (HF) primarily affect Monel alloy 400 (UNS N04400) in the nickel alloys system; others are resistant.
- Steam is known to cause SCC only in aluminum bronzes and silicon bronzes in the copper alloys system.

- Polythionic acid only cracks sensitized austenitic stainless steels and nickel alloys; SCC is avoided by solution annealing heat treatments or selection of stabilized or low-carbon alloys.

More detailed information on SCC of specific alloy systems can be found in Chapter 6.

Environments that cause SCC are usually, but not necessarily, aqueous, and specific environmental parameters must be in specific ranges for cracking to occur. These include, but are not limited to, the following:

- Temperature
- pH
- Electrochemical potential
- Solute species
- Solute concentration
- Oxygen concentration

Changing any of these environmental parameters may significantly affect the crack nucleation process or the rate of crack propagation. Although the parameters listed above are important in controlling the rate of SCC, conditions inside a propagating crack and at the crack tip, which actually control the crack propagation process, are often quite

Table 7 Some environment-alloy combinations known to result in SCC

	Alloy system								
					Stainless steels				
Environment	Aluminum alloys	Carbon steels	Copper alloys	Nickel alloys	Austenitic	Duplex	Martensitic	Titanium alloys	Zirconium alloys
Amines, aqueous	…	X	X	…	…	…	…	…	…
Ammonia, anhydrous	…	X	…	…	…	…	…	…	…
Ammonia, aqueous	…	…	X	…	…	…	…	…	…
Bromine	…	…	…	…	…	…	…	…	X
Carbonates, aqueous	…	X	…	…	…	…	…	…	…
Carbon monoxide, carbon dioxide, water mixture	…	X	…	…	…	…	…	…	…
Chlorides, aqueous	X	…	…	X	X	X	…	…	X
Chlorides, concentrated, boiling	…	…	…	X	X	X	…	…	…
Chlorides, dry, hot	…	…	…	X	…	…	…	X	…
Chlorinated solvents	…	…	…	…	…	…	…	X	X
Cyanides, aqueous, acidified	…	X	…	…	…	…	…	…	…
Fluorides, aqueous	…	…	…	X	…	…	…	…	…
Hydrochloric acid	…	…	…	…	…	…	…	X	…
Hydrofluoric acid	…	…	…	X	…	…	…	…	…
Hydroxides, aqueous	…	X	…	…	X	X	X	…	…
Hydroxides, concentrated, hot	…	…	…	X	X	X	X	…	…
Methanol plus halides	…	…	…	…	…	…	…	X	X
Nitrates, aqueous	…	X	X	…	…	…	X	…	…
Nitric acid, concentrated	…	…	…	…	…	…	…	…	X
Nitric acid, fuming	…	…	…	…	…	…	…	X	…
Nitrites, aqueous	…	…	X	…	…	…	…	…	…
Nitrogen tetroxide	…	…	…	…	…	…	…	X	…
Polythionic acids	…	…	…	X	X	…	…	…	…
Steam	…	…	X	…	…	…	…	…	…
Sulfides plus chlorides, aqueous	…	…	…	…	X	X	X	…	…
Sulfurous acid	…	…	…	…	X	…	…	…	…
Water, high-purity, hot	X	…	…	X	…	…	…	…	…

X, known to result in SCC

different from the so-called bulk environmental parameters. The pH inside cracks often differs from that in the bulk environment. In low-alloy steels containing approximately 1 wt% Cr, dissolution and hydrolysis of chromium can result in a lowering of the pH to values near 4 (Ref 11).

In the case of stainless steels, the pH value in cracks can range from 0 to 3, with the lowest pH values associated with concentrated salt solutions containing chromium and ferrous ions. The pH inside cracks of aluminum and aluminum alloys is generally in the range of 3 to 4, while the pH inside propagating cracks in titanium alloys can be as low as 1 (Ref 11).

Stress-corrosion cracking consists of a crack nucleation and propagation phase. Very little is known about the conditions that control the nucleation of a crack, other than that the thermodynamic and kinetic conditions must be right for the crack nucleate. For example, for anodically assisted SCC, metal dissolution and subsequent formation of a protective oxide film must be thermodynamically possible. The thermodynamic requirement of simultaneous dissolution and film formation has led to the identification of critical potentials at which SCC can occur. The thermodynamic conditions at which dissolution and film forming occurs is described by potential-pH (Pourbaix) diagrams. For example, the Pourbaix diagram in Fig. 55 describes the conditions at which dissolution and film formation on carbon steel can occur in different environments such as phosphate, nitrate, and carbonate/bicarbonate solutions. The effects of many of the external parameters listed above, such as pH, temperature, potential, and solute and oxygen concentration can have a great effect on thermodynamic stability and, thus, on the susceptibility to SCC. The diagram indicates that severe susceptibility to SCC is encountered when a protective film such as carbonate, phosphate, or magnetite is thermodynamically stable.

In addition to the thermodynamic stability requirements for crack nucleation and propagation, kinetic requirements also need to be met. As in the thermodynamic requirements for SCC, environmental parameters such as potential, pH, solute and oxygen concentration, temperature, and crack-tip chemistry have a strong effect on the crack nucleation and crack growth kinetics. Figure 56 shows examples of potentio-dynamic polarization curves for alloy 600, alloy 800, and type 304 stainless steel in 10% NaOH solution at 288 °C (550 °F), indicating the various potential regions for susceptibility to SCC. The figure shows that, for all three alloys, the active-passive transition region presents the critical potential range for SCC to occur. However, the critical potentials, as well as the mode of cracking, are different for each alloy.

Mechanical Factors Influencing SCC Behavior. Threshold stresses and stress-intensity factors, the presence of a stress-independent crack-growth regime, and the dependence of cracking to strain rate are important features in determining the susceptibility of alloys to SCC.

The threshold stress is typically the stress value obtained from constant-load testing below which SCC does not occur and can serve as a simple measure for susceptibility of a material to SCC in a certain environment.

The stress-intensity factor, *K*, is a parameter that describes the relationship between the applied stress and crack length for specific specimen geometries. Figure 57 shows the stress-intensity factor, *K*, as a function of the crack propagation rate, *da*/*dt*. The threshold is defined in this figure by the minimum detectable crack growth rate. The threshold stress intensity is generally associated with the development of a plastic zone at the crack tip. Stage I crack growth shows a rapid increase in crack growth rate, while in Stage II, the crack growth rate is independent of the stress intensity.

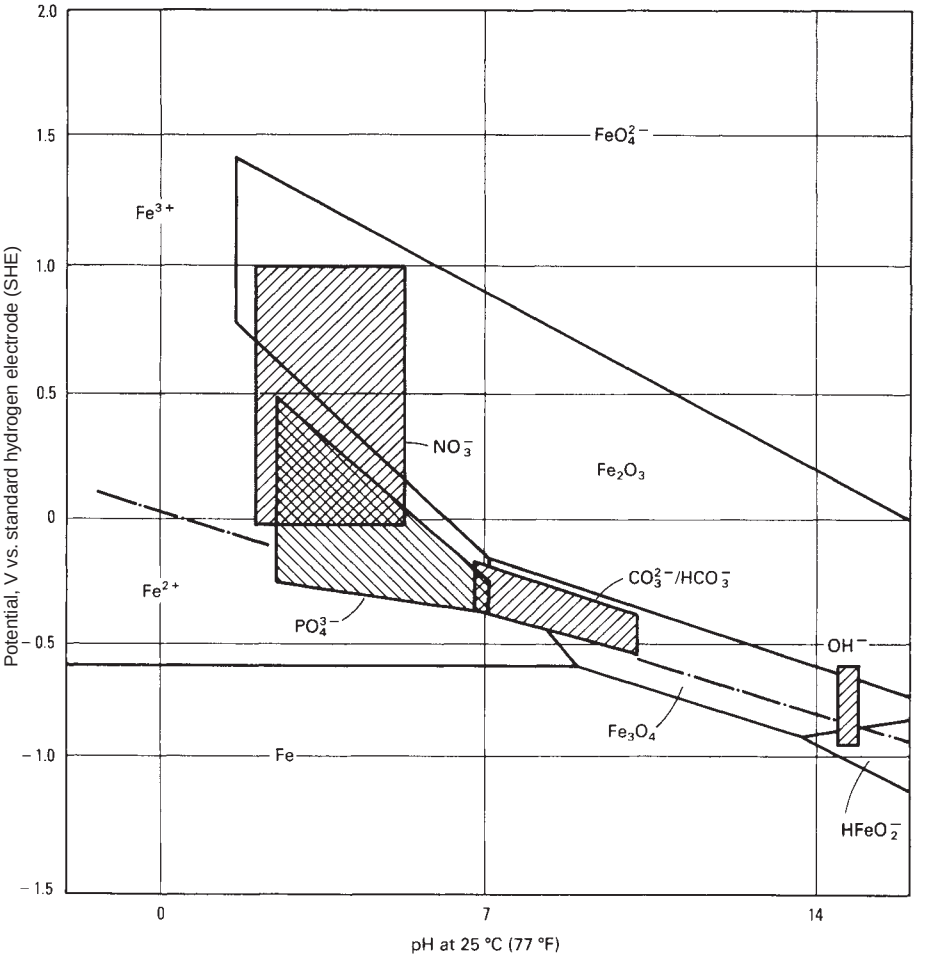


Fig. 55 Relationship between pH-potential conditions for SCC susceptibility of carbon steel in various environments and the stability regions for solid and dissolved species on the Pourbaix diagram. Note that severe susceptibility is encountered where a protective film (phosphate, carbonate, magnetite, and so on) is thermodynamically stable, but if ruptured, a soluble species (Fe^{2+}, $HFeO_2^-$) is metastable.

The stress-corrosion crack propagation is usually studied with linear elastic fracture mechanics (LEFM), which assumes little plasticity at the tip of the propagating crack, such that the stress state is triaxial or plane strain. When the plastic zone size exceeds a certain value, either by increased stress, by propagation in a ductile material, or by crack propagation in a thin member, the stress state becomes biaxial or plane

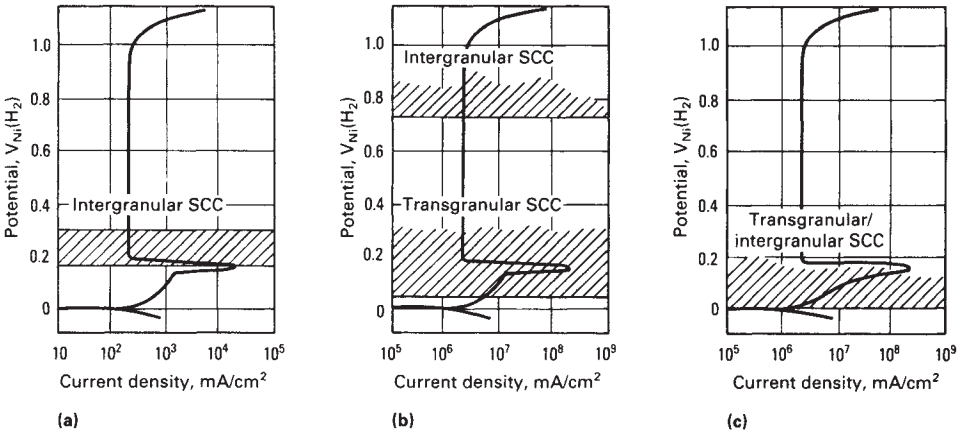


Fig. 56 Potentiokinetic polarization curve and electrode potential values at which intergranular and transgranular SCC appears in a 10% sodium hydroxide (NaOH) solution at 288 °C (550 °F). (a) Alloy 600. (b) Alloy 800. (c) AISI type 304 stainless steel

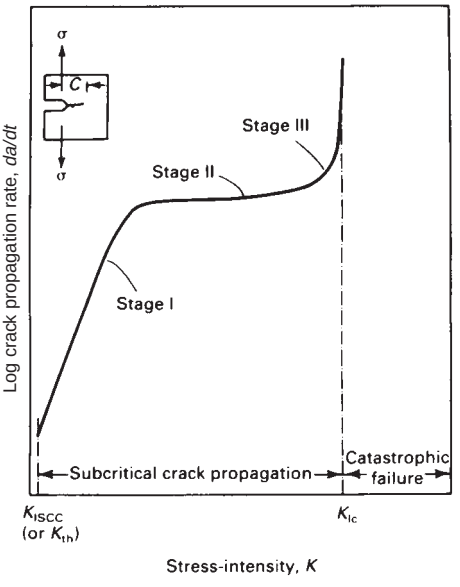


Fig. 57 Schematic of stress-corrosion crack velocity as a function of stress-intensity factor, *K*

stress, and LEFM is not applicable. Then the more fundamental parameters, the energy release rate or *J*-integral, can be applied to describe the propagating stress-corrosion crack (Ref 12).

The slow-strain-rate technique provides an excellent way to determine the susceptibility of an alloy to SCC (Ref 13, 14). However, the strain-rate behavior strongly depends on the alloy/environment combination. For example, for most materials, the critical strain rate, at which the maximum susceptibility is obtained, is 10^{-6}/s. This critical strain rate points to a cracking mechanism whereby the rate of anodic dissolution is equal to the rate of protective film formation. If a higher strain rate is applied, the mechanical fracture will be more rapid than the rate of anodic dissolution. On the other hand, when a lower strain rate is applied, anodic dissolution will continue to blunt the crack, and SCC cannot occur. When other SCC mechanisms are predominant, the critical strain rate may be at a higher value, as is often the case with internal hydrogen embrittlement, or there may be no critical value, which occurs when the susceptibility decreases with decreasing strain rate. This has been observed in cases where the mechanism of SCC is thought to be hydrogen embrittlement. More detailed descriptions of the mechanisms of SCC and the use of LEFM for studying SCC behavior can be found in *Corrosion,* Volume 13, of the *ASM Handbook.*

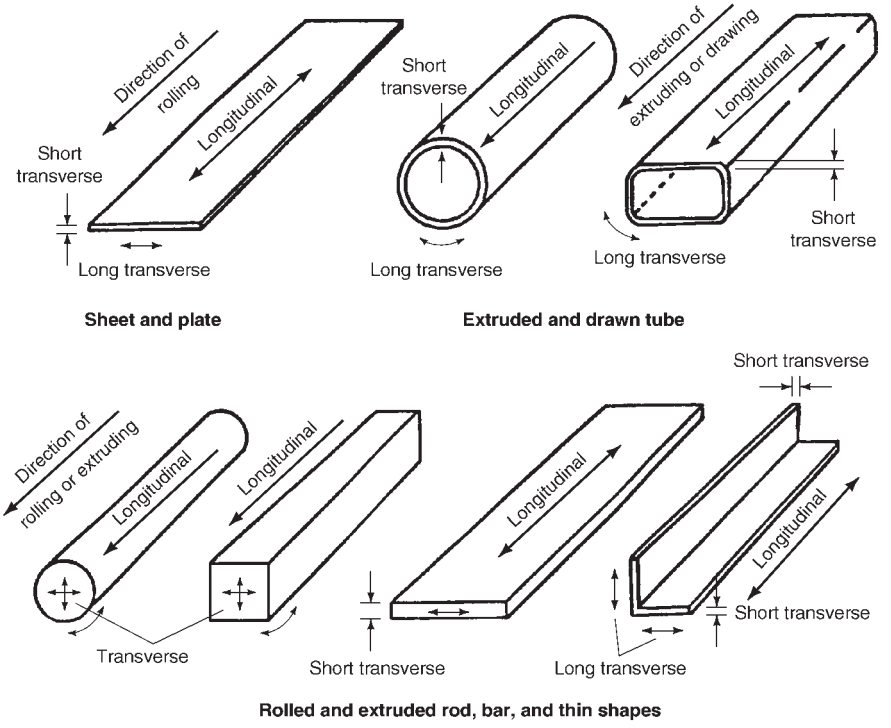


Fig. 58 Grain orientations in standard wrought forms of alloys

Evaluation of SCC. In order to determine the susceptibility of alloys to SCC, several types of testing are available. If the objective of testing is to predict the service behavior or to screen alloys for service in a specific environment, it is often necessary to obtain SCC information in a relatively short period of time, which requires acceleration of testing by increasing the severity of the environment or the critical test parameters. The former can be accomplished by increasing the test temperature or the concentration of corrosive species in the test solution and by electrochemical stimulation. Test parameters that can be changed to reduce the testing time include the application of higher stresses, continuous straining, and precracking, which allows bypassing of the crack nucleation phase of the SCC process.

Stress-corrosion specimens can be divided into two main categories, namely smooth, and precracked or notched specimens. Further distinction can be made in the loading mode, such as constant deflection, constant load, and constant extension or strain rate.

During alloy processing, operations used in the production of wrought alloys, the metal is forced in a predominant direction so that the grains are elongated in the direction of flow. Because it is important to relate the application of stress and the grain flow direction, two conventions are used to relate the two parameters. In one system, which is primarily used for smooth specimens, the three stressing directions are designated by indicating the direction of the stress, namely longitudinal (L), long-transverse (LT), transverse (T), and short-transverse (Fig. 58).

A second system, which is particularly useful for precracked specimens, indicates both the cracking plane and the direction of crack propagation. The system uses three letters (L, T, and W) to indicate three perpendicular directions, namely L for the longitudinal direction, T for the thickness direction, and W for the width direction. The crack plane is indicated by the direction normal to the crack, and the crack propagation is indicated by one of the directions L, T, or W. Figure 59 demonstrates the various orientations for a double-cantilever-beam (DCB)

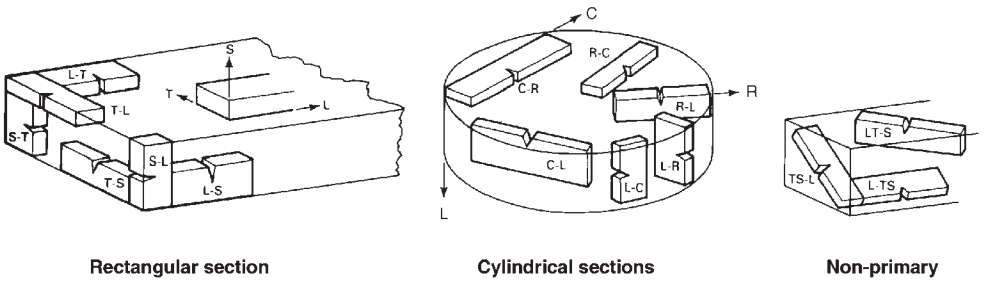


Fig. 59 Fracture plane identification in double-cantilever-beam specimens. L, direction of grain flow; T, transverse grain direction; S, short transverse grain direction; C, chord of cylindrical cross section; R, radius of cylindrical cross section; first letter, normal to the fracture plane; second letter, direction of crack propagation in fracture plane

specimen. More detailed information on SCC test specimens and test methods can be found in Ref 15.

Prevention of SCC can be accomplished by the following:

- *Changing the material:* A common method to control SCC is to select a material with greater SCC resistance to a particular environment. In other cases, the cracking may result from a specific microstructural condition of the metal (e.g., sensitized austenitic stainless steel). In this case, avoiding the susceptible microstructure can solve the problem. Often, as the strength of an alloy increases, its susceptibility to SCC increases. Use of alloys with lower strength levels can thus be an effective means of reducing the likelihood of SCC if the design/ application permits.
- *Changing the environment:* The environment can be modified to reduce the concentration of aggressive species or to reduce the temperature. Inhibitors can also be added to control SCC.
- *Changing the oxidizing potential:* Shifting the electrochemical potential of the metal's surface out of the critical potential range for cracking will prevent SCC. The potential can be shifted to more oxidizing potentials (anodic protection) or to more reducing potentials (cathodic protection).

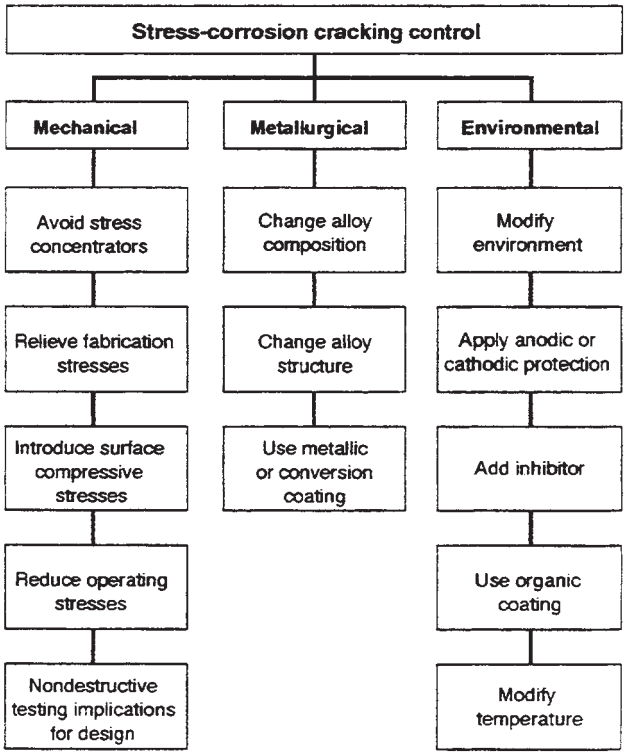


Fig. 60 Methods used to control SCC. Source: Ref 16

- *Applying protective coatings:* Coatings that isolate the metal substrate from the corrosive environment can effectively control SCC. In these cases, however, the protection depends on the integrity of the protective film.
- *Changing applied or residual stress levels:* Several approaches can be used to alleviate SCC problems. The level of tensile stresses at the metal surface can be lowered either by lowering the operating stresses, stress relieving the parts subsequent to fabrication to reduce residual stresses, or shot peening to build up compressive stresses at the metal surface. Another important consideration is to use proper grain orientations to reduce sustained stress levels on the part below the stress-corrosion threshold levels, especially in the more susceptible short-transverse direction grain directions. High-strength aluminum alloys have much lower SCC resistance in the short-transverse direction.

Figure 60 summarizes the various approaches to controlling SCC.

Corrosion Fatigue

General Description. Corrosion fatigue is a term that is used to describe the phenomenon of cracking, including both initiation and propagation, in materials under the combined actions of a fluctuating, or cyclic stress, and a corrosive environment. Corrosion fatigue depends strongly on the interactions between the mechanical (loading),

Table 8 Mechanical, metallurgical, and environmental variables that influence corrosion fatigue behavior

Variable	Type
Mechanical	Maximum stress or stress-intensity factor, σ_{max} or K_{max}
	Cyclic stress or stress-intensity range, $\Delta\sigma$ or ΔK
	Stress ratio (R)
	Cyclic loading frequency
	Cyclic load waveform (constant-amplitude loading)
	Load interactions in variable-amplitude loading
	State of stress
	Residual stress
	Crack size and shape, and their relation to component size and geometry
Metallurgical	Alloy composition
	Distribution of alloying elements and impurities
	Microstructure and crystal structure
	Heat treatment
	Mechanical working
	Preferred orientation of grains and grain boundaries (texture)
	Mechanical properties (strength, fracture toughness, etc.)
Environmental	Temperature
	Types of environments: gaseous, liquid, liquid metal, etc.
	Partial pressure of damaging species in gaseous environments
	Concentration of damaging species in aqueous or other liquid environments
	Electrical potential
	pH
	Viscosity of the environment
	Coatings, inhibitors, etc.

metallurgical, and environmental variables listed in Table 8. As shown in Fig. 61, an aggressive environment usually has a deleterious effect on fatigue life, producing failure in fewer stress cycles than would be required in a more inert environment.

Corrosion fatigue produces fine-to-broad cracks with little or no branching (Fig. 62 and 63); thus, they differ from stress-corrosion cracks, which often exhibit considerable branching. They are typically filled with dense corrosion product (Fig. 63a). The cracks may occur singly but commonly appear as families or parallel cracks. They are frequently associated with pits, grooves, or some other form of stress concentrator. Transgranular fracture paths are more common than intergranular fractures.

Prevention. All metals and alloys are susceptible to corrosion fatigue. Even some alloys that are immune to SCC, for example, ferritic stainless steels, are subject to failure by corrosion fatigue. Both temporary and permanent solutions for corrosion involve reducing or eliminating cyclic stresses, selecting a material or heat treatment with higher corrosion fatigue strengths, reducing or eliminating corrosion, or a combination of these procedures. These objectives are accomplished by changes in material, design, or environment.

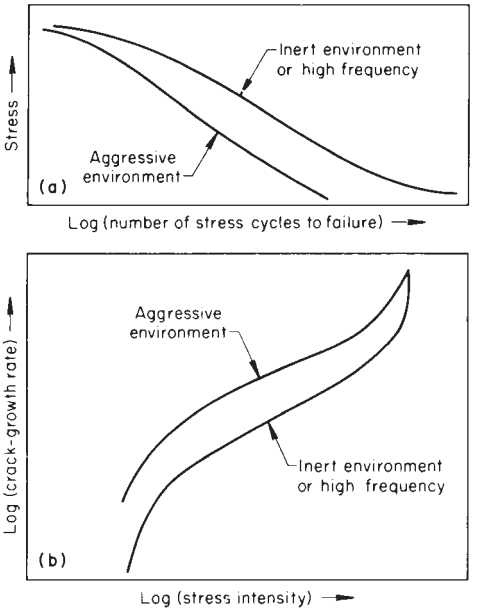


Fig. 61 Typical fatigue behavior in an aggressive environment compared with fatigue behavior in an inert environment or at high frequency. (a) Data plotted as *S-N* curves. (b) Data plotted as the crack-growth rate vs. stress-intensity range. The environmental influence is most pronounced at low and intermediate stress-intensity levels. At high stress intensity, the mechanical crack-growth driving force becomes dominant, and the influence of environment is less significant. As the stress intensity approaches the fracture toughness of the material where instability occurs, the effect of the aggressive environment becomes less significant

For permanent solutions, if a new material is selected (the same alloy with a different heat treatment or fabrication method, another alloy for the same system, or an alloy from a completely different system), basic compatibility with design requirements and with the environment to be encountered in service usually must be proved by testing. If changes in design or in mode of fabrication are selected, test specimens should reflect these changes. Any environmentally affected properties must be checked in a simulated service environment. Any alteration of the environment should also be testing at this stage. Finally, the ultimate test of a redesigned component is its service life in comparison with the life of the component that is replaced. A review of corrosion fatigue test methods can be found in the article "Corrosion Fatigue Testing" in Volume 19 of the *ASM Handbook*.

Operating stress may be lowered by reducing either the mean stress or the amplitude of the cyclic stress. This almost always involves a change in component design. Sometimes, only a minor change is required, such as increasing a fillet radius to reduce the amount of stress concentration at a critical location. In other instances, more extensive changes are required, such as significantly increasing the cross-sectional area or adding a strengthening rib. If failure has occurred because of stress raisers introduced during manufacture, changes in manufacturing processes or procedures and quality requirements may be necessary.

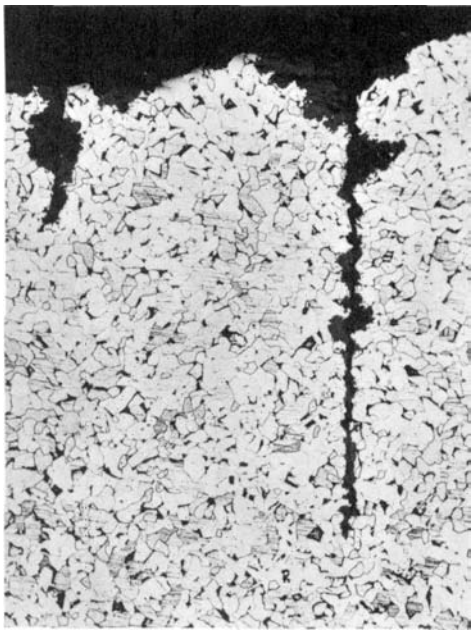
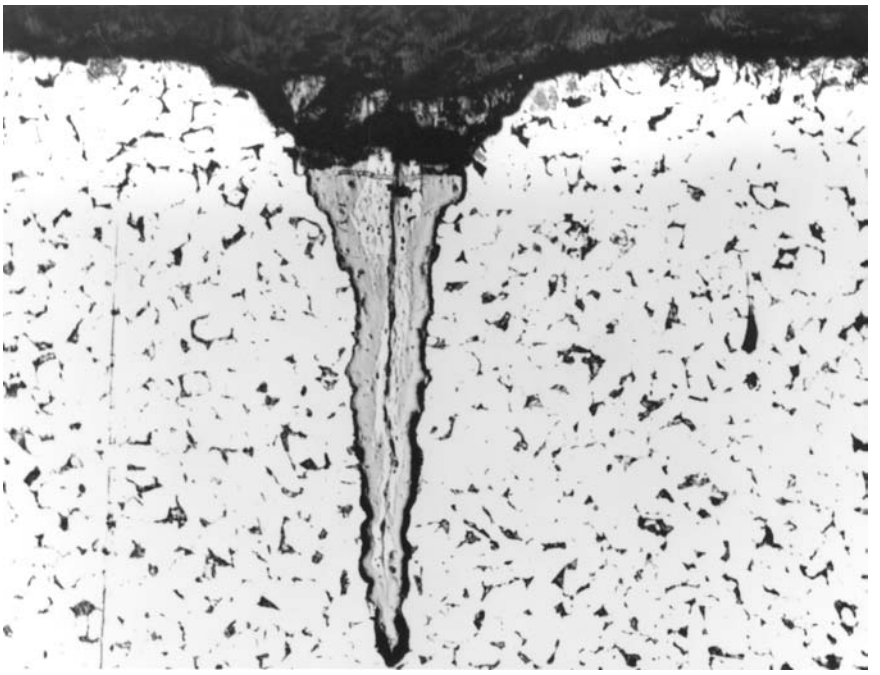
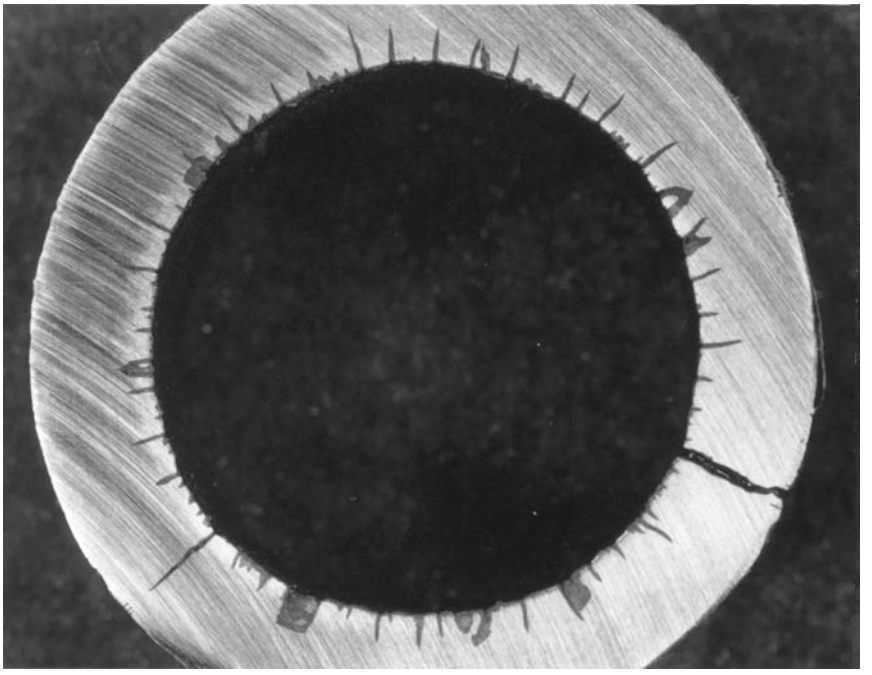


Fig. 62 Corrosion-fatigue cracks in carbon steel. A nital-etched section through corrosion-fatigue cracks that originated at hemispherical corrosion pits in a carbon steel boiler tube. Corrosion products are present along the entire length of the cracks. 250×



(a)



(b)

Fig. 63 Failure of boiler tube wall due to corrosion fatigue cracking. (a) Wedge-shaped corrosion fatigue crack filled with corrosion product. As the cyclic process continues, this crack will eventually propagate through the tube wall. (b) A family of longitudinal corrosion fatigue cracks resulting from fluctuations in internal pressure. Source: Nalco Chemical Company

Shot peening is usually effective in prolonging fatigue life in air by introducing residual compressive stresses in a metal surface, thus reducing the mean tensile stress at potential crack-initiation sites. In more aggressive environments, however, shot peening may have only limited value, because general corrosion can eventually remove the surface layer and, thus, the beneficial compressive residual stresses.

Nitriding, which also introduces compressive residual surface stresses, can improve the corrosion-fatigue resistance of steels, particularly when a relatively short life is required. For applications requiring extended life, other measures are more effective.

Material strength is generally increased by alloying, heat treatment, cold working, or selection of a material from a different alloy system. Because corrosion may reduce the fatigue strength of a material to only a small fraction of its strength in air, alloying additions or heat treatments that only increase strength, without altering the corrosion resistance of the material, may be of marginal value. Conversely, alloying that improves corrosion resistance can be effective in combating corrosion fatigue. For instance, chromium-containing steels are generally more corrosion-fatigue resistant than carbon steels.

Galvanic protection by sacrificial anodes or applied cathodic currents has been successful in reducing the influence of corrosion on fatigue of metals and alloys exposed to aqueous environments, except in such alloys as high-strength steels that are subject to hydrogen-induced delayed cracking. In similar instances, anodic polarization has been used for protection of stainless steels. With passive alloys or alloys that can be polarized to produce passive behavior, crevices must be avoided because corrosion within crevices may actually proceed more rapidly due to the anode-cathode relationship. For example, in a part made of low-carbon steel, an area under an O-ring can fail by corrosion fatigue in a caustic solution with a pH of 12 at a location where only low cyclic stresses exist. Where pitting corrosion has occurred, corrosion pits may act as stress raisers and thus accelerate fatigue failure.

Inhibitors are sometimes added to the environment or included in organic coatings to eliminate corrosion fatigue. The effect of inhibitors is believed to depend solely on their ability to reduce corrosion rates to acceptable values.

Corrosion fatigue cannot occur if there is no contact between the surface of a susceptible material and a corrosive environment; however, ordinary fatigue can occur. In most instances, the environment cannot be prevented from contacting the component; therefore, coatings are necessary. Continuity of the coating is important. Organic coatings, such as paint or plastic, are only physical barriers (unless they contain inhibitors) and therefore must be absolutely continuous to be effective. The density and the thickness of coatings are also significant factors in the prevention of corrosion fatigue. Noble-metal coatings can be effec-

tive, but only if they remain unbroken and are of sufficient density and thickness. The relatively low corrosion-fatigue strength of carbon steel is reduced still further when local breaks in a coating such as nickel occur. Presumably, noble-metal coatings that contain residual compressive stresses are more effective than coatings that contain residual tensile stresses.

Hydrogen Damage

The term hydrogen damage has been used to designate a number of processes in metals by which the load-carrying capacity of the metal is reduced due to the presence of hydrogen, often if combination with residual or applied tensile stresses. Although it occurs most frequently in carbon and low-alloy steels, many metals and alloys are susceptible to hydrogen damage. Hydrogen damage in one form or another can severely restrict the use of certain materials.

Because hydrogen is one of the most abundant elements and is readily available during the production, processing, and service of metals, hydrogen damage can develop in a wide variety of environments and circumstances. The interaction between hydrogen and metals can result in the formation of solid solutions of hydrogen in metals, molecular hydrogen, gaseous products that are formed by reactions between hydrogen and elements constituting the alloy, and hydrides. Depending on the type of hydrogen/metal interaction, hydrogen damage of metal manifests itself in one of several ways.

Specific types of hydrogen damage, some of which occur only in specific alloys under specific conditions are the following:

- Hydrogen embrittlement
- Hydrogen-induced blistering
- Cracking from precipitation of internal hydrogen
- Hydrogen attack
- Hydride formation

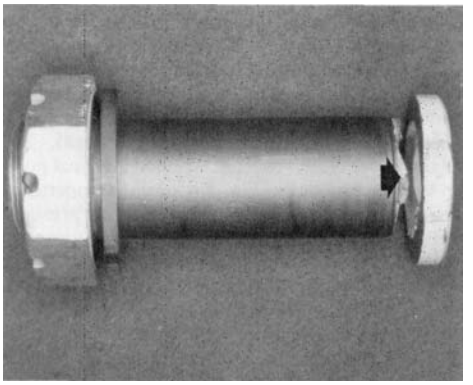
The first three types are usually observed at ambient temperatures and are closely related to one another. Hydrogen attack is an elevated-temperature phenomenon that affects carbon and alloy steels. Hydride formation produces embrittlement and cracking in transition metals such as titanium, tantalum, and zirconium.

Hydrogen Embrittlement

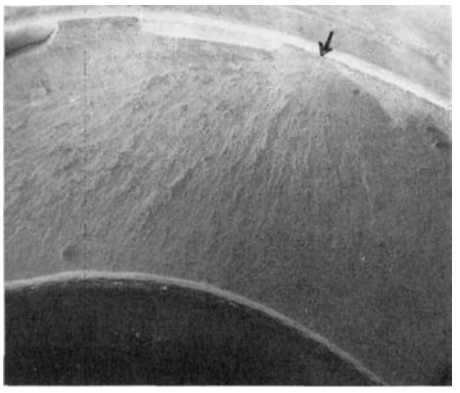
General Description. When high-strength steel containing hydrogen is stressed in tension, even if the applied stress is less than the yield

strength, it may fail prematurely in a brittle manner. This type of hydrogen damage occurs most often in high-strength steels, primarily quenched-and-tempered steels and precipitation-hardened steels. The presence of hydrogen in steel reduces the tensile ductility and causes premature failure under static load that depends on the stress and time. This phenomenon is known as hydrogen embrittlement.

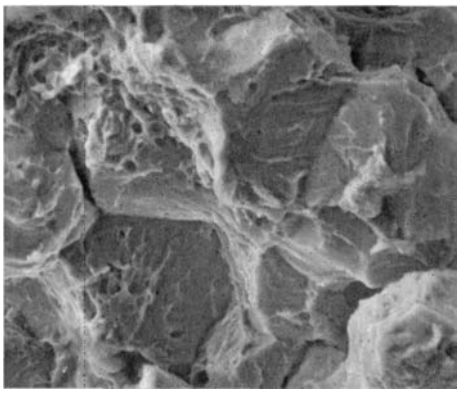
Steel can be embrittled by a very small amount of hydrogen, often a few parts per million, and hydrogen may come from various sources (e.g., acid pickling, electroplating, and aqueous corrosion), all of which are electrochemical processes involving the discharge of hydrogen ions. Unlike SCC, cracks caused by hydrogen embrittlement usually do not branch. Failure by the hydrogen embrittlement mechanism is accompanied by very little plastic deformation, and the fracture mode is often brittle intergranular fracture (Fig. 64).



(a)



(b)



(c)

Fig. 64 Hydrogen embrittlement failure of a 300 M steel space shuttle orbiter nose landing gear steering collar pin. The pin was heat treated to a 1895-MPa (275 ksi) strength level. The part was plated with chromium and titanium-cadmium. (a) Pin showing location of failure (actual size). (b) Failure origin (arrow). 9×. (c) Brittle intergranular fracture face characteristic of hydrogen embrittlement. Parts did not receive a hydrogen embrittlement relief bake due to processing error. 1380×

Cracking from Hydrogen Charging in an Aqueous Environment. When metal corrodes in a low-pH solution, the cathodic partial reaction is reduction of the hydrogen ion. Although most of the reduced hydrogen reacts to form H_2 and leaves the metal surface as gaseous hydrogen, a part of the reduced hydrogen enters into the metal as atomic hydrogen. The presence of certain chemical substances that prevent the recombination of hydrogen to form molecular hydrogen enhances the absorption of nascent (atomic) hydrogen into the metal. These substances are called cathodic poisons, and they include phosphorus, arsenic, antimony, sulfur, selenium, tellurium, and cyanide ion. Among the cathodic poisons, sulfide is the most common. Environments containing hydrogen sulfide can cause severe embrittlement of steels and some other high-strength alloys. On the other hand, corrosion inhibitors lower the corrosion rate and thus the amount of hydrogen charged into the metal.

Atmospheric and Aqueous Corrosion. Most high-strength steels are susceptible to hydrogen embrittlement when stressed and exposed to fresh or seawater and even during atmospheric exposure. The susceptibility of steels to hydrogen embrittlement generally increases with increasing tensile strength.

Steels having a tensile strength greater than about 1034 MPa (150 ksi) are much more susceptible to embrittlement. Above a tensile-strength level of 1241 MPa (180 ksi), most high-strength low-alloy steels, such as AISI 4130 and 4340, and precipitation-hardening stainless steels are susceptible to hydrogen-embrittlement cracking in marine atmospheres when the residual or applied tensile stresses are sufficiently high, and the cracking usually occurs in a form of delayed failure. Steels with tensile strengths less than 690 MPa (100 ksi) appear tpo be resistant to hydrogen-embrittlement cracking, and the structures made with such steels have been used in service without serious problems in various environments that do not contain hydrogen sulfide.

Environments Containing Hydrogen Sulfide. High-strength steel pipes used in drilling and completion of oil and gas wells may exhibit delayed failure in environments containing hydrogen sulfide. This type of failure is referred to as *sulfide stress cracking*. The basic cause of sulfide stress cracking is embrittlement resulting from hydrogen absorbed into steel during corrosion in sour environments. The presence of hydrogen sulfide in the environment promotes hydrogen absorption into steel, thereby making the environment more severe and thus more likely to cause hydrogen embrittlement. Although hydrogen sulfide gas, like gaseous hydrogen, can cause embrittlement, water ordinarily must be present for sulfide stress cracking to occur.

The susceptibility to sulfide stress cracking increases with increasing hydrogen sulfide concentration or partial pressure and decreases with increasing pH. The ability of the environment to cause sulfide stress cracking decreases markedly above pH 8 and below 101 Pa (0.001 atm)

partial pressure of hydrogen sulfide. The cracking tendency is most pronounced at ambient temperature and decreases with increasing temperature. For a given strength level (commonly measured nondestructively by hardness), tempered martensitic steels have better sulfide stress-cracking resistance than normalized-and-tempered steels, which in turn are more resistant than normalized steels. Untempered martensite demonstrates poor resistance to sulfide stress cracking. It is generally agreed that a uniform microstructure of fully tempered martensite is desirable for sulfide stress-cracking resistance. In most cases, carbon and low-alloy steels are used at hardnesses of 22 HRC or below to prevent sulfide stress cracking.

The effect of alloying elements on the sulfide stress-cracking resistance of carbon and low-alloy steels is controversial, except for one element. Nickel is detrimental to sulfide stress-cracking resistance. Steels containing more than 1% Ni are not recommended for service in sour environments.

Pickling and Electroplating. Pickling alone is not a serious problem (unless internal voids or other imperfections lead to local formation of molecular hydrogen) because the metal is not being stressed, and much of the absorbed hydrogen diffuses out of the metal. Heating at 150 to 200 °C (300 to 390 °F) for 3 h hastens the removal of hydrogen. Also, the addition of suitable inhibitors to the pickling solution eliminates or minimizes attack on the metal and the consequent generation of nascent hydrogen. Salt baths operated at about 210 °C (410 °F) can be used for descaling titanium alloys, superalloys, and refractory metals to avoid the possibility of hydrogen charging associated with pickling.

Plating solutions and plating conditions selected to produce a high-cathode efficiency minimize the amount of hydrogen generated on the metal. Because the metallic coatings plated on metal often act as barriers to effusion of hydrogen, elevated-temperature baking after plating is generally required for removal of hydrogen. Baking at 190 °C (375 °F) usually suffices, unless the coating is cadmium, through which hydrogen diffuses less readily than through other electrodeposited metals. Raising the baking temperature to accelerate effusion is not possible without reducing the protective qualities of the cadmium plate. Thus, baking time must be lengthened, particularly for steels with tensile strengths exceeding 1380 MPa (200 ksi). Baking times up to 24 h are necessary for such steels.

Cracking from Gaseous Hydrogen. Steel vessels and other equipment that contains hydrogen gas at high pressures at ambient temperature are susceptible to failure by hydrogen embrittlement. Many high-strength steels are severely embrittled in tension tests conducted in high-pressure hydrogen gas, and the cracking tendency increases with increasing pressure of hydrogen. The cracking susceptibility of steels generally increases with increasing strength.

Generally, high-strength steels and high-strength nickel alloys display severe degradation of tensile properties in hydrogen gas. Austenitic stainless steels, aluminum alloys, and alloy A-286 show very little embrittlement in this environment. Most other engineering metals and alloys are affected to a lesser degree.

Hydrogen-Induced Blistering

General Description. Hydrogen-induced blistering, also referred to as hydrogen-induced cracking (HIC) or blister cracking, is primarily found in lower-strength (unhardened) steels, typically with tensile strengths less than approximately 550 MPa (80 ksi). It is observed in steels that have been exposed to hydrogen-charging conditions, for example, pickling or corrosion in environments containing hydrogen sulfide. During such exposures, atomic hydrogen generated at the metal surface is absorbed by the metal. When hydrogen is absorbed into the metal and diffuses inward, it can precipitate as molecular hydrogen at internal voids, laminations, or inclusion/matrix interfaces, and it can build up pressure great enough to produce internal cracks. If these cracks are just below the surface, the hydrogen-gas pressure in the cracks can lift up and bulge out the exterior layer of the metal so that it resembles a blister (Fig. 65). The equilibrium pressure of the molecular hydrogen in the void, which is in contact with the atomic hydrogen in the surrounding metal, its great enough to rupture any metal or alloy.

Hydrogen-Induced Cracking of Line-Pipe Steel. Line pipe transmitting wet, sour gas can develop hydrogen-induced cracking in the pipe wall. When line-pipe steel is exposed to sour brine in the absence of applied stress, a number of cracks parallel to the longitudinal axis of

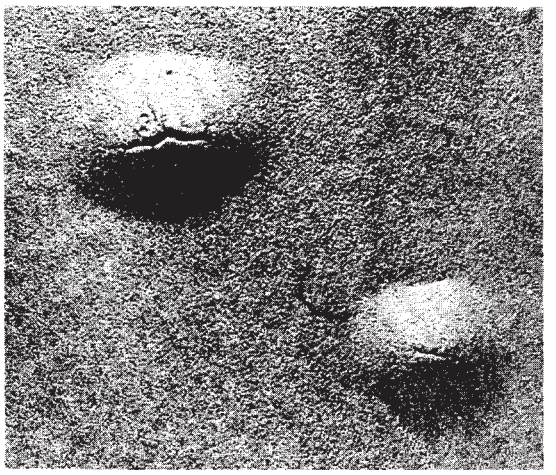


Fig. 65 Hydrogen-induced blistering in a 9.5 mm (⅜ in.) thick carbon steel (ASTM A 285 Grade C) plate that had been in service 1 year in a refinery vessel. 1½×

the pipe may develop through the wall, and the tip of one crack may link up with another in stepwise fashion. This type of cracking is called stepwise cracking (Fig. 66), and it can significantly reduce the effective wall thickness of the pipe. It is believed that a single, straight longitudinal crack is less harmful than stepwise cracks. The presence of hydrogen sulfide in the corrodent greatly promotes the absorption of hydrogen into steel.

Factors That Affect HIC. Aside from reducing the amount of hydrogen being generated by reducing the corrosion reaction, another way of controlling HIC is through material processing. Shape control of sulfide inclusions is perhaps the best way to minimize the tendency toward HIC in line-pipe steels. Elongated manganese sulfide inclusions promote crack initiation and propagation due to the high stresses at the tips of the inclusions. However, the addition of calcium or rare earths to the steel makes the sulfides spherical, and because of their hardness, they remain spherical after processing. In addition, reduction of the sulfur content is also beneficial in reducing the susceptibility of steels to HIC. Other alloying additions that reduce hydrogen permeation, such as copper up to about 0.25%, are also beneficial.

Cracking from Precipitation of Internal Hydrogen

General Description. Shatter cracks, flakes, and fish eyes are features common to hydrogen damage in forgings, weldments, and castings. They are attributed to hydrogen pickup during melting operations when the melt has a higher solubility for hydrogen than the solid alloy. During cooling from the melt, hydrogen diffuses to and precipitates in voids and discontinuities, producing the features that result from the decreased solubility of hydrogen in the solid metal. In many aspects, these features are comparable to blistering, and this could be considered a special case of that class.

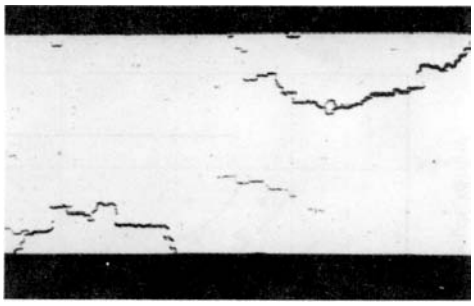


Fig. 66 Stepwise cracking of a low-strength pipeline steel exposed to hydrogen sulfide (H_2S). 6×

Hydrogen Attack

General Description. Steel exposed to high-temperature, high-pressure hydrogen appears to be unaffected for days or months and then suddenly loses its strength and ductility. This type of damage is called hydrogen attack. It is important to note that hydrogen attack is different from hydrogen embrittlement. Hydrogen attack is irreversible damage, and it occurs at elevated temperatures, whereas hydrogen embrittlement is often reversible and occurs at temperatures below 200 °C (390 °F).

In hydrogen attack of steel, absorbed hydrogen reacts internally with carbides to produce methane bubbles along grain boundaries. These bubbles subsequently grow and merge to form fissures. Failure by hydrogen attack is characterized by decarburization and fissuring at grain boundaries (Fig. 67) or by bubbles in the metal matrix. This type of hydrogen damage is most commonly experienced in steels that are subjected to elevated temperatures in petrochemicals-plant equipment that often handles hydrogen and hydrogen-hydrocarbon streams at pressures as high as 21 MPa (3 ksi) and temperatures up to 540 °C (1000 °F). The severity of hydrogen attack depends on temperature, hydrogen partial pressure, stress level, exposure time, and steel composition.

Prevention of Hydrogen Attack. The only practical way to prevent hydrogen attack is to use only steels that, based on plant experience, have been found to be resistant to this type of deterioration. The following general rules are applicable to hydrogen attack:

- Carbide-forming alloying elements, such as chromium and molybdenum, increase the resistance of steel to hydrogen attack.

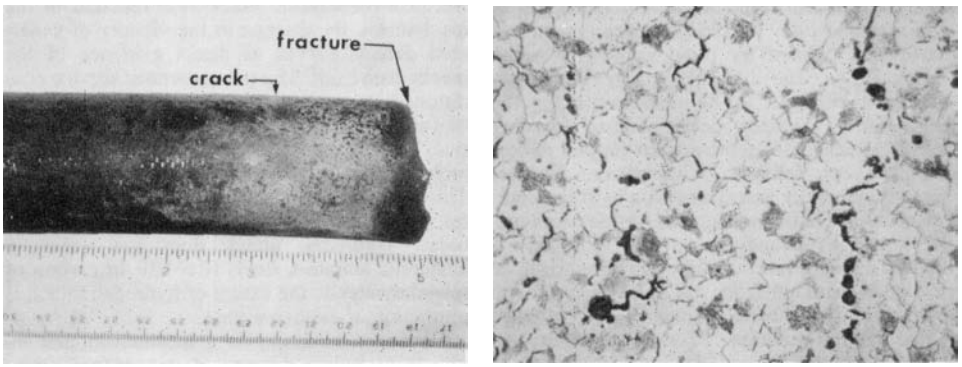


Fig. 67 Section of ASTM A 106 carbon steel pipe with wall severly damaged by hydrogen attack. The pipe failed after 15 months of service in hydrogen-rich gas at 34.5 MPa (5000 psig) and 320 °C (610 °F). (a) Overall view of failed pipe section. (b) Microstructure of hydrogen-attacked pipe near the midwall. Hydrogen attack produced grain-boundary fissures that are radially aligned.

- Increased carbon content decreases the resistance of steel to hydrogen attack.
- Heat-affected zones are more susceptible to hydrogen attack than the base or weld metal.

For most refinery and petrochemical plant applications, low-alloy chromium- and molybdenum-containing steels are used to prevent hydrogen attack. However, questions have recently been raised regarding the effect of long-term hydrogen exposure on C-0.5Mo steel. As a result, low-alloy steels are preferred over C-0.5Mo steel for new construction.

The conditions under which different steels can be used in high-temperature hydrogen service are listed in the American Petroleum Institute (API) document 941 "Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants." The principal data are presented in the form of Nelson curves, as shown in Fig. 68. The curves are periodically revised by the API Subcommittee on Materials Engineering and Inspection, and the latest edition of API 941 should be consulted to ensure that the proper steel is selected for the operating conditions encountered.

Hydride Formation

General Description. A number of transition, rare-earth alkaline-earth metals, and the alloys of these metals are subject to embrittlement and cracking due to hydride formation. Among these metals, the commercially important ones are titanium, tantalum, zirconium, uranium,

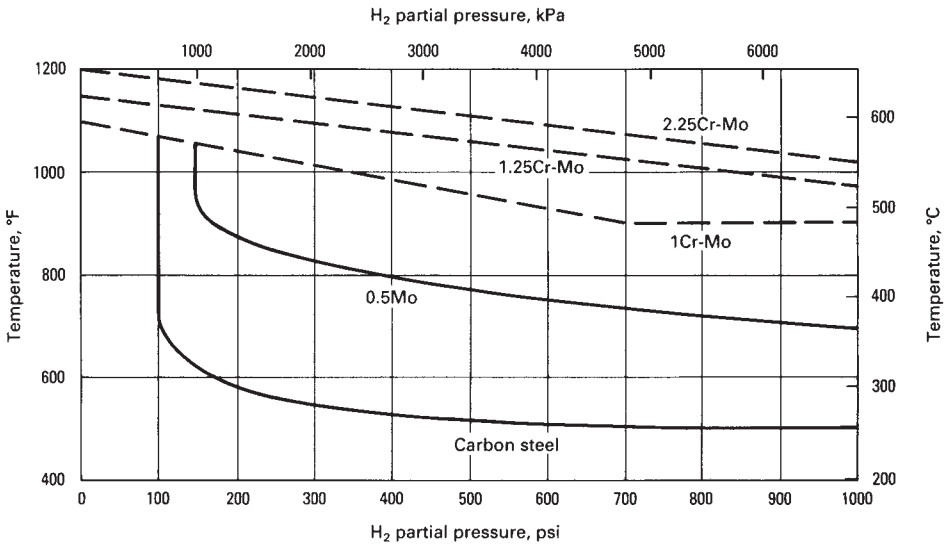


Fig. 68 Operating limits for various steels in high-temperature, high-pressure hydrogen service (Nelson curves) to avoid decarburization and fissuring



Fig. 69 Micrograph of severely hydrided unalloyed titanium. Approximately 200×

thorium, and their alloys. The presence of hydrides in these metals can cause significant increases in strength and large losses in ductility and toughness. As in other types of alloys, excess hydrogen is readily picked up during melting or welding, and hydride formation takes place during subsequent cooling. The use of vacuum melting and the modification of compositions can reduce susceptibility to hydride formation. Hydrogen can often be removed by annealing in vacuum. Welding generally requires the use of inert-gas shielding to minimize hydrogen pickup.

The hydride particles often have the form of platelets and show preferred orientation within the parent lattice (Fig. 69), depending primarily on the metal or alloy composition. The large volume change associated with hydride formation leads to a strong interaction between the hydride-formation process and externally applied stresses. Applied stresses can cause preferential alignment of hydrides or realignment. In most cases, the hydride phase has a much lower ductility than the matrix.

Prevention of Hydrogen Damage

The primary factors controlling hydrogen damage are material, stress, and environment. Hydrogen damage can often be prevented by using more resistant material, changing the manufacturing processes, modifying the design to lower stresses, or changing the environment. As described earlier, inhibitors and post-processing bake-out treatments can also be used.

Selection of materials resistant to hydrogen damage is often possible. In many applications, a lower-strength material will function just as

well mechanically as will a higher-strength material, and the use of such a material may eliminate a hydrogen-embrittlement problem.

Coatings and linings can be applied to the surface of the metal to shield it from the environment. Such coating materials should be stable in the environment.

Tempering. In high-strength steels, tempering at a higher temperature for a longer time lowers the strength and improves the toughness, and such a heat treatment would also help to reduce hydrogen content. Although such tempering treatments can improve resistance to hydrogen embrittlement, care should be exercised to avoid temper embrittlement. Temper-embrittled materials are more prone to cracking. Baking of electroplated parts reduces the possibility of hydrogen embrittlement.

Surface preparation techniques that impart residual compressive stresses to the surface are used to improve resistance to cracking when susceptible metals are subjected to the combination of hydrogen embrittlement and residual or applied tensile stress. These techniques include shot peening, grit blasting, and face milling.

Low-hydrogen welding rods should be specified for welding if hydrogen embrittlement is a potential problem. Also, it is important to maintain dry conditions in storing the rods before use and during welding because water and water vapor are major sources of hydrogen. Preheating and postweld heat treatment are also important when welding high-strength steels to prevent high residual stresses or microcracks.

Lowering the stress below the threshold value for hydrogen embrittlement is often possible. This can be achieved by increasing the cross section of parts, avoiding stress raisers in design, reducing residual stresses through heat treatment, or reducing the load. Corrosion inhibitors reduce corrosion and therefore the amount of hydrogen absorbed into the metal, and they often eliminate the cracking problem. Proper use of inhibitors in the service environment can prevent hydrogen-embrittlement failure.

Liquid-Metal Embrittlement

Liquid-metal embrittlement (LME), also known as liquid-metal cracking, is the catastrophic brittle failure of a normally ductile metal when coated with a thin film of a liquid metal and subsequently stressed in tension. Although LME is not a corrosion process or even a metal dissolution process (like that encountered when a solid metal is immersed at length in a molten metal), it is included here because it is a problem frequently encountered by materials engineers. During

LME, metals and alloys are penetrated, usually along grain boundaries, by such metals as mercury, which are liquid at room temperature, or by metals that have relatively low melting points. Examples of low-melting point metals contributing to LME are bismuth, tin, lead, cadmium, zinc, aluminum, and copper. Stress, temperature, and time are the factors that facilitate and accelerate LME. Virtually all metal and alloy systems are subject to LME by one or more of these metals at or above their melting points. More detailed information on LME can be found in *Failure Analysis and Prevention*, Volume 11 of the *ASM Handbook* (refer to p 225 to 244).

Zinc is a prime offender because of widespread use throughout industry in the form of corrosion-resistant coatings applied to carbon steels by hot-dip galvanizing, electroplating, tumbling, and spray painting. Plain carbon steels are embrittled by zinc at temperatures above 370 °C (700 °F) for long periods of time, especially when the steel is heavily stressed or cold worked.

Austenitic stainless steels and nickel-based alloys will also crack in the presence of molten zinc. These alloys usually crack instantly when welded to galvanized steel, a fairly common occurrence in the chemical-processing industry. In addition, austenitic alloy failures have occurred under the following conditions:

- In high-temperature bolting fastened with galvanized steel nuts
- During welding or heat treating of components contaminated by grinding with zinc-loaded grinding wheels, contact with zinc-coated structurals or slings, or exposure to zinc paint overspray
- During process industry plant fires involving piping and vessels (thin-wall expansion joint bellows are especially susceptible) sprayed with molten zinc from coated steel structures

Thus, it is imperative that all traces of zinc be removed from coated steel members before welding to austenitic alloys and before intimate contact with these alloys at temperatures above 370 °C (700 °F). Also, austenitic stainless steels and nickel-based alloys should be handled with non-coated steel hoist chains, cables, and structurals. They should be dressed and cleaned with new grinding wheels and stainless steel brushes, and they should be marked with materials (paints, crayons, and so on) free from zinc and other low-melting metals.

Cadmium is probably second to zinc in importance as an agent of liquid-metal embrittlement because of its applications as a corrosion-resistant coating to a variety of hardware, particularly fasteners. Failures by cadmium LME of bolting operating at temperatures above 300 °C (570 °F) and fabricated from high-strength alloy steels, such as AISI 4140 and 4340, and austenitic stainless steels are fairly common. In fact, some high-strength steels and high-

strength titanium alloys are embrittled by cadmium at temperatures below its melting point by mechanisms not yet understood. The solution to LME by cadmium is similar to that of zinc, that is, avoidance of contact with, and contamination of, susceptible metal and alloy systems at temperatures above the 321 °C (610 °F) melting point of cadmium (and at all temperatures at which high-strength steels and titanium alloys are involved).

Metal systems that are embrittled by contact with mercury include copper and its alloys, aluminum and its alloys, Nickel 200 (at elevated temperatures) and Monel Alloy 400, and titanium and zirconium and their alloys. Cracking is intergranular except in zirconium alloys; in these alloys, cracking is transgranular. Mercury LME of aluminum and copper alloys was more common years ago in the petrochemical industry when mercury-filled manometers and thermometers were extensively used. Failures or upsets would release mercury into process or service (steam, cooling water, and so on) streams, causing widespread cracking of piping, heat exchanger tube bundles, and other equipment. Under these conditions, even pure aluminum and pure copper are susceptible. With regard to the titanium system, the commercially pure grades used in the chemical-processing industry are less sensitive than the alloys. In addition, LME in aqueous solutions of mercurous salts, such as mercurous nitrate, is possible because the mercurous ion can be reduced to its elemental form at local cathodic sites.

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CHAPTER 5

Types of Corrosive Environments

CORROSIVE ENVIRONMENTS can be broadly classified as atmospheric, underground/soil, water, acidic, alkaline, and combinations of these. Complicating matters is the fact that there are important variables, for example, pH, temperature, and the presence of biological organisms, that can significantly alter the response of the material in a given environment. Take, for example, the complex interaction of various elements that make up the chemistry of the environments in which automobiles are driven. The combination of natural environments (rain, snow, humidity, marine environments, etc.) with deleterious man-made environmental contributions (road salts, atmospheric pollutants and emissions, and acid rain) provide a uniquely aggressive corrosive environment for automobiles.

The goal of this chapter is to point out the connection between the characteristics of the corrosive environment, the corrosion characteristics of various metals and materials systems, and the subsequent corrosion response. It should be noted that the corrosion literature contains a wealth of laboratory and service data on material/environmental combinations. In addition, ASM International and other associations, such as NACE International, publish useful information on corrosion in environments relevant to buildings, highways, and other structures, and components and equipment used in the chemicals processing, pulp and paper, gas and oil, electric power, automotives, aerospace, and telecommunications industries.

Characteristics of Corrosive Environments

Several important characteristics/variables of environments control corrosion behavior:

- Relative degree of acidity or alkalinity as measured by pH
- Relative degree of oxidizing or reducing conditions measured by the electrochemical potential, *E*
- Temperature of the environment
- Presence of detrimental/beneficial species
- Velocity/fluid flow rate
- Concentration of corrodent in the environment

Each of these characteristics is discussed below. Another key consideration, the effects of biological organisms like bacteria on corrosion, is addressed in a separate section.

Acidity/Alkalinity. A wide variety of acid or alkaline conditions are encountered in common environments. As shown in Fig. 1, environments can range from strong acids, represented by low pHs (e.g., pH≤1); to neutral environments with pH 7; to strong alkalis, represented by sodium hydroxide and calcium hydroxide at pH 14.

The measured pH of several common acids and alkalis are as follows:

Solutions	pH
Hydrochloric acid (1*N*)	0.1
Sulfuric acid (1*N*)	0.3
Boric acid (0.1*N*)	5.2
Sodium bicarbonate (0.1*N*)	11.6
Ammonium hydroxide (1*N*)	11.6
Sodium hydroxide (1*N*)	14

Hydrochloric acid and sulfuric acid are strong acids and have low pH values. Boric acid and sodium bicarbonate are representative of a weak acid and a weak alkaline solution, respectively. Sodium hydroxide is a strongly alkaline solution and results in high pH. The acidity or alkalinity of an environment in combination with its oxidizing/reducing characteristics is critical to the resulting corrosion behavior of various materials.

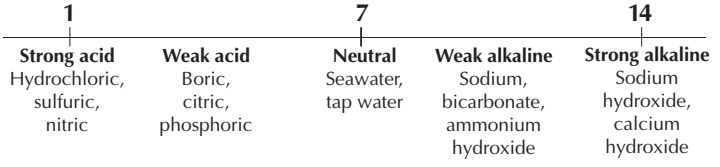


Fig. 1 The pH of several common environments

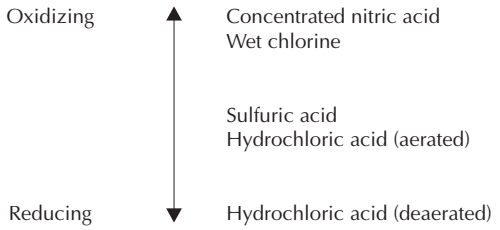


Fig. 2 Environments with a wide range of oxidizing/reducing behavior

Oxidizing/Reducing Characteristics. Environments can be characterized by their oxidizing power. An environment that is strongly oxidizing has a great tendency to oxidize materials in contact with it, while an environment that is strongly reducing has a much lesser tendency to oxidize materials.

Figure 2 illustrates the oxidizing/reducing power of several common environments. Concentrated nitric acid and wet chlorine environments are strongly oxidizing and promote the oxidation of all but the most noble metals. The oxidizing power of sulfuric acid is a function of concentration and ranges from moderately reducing for dilute acids to more strongly oxidizing for concentrated acids. Deaerated hydrochloric acid is a strongly reducing environment, and the addition of oxidizing species such as dissolved oxygen or ferric (Fe^{3+}) ions will significantly increase oxidizing power.

Figure 3 shows oxidizing power as a function of potential, *E*, and the degree of acidity or alkalinity as measured by pH. Typical ranges of oxidizing power and acidity for several environments are indicated. As stated earlier, nitric acid is a strongly oxidizing acid characterized by low pH values and high potential values. Hydrochloric acid is a reducing

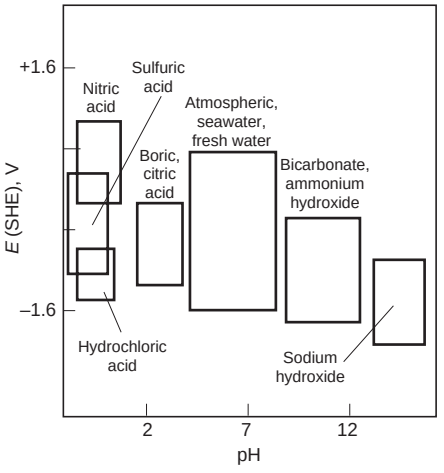


Fig. 3 Approximate locations of several common environments on a potential-pH diagram. SHE, standard hydrogen electrode

acid characterized by low pHs and lower potentials. Boric acid is a weaker acid and has a pH representative of mildly acidic solutions.

Atmospheric, seawater, and freshwater environments are typically nearly neutral and range from moderately reducing to moderately oxidizing. Sodium hydroxide is a strongly alkaline environment represented by high pH, and bicarbonate and ammonium hydroxide solutions are weak bases with somewhat lower pH values.

Metals in contact with these environments may be immune; that is, no attack is exhibited. They also may be passive, where a protective corrosion product layer provides corrosion resistance to the metal, or active, in which case corrosion rates are substantial. The relative locations of immune, passive, and active regions depend very much on the specific metal. Gold is immune over almost the entire *E*-pH diagram, as it is attacked by only strongly oxidizing environments. Magnesium is a very reactive metal and shows an active region over the bulk of the *E*-pH diagram. Titanium exhibits a strong tendency to passivate, and large portions of the diagram are covered by the passive region. A number of *E*-pH diagrams are presented and discussed in Chapter 3.

Temperature Effects. Corrosion is an activation-controlled chemical reaction, the rate of which is greatly affected by temperature. Typically, corrosion rate increases significantly as temperature increases. A rule of thumb is that the corrosion rate will double for each 10 °C (18 °F) increase in temperature. The increased corrosion rate results from increased activation energy for chemical and electrochemical reactions, increased diffusion rates in the electrolyte, and increased transport through the electrolyte or environment and across films that may be formed on the metal surface. There are observed reversals in the trends regarding temperature and corrosion rate. These are typically related to the stability of passive films that may form or break down over a fairly narrow temperature range and also can be related to the solubility of corrosive or beneficial gases and species in the environment. An important consideration with respect to temperature is the temperature of the metal surface in contact with the environment. Often the surface temperature of a heating element or heat-exchanger component can be significantly greater than the bulk environment temperature. This can result in significantly increased corrosion rates of these surfaces with respect to the corrosion rate of unheated metal surfaces in contact with the same electrolyte.

Detrimental/Beneficial Species. The presence of individual species in an environment, even at trace levels, can have a major impact on corrosion behavior. Chlorides particularly detrimental to materials that depend on a passive film for their corrosion resistance (e.g., stainless steels). In the presence of chloride ion, the passive film can break down locally and result in pitting, concentration-cell corrosion, and in some cases stress-corrosion cracking (SCC). The presence of ammonia in an

environment can greatly increase the corrosion of some alloys. The ammonia ion forms soluble complexes with copper in the metal and results in the breakdown of passive surface films on copper alloys and more rapid corrosion.

An environment can also contain beneficial species in the form of corrosion inhibitors that are intentionally added to the environment or in the form of naturally occurring species that help to control corrosion. Beneficial species can promote the development of protective films on the metal surface, or they can interact with detrimental species to reduce the corrosion tendency for the specific metal/environment combination. More detailed information regarding the use of inhibitors for corrosion control can be found in Chapter 9.

Velocity/Fluid Flow Rate. The influence of fluid flow rate, or fluid velocity, is a complex variable, and its influence on corrosion behavior is dependent on the alloy, fluid constituents, fluid physical properties, geometry, and corrosion mechanism. The presence of fluid flow can sometimes be beneficial in preventing or decreasing localized attack. For example, type 316 stainless steel has been shown to pit in quiescent seawater but not in moving seawater. When the seawater is moving, the mass transfer rate of oxygen is high enough to maintain a completely passive surface, but in the absence of flow, the mass transfer of oxygen is too slow and the surface cannot remain passive.

Under other circumstances, fluid flow can cause a type of erosion of a surface through the mechanical force of the fluid itself. This common process is called impingement, and an example of such erosion is where fluid is forced to turn its flow direction at pipe bends. When solids are present in the liquid, they can cause erosion-corrosion. Both impingement and erosion-corrosion are discussed in Chapter 4.

Effect of Concentration. The effect on corrosion rate of increasing or decreasing the concentration of corrodent in the environment to which a metal part is exposed does not follow a uniform pattern because of (a) ionization effects in aqueous solutions and the effects of even trace amounts of water in nonaqueous environments and (b) changes that occur in the characteristics of any film of corrosion products that may be present on the surface of the metal. Typical patterns of the types of corrodent-concentration effects on corrosion rate that may be encountered are illustrated in Fig. 4, which plots the variation of corrosion rate of iron as a function of the concentration of three common inorganic acids in aqueous solutions at room temperature.

The rate of corrosion of a given metal usually increases as the concentration of the corrodent increases, as shown in Fig. 4(a) for the corrosion of iron in hydrochloric acid. However, corrosion rate does not always increase with concentration, as shown in Fig. 4(b) and (c) for iron in sulfuric acid and in nitric acid respectively.

Because corrosion is electrochemical and involves anodic and cathodic reactions, process variables influence corrosion rate if they influence one or both reactions. For example, the main cathodic reaction for iron corroding in dilute inorganic acids is $2H^+ + 2e^- \rightarrow H_2$. The more hydrogen ions available, the faster the rate of the cathodic reaction. In turn, this permits a high rate of anodic dissolution: ($Fe \rightarrow Fe^{2+} + 2e^-$). This is what happens throughout the concentration range in hydrochloric acid solutions.

In both nitric acid and sulfuric acid solutions, the hydrogen ion concentration increases with acid concentration. At the higher levels of acid concentration, however, it decreases again. Iron may be used to handle concentrated sulfuric acid at ambient temperatures. Care must be taken to avoid any combination with water, because this dilutes the acid and increases the rate of attack. Also, impurities in the acid or the iron can increase the rate of attack.

The corrosion rate of iron (and steel) at room temperature in nitric acid decreases with increasing concentration above approximately 35% because of the formation of a passive oxide film on the metal surface. However, this passive condition is not completely stable.

The rate of attack for concentrations of 70% or higher, although low compared to the maximum rate shown in Fig. 4, is still greater than 1.3 mm/year (50 mils/year), making iron and steel unsuitable for use in shipping and storing nitric acids at any concentration. Nitric acid in bulk is usually stored and shipped in type 304 stainless steel, aluminum alloy 3003, or commercially pure titanium (grade 2).

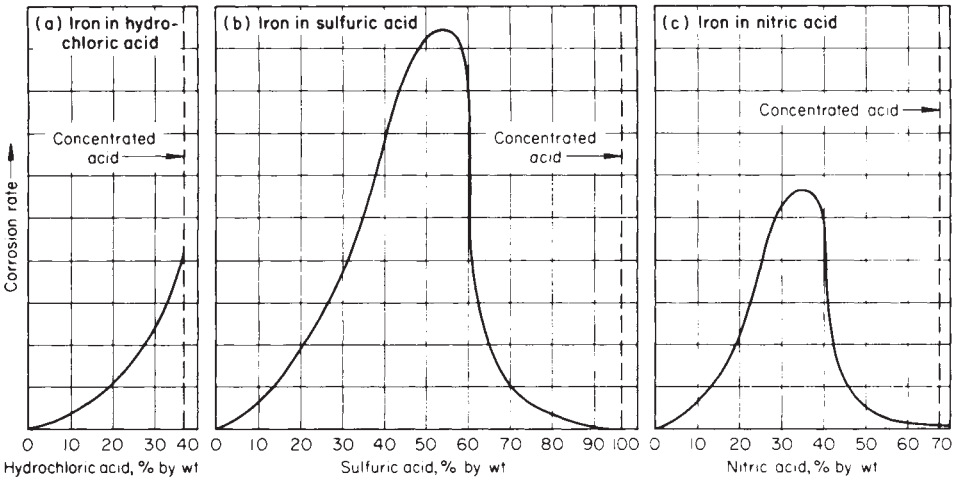


Fig. 4 Effect of acid concentration on the corrosion rate of iron completely immersed in aqueous solutions of three inorganic acids at room temperature. It should be noted that the scales for corrosion rate are not the same for all three charts. As discussed in text, the corrosion rate of iron (and steel) in nitric acid in concentrations of 70% or higher, although low compared to the maximum rate, is sufficient to make it unsafe to ship or store nitric acid in these metals.

Metals that have passivity effects, such as Monel 400 in hydrochloric acid solutions and lead in sulfuric acid solutions, corrode at an extremely low rate at low acid concentration at room temperature but lose their passivity at a certain limiting acid concentration. Above the limiting acid concentration, the corrosion rate increases rapidly with increasing acid concentration.

Biologically Influenced Corrosion

Biological organisms are present in virtually all natural aqueous environments. In seawater environments, such as tidal bays, estuaries, harbors, and coastal and open ocean seawaters, a great variety of organisms are present. Some of these are large enough to observe with the naked eye (e.g., barnacles, mussels, and clams), while others are microscopic (hence, the term microbiologically influenced corrosion, or MIC). In freshwater environments, both natural and industrial, the large organisms are missing, but there are still many microorganisms, such as bacteria and algae. MIC has been documented for metals exposed to process chemicals, foods, soils, aircraft fuels, human plasma, and sewage, in addition to seawater and freshwater.

In all these environments, organisms in the water tend to attach to and grow on the surface of structural materials, resulting in the formation of a biological film, or biofilm. The film itself can range from a

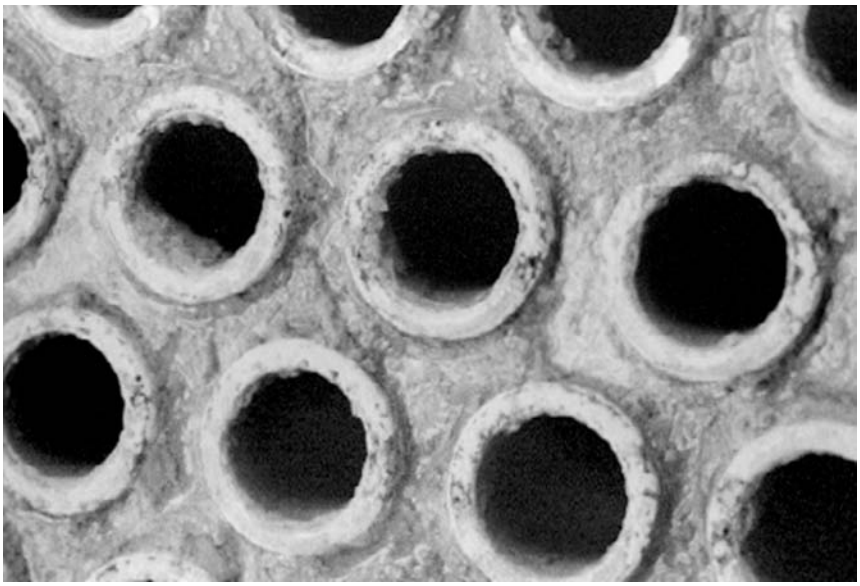


Fig. 5 A gelatinous biofouling slime layer on a heat exchanger tube sheet. The slime layer may be colored by dirt and other debris that accumulates in the gooey mass. Source: Nalco Chemical Company

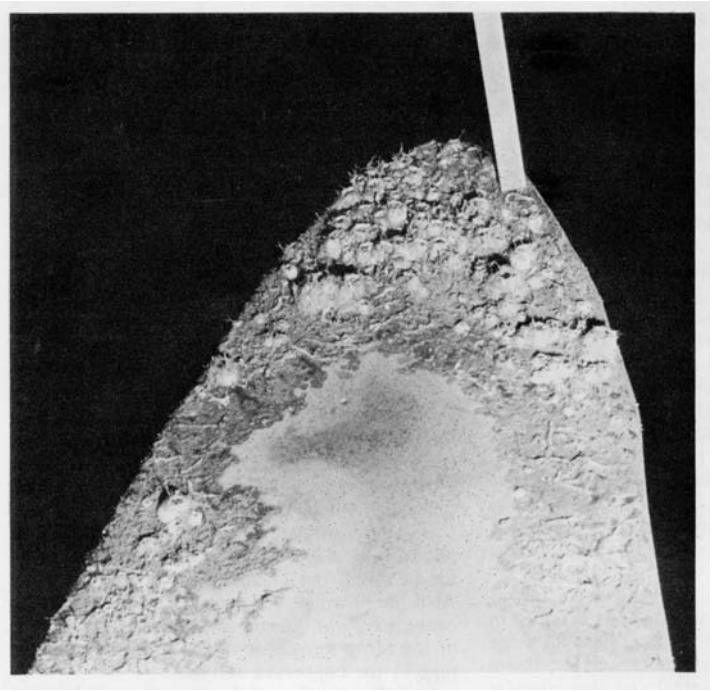


Fig. 6 Barnacles attached to the periphery of a high-strength steel rudder, which had originally been coated with an antifouling paint. During use, the paint around the edges had been removed by mechanical action, thus allowing the attachment of barnacles. Partial coverage of such macroorganisms can lead to localized corrosion. Complete coverage can sometimes provide a barrier film and limit corrosion.

microbiological slime film on freshwater heat transfer surfaces (Fig. 5) to a heavy encrustation of hard-shelled fouling organisms on structures in coastal seawater (Fig. 6).

The biofilms that form on the surface of virtually all structural metals and alloys immersed in aqueous environments have the capability to influence the corrosion of those metals and alloys. This influence derives from the ability of the organisms to change environmental variables including oxidizing power, temperature, velocity, and concentration. Thus, the value of a given parameter at the metal/water interface under the biofilm can be quite different from that in the bulk electrolyte away from the interface. The result can be the initiation of corrosion under conditions in which there would be none in the absence of the film, a change in the mode of corrosion (that is, from uniform to localized), or an increase or decrease in the corrosion rate.

Industries and Organisms Involved

The various industries that have been affected by MIC problems are listed in Table 1. Table 2 lists organisms that cause corrosion in environments

Table 1 Industries known to be affected by microbiological corrosion

Industry	Problem areas
Chemical-processing industries	Stainless steel tanks, pipelines and flanged joints, particularly in welded areas after hydrotesting with natural river or well waters
Nuclear power generation	Carbon and stainless steel piping and tanks; copper-nickel, stainless, brass and aluminum bronze cooling water pipes and tubes, especially during construction, hydrotest, and outage periods
Onshore and offshore oil and gas industries	Mothballed and waterflood systems; oil and gas handling systems, particularly in those environments soured by sulfate reducing bacteria (SRB), from produced sulfides
Underground pipeline industry	Water-saturated clay-type soils of near-neutral pH with decaying organic matter and a source of SRB
Water treatment industry	Heat exchangers and piping
Sewage handling and treatment industry	Concrete and reinforced concrete structures
Highway maintenance industry	Culvert piping
Aviation industry	Aluminum integral wing tanks and fuel storage tanks
Metal working industry	Increased wear from breakdown of machining oils and emulsions

Table 2 Microorganisms most commonly implicated in biological corrosion

Genus or species	pH range	Temperature range in °C	Oxygen requirement	Metals affected	Action
Bacteria					
Desulfovibrio (best known: *D. desulfuricans*)	4–8	10–40	Anaerobic	Iron and steel, stainless steels, aluminum, zinc, copper alloys	Utilize hydrogen in reducing SO_4^{2-} to S^{2-} and H_2S; promote formation of sulfide films
Desulfotomaculum (best known: *D. nigrificans*, also known as *Clostridium*)	6–8	10–40 (some 45–75)	Anaerobic	Iron and steel, stainless steels	Reduce SO_4^{2-} to S^{2-} and H_2S; (spore formers)
Desulfomonas	…	10–40	Anaerobic	Iron and steel	Reduce SO_4^{2-} to S^{2-} and H_2S
Thiobacillus thiooxidans	0.5–8	10–40	Aerobic	Iron and steel, copper alloys, concrete	Oxidizes sulfur and sulfides to form H_2SO_4; damages protective coatings
Thiobacillus ferrooxidans	1–7	10–40	Aerobic	Iron and steel	Oxidizes ferrous (Fe^{2+}) to ferric (Fe^{3+})
Gallionella	7–10	20–40	Aerobic	Iron and steels, stainless steels	Oxidizes ferrous (and manganous) to ferric (and manganic); promotes tubercle formation
Sphaerotilus	7–10	20–40	Aerobic	Iron and steel, stainless steels	Oxidizes ferrous (and manganous) to ferric (and manganic); promotes tubercle formation
S. natans	…	…	…	Aluminum alloys	Oxidizes ferrous (and manganous) to ferric (and manganic); promotes tubercle formation
Pseudomonas	4–9	20–40	Aerobic	Iron and steel, stainless steels	Some strains can reduce Fe^{3+} to Fe^{2+}
P. aeruginosa	4–8	20–40	Aerobic	Aluminum alloys	Some strains can reduce Fe^{3+} to Fe^{2+}
Fungi					
Cladosporium resinae	3–7	10–45 (best at 30–35)	…	Aluminum alloys	Produces organic acids in metabolizing certain fuel constituents

in which there would be none without them, accelerate corrosion, or change a relatively slow rate of general corrosion into one with rapid localized penetration of the metal.

Sulfate-reducing bacteria (SRB) are the organisms most often cited as the causative agents of MIC for several reasons. They are ubiquitous, easy to culture, and in anaerobic, sulfate-containing environments, they produce hydrogen sulfide (H_2S) that can react with iron and steel, stainless steels, copper, aluminum, and zinc. *Desulfovibrio*, *Desulfomonas*, and *Desulfotomaculum* are the three genera of SRB. Table 2 lists the characteristics of these SRB.

Sulfate-reducing bacteria frequently cause intense localized attack. As shown in Fig. 7, the resulting pits are hemispherical and often feature smooth interiors. Pits also tend to cluster together, overlapping to form irregularly dimpled surfaces.

Acid Producers. Many bacteria produce acids. Acids may be organic or inorganic depending on the specific bacterium. In either case, the acids produced lower the pH, usually accelerating attack. *Thiobacillus thiooxidans* is an aerobic organism that oxidizes various sulfur-containing compounds to form sulfuric acid (H_2SO_4). As will be described later in this chapter, these bacteria are sometimes found near the tops of tubercles. Table 2 lists the characteristics of *Thiobacillus thiooxidans*.

Iron/manganese bacteria oxidize ferrous, Fe^{2+}, iron to ferric, Fe^{3+}, iron. Ferric hydroxide, $Fe(OH)_3$, is the result. Some bacteria oxidize manganese (manganous to manganic ions) and other metals. Aerobic *Gallionella* bacteria, in particular, have been associated with the accu-



Fig. 7 Severely pitted aluminum heat exchanger tube. Pits were caused by sulfate-reducing bacteria beneath a slime layer. The edge of the slime layer is just visible as a ragged border between the light-colored aluminum and the darker, uncoated metal below. Source: Nalco Chemical Company

mulation of iron oxides in tubercles. Table 2 lists the characteristics of *Gallionella* bacteria.

Slime formers are a diverse group of aerobic bacteria. Slime layers (Fig. 5) are a mixture of bacterial secretions called extracellular polymers, other metabolic products, bacteria, gases, detritus, and water. Slime layers contribute to corrosion by forming differential oxygen cells, which lead to crevice corrosion. In addition, slime layers can be efficient scrubbers of oxygen, thus preventing oxygen from reaching the surface. This creates an ideal site for anaerobic SRB growth.

Tuberculation

As described in Chapter 4, tubercles are discreet hemispherical mounds over pits on steel surfaces. The process of biologically influenced tubercle formation is a complex one. A number of the reactions that can take place are illustrated for a ferrous alloy in Fig. 8. The volcanolike structure often starts with a deposit of slime-forming and iron-oxidizing bacteria at a point of low flow velocity. This creates an oxygen concentration cell, thus promoting dissolution of iron as Fe^{2+} under the deposit. As the Fe^{2+} ions move outward, they are oxidized to Fe^{3+}; this occurs electrochemically as they encounter higher oxygen concentrations and/or by the action of iron bacteria. The resulting corrosion product, $Fe(OH)_3$, mingles with the biodeposit to form the wall of the growing tubercle. When bacteria are present, the tubercle structure is usually less brittle and less easily removed from the metal surface than when bacteria are absent. The outside of the tubercle becomes cathodic, while the metal surface inside becomes highly anodic.

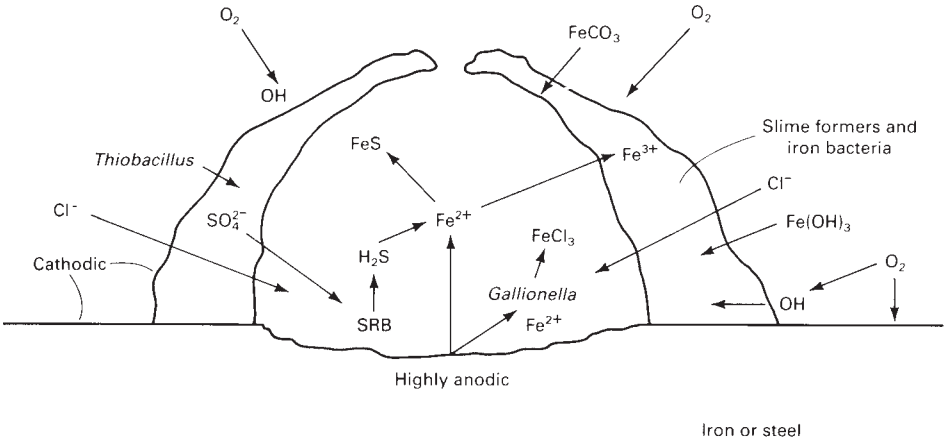


Fig. 8 Schematic diagram of electrochemical and microbial processes involved in tuberculation. Not all of these processes may be active in any given situation. Cl^-, chlorides.

As the tubercle matures, some of the biomass may start to decompose, providing a source of sulfates for SRB to use in producing H_2S in the anaerobic interior solution. In some cases, the sulfur-oxidizing bacteria may assist in the formation of the sulfates. Depending on the ions available in the water, the tubercle structure may contain some $FeCO_3$, and when SRB are present, some FeS. Finally, if there is a source of chlorides and if the iron-oxidizing bacteria *Gallionella* are present, a highly acidic, ferric chloride solution may form inside the tubercle.

Generally, not all of the above reactions will take place in any single environment. As the individual tubercles on a surface grow under the influence of any combination of reactions, they eventually combine to form a mass that severely limits flow (or even closes it off altogether), leaving a severely pitted surface underneath.

Prevention of MIC

Effective MIC prevention requires identification of the bacteria and verification that the bacteria are a factor in corrosion. Microbiologically influenced corrosion should be considered whenever extensive, repetitive pitting corrosion continues, even with an upgraded material. Preventative methods include these:

- Providing corrosion monitoring for the presence of MIC causing bacteria. Monitoring should include water and biofilm sampling to determine bacterial counts and biofilm development on surfaces.
- Providing periodic cleaning to ensure unimpeded fluid flow and to prevent crevice corrosion
- Applying biocide treatments in closed environment systems. Common biocides include chlorine, hydrogen peroxide, and ozone (see Chapter 9 for additional information on biocides).
- Using antifouling paints that contain toxic substances, usually copper compounds. They function by slowly releasing copper ions into the aqueous environment, poisoning the mussels, barnacles, and other creatures.
- Replacing the iron and steel with more corrosion-resistant materials, such as fiberglass polyvinyl chloride (PVC), polyethylene, and concrete
- Creating a nonaggressive environment around the steel by backfilling with gravel or clay-free sand to encourage good drainage (i.e., oxygenating to suppress SRB), making the environment alkaline
- Using cathodic protection, although potentials of –0.95 V (or even more negative) versus $Cu/CuSO_4$ are often required. At these potentials, the risk of hydrogen cracking or blistering should be assessed.
- Using various barrier coatings, some with corrosion inhibitors and/or biocides

Atmospheric Corrosion

Atmospheric corrosion is defined as the corrosion or natural degradation of material exposed to the air and its pollutants rather than immersed in a liquid. The rate or degree of degradation varies for different materials and is influenced by several environmental factors. Many of these factors are natural in origin, but some result from man-made sources. Among the latter sources, which are known to affect atmospheric degradation of materials, are the SO_x and NO_x compounds produced as fossil fuel combustion by-products. These species can react in the atmosphere and result in acid deposition. Although considerable public attention is focused on the effects of acid deposition on our ecosystem, the potential damage to materials may represent the largest economic impact of acid deposition. In fact, it has been reported that atmospheric corrosion accounts for more failures in terms of cost and tonnage than any other single environment.

Types of Atmospheres. Atmospheres are often broadly classified as being:

- Rural
- Industrial
- Marine

An atmosphere classified as rural is normally one that does not contain chemical pollutants but does contain organic and inorganic dusts. Its principal corrodent is moisture and, of course, oxygen and carbon dioxide. Arid or tropical atmospheres are special cases of the rural environment because of their extreme relative humidities and condensation. The rural atmosphere is generally the least corrosive.

An industrial atmosphere is typically identified as one with heavy industrial manufacturing facilities. These atmospheres can contain concentrations of sulfur dioxide, chlorides, phosphates, nitrates, or other specific industrial emissions. These emissions combine with precipitation or dew to form the liquid corrosive.

A marine atmosphere is laden with fine particles of sea salt carried by the winds and deposited on materials. The marine atmosphere is usually one of the more corrosive atmospheric environments. It has been shown that the amount of salt (chlorides) in the marine environment decreases with increasing distance from the ocean and is greatly influenced by wind direction and velocity.

Such classifications are, of course, gross oversimplifications of the situation. It is easy to list locations along the seacoast that have heavy industrial pollution in the atmosphere. Such locations are both marine and industrial. Furthermore, two decidedly rural environments can

differ widely in average yearly temperature and rainfall and can therefore have considerably different corrosive tendencies. Industrial expansion into formerly rural areas can easily change the aggressiveness of a particular location. Finally, longterm trends in the environment, such as changes in rainfall patterns, mean temperature, and perhaps acid rain, can make extrapolations from past behavior less reliable.

Other factors that limit the usefulness of atmospheric-exposure data are the general nonlinearity of weight loss due to corrosion with time and the fact that most atmospheric-corrosion data are presented as an average over the entire test panel surface. Most atmospheric-exposure

Table 3 Comparative rankings of 45 locations based on loss of weight (grams) of 10 by 15 cm (4 by 6 in.) specimens of steel

Ranking to State College, PA	Location	Two-year exposure, grams lost
1	Norman Wells, N.W.T., Canada	0.73
2	Phoenix, AZ	2.23
3	Saskatoon, Sask., Canada	2.77
4	Esquimalt, Vancouver Island, Canada	6.50
5	Detroit, MI	7.03
6	Fort Amidor Pier, Panama, C.Z.	7.10
7	Morenci, MI	9.53
8	Ottawa, Ont., Canada	9.60
9	Potter County, PA	10.00
10	Waterbury, CT	11.00
11	State College, PA	11.17
12	Montreal, P.Q., Canada	11.44
13	Melbourne, Australia	12.70
14	Halifax (York Redoubt), N.S.	12.97
15	Durham, NH	13.30
16	Middletown, OH	14.00
17	Pittsburgh, PA	14.90
18	Columbus, OH	16.00
19	South Bend, PA	16.20
20	Trial, B.C. Canada	16.90
21	Bethlehem, PA	18.3
22	Cleveland, OH	19.0
23	Miraflores, Panama, C.Z.	20.9
24	London (Battersea), England	23.0
25	Monroeville, PA	23.8
26	Newark, NJ	24.7
27	Manila, Philippine Islands	26.2
28	Limon Bay, Panama, C.Z.	30.3
29	Bayonne, NJ	37.7
30	East Chicago, IN	41.1
31	Cape Kennedy, 0.8 km (0.5 mile) from ocean	42.0
32	Brazos River, TX	45.5
33	Pilsey Island, England	50.0
34	London (Stratford), England	54.3
35	Halifax (Federal Building), N.S.	55.3
36	Cape Kennedy, 55 m (60 yd) from ocean, 60 ft elevation	64.0
37	Kure Beach, NC, 250 m (800 ft) lot	71.0
38	Cape Kennedy, 55 m (60 yd) from ocean, 9 m (30 ft) elevation	80.2
39	Daytona Beach, FL	144.0
40	Widness, England	174.0
41	Cape Kennedy, 55 m (60 yd) from ocean, ground level	215.0
42	Dungeness, England	238.0
43	Point Reyes, CA	244.0
44	Kure Beach, NC, 25 mm (80 ft) lot	260.0
45	Galeta Point Beach, Panama, C.Z.	336.0

data for steels show a decrease in the rate of attack with time of exposure so that extrapolations of such data to times longer than those covered by the exposure data can lead to an overdesign in cross section. Finally, in many cases, the average weight loss per unit area is of less concern than the time to perforation. This factor is more related to localized attack, which can be masked by the averaging of data, as is done in weight-loss determinations.

The effect of various environments on the corrosion rate is indicated in Table 3. Table 3 is a compilation of weight-loss measurements for cold-rolled steels after two years of exposure. The most startling feature of Table 3 is the extreme range of corrosion rates: Galeta Point Beach, Panama, is more than 450 times as aggressive as the site at Norman Wells, N.W.T., Canada. This difference in corrosion rate is easily greater than any effect that can be produced by small changes in composition of the steel. This again underscores the fact that in dealing with the corrosion of carbon steels, the alteration of design or environmental factors is usually more effective than changing the grade of steel.

Further examination of Table 3 shows that the marine environments tend to be near the aggressive end of the list and that cold environments are generally less aggressive than warm sites. The average yearly temperature cannot, in general, be isolated from the moisture effect, because most of the more tropical exposure sites are also in regions with high humidity. One exception is arid Phoenix, AZ.

Atmospheric Corrosion of Various Metals. The average atmospheric corrosion rates of various metals for 10 year and 20 year exposure times are presented in Table 4. Corrosion rates are given for several metals at urban industrial, marine, and rural locations. On a tonnage basis, steel is the most common metal exposed to atmospheric corrosion. Other important metals include aluminum, copper, lead, tin, nickel, and zinc. Aluminum has high corrosion resistance in rural environments

Table 4 Average atmospheric-corrosion rates of various metals for 10 year and 20 year exposure times

Corrosion rates are given in mils/year (1 mil/year = 0.025 mm/year). Values cited are one-half reduction of specimen thickness.

	Atmosphere					
	New York, NY (urban-industrial)		La Jolla, CA (marine)		State College, PA (rural)	
	Years					
Metal	10	20	10	20	10	20
Aluminum	0.032	0.029	0.028	0.025	0.001	0.003
Copper	0.047	0.054	0.052	0.050	0.023	0.017
Lead	0.017	0.015	0.016	0.021	0.019	0.013
Tin	0.047	0.052	0.091	0.112	0.018	…
Nickel	0.128	0.144	0.004	0.006	0.006	0.009
65% Ni, 32% Cu, 2% Fe, 1% Mn (Monel)	0.053	0.062	0.007	0.006	0.005	0.007
Zinc (99.9%)	0.202	0.226	0.063	0.069	0.034	0.044
Zinc (99.0%)	0.193	0.218	0.069	0.068	0.042	0.043
0.2% C Steel(a) (0.02% P, 0.05% S, 0.05% Cu, 0.02% Ni, 0.02% Cr)	0.48	…	…	…	…	…
Low-alloy steel(a) (0.1% C, 0.2% P, 0.04% S, 0.03% Ni, 1.1% Cr, 0.4% Cu)	0.09	…	…	…	…	…

(a) Kearney, NJ (near New York City)

and lower resistance in industrial and marine environments. Nickel and nickel alloys have high corrosion resistance in marine and rural environments but can exhibit attack in industrial environments containing higher levels of sulfur compounds. Zinc also exhibits its highest corrosion rates in industrial environments, with somewhat lower rates in marine environments and still lower rates in rural environments. Table 4 also provides a comparison between the 10 year corrosion rates of a carbon steel and a low-alloy steel containing alloying additions of phosphorus, nickel, chromium, and copper for increased atmospheric corrosion resistance. Such steels, referred to as weathering steels, are discussed in Chapter 6.

Effects of Moisture and Atmospheric Pollutants. Because atmospheric corrosion is an electrolytic process, the presence of an electrolyte is required. This should not be taken to mean that the steel surface must be awash with water; a very thin, adsorbed film of water is all that is required. During an actual exposure, the metal spends some portion of the time awash with water because of rain or splashing and a portion of the time covered with a thin adsorbed water film. The portion of time spent covered with the thin water film depends quite strongly on relative humidity at the exposure site (Fig. 9). This fact has led many corrosion scientists to investigate the influence of the time of wetness on the corrosion rate.

These studies have shown that the time of wetness, although an important factor, cannot be considered in isolation when estimating corrosion rates. An excellent example of this fact is demonstrated in Fig. 10, in which the weight loss of iron is plotted as a function of relative humidity for an exposure of 55 days in an atmosphere containing 0.01% sulfur dioxide (SO_2). In the lower righthand corner of Fig. 10 is the measured corrosion rate of iron exposed for the same time in an

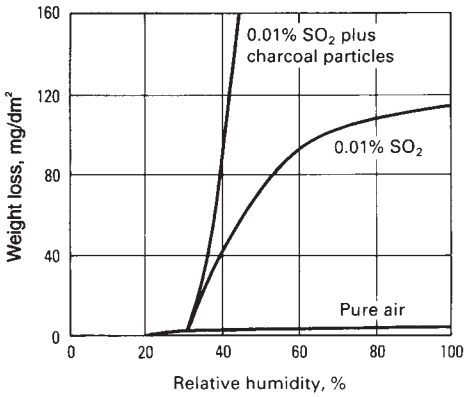


Fig. 9 Relationship between the corrosion rate of iron and the relative humidity in an environment containing 0.01% SO_2. Exposure period: 55 days. The corrosion rate of iron exposed for 55 days at 100% relative humidity is shown for comparison.

SO_2-free atmosphere at 99% relative humidity. The increase in corrosion rate produced by the addition of SO_2 to the atmosphere is substantial.

Another feature of interest is the apparent existence of a critical humidity level below which the corrosion rate is small. As shown in Fig. 10, the critical humidity in an SO_2-containing atmosphere is approximately 60%.

To better appreciate the effects of pollutants on the atmospheric corrosion of metals, one may consider once again the environmental aspects of automotive corrosion. Before 1950, corrosion of externally exposed metal on automobiles was not considered a serious problem. By 1955, initial signs of corrosion had surfaced. During the 1960s, type 430 stainless steel containing 17% Cr was failing due to pitting and crevice corrosion. This stainless steel grade was widely used for exterior trim. As a result of localized corrosion problems, a modified 434 grade with 17% Cr and 1% Mo was developed. Severe galvanic corrosion problems with painted auto body steel surfaced during the 1960s, especially in trim areas where solid stainless steel was attached to the auto body. By 1970, corrosion perforation of painted auto body steel was a problem which grew to major importance throughout the 1970s. The susceptibility and high incidence of pitting and blush and bloom (flat finish with milky appearance) of anodized aluminum exterior trim was recognized by 1980 and by 1985, type 434 stainless steel in the same application was exhibiting signs of localized corrosion unless it was properly produced. High susceptibility to cosmetic corrosion, including filiform corrosion, persisted throughout the 1990s.

Although some of these problems can be attributed to poor design and maintenance, there is also a direct correlation with atmospheric

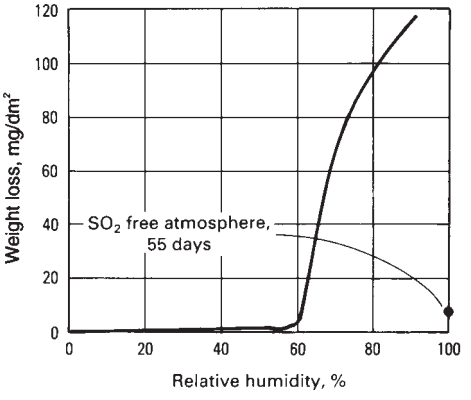


Fig. 10 Effect of relative humidity and atmospheric pollution (environment containing 0.01% SO_2) on the rusting of iron. A critical humidity near 60% relative humidity is observed.

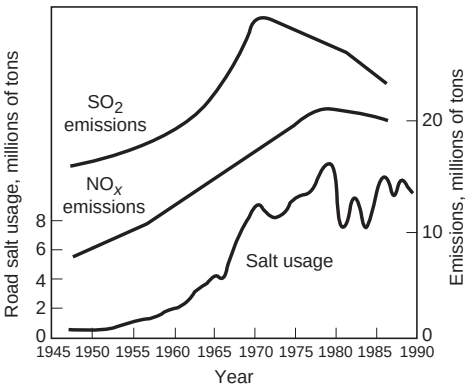


Fig. 11 Annual emissions and road salt usage in the United States

conditions. Figure 11 plots the annual emissions output and road (deicing) salt usage in the United States from 1945 through 1990. As the use of road salts (sodium chloride and calcium chloride) increased and levels of atmospheric pollutants (emissions) continued to rise, the corrosion problems summarized in the previous paragraph began to manifest themselves. Chlorides are known to be aggressive to metals and atmospheric pollutants such as SO_2, NO_x, H_2S, and NH_4, and particulate matter are known to have a negative impact on corrosion. Take, for example, the reaction involving the SO_2 molecule striking a steel surface and converting to sulfuric acid as a result of hydrolysis and oxidation. This introduces reactive ions, increased conductivity, and a lower pH. The presence of hygroscopic sulfate corrosion products also lowers the critical humidity for the corrosion reaction.

Note that the most severe automotive corrosion problems during the 1970s correspond with the highest emission levels and road salt usage shown in Fig. 11. Realization of improved corrosion performance began after the U.S. *Clean Air Act of 1977*, with public awareness of the damaging effects of road salts and better quality control by automobile manufacturers.

Corrosion Control. Atmospheric corrosion is controlled by selecting more corrosion resistant materials. For example, aluminum or stainless steels can be used where the corrosion of steel parts is undesirable. Metallic and organic coatings are commonly used on steel to provide atmospheric corrosion resistance. The metallic coatings can be sacrificial, such as zinc coating on galvanized steel, or they can be a noble metal coating that acts as a barrier. Removal of moisture from the atmosphere to levels below the critical relative humidity will control corrosion. Air conditioning is commonly used to control the relative humidity in the atmosphere for protection of communications equipment and computer components.

Underground/Soil Corrosion

Soil corrosion may be considered to encompass all corrosion taking place on buried (underground) structures. Underground storage tanks, gas and oil transmission pipelines, distribution pipelines, and many other structures buried in soil are susceptible to underground corrosion.

Ordinary steel and cast irons are the two most common metallic materials used for such underground structures. Aluminum, stainless steel, and copper are also used.

Nonmetallic materials are being used increasingly for underground applications. Concrete is used as footings, piers, tanks, and piping. Thermoplastics, most notably polyvinyl chloride (PVC), acrylonitrile-butadiene-styrene (ABS), and polyethylene (PE) have replaced metals in many piping applications. Glass fiber reinforced thermosetting plastics are used for the underground storage of a wide range of products (e.g., water and gasoline).

Factors Affecting Underground/Soil Corrosion

Important soil characteristics that control the corrosivity of soils to steel and other metals include the following:

- Aeration and water-retention (permeability) characteristics of the soil
- Dissolved salt content and resistivity of the soil
- Soil acidity
- Presence of ionic species in the soil—for example, chloride or microbiologically active species, such as bacteria

The resulting corrosion resistance depends on the combination of the corrosivity of the soil and the corrosion behavior of the metal under those conditions.

Aeration and water-retention characteristics are the chief physical attributes of soil. Coarse soils (sands and gravels) that have good drainage and ample aeration corrode steel at a rate approaching that of the local atmosphere. Clay and silt soils are characterized by fine texture, high water retention, poor aeration, and poor drainage, all of which increase corrosion rates for steel. The most severe corrosion usually takes place at low elevations in poorly drained soils such as clays and tidal marshes where there is minimal aeration. If these soils are dug up and then backfilled, drying and shrinkage cause them to become partly aerated, which, in turn, creates differential aeration cells. Salts often accumulate in the backfilled areas and lower the soil resistivity. In

contrast, corrosion occurs to a lesser degree in well-aerated, well-drained, porous soils where salts are readily washed away by the rain.

Corrosion by differential aeration can result from various conditions. For example, when a pipe passes through two soils that differ in oxygen permeability, a galvanic current flows from the more poorly aerated (anodic) surface of the pipe through the soil to the better aerated (cathodic) surface, as shown schematically in Fig. 12.

Lower oxygen concentrations commonly occur at the bottom of a buried steel structure, where the soil is more compact and farther from the source of oxygen in the atmosphere. This can give rise to an oxygen concentration cell. The lower-oxygen environment in contact with the steel at the bottom of the pipe can cause this area to become anodic with respect to the steel at the top of the pipe, which is in contact with soil that contains higher levels of oxygen. Corrosion current leaves the steel at the bottom of the pipe, resulting in corrosion at the anodes, and travels through the soil to the top of the pipe, where the cathodic reaction is the reduction of oxygen (Fig. 13). This type of corrosion also can occur if the normal water table lies between the top and bottom of a large- diameter pipe. Oxygen-concentration cells are also produced at random sites where sticks, stones, and other foreign material in the backfill contact the pipe.

Soil acidity can also influence underground corrosion. The acidity or alkalinity of most soils in the United States is stable because of the buffering action of the soluble minerals available. However, soils across the country differ in pH from less than 4.5 (very acidic) to greater than 9.5 (strongly alkaline). The corrosion response of a metal in contact with soil varies widely, depending on acidity. Steel, for example, is corroded in acidic environments but remains passive in moderately alkaline environment, whereas aluminum is passive in a neutral environment but is corroded in either extremely acidic or strongly alkaline environments.

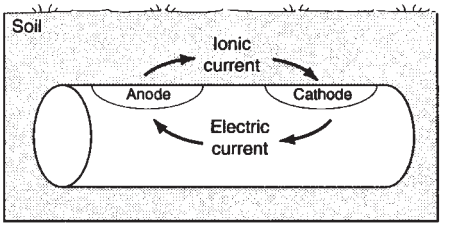


Fig. 12 Corrosion cell on a metal surface buried in soil. The corrosion current leaves the metal surface at an anode and enters the soil. The current flows from the anode to the cathode through the soil by ionic conductivity and enters the metallic structure at the cathode. The current flows from the cathode through the metallic structure to the anode by electrical conductivity and completes the corrosion cell. In most cases in naturally occurring soils, that portion of the pipe lying in the more conductive (poorly aerated) soil is the anode; that in the less conductive (well aerated) soil is the cathode

Dissolved Salts and Soil Resistivity. The most corrosive soils are those that contain large concentrations of soluble salts. Because of the presence of salts, such soils have relatively high electrical conductivites (or low electrical resistivities). The least corrosive soils have low concentrations of soluble salts and high resistivities. Resistivity measurements can be obtained readily and provide as much information on corrosion characteristics as measurements of any other single soil property. Consequently, resistivity is the property most often used to approximate the aggressiveness of a soil. Observations of soil drainage and/or measurements of pH supplement resistivity measurements. The following table lists the general relationship that exists between soil resistivity and corrosion of ferrous metals; however, because of other factors, this relationship may not always be valid.

Soil resistivity, Ω · m	Classification
<7	Very corrosive
7–20	Corrosive
20–50	Moderately corrosive
>50	Mildly corrosive to noncorrosive

Presence of Biological Species. It has been estimated that 50% of all failures of buried metal structures are due to MIC. The primary culprits are SRB and acid-producing bacteria such as *Thiobacillus* (refer to the earlier section "Biologically Influenced Corrosion" in this Chapter). In view of the effects of bacteria, the best means for modifying a natural environment is to displace organic soil, with its bacterial population and nutrients, from around the buried structure and to surround the structure with mineral backfill (gravel or clay-free sand) that provides good drainage and adequate aeration. The backfill can be treated with biocides to provide an environment that inhibits growth and reproduction.

Types of Underground/Soil Corrosion

Galvanic corrosion is a concern in soils where dissimilar materials are in contact. A classic example is the use of copper alloy (brass or

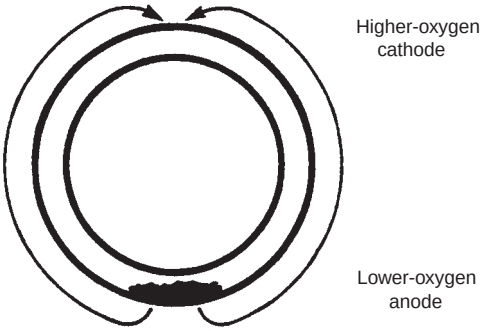


Fig. 13 An oxygen concentration cell on steel in soil

bronze) valves and fixtures with steel piping. The copper alloy component becomes a cathode and accelerates the corrosion of steel. Often the accelerated attack is most severe for the steel immediately adjacent to the copper alloy component.

Table 5 presents a galvanic series in typical neutral soil. When two dissimilar metals are electrically coupled in contact with moist soil, the more positive member of the couple becomes a cathode and the more negative member becomes an anode. The anodic member is corroded more severely. Graphite and copper alloys coupled to steel accelerate the corrosion of the latter. The more active metals in the series (magnesium, zinc, and, in some cases, aluminum) can be used to cathodically protect steel. Where aluminum is used, it must remain active.

Another observation from Table 5 is that the presence of corrosion products (rust) or mill scale on steel make the steel more cathodic. A consequence of this is that a fresh, bare steel coupled to a corroded steel or one covered with mill scale shows accelerated attack.

Stray-current corrosion is a special form of corrosion observed in buried structures. It differs from natural corrosion in that it is caused by an externally induced electrical current and is basically independent of environmental factors such as oxygen concentration or pH. Environmental factors may enhance other corrosion mechanisms involved in the total corrosion process, but the stray-current corrosion portion of the mechanism is unaffected.

Stray currents are defined as currents that follow paths other than their intended circuit. A current leaves the intended path because of poor electrical connections within the circuit of poor insulation around the intended conductive material. It then passes through soil, water, or any other suitable electrolyte to find a low-resistance path, such as a buried metal pipe or some other metal structure, and flows to and from that structure, causing accelerated corrosion. Sources of stray currents include equipment using the earth as a ground return, such as electric

Table 5 Practical galvanic series of metals and alloys in neutral soils and water

Metal or alloy(a)	Potential(b), V
Carbon, graphite, coke	+0.3
Mill scale on steel	–0.2
High-silicon cast iron	–0.2
Copper, brass, bronze	–0.2
Low-carbon steel in concrete	–0.2
Lead	–0.5
Cast iron (not graphitized)	–0.5
Low-carbon steel (rusted)	–0.2 to –0.5
Low-carbon steel (clean and shiny)	–0.5 to –0.8
Commercially pure aluminum	–0.8
Aluminum alloy (5% Zn)	–1.05
Zinc	–1.1
Magnesium alloy (Mg-6Al-3Zn-0.15Mn)	–1.16
Commercially pure magnesium	–1.75

(a) Arranged from most noble to most active. (b) Typical potential normally observed in neutral soils and water measured with respect to copper sulfate reference electrode

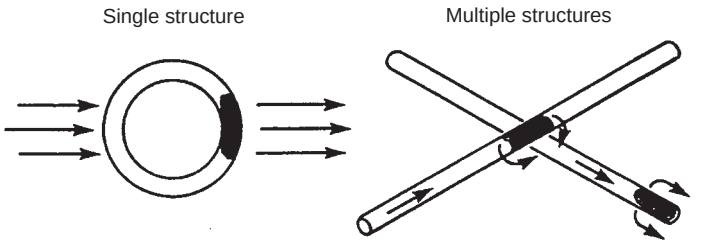


Fig. 14 Two examples of stray-current corrosion on buried structures. Black areas indicate anodic areas (i.e., current leaves structure).

railways or welding generators, as well as fixed installations that have inadvertently allowed current to escape, for example, cranes or direct current power transmission lines.

Two instances of stray-current corrosion are shown schematically in Fig. 14. Stray-current corrosion results from currents flowing through the soil that enter a buried metallic structure in one area, then leave the metallic structure, and then reenter the soil at another location. The area where the current reenters the soil becomes anodic, and rapid corrosion can occur. For the single structure shown in Fig. 14, the current flowing through the soil enters the structure on the left side, flows through the metal structure, and reenters the environment on the right side. Severe attack is observed at the area where the current reenters the environment.

For the case of multiple structures shown schematically in Fig. 14, the current flowing through the upper pipeline by electrical conductivity leaves that pipeline and jumps onto the lower pipeline, where it is electrically conducted at the end of that pipeline and reenters the soil. Severe attack is observed on both pipelines in the area where the current leaves the structure. The corrosion of the upper pipeline could be eliminated by attaching an electrically conducting bonding strap that would tie the two metallic structures together. In that case, the current flowing along the upper pipeline could go through the metallic conductor to the lower pipeline without reentering the soil and, therefore, would not affect the corrosion behavior of the pipeline in the soil.

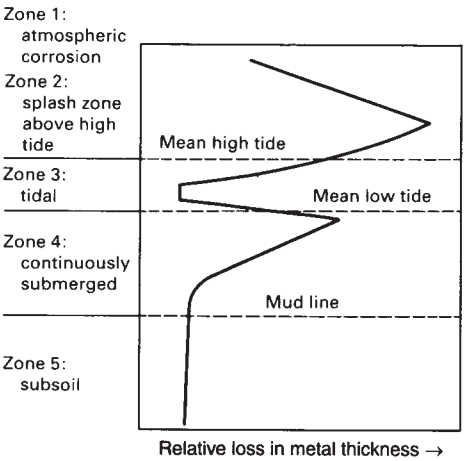
Corrosion Control

The most economical and effective method of combating corrosion of steels underground has been cathodic protection. Both applied current from rectifiers and current from sacrificial anodes have been used, either alone or in conjunction with organic coatings. More detailed information on these corrosion control methods can be found in Chapters 9 and 10.

Natural and Treated Waters

Natural waters exhibit a wide variety of dissolved ionic species—from nearly pure rain water to concentrated brines. The general classifications of natural waters are fresh, brackish, seawater, geothermal, and brines. The important factors controlling the corrosivity of a water include its acidity, oxidizing power, conductivity, and the presence of specific detrimental or beneficial species. The presence of solids in a water can also significantly affect corrosivity, as can flow rate, temperature, and presence of biological agents.

Seawater is a highly conductive environment with approximately 3.4% salt concentration. Other factors that contribute to the corrosivity of seawater include oxygen concentration, velocity, temperature, and presence of marine biological species. Figure 15 shows the relative loss of metal thickness for a steel piling after five years of exposure in seawater at Kure Beach, NC. A variety of corrosive conditions exist from the bottom of the piling in the sea to the portion of the piling exposed to marine atmospheric corrosion. In the soil (zone 5) and the continuously submerged area (zone 4), the corrosion rate is relatively low. The corrosion rate increases at the upper regions of the immersed area and the area in the tidal zone (zone 3), except for a portion immediately above the mean low-tide level and the below-the-mean high-tide level. The corrosivity increases again significantly in the splash zone (zone 2) and then drops off again in the marine atmospheric corrosion zone (zone 1). The tidal and splash zones are considered to be the most corrosive because of the higher oxygen concentration in these areas and the effect of the seawater velocity. The lower corrosion rate of the piling in zone 3 in



Corrosion zone	Description
Atmospheric zone 1	The portion of the elevated structure subject to a marine atmosphere, including sea mist and high relative humidity, but without significant wetting by splash from waves
Splash zone 2 (above high tide)	The portion above the level of mean high tide that is subject to wetting by large droplets of seawater
Tidal zone 3	The portion of the structure between mean high tide and mean low tide, alternately immersed in seawater and exposed to a marine atmosphere
Submerged zone 4	The portion of the structure from about 0.3 to 1 m (1 to 3 ft) below mean low tide down to the mud line
Subsoil zone 5	The portion below the mud line, where the structure has been driven into the ocean bottom

Fig. 15 Zones of corrosion for steel piling in seawater, and relative loss of metal thickness in each zone

Fig. 15 is reported to be due to the buildup of marine life (barnacles, for example) in this area, which provide some corrosion protection if coverage is complete (refer to Fig. 6). In addition, steel at the tidal zone may act cathodically and receive some protection from corrosion just below the tidal zone in the case of a continuous steel pile.

Treated waters are classified as potable, demineralized, boiler feed, processed, and cooling. Potable waters show a variety of corrosiveness, much of which is the result of the degree of water hardness. Calcium and magnesium salts in water can precipitate out and form hard scale on pipe surfaces. Corrosion control under these conditions involves striking a balance between sufficient scaling properties that allow a buildup of thin scale for corrosion protection but will not plug and constrict the piping system. If the degree of water hardness is very low, then there is no scaling tendency, and the water can be more corrosive. Demineralized water has soluble salts removed. As the resistivity of the water increases, the corrosion rate of metals typically decreases.

For boiler feedwater, oxygen commonly is removed by mechanical or chemical means and the pH adjusted to mildly alkaline conditions. Other inhibitors can also be added. For process water and cooling waters, a variety of chemical treatments are available to control oxygen concentration. The same benefit can be gained by the use of inhibitors. Stagnant water conditions are often more corrosive than flowing conditions. Rapid failures in stainless steel components have resulted from stagnant water, which allows the buildup of deposits with subsequent accelerated attack beneath these deposits.

Understanding Corrosion in Acids

Many of the severe corrosion problems encountered in the processing industries involve acids. These environments are naturally corrosive. Metal dissolves at the anodic areas by the oxidation reaction of metal atoms becoming metal ions in solution. The balancing reduction reaction at the cathodes is the consumption of the hydrogen ions in the acid with the evolution of hydrogen gas. The overall reaction is

$$\text{Metal} + \text{acids}(H^+) \rightarrow \text{hydrogen}(H_2) + \text{metal ions } (M^+)$$

The rate of oxidation or corrosion of the metal is often controlled by the rate of the reduction reaction. In a concentrated acid with a high concentration of hydrogen ions (H^+), there is a large capacity for consuming electrons and promoting the corrosion reaction. In the sections that follow, the corrosion behavior of steels in a variety of acids will be described.

The response of steels to these acids is a function of acid concentration and temperature. Hydrochloric, sulfuric, and nitric acids are all strong acids, and yet the corrosion behavior of steel in them differs widely. Two of the keys to understanding this diversity of behavior are the oxidizing power of the acid environment and the tendency for passivation of steel in the environment. It is useful to contrast the corrosion behavior of steel in hydrochloric acid and sulfuric acid as a function of the concentration of the acid.

Corrosion Rate Versus Concentration of Acid. The corrosion rate of steel as a function of hydrochloric acid (HCl) concentration is shown in Fig. 4(a) and schematically in Fig. 16. Hydrochloric acid is a strong and highly reducing acid. No passive film is formed in hydrochloric acid and steel corrodes by active dissolution. As the concentration of hydrochloric acid increases, the corrosion rate of the steel increases. The shape of this curve is characteristic of an activation-controlled dissolution of an active metal. The hydrochloric acid concentration is comparable to increasing oxidizing power along the *y*-axis, and the corrosion rate is comparable to the log of the current for the oxidation reaction along the *x*-axis.

Data for the corrosion of steel by sulfuric acid at room temperature are presented in Fig. 4(b) and Table 6. Very dilute sulfuric acid is only moderately corrosive. As the concentration of sulfuric acid increases from very dilute up to values from 10 to 50%, the corrosion rate increases significantly. At concentrations from 60 to 90%, the corrosion rate drops significantly and remains fairly constant. This behavior is shown schematically in Fig. 17 for the corrosion rate of steel as a function of sulfuric acid concentration. As the sulfuric acid concentration increases, the oxidizing power of the environment increases. At dilute concentrations of acid, this increased oxidizing power is accompanied by an increased corrosion rate of the steel while the steel is actively dissolving. At a critical concentration of acid, the corrosion rate drops

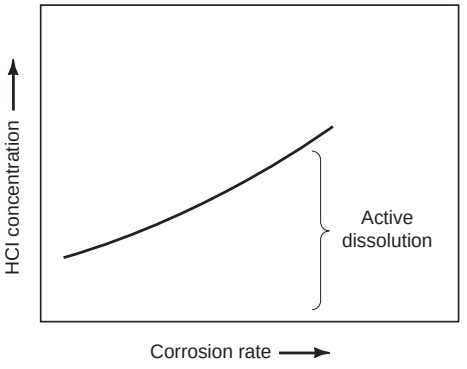


Fig. 16 Corrosion rate of steel as a function of hydrochloric acid concentration

Table 6 Corrosion of steel by sulfuric acid, H_2SO_4, at room temperature

H_2SO_4, %	Corrosion rate	
	mm/year	mils/year
0.005	0.2	8
0.05	0.4	15
0.5	3	120
1.0	5	200
3.0	22	875
5.0	30	1200
10.0	58	2300
50.0	41	1600
60.0	1.5	60
70.0	0.5	20
80.0	0.5	20
90.0	0.5	20

rapidly to a significantly lower value and remains fairly constant even at increasingly higher levels of concentration. This lower corrosion rate results from the stable passive film that builds up on steel under the more oxidizing conditions. Once the passive film forms, the corrosion rate is independent of oxidizing potential as long as the passive film is stable.

Influence of Oxidizing Power and Passivation. The differences in behavior between steel in hydrochloric acid and steel in sulfuric acid can be readily understood in terms of the oxidizing power of the environment and the relative tendency to form passive films. In hydrochloric acid, no passivity of steel is observed, and the corrosion rate continues to increase with increasing oxidizing power of the environment. In sulfuric acid, there is a critical oxidizing power at which passivity becomes stable, and the corrosion rate above this oxidizing power level drops off dramatically. The corrosion resistance of steel under these conditions depends on the tenacity and durability of the passive film. If the film is broken down mechanically or chemically, the corrosion rate of steel will greatly increase in the more concentrated sulfuric acid.

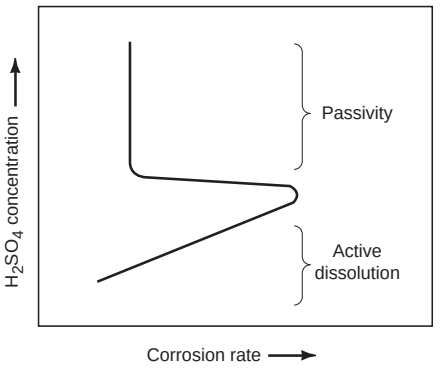


Fig. 17 Corrosion rate of steel as a function of sulfuric acid (H_2SO_4) concentration

Corrosion by Sulfuric Acid

Sulfuric acid (H_2SO_4) is the largest-volume inorganic acid currently in use and is generally considered to be the most important industrial chemical. The principal uses of H_2SO_4 are for fertilizer manufacture, petroleum refining, production of other chemicals, manufacture of rayon and other textiles, pickling steel and brass, refining metals, manufacture of pigments and colors, explosives, manufacture of coke and coal tar products including dyes and drugs, storage batteries, production of natural and synthetic rubber, and synthetic detergents.

Sulfuric acid is made by the contact process, in which elemental sulfur or sulfur-containing waste is burned to form sulfur dioxide (SO_2). Sulfur dioxide is converted to sulfur trioxide (SO_3) by contact with a vanadium catalyst. Reaction of this gas with water produces sulfuric acid:

$$SO_3 + H_2O \rightarrow H_2SO_4$$

Sulfur trioxide is soluble in 100% H_2SO_4, so if the SO_3 (gas) is bubbled through the acid, a "fuming acid" called oleum is produced. Most of the H_2SO_4 produced is shipped to the customer in three concentrations, approximately 78 and 93%, and fuming (oleum).

Materials Selection Guidelines for Sulfuric Acid

The corrosiveness of H_2SO_4 depends on many factors, particularly temperature and concentration. Strong, hot conditions present the greatest problems, and few materials except platinum, tantalum, fluorocarbon plastic, and brick-lined steel will resist 60 to 98% H_2SO_4 at 120 °C (250 °F). However, other variables also influence the resistance of materials to H_2SO_4. The presence of oxidizing or reducing contaminants, velocity effects, solids in suspension, and galvanic effects can alter the serviceability of a particular material of construction.

It is unwise to select materials of construction for equipment that will handle H_2SO_4 solely on the basis of published corrosion data unless the conditions involved are adequately and specifically covered by the reference data. Seemingly minor differences in impurities or environmental conditions can significantly affect actual service corrosion rates. Impurities such as halides generally increase corrosion. Aeration or the presence of oxidizing agents generally accelerates corrosion of nonferrous materials and reduces corrosion of stainless alloys, but the extent of these effects depends on specific conditions. Hot-wall effects are frequently overlooked, and heating coils made of the same material as the containing vessel can corrode rapidly while the condition of the vessel itself remains satisfactory.

It is therefore, advisable to consider all general corrosion data only as an indicator of relative resistance and as a guide by which the limiting conditions of materials may be further reviewed. Final selection of materials for specific equipment depends, of course, on such factors as allowable corrosion rate, desired mechanical and physical properties, fabrication requirements, availability, and cost.

Use of Steel in Sulfuric Acid

General Resistance. Ordinary carbon steel is widely used for the handling of sulfuric acid in concentrations greater than 70% under static or low-velocity conditions (<0.9 m/s, or 3 ft/s). Storage tanks, pipelines, tank cars, and shipping drums made of steel are very common for 78, 93, and 98% and stronger acids, such as oleum. Pumps and valves may be made of alloy steel because of erosion-corrosion of carbon steel. Much of the equipment if contact sulfuric acid manufacturing plants is made of plain carbon steel. Steel is rapidly attacked by the more dilute sulfuric acids. Figure 18 shows the corrosion of carbon steel by strong sulfuric acid as a function of temperature. Most of the tests were made on ordinary low-carbon steel (0.20% C) with exposure periods of 48 h. Specimens were prepared by abrading the surface with No. 120 emery cloth.

The curves in Fig. 18 comprise an isocorrosion diagram and represent corrosion rates of 5, 20, 50, and 200 mils/year (0.13, 0.5, 1.3, and 5 mm/year). These are isocorrosion or constant corrosion lines. In other words, the outlined areas represent regions where corrosion rates of 0 to 5, 5 to 20, 50 to 200, and >200 mils/year would be expected. The corrosion of steel by strong sulfuric acid is complicated because of the

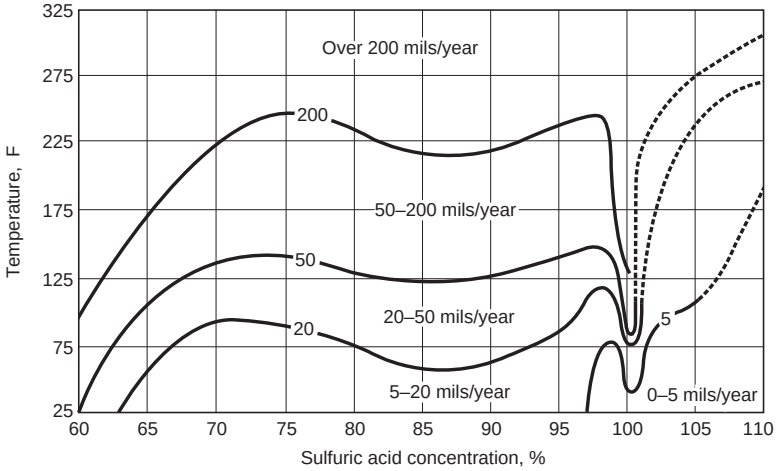


Fig. 18 Corrosion of steel by sulfuric acid as a function of concentration and temperature

peculiar dips in the curves and the rapid increase in corrosion in the neighborhood of 100 to 101% acid. The narrowness of this range means that the acids must be carefully analyzed in order to obtain reliable corrosion data. The dips (increased attack) around 85% are more gradual and less difficult to establish.

Localized attack can occur even at flow velocities within the prescribed limits (under 0.9 m/s, or 3 ft/s, as mentioned earlier). Discontinuities such as short-radiused elbows, excessive penetration of welds, and pipe mismatch may cause sufficient downstream turbulence to disturb the protective sulfate film, resulting in high corrosion rates. Weldments must be thoroughly inspected to ensure that they contain no slag, surface porosity, laps, excessive penetration, or other welding defects that might initiate accelerated corrosion. In addition, steel vessels and piping should be free of mill scale, or serious pitting or nonuniform corrosion may occur.

Hydrogen grooving is another form of localized attack that occurs on vertical or inclined surfaces exposed to the liquid phase. During the corrosion of steel by H_2SO_4, atomic hydrogen is evolved. If produced in sufficient quantities, the hydrogen combines to form small bubbles that stream along preferred paths on vertical and inclined surfaces, disrupting the soft protective iron sulfate film. Channels and deep grooves may eventually form. Grooving is commonly observed in the tops of horizontal manways on the side of storage tanks and on the top 180° of horizontal pipe runs (Fig. 19). In piping, stagnant conditions promote grooving; therefore, a minimum velocity of 0.3 m/s (1 ft/s) is often recommended.

Grooving, combined with erosion-corrosion, also occurs on the sidewalls of tanks (Fig. 20). Location of the liquid inlet in the roof near the shell has, in at least two cases, resulted in combined erosion-corrosion and hydrogen grooving, which caused catastrophic rupture of large storage tanks.

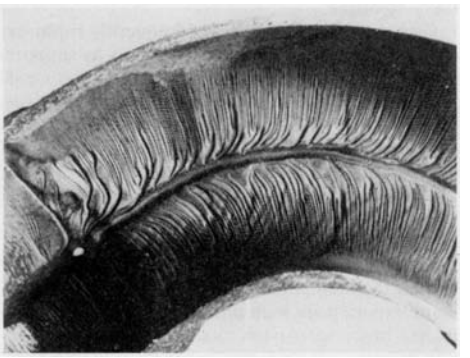


Fig. 19 Hydrogen grooving of a 75 mm (3 in.) diameter steel elbow. The elbow was sectioned; the top half is shown.

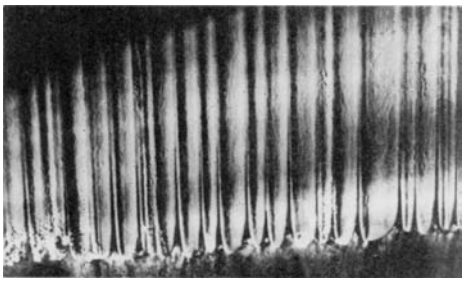


Fig. 20 Hydrogen grooving on the sidewall of an H_2SO_4 storage tank

Use of Cast Irons in Sulfuric Acid

Gray cast iron is at least as resistant to corrosion as steel in the 65 to 100% acid concentration range. Gray cast iron is also less sensitive to velocity than steel and is frequently used up to 1.7 m/s (5.6 ft/s).

Ductile irons are slightly less resistant than gray irons. Higher silicon contents (3.5% versus the normal 1.8 to 2.8%) can improve corrosion resistance.

High-Silicon Cast Iron. Another material that has long been used for handling sulfuric acid is high-silicon iron. Iron with 14.5% Si has exceptional resistance to sulfuric acid in all concentrations to 100% up to the atmospheric boiling points. Corrosion rates are normally less than 0.13 mm/year (5 mils/year).

Use of Stainless Steels in Sulfuric Acid

The common stainless steels are not often used for handling straight sulfuric acid. Type 316 stainless steel (18Cr-12Ni with 2% Mo) is sometimes used in dilute acid solutions containing other ingredients. Other stainless steels sometimes used include type 317 and silicon stainless steels containing 5 to 6% Si. The stainless steels show borderline passivity effects; therefore, they are difficult to test, and it is difficult to predict performance or give reliable and reproducible corrosion data.

The 20-type alloys are usually the first considered when a sulfuric acid environment is too corrosive for the use of steel, 300-series stainless steels, or cast iron. This group contains both wrought alloy 20Cb-3 (Fe-34Ni-20Cr-3.3Cu-2.5Mo) and cast alloy CN-7M containing 19 to 22% Cr, 27.5 to 30.5% Ni, 2.0 to 3.0% Mo, and 3.0 to 4.0% Cu. These alloys possess excellent (less than 0.13 mm/year, or 5 mils/year) corrosion resistance over the entire concentration range at temperatures up to about 50 °C (125 °F) and possess good resistance (less than 0.5 mm/year, or 20 mils/year) up to about 65 °C (150 °F). Higher temperatures can be used in the more dilute and in the strong acids.

Use of Nickel Alloys in Sulfuric Acid

The corrosion rates of nickel-base alloys, in general, increase with acid concentration up to approximately 90%. Higher concentrations of the acid are generally less corrosive. A broad view of the relative performance of various stainless steels and nickel alloys in pure sulfuric acid is illustrated in Fig. 21. In this graph, the temperatures at which the corrosion rate of an alloy in a given concentration of the acid exceeds 0.5 mm/year (20 mils/year) are plotted as isocorrosion curves. At low acid concentrations, the nickel-chromium-molybdenum alloys show a significantly higher resistance than type 316 stainless steel. Alloy 20, a high-nickel stainless steel, shows similar behavior. These high-nickel-chromium-molybdenum alloys can be used only to moderate temperatures in the intermediate and high concentrations of H_2SO_4. The nickel-molybdenum alloys B and B-2 can be used to higher temperatures for all concentrations of acid. However, in the presence of oxidizing species and in aqueous acid systems, alloys B and B-2 suffer serious corrosion.

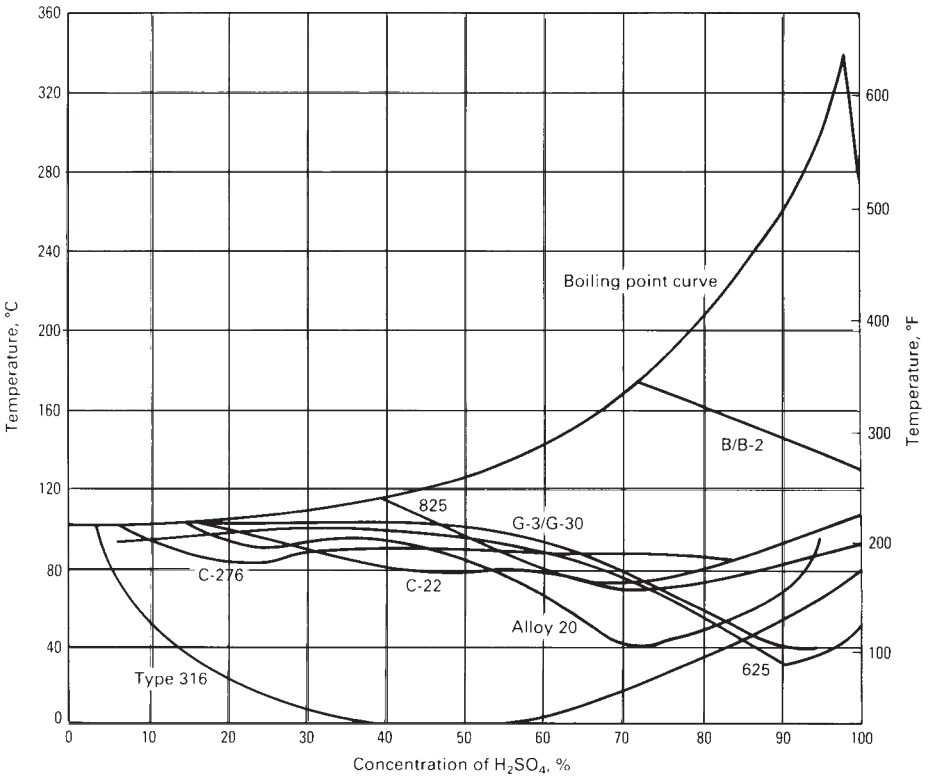


Fig. 21 Comparative behavior of several nickel-base alloys in pure sulfuric acid (H_2SO_4). The isocorrosion lines indicate a corrosion rate of 0.5 mm/year (20 mils/year).

The presence of oxidizing impurities can be beneficial to nickel-chromium-molybdenum alloys shown in Fig. 21 because these impurities can aid in the formation of passive films that retard corrosion. Another important consideration is the presence of chlorides (Cl^-). Chlorides generally accelerate the attack; the extent of acceleration differs for various alloys.

Other Metals Used in Sulfuric Acid

Zirconium has excellent resistance to sulfuric acid up 50% concentration at temperatures to boiling and above. From 50 to 65% concentration, resistance is generally very good at elevated temperatures, but the passive film is a less effective barrier.

Tantalum has resistance to sulfuric acid in all concentrations up to 98% at temperatures as high as 200 °C (390 °F). It is inert to dilute acid even at boiling temperatures and is not attacked by concentrated acids at temperatures below 150 °C (300 °F).

Lead resists sulfuric acid but its protective sulfate film is increasingly solubilized above 90% concentration. The film is easily damaged by erosion or abrasion even at low velocities, with the rate of attack increasing with concentration.

Nonmetallic Materials Used in Sulfuric Acid

Nonmetallic materials of construction have wide application in H_2SO_4. Most of these materials have good corrosion resistance to the pure acid, particularly in dilute concentrations, and are primarily restricted by their mechanical properties at temperature. They are relatively unaffected by most inorganic contaminants, except for such strongly oxidizing agents as nitric acid, peroxides, and dichromates. Commonly used materials include these:

- Brick linings (used for most severe sulfuric acid conditions)
- Polyvinyl chloride (excellent resistance to about 93% concentration at ambient temperatures)
- Plastic linings for pipe (see Table 7)
- Polyethylene (high degree of resistance up to 98% concentration at ambient temperature)
- Fluoroplastics (see Table 8)
- Glass-reinforced polyester resins (show virtually no attack in dilute sulfuric acid at 90 °C, or 200 °F, and can be used up to 75% concentration at temperatures less than 65 °C, or 150 °F)
- Carbon (used for hot acid at concentrations above 60%)
- Graphite (excellent corrosion resistance to all but highly oxidizing concentrations)

Table 7 Suitability of plastic-lined piping systems in sulfuric acid, H_2SO_4

Material	Maximum temperature(a) °C	Maximum temperature(a) °F	Concentration of H_2SO_4, %
Polyvinylidene chloride (PVDC)	52	126	<16
	24	75	30
	NR	NR	>60
Polypropylene (PP)	93	200	<60
	80	175	93
	65	150	96
	50	120	98
Polyvinylidene fluoride (PVDF)	120	250	<16
	105	220	30–60
	80	175	85–93
	65	150	94–98
Polytetrafluoroethylene (PTFE)	260	500	0–100

(a) Temperature may be further limited by mechanical conditions under vacuum. NR, not rated

Table 8 Suitability of fluorinated plastic linings in H_2SO_4

Material	Maximum temperature °C	Maximum temperature °F	H_2SO_4 concentration, %
Polytetrafluoroethylene (PTFE)	260	500	0–100
Perfluoroalkoxy (PFA)	260	500	0–100
Fluorinated ethylene propylene (FEP)	205	400	0–100
Ethylene-chlorotrifluoroethylene (ECTFE)	150	300	<98
Ethylene-tetrafluoroethylene (ETFE)	150	300	<98
Polyvinylidene fluoride (PVDF)	120	250	<16
	105	220	30–60
	80	175	85–93
	65	150	94–98

- Rubber linings, for example, butyl rubber and neoprene (good resistance to 50% concentration at modest temperatures and resistant to 75% acid at ambient temperature)
- Glass linings (glass-lined steel widely used for sulfuric acid service)

Corrosion by Nitric Acid

Nitric acid (HNO_3) is typically produced by the air oxidation of ammonia (NH_3). This catalyzed reaction takes place at very high temperatures. The gaseous oxidation product is condensed to an aqueous liquid of about 65% concentration. During the high temperature oxidation, corrosion of the plant materials is of secondary concern. The elevated operating temperatures dictate that the high-temperature properties of the materials are the primary design consideration. Corrosion considerations prevail during and after condensation and at lower temperatures.

The concentration of HNO_3 up to 99% requires secondary processing to remove excess water. This involves mixing 65% HNO_3 with another substance having a greater affinity for water (such as H_2SO_4) and then separating the mixed acids by distillation and condensation processes.

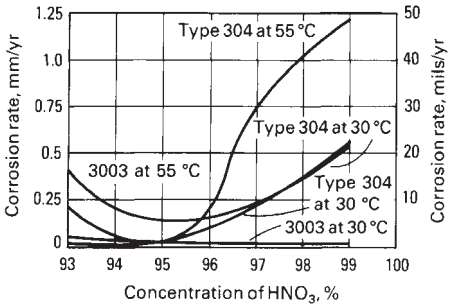


Fig. 22 Comparison of corrosion of aluminum alloy 3003 and type 304 stainless steel in HNO_3

Materials Selection Guidelines for Nitric Acid

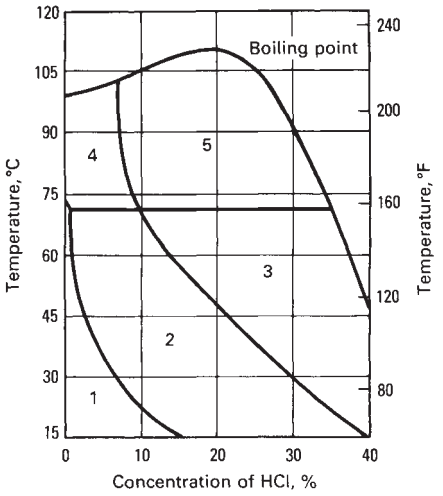
Commercially produced HNO_3 is available in concentrations from 52 to 99%. Nitric acid over 86% is described as fuming. Nitric acid up to 95% is stored and shipped in type 304 stainless steel. Concentrated acid above 95% is handled in Aluminum Association (AA) aluminum alloys 1100 or 3003. Figure 22 shows the reason for this; the corrosion rate of type 304 stainless steel increases rapidly above 95% concentration, while that of aluminum 3003 remains essentially constant to 100%.

Nitric acid is a strong oxidizing agent and attacks most metals, such as iron, by oxidizing the metal to the oxide. A secondary effect of oxidation is the generation of hydrogen at the metal/acid interface, which can cause hydrogen embrittlement of some materials, for example, high-strength steels. Metals and alloys that are able to form adherent oxide films, such as austenitic stainless steels and aluminum alloys, are protected by their oxide films from corrosion by HNO_3.

Corrosion by Hydrochloric Acid

Hydrochloric acid is an important mineral acid with many uses, including acid pickling of steel, acid treatment of oil wells, chemical cleaning, and chemical processing. It is made by absorbing hydrogen chloride in water. Most acid is the by-product of chlorinations. Pure acid is produced by burning chlorine and hydrogen. Hydrochloric acid is available in technical, recovered, food-processing, and reagent grades. Reagent grade is normally 37.1%.

Hydrochloric acid is a corrosive, hazardous liquid that reacts most metals to form explosive hydrogen gas and causes severe burns and irritation to the eyes and mucous membranes. Safe handling procedures are available from various manufacturers and from safety data sheets available from the Chemical Manufacturers Association (Arlington, VA).



Zone	Metal
1	ACI CN-7M(a)(b)(c)
	Monel(b)(c)(d)
	Copper(b)(c)(d)
	Nickel 200(b)(c)(d)
	Silicon bronze(b)(c)(d)
	Silicon cast iron(b)(e)
	Tungsten
	Titanium, grade 7
	Titanium, grade 2(f)
2	Silicon bronze(c)(d)
	Silicon cast iron(b)(e)
3	Silicon cast iron(b)(e)
4	Tungsten
	Titanium, grade 7(g)
All zones (including 5)	Platinum
	Tantalum
	Silver(b)(c)
	Zirconium(b)(c)
	Hastelloy B-2(b)(c)
	Molybdenum(b)(c)

(a) <2% HCl at 25 °C (75 °F). (b) No $FeCl_3$ or $CuCl_2$ contamination. (c) No free chlorine. (d) No aeration. (e) Contains chromium, molybdenum, and nickel. (f) <10% HCl at 25 °C (75 °F). (g) <5% HCl at boiling temperature

Fig. 23 Alloys with reported corrosion rates of <0.5 mm/year (<20 mils/year) in HCl

Materials Selection Guidelines for Hydrochloric Acid

Concentrated HCl is transported and stored in rubber-lined tanks, although custom-fabricated polyester reinforced thermoset plastic (RTP) storage tanks have been used. Pipelines are usually plastic-lined steel. Processes involving aqueous acid are commonly carried out in glass-lined steel equipment. Nonmetallic materials are normally preferred because of the corrosive action of this strongest of acids on most metals.

Candidate metals and alloys for handling HCl are shown in Fig. 23. Suitable materials are judged to be those with a corrosion rate under 0.5 mm/year (20 mils/year) when exposed to uncontaminated HCl. In practice, contamination is not uncommon and can be catastrophic. Selection of a candidate metal should be based on extensive corrosion testing or, preferably, field experience, using the grade of acid that will be available.

Corrosion by Hydrogen Fluoride and Hydrofluoric Acid

Anhydrous hydrogen fluoride (AHF) and aqueous hydrofluoric acid (HF) are of great industrial importance. Anhydrous hydrogen fluoride is the foundation of the multibillion dollar fluorocarbon industry, which encompasses essentially all refrigerants, a fire-extinguishing agent, ultrasonic cleaning fluids, fluorocarbon plastics, and fluorocarbon elastomers. A popular process for alkylation of petroleum to enhance yields

of gasoline depends on the use of AHF. Aqueous HF is used in large quantities to pickle stainless steels, to acid treat wells, and to etch glass.

Aqueous HF and AHF are hazardous chemicals. Fluoride salts, although added to potable waters to prevent tooth decay, are toxic in higher concentrations. Painful, persistent burns result from contact with aqueous HF or AHF, and inhalation of high concentrations of the vapors causes lung damage. The Occupational Safety and Health Administration has ruled that an employee's exposure to HF vapor in any 8 h work shift of a 40 h work week shall not exceed a time-weighted average of 3 ppm HF vapor by volume.

Materials Selection Guidelines for Hydrofluoric Acid

From the standpoint of corrosion, hydrofluoric acid is unique in its behavior compared to most other acids. The high-silicon cast irons, stoneware, and glass are generally resistant to most acids, but all are readily attacked by hydrofluoric acid. Magnesium shows rather poor corrosion resistance to many acids, but resists attack by hydrofluoric acid; in fact, shipping containers for this acid are often made of magnesium. Below 1% concentration, some attack occurs, but in concentrations of 5% and above, magnesium is practically immune to corrosion. The magnesium passivates, apparently because of the formation of a surface fluoride film, and corrosion of the metal is thus retarded. This same surface effect also applies to other metals and alloys that resist corrosion by hydrofluoric acid.

Steels. Carbon steels have useful corrosion resistance from 64 to 100% HF at ambient temperatures. Low-alloy steels have higher corrosion rates than do plain carbon steels. Both hardened (>22 HRC) carbon and low-alloy steels are subject to hydrogen embrittlement in HF. Hydrogen blistering and stepwise cracking of plate and pipelines have been reported.

Alloy 400 (Ni-31.5Cu-1.25Fe) possesses good corrosion resistance to all concentrations of HF up to temperatures of about 120 °C (250 °F). However, the presence of oxygen in the solution is detrimental and can cause stress-corrosion cracking (SCC). Oxidizing salts also tend to increase the corrosion of nickel-copper alloys.

Copper-nickel alloy (70Cu-30Ni, C71500) is generally suitable for hot and cold dilute solutions and for higher concentrations up to about 65 °C (150 °F). Copper-nickel alloys are more sensitive to aeration and oxidizing salts in HF than are nickel-copper alloys.

Lead shows fairly good resistance to HF in concentrations below 60% at room temperature. Stronger acids attack lead.

High-Alloy Stainless Steels and High-Performance Nickel Alloys. Aerated HF or acid containing oxidizing salts, such as ferric or cupric ions, presents a problem, since the nickel-copper and copper-nickel

alloys are unstable. In these cases, the use of nonmetallics and high-alloy stainless steels such as 20Cb-3 should be considered. The Hastelloys (C-276, B-2, G, and G-3), Inconel 626, and Incoloy 825 also have good resistance to HF and to high-temperature HF vapors.

Precious metals, including gold, silver, and platinum, are all more or less unaffected by HF of any concentration at ambient temperatures, and in most cases, to the boiling point or higher.

Plastics, such as polyethylene, polypropylene, polyvinylidene fluoride and carbon-filled phenolics are limited to a maximum concentration of about 70% HF. Polyvinyl chloride is limited to about 50% concentration. Elastomers (rubbers) are also useful up to about 50 to 70% acid.

Corrosion by Phosphoric Acid

Phosphoric acid (H_3PO_4) is obtained by two different means. The wet-process acid is obtained by reacting phosphate rock with concentrated sulfuric acid and concentrating the resulting dilute acid by evaporation. The furnace acid is obtained by calcining the phosphate rock to produce elemental phosphorus, which is then oxidized and reacted with water to produce phosphoric acid. This latter acid is very pure and is used as reagent grade.

The wet-process acid is used to make phosphatic fertilizers and usually contains a number of impurities, such as HF, H_2SO_4, and SiO_2. The percentage of these impurities depends on the source of the rock, the process of reaction with H_2SO_4, and the state of concentration of the H_3PO_4.

Particularly sensitive to the impurities in wet-process acid are the stainless steels, which are widely employed in H_3PO_4 service.

In addition, a given alloy can corrode at different rates in wet-process acids from different manufacturers. Because of these differences, any comparison between alloys in this type of acid must be made from tests conducted in the same batch of acid from the same source. The wet-process acid can be considerably more corrosive than the reagent grade acid.

When heated to temperatures above 200 °C (390 °F), phosphoric acid loses its water of constitution, and salts of the resulting dehydrated acids are used in preparing some liquid fertilizers and some detergents. Use of these salts in detergents, however, has been severely restricted in an attempt to reduce pollution by phosphates. Phosphoric acid is also used in soft drinks and flavored syrups, in pharmaceuticals, in water treatment, in animal feeds, and for pickling of rustproof metals.

Table 9 Results of plant corrosion test in a H_3PO_4 evaporator

Specimens were exposed for 42 days to 53% H_3PO_4 containing 1 to 2% H_2SO_4 and 1.2 to 1.5% flouride at 120 °C (250 °F). No pitting was observed.

	Corrosion rate	
Alloy	mm/yr	mils/yr
20Cb-3	0.12	4.7
C	0.13	5
825	0.16	6.2
Type 317 stainless steel	0.26	10.4
400	0.64	25
Type 316 stainless steel	1.1	44
600	>33(a)	>1300(a)
B	>33(a)	>1300(a)

(a) Specimen was destroyed

Materials Selection Guidelines for Phosphoric Acid

Two of the most widely used materials for phosphoric acid service are type 316 stainless steel and the 20-type alloys (e.g., 20Cb-3). These alloys show very little attack in concentrations up to 85% and temperatures up to and including boiling. Other stainless steels used for wet-process phosphoric acid service include 317L and iron-nickel-chromium-molybdenum alloys 904L, alloy 28, 20Mo-4, and 20Mo-6 (Chapter 6 provides chemical compositions). Nickel-base alloys such as Incoloy 825, Inconel 625, and Hastelloy alloys G-3 and C-276 are also used for severe service conditions. Table 9 compares the corrosion resistance of stainless steels and nickel-base alloys in dilute phosphoric acid.

Lead and its alloys are also used at temperatures up to 200 °C (400 °F) and at concentrations up to 80% for pure and 85% for impure acid. Lead forms an insoluble phosphate on the surface that provides protection.

High-silicon irons, glass, and stoneware show good resistance to pure acids. Rubber and plastics show good resistance but are largely limited to temperatures of about 80 °C (175 °F). Carbon and graphite are suitable at higher temperatures.

Copper and high-copper alloys are not widely used in handling phosphoric acid. High-nickel-molybdenum alloys exhibit good resistance to pure acids but are attacked when aeration and oxidizing impurities are present. Aluminum, cast iron, steel, brass, and the ferritic and martensitic stainless steels do not possess sufficient corrosion resistance.

Corrosion by Organic Acids

Organic acids constitute another group of important chemicals currently in use in industry. These acids are produced more as precursors for other chemicals than for end use as organic acids. Acetic acid is the

most well-known member of the group and is produced in the largest volume; hence, it is emphasized in this section.

The subject of corrosion by organic acids is complicated not only by the numerous acids to be considered but also by the fact that the acids typically are not handled as a pure chemical but, rather, as process mixtures with inorganic acids, organic solvents, salts, and mixtures of several organic acids.

Acetic Acid

As stated above, acetic acid is the most important organic acid in terms of quantity produced and used. Many other organic acids show similar corrosion behavior and, in the absence of data, an approximation as to their corrosion behavior can usually be made by comparing them to acetic acid.

The materials most suitable for acetic acid service are copper and the bronzes, 1100 and 3003 aluminum, type 304 and 316 stainless steel, 20-type alloys, high-silicon cast irons, Hastelloy C-276, and Chlorimet 3. These metals and alloys are specified for the majority of plant equipment handling acetic acid.

Copper is widely used as a material of construction for acetic acid applications. More copper equipment is probably in service than any other material, although the austenitic stainless steels have replaced copper to some extent in recent years, particularly for oxidizing conditions. Copper-silicon alloys, copper-aluminum alloys, and the bronzes are also used where better mechanical or other properties are required.

In general, copper and its alloys are suitable for concentrations below 99% with temperatures below boiling and for hot vapors, provided that aeration or oxidizing conditions are absent. Hot glacial acid (pure acetic acid containing less than 1% water) is destructive. In one interesting case involving corrosion tests in a column handling hot, 75% acetic acid vapors, copper showed practically no corrosion, and types 304 and 316 stainless steel were badly attacked. Copper presents a fabrication problem, because it is relatively difficult to obtain sound welds, and silver-soldered joints often suffer galvanic corrosion at the expense of the copper. However, use of the inert-gas shielded tungsten-arc process for welding essentially eliminates both of these problems. This method of welding is now preferred over silver soldering for shop fabrication of copper equipment. Copper is also susceptible to erosion-corrosion.

Aluminum has definite limitations. In general it is corroded by hot or warm acids that are not concentrated, but it shows good resistance to hot, glacial acetic acid provided that the acid does not contain substantial quantities of acetic anhydride. The corrosion resistance increases with concentration in the higher concentration range. Aluminum is suitable for all concentrations at room temperature. A small amount

(0.01%) of water must be present in order to develop a protective film. Increasing concentrations permit the use of higher temperatures. An advantage of aluminum equipment is that colored corrosion products are not formed, and thus there is less tendency for contamination of the product.

High-Alloy Materials. The austenitic stainless steels and 20-type alloys are preferred over copper, nickel, and their alloys if aeration or oxidizing conditions exist. Type 304 is suitable for dilute and intermediate concentrations in boiling acid, but it shows appreciable attack in more concentrated boiling acid. Type 316 is suitable for boiling acid in all concentrations, although failures have occurred under reducing conditions. These 18-8 stainless alloys show borderline passivity in acetic acid and may exhibit either good resistance or destructive attack in the same corrosive environment. The presence of molybdenum in stainless steel greatly increases their corrosion resistance to acetic acid—even in the straight chromium steels, which in themselves are poorly resistant.

Alloy 20 and Duriron (high-silicon cast iron) are resistant to all concentrations, including glacial, at up to and including boiling temperatures. Alloy 20 is considerably more resistant to acetic acid than types 304 and 316. It thus allows a greater margin of safety with regard to strongly reducing conditions, contamination of product, and impurities such as sulfuric or formic acids. Alloy 20 also possesses better resistance to erosion-corrosion than types 304 and 316, copper, and aluminum. Consequently, it is a desirable material for pumps and valves. Wrought alloy 20Cb-3 finds wide application in columns, bubble caps, pump shafts, tanks, and other vessels where corrosion conditions are too severe for the more common wrought materials. Duriron is widely used for pumping hot acetic acids. For temperatures above the atmospheric boiling point, Duriron pumps are sometimes kept warm by means of copper tubing that contains steam.

Nickel and Monel are used if the temperature of the acid is below boiling and sometimes in glacial acid service. These alloys are susceptible to attack under oxidizing. Hastelloy C-276 and Chlorimet 3 are sometimes used for handling hot acetic acids when severely corrosive conditions exist and when the cost of these materials can be justified.

Effect of Temperature. Acetic acid exhibits unusual corrosion behavior with regard to temperature effects. The corrosion resistance of metals and alloys usually decreases with increasing temperature. However, copper and the stainless steels switch position as the temperature is increased. For example, copper and 18-8 or 18-8Mo, stainless steels show low corrosion rates at room temperature. At boiling temperatures, the stainless steels are superior. However, at temperatures above boiling, the stainless steels are rapidly attacked, but copper shows negligible corrosion (provided that aeration is

absent). In fact, during an investigation of a corrosion problem involving a high-temperature, high-pressure heat exchanger it was found that one end of the exchanger was corrosive to 18-8Mo and not to copper; the opposite was true at the other end. This was due to the temperature drop along the tubes. The stainless alloys exhibit borderline passivity at high temperatures, and considerable care must be exercised in selection.

Other Organic Acids

Formic acid shows corrosion characteristics similar to those of acetic acid. The main exception is aluminum, which should not be used in handling formic acid.

Maleic and lactic acid are also similar to acetic acid, except that they are more aggressive toward sensitized 18-8 stainless and attack it intergranularly. Type 316 is a preferred material for handling fatty acids in the soap industry, particularly at higher temperatures.

Corrosion by Alkalis

Common alkalis such as caustic soda (sodium hydroxide, NaOH) and potassium hydroxide are not particularly corrosive and can be handled in steel in most applications where contamination is not a problem. However, SCC and severe uniform corrosion must be guarded against at higher concentrations and temperatures. Sometimes rubber-based and other organic coatings and linings are applied to steel equipment to prevent iron contamination.

Materials Selection Guidelines for Alkalis

Carbon steel is used to store up to 50% caustic soda at temperatures from ambient to about 95 °C (200 °F). Figure 24 shows ranges of behavior of steel as a function of temperature and caustic concentration. At lower temperatures in area A, carbon steel can be used without stress relief. At higher temperatures, carbon steel can be used with stress relief of welds and bends to lower the residual stresses and to decrease the likelihood of SCC. In area C at still higher temperatures, steel is no longer recommended; nickel alloys should be considered for these applications. The danger zone for steel in concentrated caustic can also be rationalized in terms of the potential-pH diagram. In Chapter 3, the potential-pH diagram for iron was presented, and a triangle of active corrosion was predicted in highly alkaline environments. If the conditions of the environment are within this region, either SCC or localized

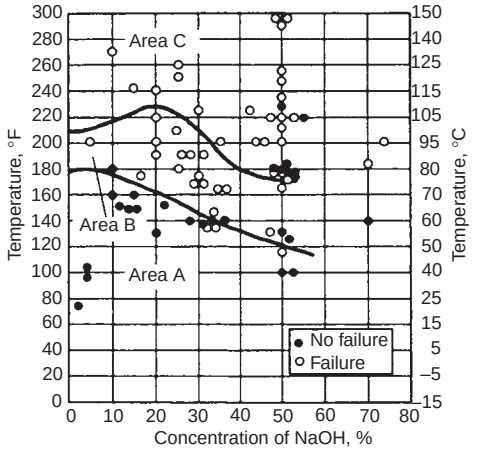


Fig. 24 NACE caustic soda chart superimposed over the data on which it is based (MTI Publication No. 15, 1985). Area A, carbon steel, no stress relief necessary; stress-relieved welded steam-traced lines. Area B, carbon steel; stress-relieved welds and bends. Area C, application of nickel alloys to be considered in this area

corrosion can occur. In severe cases, rapid uniform corrosion often referred to as caustic gouging can be observed.

Nickel and nickel alloys are extensively used for combating corrosion by caustic soda. Nickel is suitable under practically all conditions of concentration and temperature. In fact, corrosion resistance to alkalis is almost directly proportional to the nickel content of an alloy. For example, as little as 2% Ni in cast iron is beneficial. Monel (alloy 400), the austenitic stainless steels containing 8 to 20% Ni, and other nickel-bearing alloys are used in many applications involving high temperatures or control of contamination. Aluminum is unsuitable for equipment that handles caustic. Aluminum and its alloys are rapidly attacked by even dilute caustic environments.

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CHAPTER **6**

Corrosion Characteristics of Structural Materials

ALL MATERIALS, including metals and their alloys, plastics, and ceramics, are susceptible to corrosion or some form of environmental degradation. Although no single material is suitable for all applications, usually there are a variety of materials that will perform satisfactorily in a given environment. As described in Chapter 8, selection of the proper material may not simply be a matter of selecting the most corrosion resistant material. For example, carbon steels are the most common materials of construction, not because of their corrosion resistance, which is usually fair to poor, but because of their excellent mechanical properties, weldability, and low cost. When used in corrosive environments, steels usually require some form of corrosion protection, such as protective coatings, cathodic protection, or a combination of these corrosion prevention methods.

The intent of this chapter is to (a) review the corrosion behavior of the major classes of metals and alloys as well as some nonmetallic materials, (b) describe typical corrosion applications, (c) present some unique weaknesses of various types of materials, (d) point out some unique material characteristics that may be important in material selection, and (e) discuss, where appropriate, the characteristic forms of corrosion that attack specific materials. Complementary information on the forms of corrosion that affect different alloys can be found in Chapter 4. Two excellent references for more detailed information

on the corrosion behavior of various alloys are Corrosion, Volume 13 of the *ASM Handbook*, and the *Handbook of Corrosion Data*, 2nd edition, both of which are published by ASM International. The selected references at the conclusion of this chapter should also be consulted.

Carbon Steels

Carbon steels contain up to approximately 1.0% C and alloy contents of generally less than 2% by weight. Despite its relatively limited corrosion resistance, very large amounts of carbon steels are used in marine applications, nuclear and fossil fuel power plants, and transportation, chemical processing, mining, construction, and metal- processing equipment. All of these areas present unique corrosion problems.

Corrosive Service

As a rule, only the low-carbon, or mild, steels containing 0.08 to 0.28% C are considered for resistance to corrosion. They are generally more corrosion resistant than the medium-carbon (0.28 to 0.55% C) and high-carbon (0.50 to 1.0% C) groups. More importantly, they are more amenable to welding and forming, a common requirement for building structures of a variety of types.

Without some sort of surface protection, carbon steels are hardly worth considering for resisting attack by very aggressive chemicals, simply because this kind of attack is so very rapid. However, carbon steel in vast quantities has been successfully used in corrosive atmospheres and waters.

The two conditions necessary to initiate corrosion of low-carbon steel within natural environments are water and oxygen. After these essentials, a number of variables can affect the corrosion process. For example, samples of mild steels that are wholly immersed corrode faster if uninhibited water is moving around them than if the water is stagnant, but less rapidly where velocity is high if an inhibitor is present. Another of the many variables is the process called “cycling.” Water pipes and tanks corrode much more slowly if the immersed surface remains completely submerged as opposed to alternating between submersion and partial or total exposure.

Carbon steels perform well in dry, rural atmospheres, but the rate of corrosion increases quickly in high-humidity saline or industrial atmospheres. The useful service life of carbon steels has been recorded for boiler service of up to 25 years where the conditions are controlled. It is thus obvious that stainless steels, copper-base alloys, and other highly

corrosion-resistant alloys are not always required for many such applications.

Corrosive Environments. There are a number of major corrosive conditions into which carbon steels can be successfully introduced. These include the following:

- Atmospheric corrosion, including humidity, and both natural and man-made pollutants
- Soil corrosion, as determined by such factors as moisture content, level of electrical conductivity, acidity level, amount of dissolved salts, and aeration
- Corrosion in concrete, as caused primarily by chloride ions, and most successfully combated by cathodic protection
- Boiler service, which is a specialized form of aqueous corrosion that also involves elevated temperatures
- Corrosion in molten nitrate salts, which are used for heat treatment baths (plain carbon and low-alloy steels form protective iron oxide films that effectively protect the metal surface to approximately 500 °C, or 930 °F)
- Corrosion in sulfuric acid at ambient temperatures and in the concentration range of 65 to 100%

Protection of Steel from Corrosion

General Considerations. Corrosion protection is often an essential consideration when selecting carbon or alloy steel for a given structural application. Corrosion can reduce the load-carrying capacity of a component either by generally reducing its size (cross section) or by pitting. Pitting not only reduces the effective cross section in the pitted region but can also introduce stress raisers that may initiate cracks. Any technique that reduces or eliminates corrosion will extend the life of a component and increase its reliability.

Overall economics, environmental conditions, degree of protection needed for the projected life of the part, consequences of unexpected service failure, and importance of appearance are the chief factors that determine not only whether a steel part needs to be protected against corrosion, but also the most effective and economical method of providing the protection. There are two primary methods of minimizing the corrosion of steels. The first is to separate the reacting phases, and the second is to reduce the reactivity of the reacting phases. The separation of the reacting phases can be accomplished by using metallic, inorganic, or organic coatings and film-forming inhibitors. Reactivity can be reduced by alloying, anodic or cathodic protection, and chemical treatment of the environment.

Some methods of protection combine two or more elements. For example, a baked epoxy paint applied over a chromate conversion coating on a galvanized steel part is, in reality, a combination of three types of corrosion protection. The epoxy paint provides a physical barrier to the corroding medium, the chromate conversion coating provides an inhibitor if the medium somehow penetrates the paint, and the galvanized coating (zinc) is an effective sacrificial anode (galvanic device) that diverts corrosion from the underlying steel part. A guide to the corrosion protection of carbon steels is provided in Table 1.

In addition to the corrosion prevention methods described above, design and material selection are important to the overall corrosion performance of a part. Many exterior steel structures—highway guardians and electric transmission towers, for example—have been designed to prevent rain from collecting on horizontal surfaces, in depressions, or at joints. Galvanic couples usually are not a serious consideration when steel is exposed to the atmosphere, but they become very important when a strong electrolyte, such as seawater, is involved.

Table 1 Guide to corrosion prevention for carbon steels in various environments

Preventive method	Atmosphere	Soil	Fresh water	Seawater	Steam systems	Acids and pickling baths
Metal coatings: electroplating, galvanizing, thermal spraying	Galvanizing very effective; plating with other metals used for both decorative appearance and corrosion protection	Not recommended	Galvanizing used in potable water	Not recommended	Not recommended	Not recommended
Painting: chemical treatment, priming, and painting	Most economical and effective corrosion prevention	Seldom used	Fairly effective	Special paint systems used	Not recommended	Not recommended
Cathodic protection	Not recommended	Most economical and effective method, especially with organic coatings other than paint	Fairly effective with organic coatings	Very effective	Not recommended	Effective under special conditions
Inhibitors: liquid and vapor	Not recommended	Not recommended	Effective in some applications, especially cooling waters	Fairly effective in some applications	Very effective	Very effective
Alloying additions to steel	Very effective, especially copper-bearing and HSLA steels	Not effective	Not effective	Only effective with much alloying	Chromium-molybdenum steels are very effective	Only effective with much alloying
Removal of oxygen from environment	Not recommended	Not recommended	Seldom used	Very effective, especially in desalination and hot seawater	Very effective	Not recommended
Removal of more noble metals and elimination of galvanic couples	Usually not necessary	Fairly effective	Effective	Necessary	Advisable	Not effective
Organic coatings other than paint	Seldom used to replace painting	Used to advantage with cathodic protection	Fairly effective with cathodic protection	Used to advantage with cathodic protection	Not recommended	Have been used

Protective Coatings. Many types of coatings are applied to enhance the corrosion resistance of carbon steels, particularly in outdoor atmospheres. Commonly used coatings include the following:

- Rust-preventative temporary coatings, for example, oils containing rust inhibitors
- Organic coatings (paints and plastic or rubber linings)
- Hot-dip galvanized and electrogalvanized coatings
- Thermal spray coatings (zinc, aluminum, or zinc-aluminum alloys)
- Electroless and electroplated coatings, for example, nickel-phosphorus, nickel, chromium, nickel-chromium-copper, zinc, and cadmium
- Clad coatings, for example, roll-bonded stainless steel on carbon steel
- Pack cementation coatings for improved high-temperature oxidation resistance

Each of these coating methods is described in Chapter 9.

Inhibitors find their major uses in acid-pickling solutions, acidic service environments, steam systems, and neutral and near-neutral aqueous solutions. Inhibitors may be organic or inorganic compounds, and they are usually dissolved in aqueous environments. Inhibitors have been added to chemical-conversion treatment baths and to paint primers. Vapor-phase inhibitors are used in confined atmospheres.

Some of the most effective inorganic inhibitors are chromates, nitrates, silicates, carbonates, phosphates, and arsenates (it should be noted that environmental concerns have significantly impacted on the use of chromates). Among the many organic inhibitors are amines, heterocyclic nitrogen compounds, sulfur compounds (such as thioethers, thioalcohols, thioamides, thiourea, and hydrazine), some natural compounds (such as glue and proteins), and mixtures of two or more compounds. See Chapter 9 for additional information on inhibitors.

Cathodic Protection. The most economical method for protecting underground or underwater steel structures from corrosion is usually cathodic protection. The use of cathodic protection for long-term corrosion prevention for underground pipelines, oil and gasoline tanks, offshore drilling rigs, wellhead structures, steel piling, piers, bulkheads, offshore pipelines, gathering systems, drilling barges, and other underground and underwater structures is now a fairly standard procedure.

In the cathodic protection method, a direct electrical current is applied to the steel structure. The direct current can be supplied either by galvanic action from sacrificial anodes or by impressed current from a rectifier. Coatings of coal tar, coal tar/epoxy, or fusion-bonded epoxy powders are generally used on steel structures in conjunction with cathodic protection to lessen the amount of current required; with such

coatings the current need only protect the steel at holidays or flaws in the coating. More detailed information on cathodic protection can be found in Chapter 10.

Weathering Steels

Weathering steels are a subset of high-strength low-alloy (HSLA) steels, which contain small amounts of alloying elements such as copper and phosphorus for improved atmospheric corrosion resistance. The original architectural grade is covered by ASTM A 242, "Standard Specification for High-Strength Low-Alloy Structural Steel," while the heavier structural grades are covered by ASTM A 588, "Standard Specifications for High-Strength Low-Alloy Structural Steel with 50 ksi (345 MPa) Minimum Yield Point to 4 in. (100 mm) Thick." Chemical composition variations among the four grades of A 588 are listed in Table 2. Other HSLA steels are microalloyed to provide specific desirable combinations of properties such as strength, toughness, formability, and weldability.

Characteristics of the Protective Oxide Film. On alternate wetting and drying, the weathering steels develop a thick, protective oxide film, and their corrosion rate decreases to much lower values than those for carbon steel. This alternate wetting and drying cycle produces a protective oxide film on weathering steel, but it produces a more porous nonprotective oxide film on carbon steel. Repeated cycles of this type ultimately result in complete coverage of the surface and a slowing of the corrosion rate. This behavior can be best expressed by the time/corrosion curves shown in Fig. 1.

The key to the development of the protective oxide film is the alternate wetting and drying cycle typified by normal night and day exposure. Under conditions of long-term immersion in fresh water or seawater, the corrosion rate is the same as that for carbon steel—about 0.13 mm/year (5 mils/year). Similarly, burial in soil having varying moisture levels will result in behavior similar to that of carbon steel. The lack of a drying cycle inhibits the formation of the characteristic oxide film. The implication then is to avoid structural features such as pockets that can

Table 2 Compositional limits for weathering steel grades (ASTM A 588) used in building and bridge construction

Grade	UNS designation	Heat compositional limits(a), %									
		C	Mn	P	S	Si	Cr	Ni	Cu	V	Other
A	K11430	0.10–0.19	0.90–1.25	0.04	0.05	0.15–0.30	0.40–0.65	…	0.25–0.40	0.02–0.10	…
B	K12043	0.20	0.75–1.25	0.04	0.05	0.15–0.30	0.40–0.70	0.25–0.50	0.20–0.40	0.01–0.10	…
C	K11538	0.15	0.80–1.35	0.04	0.05	0.15–0.30	0.30–0.50	0.25–0.50	0.20–0.50	0.01–0.10	…
K	…	0.17	0.5–1.20	0.04	0.05	0.25–0.50	0.40–0.70	0.40	0.30–0.50	…	0.10 Mo, 0.005–0.05 Nb

(a) If a single value is shown, it is a maximum unless otherwise stated.

retain water for lengthy periods and to paint and portion of a structure, such as a column, that will be in the soil and subject to rain or snow drainage.

Advantages and Limitations. Weathering steels are useful structural materials, falling midway between painted carbon steel and the stainless steels in terms of corrosion resistance. Depending on environmental conditions, they can be used in the unpainted or the painted condition. Weathering steels contribute synergistically to extending the service life of protective coatings, resulting in lower maintenance costs. Weathering steels are popular in architectural applications and in sculpture.

The primary limitations of weathering steels involve frequent and long-term contact with water caused by the inadvertent creation of pockets and crevices that trap and retain moisture. Below-deck structural members on bridges can be attacked by deicing salt solutions that leak through poorly maintained expansion-joint devices. Bridge structures located close to the Gulf Coast shoreline are subject to constant onshore breezes, which, on contact with the structure, deposit sea salt residues in areas where they cannot be washed away by rain.

Like any carbon steel material used in below-ground applications, weathering steels require a protective coating when constantly immersed in fresh water or seawater. The protective oxide coating can develop only under conditions of alternate wetting and drying that occur in normal day and night exposure.

To avoid staining caused by the drainage of moisture that contains particles of rust, techniques of retention and diversion must be employed. Finally, field installations at ground level should be protected from the destructive effects of damp shrubbery, grass, and field crops. Clear space is necessary so that the structure can maintain a dry state except during intermittent periods of rain and snow.

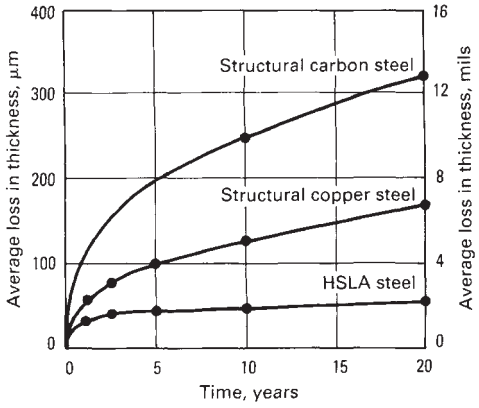


Fig. 1 Atmospheric corrosion versus time in a semiindustrial or industrial environment

Alloy Steels

Alloy (or low-alloy) steels constitute a category of ferrous materials with mechanical properties superior to those of ordinary carbon steels; this is the result of additions of alloying elements such as chromium, nickel, and molybdenum. Total alloy content can range from 0.5 to 1% and up to levels just below those of stainless steels. For many alloy steels, the primary function of the alloying elements is to increase hardenability in order to optimize mechanical properties and toughness after heat treatment. In some cases, however, alloy additions are used to reduce environmental degradation under certain specified service conditions.

Chromium-molybdenum steels are more corrosion resistant than carbon steels. Chromium concentrations typically range from 1 to 9%, and molybdenum concentrations range from 0.5 to 1%. Such steels are used extensively in higher-temperature applications—for example, boiler tubes in electric power plants. The resistance of chromium-molybdenum steels to high-temperature hydrogen damage is often more important than aqueous corrosion resistance. Prevention of high-temperature hydrogen damage is discussed in Chapter 4.

High-strength steels are used in applications where weight reduction is critical. Higher strength levels are developed by cold work, quenching and tempering, and precipitation hardening. As strength levels increase above approximately 1050 MPa (150 ksi), environmental cracking becomes a major consideration. In the presence of hydrogen sulfide, the level of concern is above approximately 700 MPa (100 ksi).

Cast Irons

Cast iron is a generic term applied to a large family of ferrous alloys. Cast irons are primarily alloys of iron that contain more than 2% C and 1% or more Si. Low raw material costs and relative ease of manufacture make cast irons the least expensive of the engineering metals. Cast irons can be cast into intricate shapes because of their excellent fluidity and relatively low melting points and can be alloyed for improvement of corrosion resistance and strength. With proper alloying, the corrosion resistance of cast irons can equal or exceed that of stainless steels and nickel-base alloys.

Because of the excellent properties obtainable with these low-cost engineering materials, cast irons find wide application in environments that demand good corrosion resistance, including water, soils, acids, alkalis, saline solutions, organic compounds, sulfur compounds, and

liquid metals. In some services, alloyed cast irons are the only economical material of construction.

Commercially Available Cast Irons

The form and shape in which carbon occurs determine the type of cast iron. Table 3 identifies the classifications of cast iron: white, malleable, gray, ductile, and compacted graphite. Based on corrosion resistance, cast irons can be grouped into five basic categories. Each is discussed below.

Unalloyed gray, ductile, malleable, and white cast irons represent the largest category. All of these materials have carbon and silicon contents of 3% or less and no deliberate additions of nickel, chromium, copper, or molybdenum. As a group, these materials exhibit corrosion resistance that equals or slightly exceeds that of unalloyed steels, but they show the highest rates of attack among the cast irons. These materials are available in a wide variety of configurations and alloys.

Low and moderately alloyed irons contain the iron and silicon contents of unalloyed cast irons plus up to several percent of nickel, copper, chromium, or molybdenum. As a group, these materials exhibit two to three times the service life of unalloyed cast irons.

High-nickel austenitic cast irons, commonly referred to as Ni-Resists, contain large percentages of nickel (18 to 36%) and copper and are fairly resistant to concentrated sulfuric (H_2SO_4) and phosphoric (H_3PO_4) acids at slightly elevated temperatures, hydrochloric acid (HCl) at room temperature, and organic acids such as acetic (CH_3COOH), oleic, and stearic. When nickel levels exceed 18%, austenitic cast irons are nearly immune to alkalis or caustics, although stress-corrosion cracking (SCC) can occur. High-nickel cast irons can be nodularized to yield ductile irons.

High-chromium cast irons are basically white cast irons, alloyed with 12 to 30% chromium. Other alloying elements may also be added to improve resistance to specific environments. When chromium levels exceed 20%, high-chromium cast irons exhibit good resistance to oxidizing acids, particularly nitric acid (HNO_3). High-chromium irons are not resistant to reducing acids. They are used in saline solutions, organic acids, and marine and industrial atmospheres. These materials display excellent resistance to abrasion, and with proper alloying additions they

Table 3 Cast iron classification based on carbon form and shape

Type of cast iron	Carbon form and shape
White	Iron carbide compound
Malleable	Irregularly shaped nodules of graphite
Gray	Graphite flakes
Ductile	Spherical graphite nodules
Compacted graphite	Short, fat interconnected flakes (intermediate between ductile and gray cast iron)

can also resist combinations of abrasives and liquids, including some dilute acid solutions.

High-silicon cast irons are principally alloyed with 12 to 18% Si, with more than 14.2% Si needed to develop excellent corrosion resistance. Chromium and molybdenum are also used in combination with silicon to develop corrosion resistance to specific environments. High-silicon cast irons represent the most universally corrosion resistant alloys available at moderate cost. When silicon levels exceed 14.2%, these cast irons exhibit excellent resistance to H_2SO_4, HNO_3, HCl, CH_3COOH, and most other mineral and organic acids and corrosives.

These materials display good resistance in oxidizing and reducing environments and are not appreciably affected by concentration or temperature. Exceptions to universal resistance are hydrofluoric acid (HF), fluoride salts, sulfurous acid (H_2SO_3), sulfite compounds, strong alkalis, and alternating acid-alkali conditions.

High-silicon cast irons are defined in ASTM standards A 518 and A 861. In addition, some proprietary compositions not included in these standards, such as alloy SD77 (Fe-4Cr-3Mo-16Si-1Mn-1C), are manufactured for high-temperature HCl service.

Graphitic Corrosion

A form of corrosion unique to cast irons is a selective leaching attack commonly referred to as graphitic corrosion. Graphitic corrosion is observed in gray cast irons in relatively mild environments, where selective leaching of iron leaves a graphite network. Selective leaching occurs because the graphite is cathodic to iron, and the gray iron structure establishes an excellent galvanic cell. This form of corrosion generally occurs only when corrosion rates are low. If the metal corrodes more rapidly, the entire surface, including the graphite, is removed, and uniform corrosion occurs.

Graphitic corrosion can cause significant problems. Although no dimensional changes occur, the cast iron loses its strength and metallic properties. Thus, without detection, a potentially dangerous situation may develop in pressure-containing applications. Examples of graphitic corrosion can be found in Chapter 4.

Graphitic corrosion is often erroneously referred to as graphitization. Graphitization is a microstructural change that sometimes occurs in carbon or low-alloy steels that are subjected to moderately high temperatures (~455 to 595 °C, or 850 to 1100 °F) for extended periods of time (≥40,000 h). Graphitization results from the decomposition of pearlite into ferrite and carbon (graphite) and can embrittle steel parts, especially when the graphite particles form along a continuous zone through a load-carrying member.

Stainless Steels

Stainless steels are iron-base alloys containing at least 11% chromium. With increasing chromium content and the presence or absence of some 10 to 15 other elements, stainless steels can provide and extraordinary range of corrosion resistance. Various grades have been used for many years in environments as mild as open air in architectural applications and as severe as the chemically active product streams in the chemical-processing industries.

Stainless steels are categorized in five distinct families according to their crystal structure and strengthening precipitates. Each family exhibits its own general characteristic in terms of mechanical properties and corrosion resistance. Within each family is a range of grades that vary in composition, corrosion resistance, and cost.

Stainless steels are susceptible to several forms of localized corrosive attack. The avoidance of such localized corrosion is the focus of most of the effort involved in selecting stainless steels. Furthermore, the corrosion performance of stainless steels can be strongly affected by design, fabrication, surface conditioning, and maintenance practices.

The selection of a grade of stainless steel for a particular application involves many factors, but most often begins with corrosion resistance. It is not enough merely to consider the design conditions. First, the probable service environment must be characterized, including anticipated excursions or upsets in service conditions. The suitability of various grades can be estimated from laboratory tests or from documentation of field experience in comparable environments. Once grades with adequate corrosion resistance have been identified, mechanical properties, ease of fabrication, the types and degree of risk present in the application, the availability of the necessary product forms, and cost can be considered.

Stainless Steel Families

The five major families of stainless steels are defined by crystallographic structure. Each family is distinct with regard to typical mechanical properties. Furthermore, each tends to share a common nature in terms of resistance/susceptibility to particular forms of corrosion. Table 4 lists the SAE/AISI grades of stainless steel, their UNS designations, and chemical compositions. Table 5 lists several proprietary and nonstandard stainless steels. Figure 2 provides a useful summary of some of the compositional and property linkages in the stainless steel families.

Ferritic Stainless Steels. The simplest stainless steels contain only iron and chromium. Chromium is a ferrite stabilizer; therefore, the stability

Table 4 Compositions of AISI standard grades of stainless steels

UNS designation	AISI type	Composition(a), % C	Mn	P	S	Si	Cr	Ni	Mo	Others
Austenitic grades										
S20100	201	0.15	5.60–7.50	0.06	0.03	1.00	16.00–18.00	3.50–5.50	…	0.25N
S20200	202	0.15	7.50–10.0	0.06	0.03	1.00	17.00–19.00	4.00–6.00	…	0.25N
S20500	205	0.12–0.25	14.00–15.50	0.03	0.03	0.50	16.50–18.00	1.00–1.75	…	0.32–0.40N
S30100	301	0.15	2.00	0.045	0.03	1.00	16.00–18.00	6.00–8.00	…	…
S30200	302	0.15	2.00	0.045	0.03	1.00	17.00–19.00	8.00–10.00	…	…
	302B	0.15	2.00	0.045	0.03	2.00–3.00	17.00–19.00	8.00–10.00	…	…
S30300	303	0.15	2.00	0.2	0.15	1.00	17.00–19.00	8.00–10.00	0.60	…
	303Se	0.15	2.00	0.2	0.06	1.00	17.00–19.00	8.00–10.00	…	0.15Se min
S30400	304	0.08	2.00	0.045	0.03	1.00	18.00–20.00	8.00–10.50	…	…
S30403	304L	0.03	2.00	0.045	0.03	1.00	18.00–20.00	8.00–12.00	…	…
S30430	S30430	0.08	2.00	0.045	0.03	1.00	17.00–19.00	8.00–10.00	…	3.00–4.00Cu
	304N	0.08	2.00	0.045	0.03	1.00	18.00–20.00	8.00–10.50	…	0.10–0.16N
S30500	305	0.12	2.00	0.045	0.03	1.00	17.00–19.00	10.50–13.00	…	…
S30800	308	0.08	2.00	0.045	0.03	1.00	19.00–21.00	10.00–12.00	…	…
S30900	309	0.2	2.00	0.045	0.03	1.00	22.00–24.00	12.00–15.00	…	…
	309S	0.08	2.00	0.045	0.03	1.00	22.00–24.00	12.00–15.00	…	…
S31000	310	0.25	2.00	0.045	0.03	1.50	24.00–26.00	19.00–22.00	…	…
	310S	0.08	2.00	0.045	0.03	1.50	24.00–26.00	19.00–22.00	…	…
S31400	314	0.25	2.00	0.045	0.03	1.50–3.00	23.00–26.00	19.00–22.00	…	…
S31600	316	0.08	2.00	0.045	0.03	1.00	16.00–18.00	10.00–14.00	2.00–3.00	…
	316F	0.08	2.00	0.2	0.10 min	1.00	16.00–18.00	10.00–14.00	1.75–2.50	…
S31603	316L	0.03	2.00	0.045	0.03	1.00	16.00–18.00	10.00–14.00	2.00–3.00	…
	316N	0.08	2.00	0.045	0.03	1.00	16.00–18.00	10.00–14.00	2.00–3.00	0.10–0.16N
S31700	317	0.08	2.00	0.045	0.03	1.00	18.00–20.00	11.00–15.00	3.00–4.00	…
S31703	317L	0.03	2.00	0.045	0.03	1.00	18.00–20.00	11.00–15.00	3.00–4.00	…
S32100	321	0.08	2.00	0.045	0.03	1.00	17.00–19.00	9.00–12.00	…	Ti:5×C min
	329	0.10	2.00	0.04	0.03	1.00	25.00–30.00	3.00–6.00	1.00–2.00	…
	330	0.08	2.00	0.04	0.03	0.75–1.50	17.00–20.00	34.00–37.00	…	0.10Ta, 0.20Nb
S34700	347	0.08	2.00	0.045	0.03	1.00	17.00–19.00	9.00–13.00	…	Nb:10×C min
S34800	348	0.08	2.00	0.045	0.03	1.00	17.00–19.00	9.00–13.00	…	Nb:10×C min
	384	0.08	2.00	0.045	0.03	1.00	15.00–17.00	17.00–19.00	…	…
Ferritic grades										
S40500	405	0.08	1.00	0.04	0.03	1.00	11.50–14.50	…	…	0.10–0.30Al
S40900	409	0.08	1.00	0.045	0.045	1.00	10.50–11.75	…	…	Ti:6×C–0.75
S42900	429	0.12	1.00	0.04	0.03	1.00	14.00–16.00	…	…	…
S43000	430	0.12	1.00	0.04	0.03	1.0	16.00–18.00	…	…	…
	430F	0.12	1.25	0.06	0.15	1.00	16.00–18.00	…	0.60	…
	430FSe	0.12	1.25	0.06	0.06	1.00	16.00–18.00	…	…	0.15Si min
S43400	434	0.12	1.00	0.04	0.03	1.00	16.00–18.00	…	0.75–1.25	…
S43600	436	0.12	1.00	0.04	0.03	1.00	16.00–18.00	…	0.75–1.25	Nb:5×C–0.70
S44200	442	0.20	1.00	0.04	0.03	1.00	18.00–23.00	…	…	…
S44400	444	0.25	1.00	0.04	0.03	1.00	17.50–19.50	…	…	(Ti+Nb): 0.2+4(C+N)–0.8
S44600	446	0.20	1.50	0.04	0.03	1.00	23.00–27.00	…	…	0.25N
Martensitic grades										
S40300	403	0.15	1.00	0.04	0.03	0.50	11.50–13.00	…	…	…
S41000	410	0.15	1.00	0.04	0.03	1.00	11.50–13.50	…	…	…
S41400	414	0.15	1.00	0.04	0.03	1.00	11.50–13.50	1.25–2.50	…	…
S41600	416	0.15	1.25	0.06	0.15 min	1.00	12.00–14.00	…	0.60	…
	416Se	0.15	1.25	0.06	0.06	1.00	12.00–14.00	…	…	0.15Se min
S42000	420	0.15 min	1.00	0.04	0.03	1.00	12.00–14.00	…	…	…
	420F	0.15 min	1.25	0.06	0.15 min	1.00	12.00–14.00	…	0.60	…
S42200	422	0.20–0.25	1.00	0.025	0.025	0.75	11.00–13.00	0.50–1.00	0.75–1.25	0.15–0.30V, 0.75–1.25W
S43100	431	0.20	1.00	0.04	0.03	1.00	15.00–17.00	1.25–2.50	…	…
	440A	0.60–0.75	1.00	0.04	0.03	1.00	16.00–18.00	…	0.75	…
	440B	0.75–0.95	1.00	0.04	0.03	1.00	16.00–18.00	…	0.75	…
	440C	0.95–1.20	1.00	0.04	0.03	1.00	16.00–18.00	…	0.75	…
Precipitation-hardening grades										
S13800	PH 13-8 Mo	0.05	0.20	0.010	0.008	0.10	12.25–13.25	7.50–8.50	2.00–2.50	0.90–1.35Al, 0.01N
S15500	PH 15-5	0.07	1.00	0.04	0.03	1.00	14.00–15.50	3.50–5.50	…	2.50–4.50Cu, 0.15–0.45Nb
S17400	PH 17-4	0.07	1.00	0.04	0.03	1.00	15.50–17.50	3.00–5.00	…	3.00–5.00Cu, 0.15–0.45Nb
S17700	PH 17-7	0.09	1.00	0.04	0.04	0.04	16.00–18.00	6.50–7.75	…	0.75–1.50Al

(a) Maximum unless otherwise indicated; all compositions include balance of iron.

of the ferritic structure increases with chromium content. Ferrite has a body-centered cubic crystal structure, and it is characterized as magnetic and relatively high in yield strength but low in ductility and work hardenability. Ferrite shows an extremely low solubility for such interstitial elements as carbon and nitrogen. The ferritic grades exhibit a transition from ductile-to-brittle behavior over a rather narrow temperature

Table 5 Compositions of some proprietary and nonstandard stainless steels

UNS designation	Common name	Composition(a), %								
		C	Mn	P	S	Si	Cr	Ni	Mo	Others
Austenitic grades										
S24100	18Cr-2Ni-12Mn	0.15	11.0–14.0	0.060	0.03	1.00	16.50–19.50	0.5–2.50	…	0.2–0.45N
S20910	Nitronic 50 (22-13-5)	0.06	4.0–6.0	0.040	0.03	1.00	20.50–23.50	11.50–13.50	1.50–3.00	0.1–0.3Nb, 0.2–0.4N, 0.1–0.3V
S30345	303Al MODIFIED	0.15	2.00	0.050	0.11–0.16	1.00	17.00–19.00	8.00–10.00	0.40–0.60	0.60–1.00Al
	303BV(b)	0.11	1.75	0.03	0.14	0.35	17.75	9.00	0.50	0.75Al
	302HQ-FM	0.06	2.00	0.04	0.14	1.00	16.00–19.00	9.00–11.00	…	1.3–2.4Cu
S30430	302HQ	0.10	2.00	0.045	0.03	1.00	17.00–19.00	8.00–10.00	…	3.0–4.0Cu
S30453	304LN	0.03	2.00	0.045	0.03	1.00	18.00–20.00	8.00–12.00	…	0.1–0.16N
S31653	316LN	0.03	2.00	0.045	0.03	1.00	16.00–18.00	10.00–14.00	2.00–3.00	0.1–0.16N
S31753	317LN	0.03	2.00	0.045	0.30	1.00	18.00–20.00	11.00–15.00	3.00–4.00	0.1–0.2N
S31725	317LM	0.03	2.00	0.045	0.03	0.075	18.00–20.00	13.00–17.00	4.00–5.00	0.1N, 0.75Cu
	317LMN	0.03	2.00	0.045	0.03	0.075	18.00–20.00	13.00–17.00	4.00–5.00	0.1–0.2N
N08904	904L	0.02	2.00	0.045	0.035	1.00	19.00–23.00	23.0–28.0	4.00–5.00	1.0–2.0Cu
N08700	JS700	0.04	2.00	0.04	0.03	1.00	19.00–23.00	24.0–26.0	4.3–5.0	0.5Cu, Nb:(8×C) – 1.00, 0.005Pb, 0.035Sn
	JS777	0.025	1.70	0.03	0.03	0.50	19.00–23.00	24.0–26.0	4.00–5.00	2.10Cu, 0.25Nb
N08020	20Cb-3	0.07	2.00	0.045	0.035	1.00	19.00–21.00	32.00–38.00	2.00–3.00	3.0–4.0Cu, (8×C)Nb
N08024	20Mo-4	0.03	1.00	0.035	0.035	0.50	22.5–25.00	35.00–40.00	3.50–5.00	0.5–1.5Cu, 0.15–0.35Nb
N08026	20Mo-6	0.03	1.00	0.03	0.03	0.50	22.00–26.00	33.0–37.20	5.00–6.70	2.0–4.0Cu
N08028	Alloy 28	0.03	2.50	0.03	0.03	1.00	26.00–28.00	29.5–32.5	3.0–4.0	0.6–1.4Cu
N08367	AL-6×N	0.03	2.0	0.04	0.03	1.00	20.0–22.0	23.50–25.50	6.0–7.0	0.18–0.25N
S31254	254SMO	0.02	1.00	0.03	0.01	0.80	19.50–20.50	17.50–18.50	6.0–6.5	0.5–1.0Cu, 0.18–0.22N
Ferritic grades										
S44627	E-Brite	0.01	0.40	0.02	0.02	0.40	25.0–27.0	0.50	0.75–1.50	0.05–0.2Nb, 0.2Cu, 0.015N
S44635	MONIT	0.025	1.00	0.04	0.03	0.75	24.5–26.0	3.50–4.50	3.50–4.50	0.035N, Nb+Ti:0.20 + 4(C+N)-0.80
S44660	Sea-Cure	0.025	1.00	0.04	0.03	1.00	25.0–27.0	1.50–3.50	2.50–3.50	0.035N, Nb+Ti:0.20+4(C+N)-0.80
S44735	AL-29-4C	0.03	1.00	0.04	0.03	1.00	28.0–30.0	1.00	3.60–4.20	0.045N, Nb+Ti:6(C+N)
S4473S	Usinor 290 Mo	0.03	1.00	0.04	0.03	1.00	28.0–30.0	1.00	3.60–4.20	0.045N, Nb+Ti:6(C+N)
S44800	AL-29-4-2	0.01	0.30	0.025	0.02	0.20	28.0–30.0	2.0–2.5	3.50–4.20	0.15Cu, 0.02N, C+N:0.025 max
Duplex grades										
S31803	2205	0.03	2.00	0.03	0.02	1.00	21.0–23.0	4.50–6.50	2.50–3.50	0.08–0.2N
S31200	44LN	0.03	2.00	0.045	0.03	1.00	24.0–26.0	5.50–6.50	1.20–2.00	0.14–0.2N
S31260	DP-3	0.03	1.00	0.03	0.03	0.75	24.0–26.0	5.50–7.50	2.50–3.50	0.2–0.8Cu, 0.1–0.3N
S31500	3RE60	0.03	1.20–2.00	0.03	0.03	1.4–2.0	18.0–19.0	4.25–5.25	2.50–3.00	…
S32550	Ferralium 255	0.04	1.50	0.04	0.03	1.00	24.0–27.0	4.50–6.50	2.00–4.00	1.5–2.5Cu, 0.1–0.25N
S32950	7Mo-PLUS	0.03	2.00	0.035	0.01	0.60	26.0–29.0	3.50–5.20	1.00–2.50	0.15–0.35N
Martensitic grades										
S41040	XM-30	0.15	1.00	0.04	0.03	1.00	11.50–13.50	…	…	0.05–0.2Nb
S41610	XM-6	0.15	2.50	0.06	0.15	1.00	12.00–14.00	…	0.60	…
Precipitation-hardenable grades										
S45000	Custom 450	0.05	1.00	0.03	0.03	1.00	14.00–16.00	5.00–7.00	0.5–1.00	1.25–1.75Cu, Nb:8×C min
S45500	Custom 455	0.05	0.50	0.04	0.03	0.50	11.0–12.50	7.50–9.50	0.50	0.1–0.5Nb, 1.50–2.50Cu, 0.8–1.40Ti

(a) Maximum unless otherwise indicated; all compositions contain balance of iron. (b) Nominal composition

range. At higher carbon and nitrogen contents, and especially at higher chromium levels, this ductile-to-brittle transition can occur above ambient temperature. This possibility severely restricted the use of ferritic grades before the development of improved stainless steel refining practices. The ferritic family was previously limited to type 446 for oxidation-resistant applications and to types 430 and 434 for such corrosion applications as automotive trim. The fact that these grades were readily sensitized to intergranular corrosion as a result of welding or thermal exposure further limited their use.

Improved refining processes allow significantly reduced levels of carbon and nitrogen. This newer generation of ferritic stainless steels includes type 444 and the more highly alloyed ferritic grades shown in Table 5. At the low but effective carbon levels, these grades are tougher and more weldable than the first generation of ferritic stainless steels. Nevertheless, limited toughness generally restricts their use to sheet or lighter-gage tubulars.

Ferritic stainless steels are highly resistant and in some cases immune to chloride stress-corrosion cracking (SCC). These grades are frequently considered for thermal transfer applications.

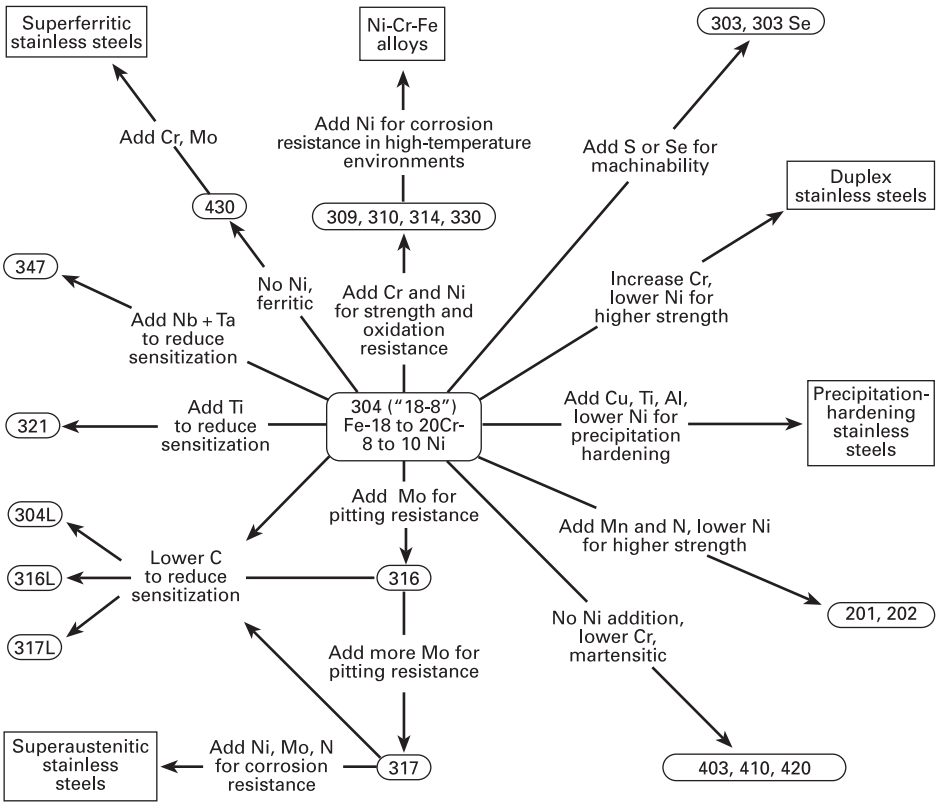


Fig. 2 Compositional and property linkages in the stainless steel family of alloys

Austenitic Stainless Steels. The detrimental effects of carbon and nitrogen in ferrite can be overcome by changing the crystal structure to austenite, a face-centered cubic crystal structure. This change is accomplished by adding austenite stabilizers—most commonly nickel, but also manganese and nitrogen. Austenite is characterized as nonmagnetic, and it is usually relatively low in yield strength with high ductility, rapid work-hardening rates, and excellent toughness. These desirable mechanical properties, combined with ease of fabrication, have made the austenitic grades, especially type 304, the most common of the stainless grades.

Improved corrosion resistance is obtained by adding molybdenum. With nitrogen additions, it is possible to produce austenitic grades with up to 6% Mo for improved corrosion resistance in chloride environments. Other special types include the high-chromium grades for high-temperature applications and the high-nickel grades for inorganic acid environments.

The austenitic stainless steels can be sensitized to intergranular corrosion by welding or by longer-term thermal exposure. These thermal exposures lead to the precipitation of chromium carbides in grain boundaries and to the depletion of chromium adjacent to these carbides. Sensitization can be greatly delayed or prevented by the use of lower-carbon L-grades (<0.03% C) or stabilized grades, such as types 321 and 347, which include additions of carbide-stabilizing elements (titanium and niobium, respectively).

The common austenitic grades, type 304 and 316, are especially susceptible to chloride SCC. All austenitic stainless steels exhibit some degree of susceptibility, but several of the high-nickel, high-molybdenum grades are satisfactory with respect to stress-corrosion attack in most engineering applications.

Martensitic Stainless Steels. With lower chromium levels and relatively high carbon levels, it is possible to obtain austenite at elevated temperatures and then, with accelerated cooling, to transform this austenite to martensite, which has a body-centered tetragonal structure. Just as with plain carbon and low-alloy steels, this strong, brittle martensite can be tempered to favorable combinations of high strength and adequate toughness. Because of the ferrite-stabilizing character of chromium, the total chromium content, and thus the corrosion resistance, of the martensitic grades is somewhat limited. In recent years, nitrogen, nickel, and molybdenum additions at somewhat lower carbon levels have produced martensitic stainless steels with improved toughness and corrosion resistance.

The duplex stainless steels can be thought of as chromium-molybdenum ferritic stainless steels to which sufficient austenite stabilizers have been added to produce a balance of ferrite and austenite at room temperature. Such grades can have the high chromium and molybdenum

contents responsible for the excellent corrosion resistance of ferritic stainless steels, as well as the favorable mechanical properties of austenitic stainless steels. In fact, the duplex grades with about equal amounts of ferrite and austenite have excellent toughness, and their strength exceeds either phase present singly.

First-generation duplex grades, such as type 329, achieve this phase balance primarily by nickel additions. The addition of nitrogen to the second generation of duplex grades restores the phase balance more rapidly and minimizes chromium and molybdenum segregation without annealing. The newer duplex grades combine high strength, good toughness, high corrosion resistance (including good resistance to chloride SCC), and good production economy in the heavier product forms.

The precipitation-hardening stainless steels are chromium-nickel grades that can be hardened by an aging treatment at a moderately elevated temperature. These grades may have austenitic, semiaustenitic, or martensitic crystal structures. In the solution-annealed condition, these grades have properties similar to those of the austenitic grades and are thus readily formed. Hardening is achieved after fabrication within a relatively short time at 480 to 620 °C (900 to 1150 °F). The precipitation-hardened grades must not be subjected to further exposure to elevated temperature by welding or environment, because the strengthening can be lost by overaging of the precipitates.

Mechanism of Corrosion Resistance

The mechanism of corrosion resistance for stainless steels differs from that for carbon steels and alloy steels. Stainless steels form a thin, protective film on the surface. In the protective state, the stainless steel is passive. The corrosion resistance depends on the integrity and durability of the passive film. Breakdown of the film leads to localized corrosion—for example, pitting or crevice corrosion.

Passivity exists under certain conditions in particular environments. The range of conditions over which passivity can be maintained depends on the precise environment and on the family and composition of the stainless steel. When conditions are favorable for maintaining passivity, stainless steels exhibit extremely low corrosion rates. If passivity is destroyed under conditions that do not permit restoration of the passive film, stainless steels will corrode much like a carbon or low-alloy steel, except that the corrosion attack is likely to be highly localized.

The presence of oxygen is essential to the corrosion resistance of stainless steel. Resistance is at its maximum when the stainless steel is boldly exposed and the surface is maintained free of deposits by a flowing bulk environment. Covering a portion of the surface—for example, by biofouling, painting, or installing a gasket—produces an oxygen-

depleted region under the covered region. The oxygen-depleted region is anodic relative to the well-aerated boldly exposed surface, and a higher level of alloy content in the stainless steel is required to prevent corrosion.

With appropriate grade selection, stainless steels perform for very long times with minimal corrosion, but an inadequate grade can corrode and perforate more rapidly than plain carbon steels fail by uniform corrosion. Selection of the appropriate grade of stainless steel is then a balancing of the desire to minimize cost and the risk of corrosion damage by excursions during operation or downtime.

Forms of Corrosion of Stainless Steels

The localized forms of corrosion—pitting, crevice corrosion, intergranular corrosion, SCC, and erosion-corrosion—are of greatest concern for stainless steels.

Pitting is a localized attack that can produce penetration of a stainless steel with almost negligible weight loss to the total structure. Pitting is associated with a local discontinuity of the passive film. The source of this discontinuity can be mechanical imperfection, and inclusion, or surface damage, or a local chemical breakdown of the film. Chloride is the most common agent for initiation of pitting. Once a pit is formed, the local chemical environment is substantially more aggressive than the bulk environment.

Pitting initiation can also be influenced by surface condition, including the presence of deposits, and by temperature. For a particular environment, a grade of stainless steel may be characterized by a single temperature, or a very narrow range of temperatures, above which pitting will initiate and below which pitting will not initiate. If the range of operating conditions can be accurately characterized, a meaningful laboratory evaluation is possible. Formation of deposits in service can reduce the pitting temperature. Frequent cleaning can prolong equipment life by removing deposits. The relative resistance to pitting corrosion of a range of commercial stainless steels is shown in Fig. 3.

Although chloride is known to be the primary agent of pitting attack, it is not possible to establish a single critical chloride limit for each grade. The corrosivity of a particular concentration of chloride solution can be profoundly affected by the presence or absence of other chemical species that can accelerate or inhibit corrosion. Chloride concentration may increase where evaporation or deposits occur. Because of the nature of pitting attack—rapid penetration with little total weight loss—significant amounts of pitting are rarely acceptable in practical applications.

Crevice corrosion occurs at restricted areas or in occluded regions. Any crevice, whether the result of a metal-to-metal joint, a gasket,

fouling, or deposits, tends to restrict oxygen access, resulting in attack. In practice, it is extremely difficult to avoid all crevices. Higher-chromium, and especially higher-molybdenum, grades are more resistant to crevice attack. Just as there is a critical pitting temperature for a particular environment, there is also a critical crevice temperature (Fig. 4).

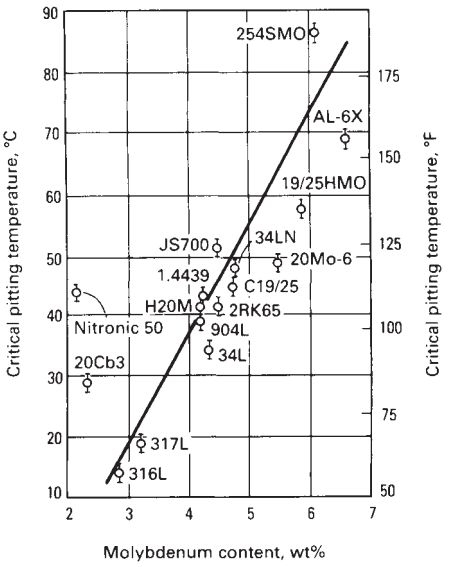


Fig. 3 Effect of molybdenum content on the $FeCl_3$ critical pitting temperature of commercial stainless steels. The more resistant steels have higher critical pitting temperatures

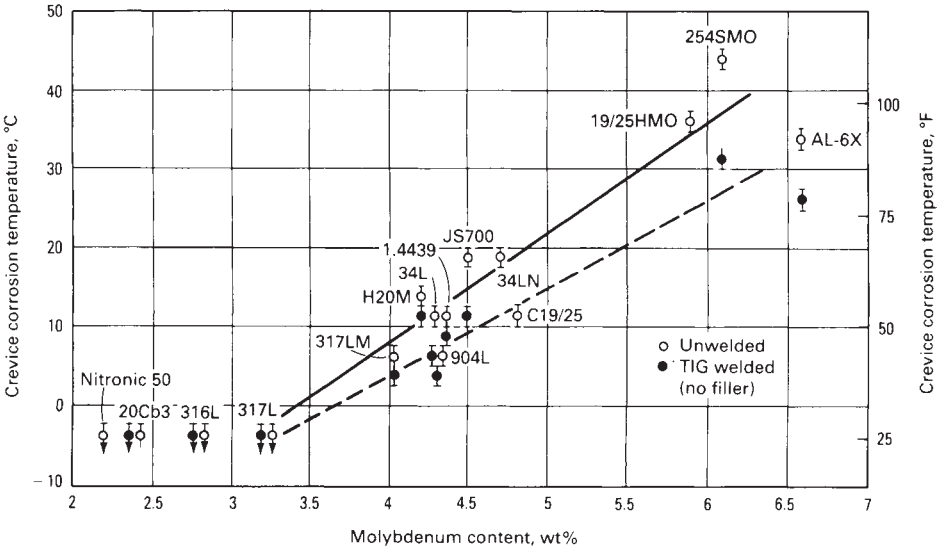
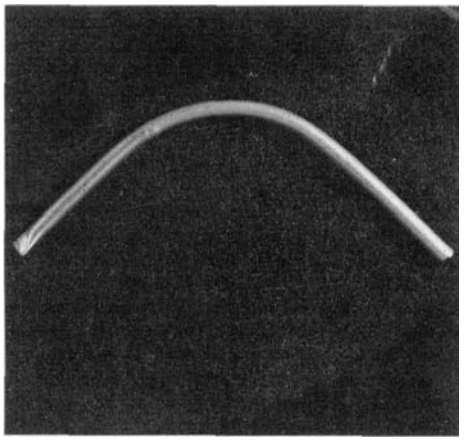


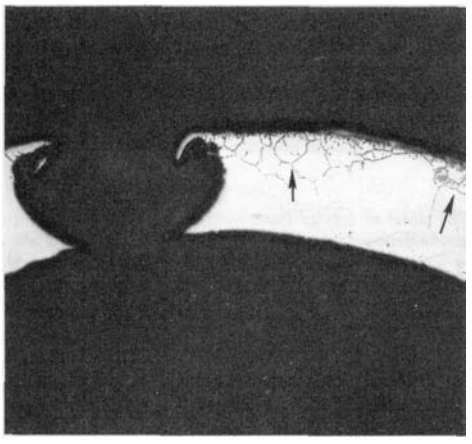
Fig. 4 Effect of molybdenum content on the crevice corrosion temperature of commercial stainless steels. The more resistant steels have higher crevice corrosion temperatures in the $FeCl_3$ test.

This temperature is specific to the geometry and nature of the crevice and to the precise corrosion environment for each grade. The critical crevice temperature can be useful in selecting an adequately resistant grade for a particular application.

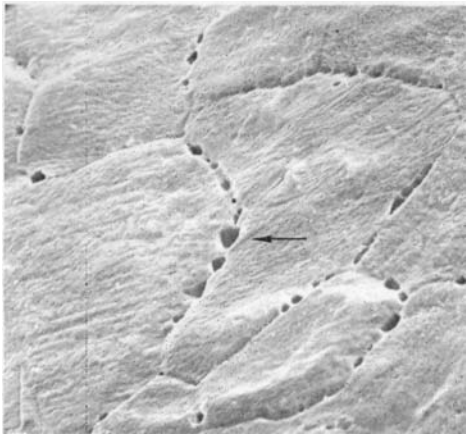
Intergranular corrosion is a preferential attack at the grain boundaries of a stainless steel. It is generally the result of sensitization. This condition occurs when a thermal cycle leads to grain-boundary precipitation of a carbide, nitride, or intermetallic phase without providing sufficient time for chromium diffusion to fill the locally depleted region. Figure 5 illustrates the occurrence of intergranular corrosion in a brazed type 304L tube.



(a)



(b)



(c)

Fig. 5 Intergranular corrosion of a type 304L stainless steel tube in a shuttle orbiter ammonia boiler. (a) Test performed to show tube ductility. 1×. (b) Cross section through the thin-wall (0.2 mm, or 8 mils) tube revealing sensitization on outside diameter due to carbonaceous deposit formed during brazing. 75×. (c) Surface SEM showing grain-boundary carbides are being removed from outside diameter during corrosion. 980×

Stress-corrosion cracking is a corrosion mechanism in which the combination of a susceptible alloy, sustained tensile stress, and a particular environment leads to cracking of the metal. Stainless steels are particularly susceptible to SCC in chloride environments; temperature and the presence of oxygen tend to aggravate chloride SCC of stainless steels. More ferritic and duplex stainless steels are either immune or highly resistant to SCC. All austenitic grades, especially types 304 and 316, are susceptible to some degree. Most martensitic and precipitation-hardening steels are also particularly susceptible. Stress corrosion is difficult to detect while in progress (even when pervasive) and can lead to rapid catastrophic failures of pressurized equipment.

It is difficult to alleviate the environmental conditions that lead to SCC. The level of chlorides required to produce stress corrosion is very low. In operation, there can be evaporative concentration or a concentration in the surface film on a heat-rejecting surface. Temperature is often a process parameter, as in the case of a heat exchanger. Tensile stress is one parameter that might be controlled. However, the residual stresses associated with fabrication, welding, or thermal cycling, rather than design stresses, are often responsible for SCC, and even stress-relieving heat treatments do not completely eliminate these residual stresses.

Erosion-Corrosion. Corrosion of a metal or alloy can be accelerated when there is an abrasive removal of the protective oxide layer. This form of attack is especially significant when the thickness of the oxide layer is an important factor in determining corrosion resistance. In the case of a stainless steel, erosion of the passive film can lead to severe acceleration of attack.

Corrosion in Various Applications

Food and Beverage Industry. Stainless steels have been relied upon in these applications because of the lack of corrosion products that could contaminate the process environment, and because of the superior cleanability of the stainless steels. The corrosive environments often involve moderately to highly concentrated chlorides on the process side, often mixed with significant concentrations of organic acids. The water side can range from steam heating to brine cooling. Purity and sanitation standards require excellent resistance to pitting and crevice corrosion.

Foods such as vegetables represent milder environments and can generally be handled by using type 304 stainless steel. Sauces and pickle liquors, however, are more aggressive and can pit even type 316 stainless steel. For improved pitting resistance, such alloys as 22Cr-13Ni-5Mn, 904L, 20Mo-4, 254SMO, Al-6XN, and MONIT stainless steels may be considered.

Stainless steel equipment should be cleaned frequently to prolong its service life. The equipment should be flushed with fresh water, scrubbed with a nylon brush and detergent, and then rinsed. On the other hand, consideration should be given to the effect of very aggressive cleaning procedures on stainless steels, as in the chemical sterilization of commercial dishwashers. In some cases, it may be necessary to select a more highly alloyed stainless steel grade to deal with these brief exposures to highly aggressive environments.

Pharmaceutical Industry. The production and handling of drugs and other medical applications require exceedingly high standards for preserving the sterility and purity of process streams. Process environments can include complex organic compounds, strong acids, chloride solutions comparable to seawater, and elevated processing temperatures. Higher-alloy grades, such as type 316 or higher, may be required instead of type 304 in order to prevent even superficial corrosion. Electropolishing may be desirable to reduce or prevent adherent deposits and the possibility of underdeposit corrosion. Superior cleanability and ease of inspection make stainless steel the preferred material in such applications.

Orthopedic Devices. Stainless steels have also found application as orthopedic implants. Material is required that is capable of moderately high strength and resistance to wear and fretting corrosion, as well as pitting and crevice attack. Vacuum-melted type 316 stainless steel has been used for temporary internal fixation devices, such as bone plates, screws, pins, and suture wire. Higher purity, improved electropolishing, and increased chromium content (17 to 19%) improve corrosion resistance.

Oil and Gas Industry. Stainless steels were not frequently used in oil and gas production until the tapping of sour reservoirs (those containing hydrogen sulfide [H_2S]) and the use of enhanced recovery systems in the mid-1970s. Sour environments can result in sulfide SCC of susceptible materials. This phenomenon generally occurs at ambient or slightly elevated temperatures; it is difficult to establish an accurate temperature maximum for all alloys. Factors affecting SCC resistance include material variables, pH, H_2S concentration, total pressure, maximum tensile stress, temperature, and time.

In addition to the lower-temperature SCC, resistance to cracking in high-temperature environments is required in many oil-field applications. Most stainless steels, including austenitic and duplex grades, are known to be susceptible to elevated-temperature cracking, probably by a mechanism similar to chloride SCC. Failure appears to be accelerated by H_2S and other sulfur compounds. Increased susceptibility is noted in material of higher yield strength, for example, because of the high residual tensile stresses imparted by some cold-working operations.

In refinery applications, the raw crude contains such impurities as sulfur, water, salts, organic acids, and organic nitrogen compounds. These

and other corrosives and their products must be considered when selecting stainless steels for the various refinery steps. Raw crude is separated into materials such as petroleum gas and various oils by fractional distillation. These materials are then treated to remove impurities, including carbon dioxide (CO_2), ammonia (NH_3), and H_2S, and to optimize produce quality. Refinery applications of stainless steels often involve heat exchangers.

Power Industry. Stainless steels are used in the power industry for generator components, feedwater heaters, boiler applications, heat exchangers, condenser tubing, flue gas desulfurization (FGD) systems, and nuclear power applications.

Stainless steels have been widely used in tubing for surface condensers and feedwater heaters. Both of these are shell-and-tube heat exchangers that condense steam from the turbine on the shell side. In these heat exchangers, the severity of corrosion increases with higher temperatures and pressures. Stainless steels must be chosen to resist chloride pitting. The amount of chloride that can be tolerated is expected to be higher with higher pH and cleaner stainless steel surfaces (i.e., those without deposits). Several high-performance stainless steels have been used to resist chloride pitting in brackish water or seawater. High-performance austenitic grades have been useful in feedwater heaters, although duplex stainless steels may also be considered because of their high strength. Ferritic stainless steels have proved to be economically competitive in exchangers and condensers. High-performance austenitic and ferritic grades have been satisfactory for seawater-cooled units.

A wide variety of alloys have been used in scrubbers, which are located between the boiler and smokestack of fossil fuel power plants to treat effluent gases and to remove sulfur dioxide (SO_2) and other pollutants. Typically, fly ash is removed, and the gas travels through an inlet gas duct and then the quencher section. Next, SO_2 is removed in the absorber section, most often using either a lime or limestone system. A mist eliminator is employed to remove suspended droplets, and the gas proceeds to the treated-gas duct, reheater section, and stack.

Two important considerations in the selection of stainless steels for resistance to pitting in scrubber environments are pH and chloride level. Stainless steels are more resistant at higher pH and lower chloride levels. Environments that cause pitting or crevice attack of type 316 stainless steel can be handled by using higher-alloy materials, for example, those with increased molybdenum and chromium.

Pulp and Paper Industry. Various alloys are selected for the wide range of corrosion conditions encountered in pulp and paper mills. Paper mill headboxes are typically fabricated from type 316L stainless steel plate with superior surface finish and are sometimes electropolished to prevent scaling, which may affect pulp flow. Evaporators

and reheaters must deal with corrosive liquors and minimize scaling to provide optimum heat transfer. Type 304 stainless steel ferrite-free welded tubing has been used in kraft black liquor evaporators. Bleach plants have used stainless steels. Tightening of environmental regulations has generally increased temperature, chloride level, and acidity in paper plants, and this requires grades of stainless steel that are more highly alloyed than those used in the past.

Transportation Industry. Stainless steels are used in a wide range of components in transportation that are both functional and decorative. Bright automobile parts, such as trim, fasteners, wheel covers, mirror mounts, and windshield wiper arms, have generally been fabricated from 17Cr or 18Cr-8Ni stainless steel or similar grades.

Stainless steels also serve many nondecorative functions in automotive design. Small-diameter shafts of type 416 and, occasionally, type 303 stainless steels have been used in connection with power equipment, such as windows, door locks, and antennas. Solenoid grades, such as type 430FR, have also found application. Type 409 has been used for mufflers and catalytic converters for many years and is now being employed throughout the exhaust system.

In railroad cars, external and structural stainless steels provide durability, low-cost maintenance, and superior safety through crashworthiness. The fire resistance of stainless steel is a significant safety advantage. For tank trucks, type 304 has been the most frequently used stainless steel, but type 316 and higher-alloyed grades have been used where appropriate to carry more corrosive chemicals safely over the highways.

Stainless steels are used for seagoing chemical tankers, with types 304, 316, 317, and alloy 2205 being selected according to the corrosivity of the cargoes carried. Conscientious adherence to cleaning procedures between cargo changeovers has allowed these grades to provide many years of service with a great variety of corrosive cargoes.

In aerospace, quench-hardenable and precipitation-hardenable stainless steels have been used for various applications. Heat treatments are chosen to optimize the combination of strength, fracture toughness, and resistance to SCC.

Architectural applications have typically employed types 430 and 304 stainless steels. In bold exposure, these grades are generally satisfactory; however, in marine and industrially contaminated atmospheres, type 316 is often suggested and has performed well.

Nickel and Nickel-Base Alloys

Nickel and nickel-base alloys are important to modern industry because of their ability to withstand a wide variety of severe operating

conditions involving corrosive environments, high temperatures, high stress, or combinations of these factors. There are several reasons for these capabilities. Pure nickel is ductile and tough. Nickel and its alloys are readily fabricated by conventional methods. Nickel has good resistance to corrosion in the normal atmosphere, in fresh water, and in deaerated nonoxidizing acids, and it has excellent resistance to corrosion by caustic alkalis.

Compared to stainless steels, nickel can accommodate larger amounts of alloying elements in solid solution, chiefly chromium, molybdenum, and tungsten. Therefore, nickel-base alloys generally can be used in more severe environments than the stainless steels. The nickel-base alloys range in composition from commercially pure nickel to complex alloys containing many alloying elements.

A distinction is usually made between those alloys that are primarily used for high-temperature strength, commonly referred to as superalloys, and those that are primarily used for corrosion resistance. The distinction is not sharp, because some of the first type are used in corrosion service and some of the second in high-temperature service. Most of the corrosion resistant alloys are primarily single-phase alloys that can be strengthened by cold working. A partial list of nickel-base alloys and their compositions is given in Table 6.

The types of corrosion of greatest importance with regard to nickel-base alloys are uniform corrosion, pitting and crevice corrosion, intergranular corrosion, and galvanic corrosion. Stress-corrosion cracking (SCC), corrosion fatigue, and hydrogen embrittlement are also common modes of attack. High-temperature halogen ion solutions, high-temperature waters, and high-temperature alkaline environments can cause environmentally assisted cracking. In order to estimate the performance of a set of alloys in a given environment, the composition and, for liquid environments, the electrochemical interaction between the environment and the alloy must be known. A case in point is the nickel-molybdenum alloy B-2. The alloy performs exceptionally well in pure, deaerated H_2SO_4 but deteriorates rapidly in the presence of oxidizing impurities, such as oxygen (air) and ferric ions (Fe^{3+}).

Effects of Major Alloying Elements

The roles of the major alloying elements used to promote corrosion resistance in nickel-base alloys are summarized below.

Copper. Additions of copper improve the resistance of nickel to nonoxidizing acids. In particular, alloys containing 30 to 40% Cu are resistant to nonaerated H_2SO_4. Additions of 2 to 3% Cu to nickel-chromium-molybdenum-iron alloys have been found to improve resistance to HCl.

Chromium additions impart improved resistance to oxidizing media such as HNO_3 and chromic acid (H_2CrO_4). Chromium also improves resistance to high-temperature oxidation and to attack by hot sulfur- bearing gases.

Iron is typically used in nickel-base alloys to reduce costs while maintaining strength and toughness.

Molybdenum in nickel substantially improves resistance to nonoxidizing acids and to pitting and crevice corrosion.

Table 6 Nominal chemical compositions of some typical nickel-base alloys

Common alloy designation	UNS designation	Chemical composition, %										
		C(a)	Nb	Cr	Cu	Fe	Mo	Ni	Si(a)	Ti	W	Other
Nickel												
200	N02200	0.1	…	…	0.25 max	0.4 max	…	99.2 min	0.15	0.1 max	…	…
201	N02201	0.02	…	…	0.25 max	0.4 max	…	99.0 min	0.15	0.1 max	…	…
Nickel-copper												
400	N04400	0.15	…	…	31.5	1.25	…	bal	0.5	…	…	…
R-405	N04405	0.15	…	…	31.5	1.25	…	bal	0.5	…	…	0.0435
Nickel-molybdenum												
B-2	N10665	0.01	…	1.0 max	…	2.0 max	28	bal	0.1	…	…	…
B	N10001	0.05	…	1.0 max	…	5.0	28	bal	1.0	…	…	…
Nickel-chromium-iron												
600	N06600	0.08	…	16.0	0.5 max	8.0	…	bal	0.5	0.3 max	…	…
601	N06601	…	…	23.0	…	14.1	…	bal	…	…	…	1.35Al
800	N08800	0.1	…	21.0	0.75 max	44.0	…	32.5	1.0	0.38	…	…
800H	N08810	0.08	…	21.0	0.75 max	44.0	…	32.5	1.0	0.38	…	…
Nickel-chromium-iron-molybdenum												
825	N08825	0.05	…	21.5	2.0	29.0	3.0	42	0.5	1.0	…	…
G	N06007	0.05	2.0	22.0	2.0	19.5	6.5	43	1.0	…	1.0 max	…
G-2/2550	N06975	0.03	…	24.5	1.0	20.0	6.0	48	1.0	1.0	…	…
G-3	N06985	0.015	0.8	22.0	2.0	19.5	7.0	44	1.0	…	1.5 max	…
H	…	0.03	…	22.0	…	19.0	9.0	42	1.0	…	2.0	…
G-30	N06030	0.03	0.8	29.5	2.0	15.0	5.5	43	1.0	…	2.5	…
Nickel-chromium-molybdenum-tungsten												
N	N10003	0.06	…	7.0	0.35 max	5.0 max	16.5	71	1.0	0.5 max	0.5 max	…
W	N10004	0.12	…	5.0	…	6.0	24.0	63	1.0	…	…	…
625	N06625	0.1	4.0	21.5	…	5.0 max	9.0	62	0.5	…	…	…
690	N06690	0.02	…	29.0	…	10.0	…	61	…	0.3	…	…
C-276	N10276	0.01	…	15.5	…	5.5	16.0	57	0.08	…	4.0	…
C-4	N06455	0.01	…	16.0	…	3.0 max	15.5	65	0.08	…	…	…
C-22	N06022	0.015	…	22.0	…	3.0 max	13.0	56	0.08	…	3.0	…
ALLCORR	N06110	0.15	2.0 max	30.0	…	…	10.0	53	…	1.5 max	4.0 max	…
Nickel-silicon												
D	…	0.12	…	1.0 max	3.0	2.0 max	…	86	9.5	…	…	…
Precipitation-hardening												
K-500	N05500	0.25	…	…	29.0	2.0 max	…	63	0.5 max	0.6	…	2.7Al
R-41	N07041	0.09	…	19.0	…	5.0 max	10.0	52	0.5 max	3.1	…	1.5Al
718	N07718	0.05	5.0	18.0	…	19	3.0	53	…	0.4 max	…	…
X-750	N07750	…	0.9	15.5	…	7.0	…	bal	…	2.5	…	…
925	N09925	0.02	…	21.0	2.0	28	3.0	43.0	…	2.1	…	…

(a) Maximum

Tungsten behaves similarly to molybdenum in providing improved resistance to nonoxidizing acids and to localized corrosion.

Silicon is typically present only in minor amounts in most nickel-base alloys. The use of silicon as a major alloying element greatly improves the resistance of nickel to hot, concentrated H_2SO_4. Alloys containing 9 to 11% Si are produced for such service in the form of castings.

Cobalt. Because of its higher cost and lower availability, cobalt is not generally used as a primary alloying element in materials designed for aqueous corrosion resistance. However, it is an important alloying ingredient in high-temperature alloys and prosthetic devices.

Niobium and tantalum were originally added to corrosion-resistant alloys as stabilizing elements to tie up carbon and prevent intergranular corrosion attack due to grain-boundary carbide precipitation. Additions of these elements also reduce the tendency of nickel-base alloys toward hot cracking during welding.

Aluminum and tantalum are often used in minor amounts in corrosion resistant alloys for the purpose of deoxidation or to tie up carbon and/or nitrogen, respectively. When added together, these elements enable the formulation of age-hardenable high-strength alloys for low-temperature and elevated-temperature service.

Chemical-Processing Applications

Caustic Soda. A major use for Nickel 200 is in the production of caustic soda (NaOH). Nickel 200 exhibits outstanding corrosion resistance to NaOH at concentrations up to anhydrous at boiling or molten temperatures (see Fig. 6). Caustic soda is normally produced at a concentration of 11 to 15% and can be further concentrated by evaporation to 50% or higher. As NaOH concentration and temperature increase during the evaporation process or during other chemical-processing conditions, its corrosivity increases dramatically. Similarly, increasing the nickel content of nickel-base alloys increases resistance to general corrosion and SCC in caustic. Thus, a number of nickel-base alloys can be used for handling NaOH, depending on solution concentration and temperature.

At temperatures above 315 °C (600 °F), Nickel 200 is replaced by Nickel 201 because of its low-carbon content. Nickel 200 is more prone to intergranular attack at elevated temperatures. In the handling of brines in NaOH production as well as the commercial production of salt, alloy 400 has performed well in a variety of components, such as heat exchangers, vacuum pans, heater tubes, rotary dryers, and transfer piping. In acidic salt environments, however, high-molybdenum nickel alloys, such as 825, 625, G-3, G-30, C-22, and C-276, are used.

Mineral Acids. The production of mineral acids requires the use of nickel alloys. In the production and handling of H_2SO_4, alloys 825 and 400 and alloy 20-type materials are used. When the acid becomes contaminated with halides, high-molybdenum alloys are used, such as alloys G, 625, C-22, C-4, C-276, and ALLCORR. These alloys also are specified where H_2SO_4 is used in the production of other chemicals, such as H_3PO_4, HF, titanium dioxide (TiO_2), and ammonium sulfate [$(NH_4)_2SO_4$], and in the refining of copper and nickel ores. Hydrochloric acid is best handled by alloy B-2, especially at elevated temperatures. Some alloys suitable for handling various concentrations of H_3PO_4 are 825, G-3, G-30, and 625.

The extreme reactivity of HF excludes many materials from equipment for producing HF and from equipment for processes that employ HF as a catalyst or reagent. Alloy 400 is used in valves for HF alkylation, storage tanks, and retorters. For applications involving HF and H_2SO_4, alloys 825, 625, G-3, and C-276 are used.

Nickel alloys are extensively used in the production of HNO_3. Alloy 617 is used in the catalyst-support grids in high-pressure plants because of its high-temperature strength and corrosion resistance. In older, lower-pressure plants, alloys 600 and 601 are used. Alloy 800 is used in the heat-exchanger train. Under reboiling conditions, alloy 690 has performed exceptionally well.

Seawater Applications

Nickel 200, alloy 400, and nickel-base alloys containing chromium and iron are very resistant to flowing seawater, but in stagnant or

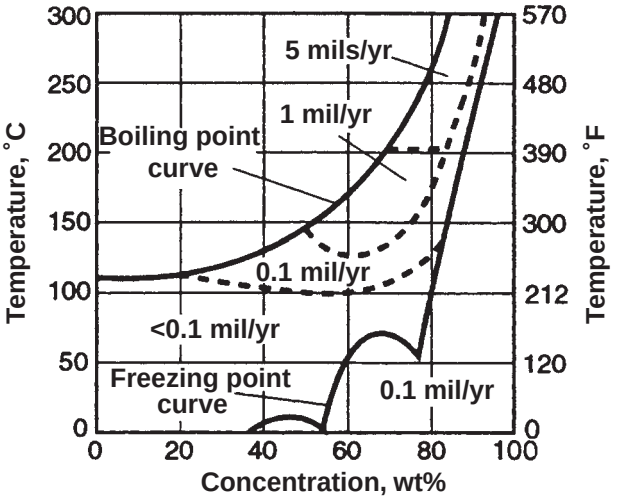


Fig. 6 Corrosion rates for Nickel 200 in caustic soda. 1 mil/yr = 0.0254 mm/yr

very-low-velocity seawater, pitting or crevice corrosion can occur, especially beneath fouling organisms or other deposits. In moderate-velocity and high-velocity seawater or brackish water, alloy 400 is frequently used for pump and valve trim and for transfer piping. It has excellent resistance to cavitation erosion and exhibits corrosion rates of less than 0.025 mm/year (0.9 mil/year). Alloy 400 sheathing also provides economical seawater splash-zone protection to steel offshore oil and gas platforms, pilings, and other structures. Age-hardening alloy K-500 is frequently used for high-strength fasteners and pump and propeller shafting in freshwater and seawater applications.

Other nickel-base alloys containing chromium and molybdenum offer increased resistance to localized corrosion in stagnant seawater. Table 7 compares the corrosion resistance of several nickel-base alloys and type 316 stainless steel in ambient-temperature seawater.

Applications in Pulp and Paper Mills

Nickel alloys are used in the highly corrosive conditions found in pulp and paper mills. Alloys 600 and 800 have been utilized for more than 25 years for digester liquor heater tubing, because their high nickel content provides excellent resistance to chloride SCC. Alloy 600 has been used for reactor vessels, transfer lines, and piping employed in the disposal of organic wastes in unevaporated black liquor.

The bleaching circuit and pollution control areas are the most demanding corrosive environments in the pulp and paper mill process. Alloys used in these areas must be resistant to the oxidizing conditions of high-temperature, low-pH liquors that contain chlorine, chlorine dioxide, oxygen, hypochlorate, peroxides, and chlorides. Only the high-molybdenum alloys 625, C-276 and C-22 are resistant to corrosion by these aggressive liquors. In equipment used to clean off gas from recovery boilers, alloys 825, 625, G, and C-276 have been used, depending on the severity of the conditions. Typical conditions include acid mists, low-pH liquors containing chlorides and organics, and occasionally high temperatures.

Table 7 Resistance of various nickel-base alloys and Type 316 stainless steel to stagnant seawater

3-yr exposure tests.

Alloy	Maximum pit depth, mm (mils)
625	Nil
825	0.025 (0.98)
K-500	0.864 (34)
400	1.067 (42)
AISI Type 316	1.575 (62)

Flue Gas Desulfurization Applications

During the period of rapid growth in the utilization of flue gas desulfurization (FGD) equipment, the industry experienced severe corrosion problems at nearly every operating FGD system. Catastrophic failures were reported for coatings and linings on carbon steel, nonmetallic, stainless steel, and occasionally nickel alloy components. The corrosion problems were caused by hot HNO_3, sulfurous (H_2SO_3) acids, H_2SO_4, HCl, and HF; chlorides; fluorides; and crevice conditions.

A wide variety of nickel alloys are used in FGD applications. Alloys 825 and G are significantly more corrosion resistant in H_2SO_3 and H_2SO_4 than austenitic stainless steels. Because of their higher molybdenum levels, alloys 625, ALLCORR, G, and C-276 are used to combat pitting and crevice corrosion. These nickel alloys have been successfully used in such FGD components as quenchers, absorber towers, dampers, stack gas reheaters, wet inlet duct fans and fan housings, outlet ducting, and stack liners. Thin-gage steel with nickel alloy cladding is used in new construction, and nickel alloy sheet liners are used in the repair of existing FGD components.

Sour Gas Applications

Sour gas is defined by NACE International Material Recommendation MR-01-75 as gas in a well that is handled at an absolute pressure of greater than 0.45 MPa (65 psi), with a partial pressure of H_2S greater than 345 Pa (0.05 psi). This combination can cause sulfide stress cracking, a problem that is complicated by the fact that the environment normally also contains brackish water and carbon dioxide CO_2 and is found at 65 to 245 °C (150 to 475 °F), depending on the depth and location of the well.

Nickel alloys most resistant to these environments contain a minimum of 42% Ni (to resist chlorides), a high level of chromium, and at least 3% Mo; examples include alloys 825, 925, 2550, 28, G-3, and C-276. These alloys are normally furnished for production tubing with minimum yield strengths of 758 or 862 MPa (110 or 125 ksi). Yield strengths up to 1080 MPa (157 ksi) minimum have also been used; such strength levels are obtained through cold work.

High-Temperature Applications

Nickel-base alloys are used extensively in high-temperature applications, including the handling of fused salts, heat treating, and petrochemical production and refining. Such applications demand a combination of corrosion resistance and high-temperature resistance. Heat-resistant superalloys are used in aircraft gas turbine engines.

Copper and Copper-Base Alloys

Copper and copper-base alloys are used in many environments and applications because of their excellent corrosion resistance, coupled with combinations of other desirable properties, such as superior electrical and thermal conductivity, ease of fabricating and joining, wide range of attainable mechanical properties, and resistance to biofouling. Copper corrodes at negligible rates in unpolluted air, water, and deaerated, nonoxidizing acids. Copper alloy artifacts have been found in nearly pristine condition after having been buried in the earth for thousands of years, and copper roofing in rural atmospheres has been found to corrode at rates of less than 0.4 mm (15 mils) in 200 years.

Copper-base alloys resist many saline solutions, alkaline solutions, and organic chemicals. However, copper is susceptible to more rapid attack in oxidizing acids, oxidizing heavy-metal salts, sulfur, NH_3, and some sulfur and NH_3 compounds. Resistance to acid solutions depends primarily on the severity of the oxidizing conditions in a particular solution. Reaction of copper with sulfur and sulfides to form copper sulfide (CuS or Cu_2S) usually precludes the use of copper and copper alloys in environments known to contain certain sulfur species.

The corrosion behavior of copper-base alloys can be better understood by examining the potential-pH diagram for copper presented in Fig. 7. Copper is a relatively noble metal compared with iron. The immune region for copper extends to cover mildly oxidizing conditions. Copper-base alloys are immune from corrosion in environments such as deaerated HCl, but the addition of oxygen or other oxidizing species will cause corrosion.

Furthermore, copper exhibits a passive range from neutral to mildly alkaline conditions, that is, conditions of pH 7 to 12. In such solutions, copper will be thermodynamically stable (immune) under reducing

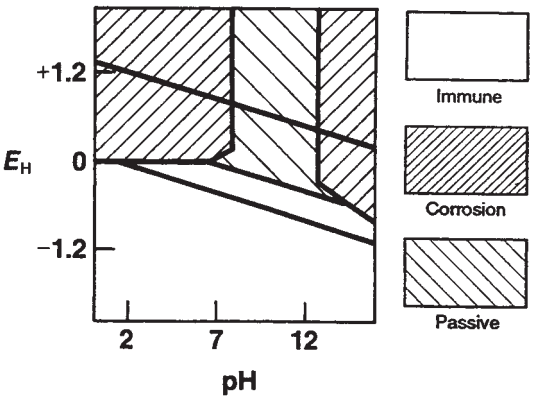


Fig. 7 Potential-pH diagram for copper

conditions. Copper-base alloys corrode in oxidizing acids and in strongly alkaline solutions.

Effects of Alloy Composition

Copper-base alloys are traditionally classified under the groupings in Table 8. Copper and high-copper alloys have excellent resistance to seawater corrosion and biofouling but are susceptible to erosion-corrosion at high water velocities. The high-copper alloy are used primarily in applications that require enhanced mechanical performance with good thermal or electrical conductivity. A number of alloys in this category have been developed for use in electronic applications—for example, contact clips, springs, and lead frames.

Brasses are basically copper-zinc alloys and are the most widely used group of copper-base alloys. The resistance of brasses to corrosion by aqueous solutions does not change markedly if the zinc content does not exceed about 15%; above 15% Zn, dealloying may occur. Dealloying is the preferential dissolution of zinc from the copper-zinc alloy. This phenomenon is also called dezincification (refer to Chapter 4 for detailed information). Quiescent or slowly moving saline solutions, brackish waters, and mildly acidic solutions are environments that

Table 8 Generic classification of copper alloys

Generic name	UNS No.	Composition
Wrought alloys		
Coppers	C10100–C15760	>99% Cu
High-copper alloys	C16200–C19600	>96% Cu
Brasses	C20500–C28580	Cu-Zn
Leaded brasses	C31200–C38590	Cu-Zn-Pb
Tin brasses	C40400–C49080	Cu-Zn-Sn-Pb
Phosphor bronzes	C50100–C52400	Cu-Sn-P
Leaded phosphor bronzes	C53200–C54800	Cu-Sn-Pb-P
Copper-phosphorus and copper-silver-phosphorus alloys	C55180–C55284	Cu-P-Ag
Aluminum bronzes	C60600–C64400	Cu-Al-Ni-Fe-Si-Sn
Silicon bronzes	C64700–C66100	Cu-Si-Sn
Other copper-zinc alloys	C66400–C69900	…
Copper-nickels	C70000–C79900	Cu-Ni-Fe
Nickel silvers	C73200–C79900	Cu-Ni-Zn
Cast alloys		
Coppers	C80100–C81100	>99% Cu
High-copper alloys	C81300–C82800	>94% Cu
Red and leaded red brasses	C83300–C85800	Cu-Zn-Sn-Pb (75–89% Cu)
Yellow and leaded yellow brasses	C85200–C85800	Cu-Zn-Sn-Pb (57–74% Cu)
Manganese bronzes and leaded manganese bronzes	C86100–C86800	Cu-Zn-Mn-Fe-Pb
Silicon bronzes, silicon brasses	C87300–C87900	Cu-Zn-Si
Tin bronzes and leaded tin bronzes	C90200–C94500	Cu-Sn-Zn-Pb
Nickel-tin bronzes	C94700–C94900	Cu-Ni-Sn-Zn-Pb
Aluminum bronzes	C95200–C95810	Cu-Al-Fe-Ni
Copper-nickels	C96200–C96800	Cu-Ni-Fe
Nickel silvers	C97300–C97800	Cu-Ni-Zn-Pb-Sn
Leaded coppers	C98200–C98800	Cu-Pb
Miscellaneous alloys	C99300–C99750	…

often lead to the dealloying of unmodified brasses. Susceptibility to SCC is significantly increased by increasing zinc content.

Tin Brasses. Tin additions significantly increase the corrosion resistance of some brasses, especially resistance to dealloying. Admiralty metal is a variation of cartridge brass (C26000) that is produced by adding about 1% Sn to the basic Cu-30Zn composition. Similarly, naval brass is the alloy resulting from the addition of 0.75% Sn to the basic Cu-40Zn composition of Muntz metal (C28000).

Aluminum Brasses. An important constituent of the corrosion film on a brass that contains a few percent aluminum in addition to copper and zinc is aluminum oxide (Al_2O_3). This compound markedly increases resistance to impingement attack in turbulent high-velocity saline water.

Inhibited Alloys. The addition of phosphorus, arsenic, or antimony (typically 0.02 to 0.10%) to admiralty metal, naval brass, or aluminum brass produces high resistance to dealloying. Inhibited alloys have been used extensively for components (e.g., condenser tubes) that must experience years of continuous service between shutdowns for repair or replacement.

Phosphor Bronzes. The addition of tin and phosphorus to copper produces good resistance to flowing seawater and to most nonoxidizing acids, with the exception of HCl. Alloys containing 8 to 10% Sn have high resistance to impingement attack. Phosphor bronzes are much less susceptible to SCC than brasses and are similar to copper in resistance to sulfur attack.

Copper Nickels. Alloy C71500 (Cu-30Ni) has the best general resistance to aqueous corrosion of all the commercially important copper-base alloys, but C70600 (Cu-10Ni) is often selected because if offers good resistance at lower cost. Both of these alloys, although well suited to applications in the chemical industry, have been used most extensively for condenser tubes and heat-exchanger tubes in recirculating steam systems. They are superior to coppers and to other copper alloys in resisting acid solutions and are highly resistant to SCC and impingement corrosion.

Nickel Silvers. The two most common nickel silvers are C75200 (Cu-18Ni-17Zn) and C77000 (Cu-18Ni-27Zn). (Note that nickel silvers do not contain silver.) They have good resistance to corrosion in both fresh and salt waters. Primarily because their relatively high-nickel contents inhibit dezincification, C75200 and C77000 are usually much more resistant to corrosion in saline solutions than brasses of similar copper content.

Aluminum Bronzes. Bronzes that contain 5 to 12% Al have excellent resistance to impingement corrosion and high-temperature oxidation. Aluminum bronzes are used for beater bars and for blades in wood

pulp machines because of their ability to withstand mechanical abrasion and chemical attack by sulfite solutions.

Types of Attack

Coppers and copper alloys, like most other metals and alloys, are susceptible to several forms of corrosion, depending primarily on environmental conditions. Table 9 lists the identifying characteristics of the forms of corrosion that commonly attack copper metals as well as the most effective means of combating each.

Applications of Copper-Base Alloys

Copper and copper-base alloys provide superior service in many of the applications included in the following general classifications:

- Applications that require resistance to atmospheric exposure, including architectural uses, such as roofing, hardware, building fronts, grillwork, handrails, lock bodies, doorknobs, and kick plates
- Freshwater supply lines and plumbing fittings, which require superior resistance to corrosion caused by various types of waters and soils
- Marine applications—including freshwater and seawater supply lines, heat exchangers, condensers, shafting, valve stems, and marine hardware—in which resistance to seawater, hydrated salt deposits, and biofouling from marine organisms is important

Table 9 Guide to corrosion of copper alloys

Form of attack	Characteristics	Preventive measures
General thinning	Uniform metal removal	Select proper alloy for environmental conditions based on weight loss data.
Galvanic corrosion	Corrosion preferentially near a more cathodic metal	Avoid electrically coupling dissimilar metals. Maintain optimum ratio of anode to cathode area. Maintain optimum concentration of oxidizing constituent in corroding medium.
Pitting	Localized pits, tubercles; water line pitting; crevice corrosion; pitting under foreign objects or dirt	Alloy selection, design to avoid crevices, keeping metal clean
Impingement, erosion-corrosion, cavitation	Erosion attack from turbulent flow plus dissolved gases, generally as lines of pits in direction of fluid flow	Design for streamlined flow; keep velocity low. Remove gases from liquid phase and use erosion-resistant alloy.
Fretting	Chafing or galling, often occurring during shipment	Lubricate contacting surfaces; interleave sheets of paper between sheets of metal. Decrease load on bearing surfaces.
Intergranular corrosion	Corrosion along grain boundaries without visible signs of cracking	Select proper alloy for environmental conditions based on metallographic examination of corrosion specimens.
Dealloying	Preferential dissolution of zinc or nickel, resulting in a layer of sponge copper	Select proper alloy for environmental conditions based on metallographic examination of corrosion specimens.
Corrosion fatigue	Several transgranular cracks	Select proper alloy based on fatigue tests in service environment. Reduce mean or alternating stress.
SCC	Cracking, usually intergranular but sometimes transgranular, that is often fairly rapid	Select proper alloy based on stress-corrosion tests; reduce applied or residual stress. Remove mercury compounds or NH_3 from environment.

- Heat exchangers and condensers in marine service, stream power plants, and chemical-processing applications, as well as liquid-to-gas or gas-to-gas heat exchangers in which either process stream may contain a corrosive contaminant
- Industrial and chemical plant processing equipment exposed to a variety of organic and inorganic chemicals
- Electrical wiring, hardware, and connectors; printed circuit boards; and electronic applications that require demanding combinations of electrical, thermal, and mechanical properties, such as semiconductor packages, lead frames, and connectors

Aluminum and Aluminum-Base Alloys

Aluminum, as indicated by its position in the electromotive force (emf) series, is a thermodynamically reactive metal; among structural metals, only beryllium and magnesium are more reactive. Aluminum owes its excellent corrosion resistance and its status as one of the primary nonferrous metals of commerce to the barrier oxide film that is bonded strongly to its surface. This passive film, if damaged, forms again immediately in most environments. On a surface freshly abraded and then exposed to air, the barrier oxide film is only 1 nm (10 Å) thick but is highly effective in protecting the aluminum from corrosion.

The conditions for thermodynamic stability of the oxide film are expressed by the potential-pH diagram shown in Fig. 8. Aluminum is passive (i.e., is protected by an oxide film) in the pH range of about 4 to 8.5. The limits of this range, however, vary somewhat with temperature, with the specific form of oxide film present, and with the presence of substances that can form soluble complexes or insoluble salts with aluminum.

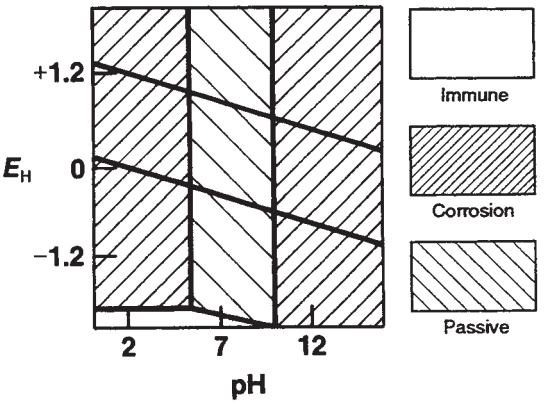


Fig. 8 Potential-pH diagram for aluminum

Beyond the limits of its passive range, aluminum corrodes in aqueous solutions, because the oxides it forms are soluble in many acids and bases, yielding Al^{3+} ions in the former and aluminate (AlO^{2-}) ions in the latter. In some instances, however, corrosion does not occur outside the passive range—for example, when the oxide film is not soluble or when the film is maintained by the nature of the solution.

Effects of Alloy Composition

The alloy series designations for commercial wrought aluminum alloys are listed in Table 10 and are discussed below.

1*xxx* Alloys. Wrought aluminums of the 1*xxx* series contain at least 99% Al and conform to composition specifications that set maximum individual, combined, and total contents for several elements present. The corrosion resistance of all 1*xxx* compositions is high but, under many conditions, resistance decreases slightly with increasing impurity content.

2*xxx* alloys, in which copper is the major alloying element, are less resistant to corrosion than alloys of the other series, which contain much lower amounts of copper. Alloys of this type were the first heat treatable, high-strength aluminum-base materials.

3*xxx* alloys (aluminum-manganese and aluminum-manganese-magnesium) have very high corrosion resistance.

4*xxx* Alloys. Elemental silicon is present as second-phase constituent particles in wrought alloys of the 4*xxx* series, in brazing and welding alloys, and in casting alloys of the 3*xx.x* and 4*xx.x* series. Silicon is cathodic to the aluminum solid-solution matrix by several hundred millivolts and accounts for a considerable volume fraction of most of the silicon-containing alloys. However, the effects of silicon on the corrosion resistance of these alloys are minimal because of the low corrosion current density that results from the high polarization of the silicon particles.

Table 10 Wrought aluminum alloy series designations

Aluminum Association series	Type of alloy composition	Strengthening method	Tensile strength range	
			MPa	ksi
1*xxx*	Al	Cold work	70–175	10–25
2*xxx*	Al-Cu-Mg (1–2.5% Cu)	Heat treat	170–310	25–45
2*xxx*	Al-Cu-Mg-Si (3–6% Cu)	Heat treat	380–520	55–75
3*xxx*	Al-Mn-Mg	Cold work	140–280	20–40
4*xxx*	Al-Si	Cold work (some heat treat)	105–350	15–50
5*xxx*	Al-Mg (1–2.5% Mg)	Cold work	140–280	20–40
5*xxx*	Al-Mg-Mn (3–6% Mg)	Cold work	280–380	40–55
6*xxx*	Al-Mg-Si	Heat treat	150–380	22–55
7*xxx*	Al-Zn-Mg	Heat treat	380–520	55–75
7*xxx*	Al-Zn-Mg-Cu	Heat treat	520–620	75–90
8*xxx*	Al-Li-Cu-Mg	Heat treat	280–560	40–80

5*xxx* alloys (aluminum-magnesium-manganese, aluminum-magnesium-chromium, and aluminum-magnesium-manganese-chromium) have high resistance to corrosion. This accounts in part for their use in a variety of building products and chemical-processing and food-handling equipment, as well as in applications involving exposure to seawater. Alloys in which the magnesium is present in amounts that remain in solid solution are generally as resistant to corrosion as commercially pure aluminum and are more resistant to salt water and some alkaline solutions, such as those of sodium carbonate and amines.

6*xxx* Alloys. Moderately high strength and very good corrosion resistance make the heat treatable wrought alloys of the 6*xxx* series (aluminum-magnesium-silicon) highly suitable for various structural, building, marine, machinery, and processing equipment applications. In general, the level of resistance decreases somewhat with increasing copper content.

When the magnesium and silicon contents in a 6*xxx* alloy are balanced, corrosion by intergranular penetration is slight in most commercial environments. If the alloy contains high levels of silicon or cathodic impurities, susceptibility to intergranular corrosion increases.

7*xxx* alloys contain major additions of zinc, along with magnesium or magnesium plus copper in combinations that develop various levels of strength. Those alloys containing copper have the highest strength and have been used as construction materials, primarily in aircraft applications. Usage of the copper-free alloys has increased; applications include automotive parts (such as bumpers), structural members and armor plate for military vehicles, and components for other transportation equipment.

The 7*xxx* wrought alloys are among the aluminum alloys most susceptible to SCC and exfoliation. All 7*xxx* alloys are more resistant to general corrosion than 2*xxx* alloys but less resistant than wrought alloys of other groups.

Modes of Corrosion That Attack Aluminum

Pitting. Because aluminum depends on a protective film for corrosion resistance, it is susceptible to localized forms of corrosion. Pitting occurs at local sites of passive film breakdown. The resistance of aluminum to pitting depends significantly on its purity; the purest metal is the most resistant with the following alloys in decreasing order of resistance:

- 1*xxx* pure aluminum grades
- 5*xxx* alloys (particularly alloys with less than 3% Mg)
- 3*xxx* alloys
- 6*xxx* alloys

- 7*xxx* alloys (must be clad)
- 2*xxx* alloys (must be clad)

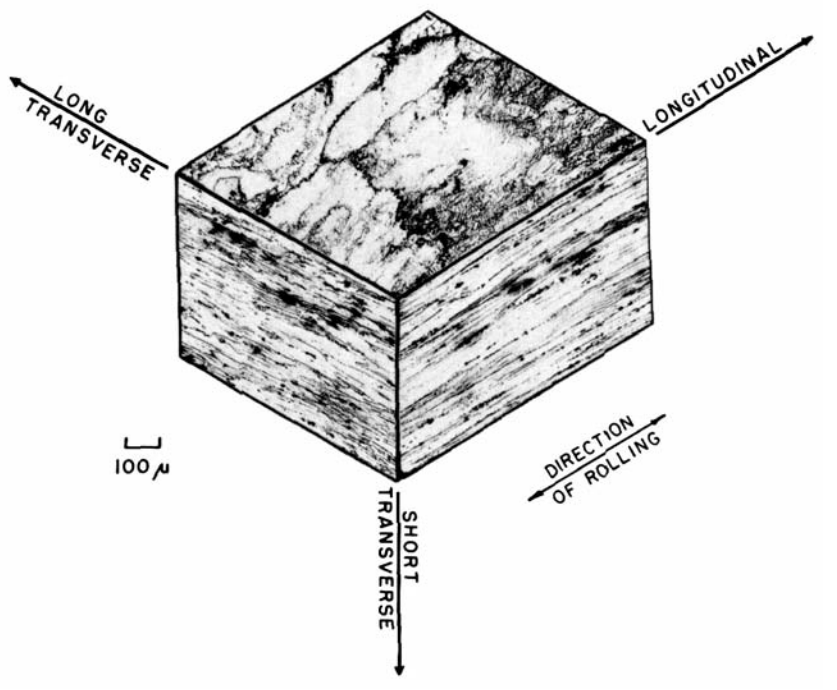
Intergranular Corrosion. Aluminum-base alloys can be susceptible to intergranular attack. The likelihood and severity of attack depends on the composition and structure of the alloy and the corrosivity of the environment.

The location of the anodic path varies with the different alloy systems. In 2*xxx* series alloys, the location of the anodic path is a narrow band on either side of the grain boundary that is depleted in copper; in 5*xxx* series alloys, it is the anodic constituent Mg_2Al_3 when that constituent forms a continuous path along a grain boundary. In copper-free 7*xxx* series alloys, the path is generally considered to be the anodic zinc-bearing and magnesium-bearing constituents on the grain boundary. In the copper-bearing 7*xxx* alloys, it appears to be the copper-depleted bands along the grain boundaries. The 6*xxx* alloys generally resist this type of corrosion, although slight intergranular attack has been observed in aggressive environments.

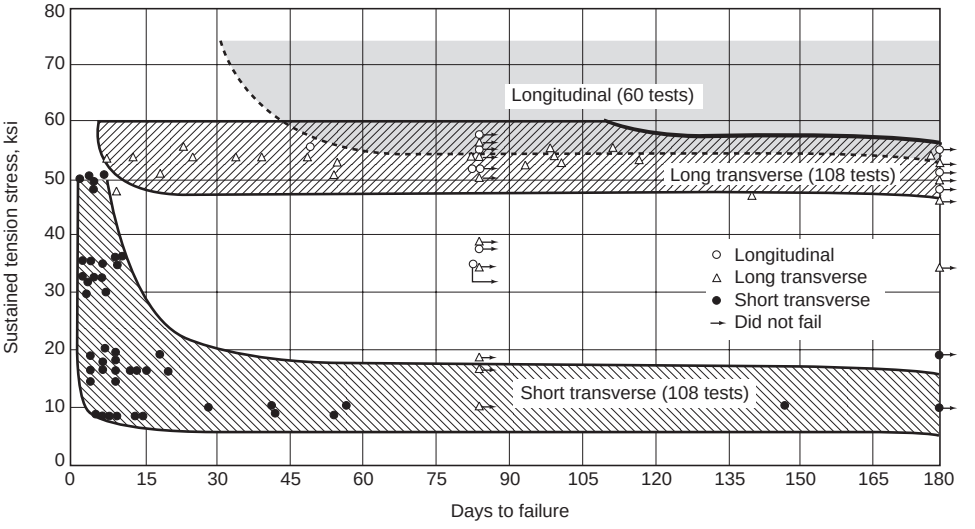
Alloys that do not form second-phase microconstituents at grain boundaries, or those in which the constituents have corrosion potential similar to the matrix ($MnAl_6$), are not susceptible to intergranular corrosion. Examples of alloys of this type are 1100, 3003, and 3004.

Stress-Corrosion Cracking. Only aluminum alloys that contain appreciable amounts of soluble alloying elements, primarily copper, magnesium, silicon, and zinc, are susceptible to SCC. These include the heat treatable 2*xxx* and 7*xxx* alloys and 5*xxx* alloys containing >3% Mg. For most commercial alloys, tempers have been developed that provide a high degree of immunity to SCC in many environments. Stress-corrosion cracking behavior is strongly dependent on both the heat treatment and the composition of the alloy. Tabulations of the relative susceptibilities of aluminum alloys are available in ASTM G 64, "Classification of Resistance to Stress-Corrosion Cracking of High-Strength Aluminum Alloys."

Other important considerations include the effects of grain structure and stress direction. Many wrought aluminum alloy products have highly directional grain structures (Fig. 9a). Such products are highly anisotropic with respect to resistance to SCC (Fig. 9b). Resistance, which is measured by magnitude of tensile stress required to cause cracking, is highest when the stress is applied in the longitudinal direction, lowest in the short-transverse direction, and intermediate in other directions. These differences are most noticeable in the more susceptible tempers but are usually much lower in tempers produced by extended precipitation treatments, such as T6 and T8 tempers for 2*xxx* alloys and T73, T736, and T76 tempers for 7*xxx* alloys.



(a)



(b)

Fig. 9 Effects of grain structure and stress direction on the SCC resistance of aluminum alloys. (a) Composite micrograph showing grain structure of a 38 mm (1.5 in.) alloy 7075-T6 plate. (b) the relative resistance to stress-corrosion cracking of 7075-T6 plate is influenced by direction of stressing. Samples are alternatively immersed in 3.5% NaCl. Plate thickness: 6.4 to 38 mm (¼ to 3 in.)

Deposition of More Noble Metals. Ions of several metals have reduction potentials that are more cathodic than the solution potential of aluminum and, therefore, can be reduced to the metallic form by aluminum. Reduction of only a small amount of these ions can lead to severe localized corrosion of aluminum, because the metal reduced from them plates onto the aluminum and sets up galvanic cells. The more important heavy metals are copper, lead, mercury, nickel, and tin. The effects of these metals on aluminum are of greatest concern in acidic solutions; in alkaline solutions, these metals have much lower solubilities and are thus much less severe.

Exfoliation Corrosion. In certain tempers, wrought products of aluminum alloys of the 2*xxx* and 7*xxx* series are subject to corrosion by exfoliation. Exfoliation is a form of intergranular corrosion in which attack proceeds along selective subsurface paths parallel to the surface. Layers of uncorroded metal between the selective paths are split apart and pushed above the original surface by the voluminous corrosion product formed along the paths of attack. More detailed information on exfoliation of susceptible aluminum alloys/tempers can be found in Chapter 4.

Corrosion Protection of Aluminum

Alclad. In alclad products, the difference in solution potential between the core alloy and the cladding alloy is used to provide cathodic protection to the core. These products, primarily sheet and tube, consist of a core clad on one or both surfaces with a metallurgically bonded layer of an alloy that is anodic to the core alloy. The thickness of the cladding layer is usually less than 10% of the overall thickness of the product. Cladding alloys are generally of the non-heat-treatable type, although heat treatable alloys are sometimes used for higher strength.

Composition relationships of core and cladding alloys are generally designed so that the cladding is 80 to 100 mV more anodic than the core. Table 11 lists several core alloy/cladding alloy combinations for common alclad products. Because of the cathodic protection provided by the cladding, corrosion progresses only to the core-and-cladding interface and then spreads laterally. This is highly effective in elimination of perforation of thin-wall products.

Table 11 Combinations of aluminum alloys used in several alclad products

Core alloy	Cladding alloy
2014	6003 or 6053
2024	1230
2219	7072
3003	7072
3004	7072 or 7013
6061	7072
7075	7072, 7008, or 7011
7178	7072

Organic Coatings. Aluminum is an excellent substrate for organic coatings if the surface is properly cleaned and prepared. For many applications, such as indoor decorative parts, the coating can be applied directly to a clean surface. However, a suitable prime coat, such as a wash primer or a zinc chromate primer, usually improves the performance of the finish coat.

For applications involving outdoor exposure, a surface treatment such as anodizing or chemical conversion coating is required prior to the application of a primer and a finish (top) coat, such as an epoxy or polyurethane. Some new one-step, self-priming polyurethane top coats are also available as are low volatile-organic compound (VOC) high-performance primers (e.g., epoxy polyamide).

Other examples of organic coatings applied to aluminum include those listed:

- Antifouling paints to prevent growth of algae, barnacles, and other sea organisms
- Clear protective coatings (lacquers) applied to beverage and food containers
- Adhesively bonded appliqué films for enhanced weather resistance
- Nonstick coatings on cooking utensils

Anodizing is an electrolytic oxidation process that produces on an aluminum surface an integral coating of amorphous aluminum oxide that is much thicker than the natural barrier layer. The anodic coatings used for decoration and/or protection of aluminum have a thin, nonporous barrier-type layer adjacent to the metal interface and a porous outer layer that can be sealed by hydrothermal treatment in water or in a metal salt solution to increase its protective value. The entire coating adheres tightly to the aluminum substrate, resists abrasion, and when adequate in thickness, provides greatly improved protection against weathering and other corrosive conditions. For outdoor applications of aluminum parts, a coating thickness of 5 to 7.6 μm (0.2 to 0.3 mil) is normally specified for bright automotive trim and 17 to 30 μm (0.7 to 1.2 mils) for architectural product finishes.

Cathodic Protection. In some applications, aluminum alloy parts, assemblies, structures, and pipelines are cathodically protected. Because the usual cathodic reaction produces hydroxyl ions, the current on these alloys should not be high enough to make the solution sufficiently alkaline to cause significant corrosion.

The criterion for cathodic protection of aluminum in soils and waters has been published by NACE International (“Recommended Practice for Cathodic Protection of Aluminum Pie Buried in Soil or Immersed in Water”). The suggested practice is to shift the potential at least –0.15 V

but not beyond the value of –1.20 V as measured against a saturated copper sulfate ($Cu/CuSO_4$) reference electrode.

Applications of Aluminum-Base Alloys

Structural. Aluminum alloys are used extensively for structural and architectural applications. Their light weight and high strength are advantageous in aerospace, automotive, and marine applications. Alloys are available in a range of shapes, including sheet, rod, tube, bar, and plate.

Foods, Pharmaceuticals, and Chemicals. The widespread use of aluminum in the processing, handling, and packaging of foods, beverages, and pharmaceutical and chemical products is based on economic factors and the excellent compatibility of aluminum with many of these products. In addition to high corrosion resistance, many of these applications depend on the nontoxicity of aluminum and its salts, as well as on its freedom from catalytic effects that cause product discoloration. The largest amount of aluminum is used for beverage cans, with a smaller amount used for food packaging. Aluminum cans generally have both internal and external organic coatings, primarily for decoration and for protection of product taste.

Large quantities of aluminum foil, either uncoated or with plastic coatings, are used in flexible packages. Coated foil is also used with fiberboard in the construction of rigid containers. The foil in such containers, because of its extreme thinness, must be coated; only the slightest corrosion can be tolerated, and perforation must not occur even during long periods of storage. Packaging foils are produced from unalloyed aluminum.

Aluminum alloy household cooking utensils, usually made of alloy 3003, have been used for many years. Ceramic coatings are often applied to the exteriors of cooking utensils for aesthetic reasons, and polymeric (Teflon) coatings to the food-contacting surfaces for nonsticking characteristics. Some alkaline cleaners cause excessive corrosion and should not be used unless they are inhibited effectively.

Aluminum-base alloys are used in the processing, handling, and packaging of a wide variety of chemical products. Resistance of aluminum and its alloys to many foods and chemicals, representing practically all classifications, has been established by laboratory testing and, in many cases, by service experience. Data are readily available from handbooks, proprietary literature, and trade association publications.

Much of the data from laboratory tests are for chemicals of high purity. Caution should be exercised in using these data to predict the performance of aluminum alloys in contact with commercial grades of chemicals. Corrosion of aluminum alloys by inorganic chemicals is frequently caused by such impurities as copper, lead, mercury, and nickel.

Corrosion by organic chemicals often results from the presence of inorganic chemicals and other organic chemicals. The combined effect of impurities may exceed the sum of their individual effects.

Sacrificial Anodes. The reactive nature of aluminum is used commercially. For example, sacrificial aluminum anodes for cathodic protection are used to protect steel in seawater. These anodes are used in environments where the aluminum remains active. As the aluminum anodes become passive, their effectiveness for cathodic protection is lost. Most aluminum sacrificial anodes are cast Al-Zn-Sn, Al-Zn-In, or Al-Zn-Hg alloys containing about 94 to 95% Al and 3.5 to 5% Zn.

Titanium and Titanium-Base Alloys

Titanium-base alloys were originally developed in the early 1950s for aerospace applications, where their high strength-to-density ratios were especially attractive. Although titanium alloys are still vital to the aerospace industry, recognition of the excellent resistance of titanium to many highly corrosive environments, particularly oxidizing and chloride-containing process streams, has led to widespread nonaerospace applications. Because of the decreasing cost and increasing availability of titanium alloy products, many titanium alloys have become standard engineering materials for a host of common industrial applications.

The designations and nominal compositions of several commercial titanium-base alloys are listed in Table 12. These titanium alloys are commonly used in industrial applications where corrosion resistance is of primary concern. With the exception of the Ti-6Al-4V alloy, these alloys consist of single alpha-phase (hexagonal close-packed crystal structure) or near-alpha alloys containing relatively small amounts of beta phase (body-centered cubic crystal structure) in an alpha matrix. Other titanium alloys have been developed for aerospace purposes. In such alloys, significantly increased strengths are achieved by solid-solution alloying and stabilization of two-phase structures.

Table 12 Designations and nominal compositions of several titanium-base alloys

Common alloy designation	UNS No.	Nominal composition, %	ASTM grade	Alloy type
Grade1	R50250	Unalloyed titanium	1	α
Grade 2	R50400	Unalloyed titanium	2	α
Grade 3	R50550	Unalloyed titanium	3	α
Grade 4	R50700	Unalloyed titanium	4	α
Ti-Pd	R52400/R52250	Ti-0.15Pd	7–11	α
Grade 12	R53400	Ti-0.3Mo-0.8Ni	12	Near-α
Ti-3-2.5	…	Ti-3Al-2.5V	9	Near-α
Ti-6-4	R56400	Ti-6Al-4V	5	α-β

Mechanism of Corrosion Resistance

The excellent corrosion resistance of titanium-base alloys results from the formation of very stable, continuous, highly adherent, and protective oxide films on metal surfaces. Because titanium metal itself is highly reactive and has an extremely high affinity for oxygen, these beneficial surface oxide films form spontaneously when fresh metal surfaces are exposed to air and/or moisture. In fact, a damaged oxide film can generally reheal itself instantaneously if at least traces (parts per million) of oxygen or water (moisture) are present in the environment. However, anhydrous conditions in the absence of an oxygen source may result in titanium corrosion, because the protective film may not be regenerated if damaged.

The nature, composition, and thickness of the protective surface oxides that form on titanium alloys depend on environmental conditions. Although these naturally formed films are typically less than 10 nm (100 Å) thick and are invisible to the eye, titanium dioxide (TiO_2) is highly chemically resistant and is attacked by very few substances. Solutions that attack titanium include hot, concentrated HCl, H_2SO_4, NaOH, and (most notably) HF. The potential-pH diagram for the titanium-water system of 25 °C (75 °F) is shown in Fig. 10 and depicts the wide region over which the passive TiO_2 film is predicted to be stable, based on thermodynamic (free energy) considerations. Oxide stability over the full pH scale is indicated over a wide range of highly oxidizing to mildly reducing potentials, whereas oxide film breakdown and the resultant corrosion of titanium occur under reducing acidic conditions. Under strongly reducing (cathodic) conditions, titanium hydride formation is predicted.

Thus, successful use of titanium alloys can be expected in mildly reducing to highly oxidizing environments in which protective TiO_2 and Ti_2O_3 films form spontaneously and remain stable. On the other hand,

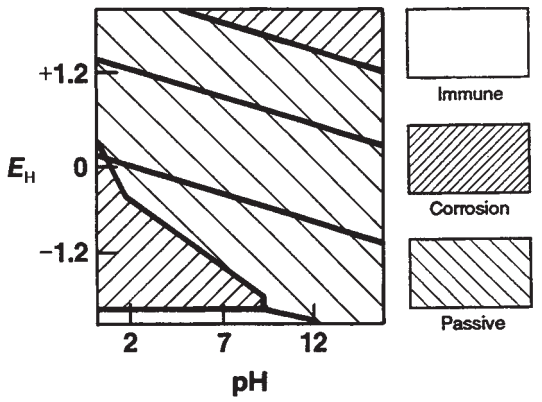


Fig. 10 Potential-pH diagram for titanium

uninhibited, strongly reducing acidic environments may attack titanium, particularly as temperature increases.

Modes of Corrosion That Attack Titanium

The primary forms of corrosion that have been observed on titanium alloys include general corrosion, crevice corrosion, pitting, hydrogen damage, and SCC. Generally, no corrosion is experienced in atmospheric exposure.

General corrosion becomes a concern in reducing acid environments, particularly as acid concentration and temperature increase.

Crevice Corrosion. Titanium alloys may be subject to localized attack in tight crevices exposed to hot (>70 °C [160 °F]) chloride-, bromide-, iodide-, fluoride-, or sulfate-containing solutions. Crevices can stem from adherent process-stream deposits or scales, metal-to-metal joints (e.g., poor weld joint design or tube-to-tubesheet joints), and gasket-to-metal flange and other seal joints.

Hydrogen Damage. Titanium alloys are widely used in hydrogen-containing environments and under conditions in which galvanic couples or cathodic charging (impressed current) causes hydrogen to be evolved on metal surfaces. Although in most cases these alloys provide excellent performance, hydrogen embrittlement has been observed.

The surface oxide film of titanium is a highly effective barrier to hydrogen penetration. Traces of moisture or oxygen in environments that contain hydrogen gas effectively maintain this protective film, thus avoiding or limiting hydrogen uptake. On the other hand, anhydrous hydrogen atmospheres may lead to absorptions, particularly as temperatures and pressures increase.

In alpha alloys and alpha-beta alloys, excessive hydrogen uptake can induce the precipitation of titanium hydride in the alpha phase. These acicular hydride platelets are brittle. Small amounts of hydride precipitates are not detrimental from an engineering standpoint in most cases, but hydride precipitates severely reduce alloy ductility and toughness when present in greater amounts.

Three general conditions must exist simultaneously for the hydrogen embrittlement of alpha alloys to occur:

- A mechanism for generating nascent (atomic) hydrogen on a titanium surface. This may be from a galvanic couple, an impressed cathodic current, corrosion of titanium, or severe continuos abrasion of the titanium surface in an aqueous medium.
- Metal temperature above approximately 80 °C (175 °F), where the diffusion rate of hydrogen into alpha titanium is significant
- Solution pH less than 3 or greater than 12, or impressed potentials more negative than –0.70 V saturated calomel electrode (SCE)

The key to preventing hydrogen embrittlement is simply to avoid one or more of these conditions: (a) galvanic couples with active metals, (b) cathodic charging of hydrogen when temperatures exceed 80 °C (175 °F), and (c) high-temperature alkaline conditions.

Stress-Corrosion Cracking. With respect to SCC, it is important to distinguish between the two classes of titanium alloys. The first class, which includes ASTM grades 1, 2, 7, 11, and 12, is immune to SCC except in a few specific environments, including anhydrous methanol/halide solutions, nitrogen tetroxide (N_2O_4), red fuming HNO_3, and liquid or solid cadmium. The second class of titanium alloys, including those used for aerospace applications, has been found to be susceptible to several additional environments, most notably aqueous chloride solutions.

Corrosion Protection of Titanium

Methods of expanding the corrosion resistance of titanium into reducing environments include the following:

- Increasing the surface oxide film thickness by anodizing or thermal oxidation
- Anodically polarizing the alloy (anodic protection) by impressed anodic current or galvanic coupling with a more noble metal in order to maintain the surface oxide film
- Applying precious metal (or certain metal oxide) surface coatings
- Alloying titanium with beneficial elements
- Adding oxidizing species (inhibitors) to the reducing environment to permit oxide film stabilization

Of these methods, the last two have proved to be very practical and effective, and are most widely used in actual service.

Alloying titanium with precious metals (such as palladium), nickel, and/or molybdenum or coating titanium with certain precious metals (or their oxides) facilitates passivity by shifting alloy potential in the noble, or positive, direction. For example, the crevice corrosion resistance of titanium-palladium alloys in reducing acids and hot brines is significantly improved compared with unalloyed titanium.

Various dissolved oxidizing species in normally reducing media also shift the alloy potential in the noble direction. Many of these species, which include a host of multivalent transition metal ions, are very potent inhibitors and may be effective at concentrations of 100 ppm or less.

Applications of Titanium-Base Alloys

Titanium-base alloys are widely used for aerospace, chemical-processing, and marine environments where high strength-to-weight ratios are

beneficial and where corrosion resistance to oxidizing environments is required. The alloys are available in structural shapes and castings. Titanium is also used for implant devices and equipment.

Zinc and Zinc-Base Alloys

Zinc is an active metal. In aqueous solutions, zinc will either corrode (i.e., in acid or alkaline solutions) or will form a protective film for corrosion resistance (i.e., in mildly alkaline solutions).

Because of its reactive nature, the greatest use of zinc is as a protective, sacrificial coating for steel. The zinc coating may be exposed directly to the environment or may also be coated itself, as in the case of prepainted and galvanized steel.

Zinc can be applied as a coating by a number of processes, which are listed in Table 13 along with typical coating thicknesses. The effective life for protection by zinc coatings is directly dependent on the coating thickness (Fig. 11). Zinc-protected steel is used for building panels, appliances, automotive body panels, fasteners, and hardware items.

The reactive nature of zinc also allows it to be used for sacrificial anodes in cathodic protection systems. The active zinc anodes are electrically coupled to the metal to be protected. Cathodic protection by zinc is used in seawater, brackish water, fresh water, and in some soils. It is important that the zinc remain active. If the zinc passivates, as it will in certain soils, the sacrificial protection to steel is lost.

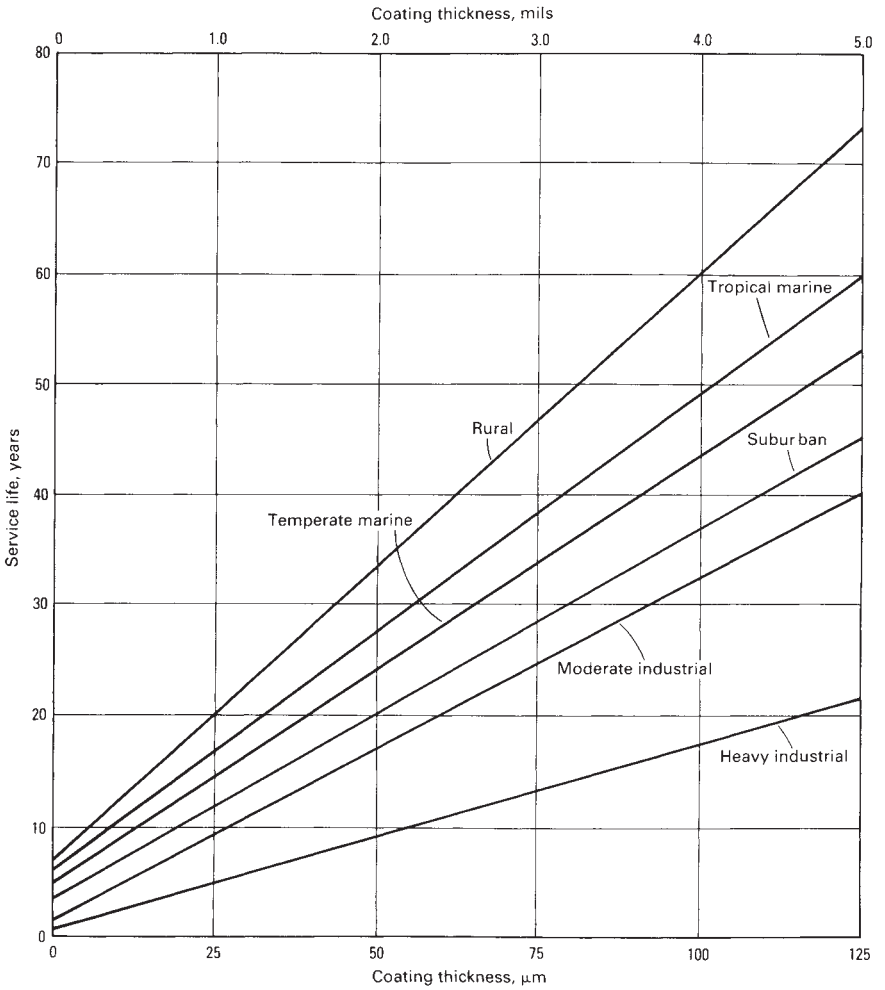
Zinc alloys are also used for applications such as die castings. For these uses, zinc must be protected from corrosion, typically by coatings.

Magnesium and Magnesium-Base Alloys

Magnesium is the most active of metals used for structural applications, being more active than either zinc or aluminum. Because of this

Table 13 Typical zinc coating processes and thicknesses

Method	Process	Coating thickness, μm (mils)	Applications
Electrogalvanizing	Electrolysis	0.5–4 (0.02–1.65)	Interior; appliance panels, studs, acoustical ceiling members
Zinc plating	Electrolysis	39 (1.53)	Interior or exterior: fasteners and hardware items
Mechanical plating	Peening	2.5–145 (0.098–5.75)	Interior or exterior: fasteners and hardware items
Thermal spraying	Hot-zinc spray	84–210 (3.32–8.33)	Interior or exterior: items that cannot be galvanized because of size or must be performed on-site
Continuous galvanizing	Hot dip	50 (2.0)	Interior or exterior: roofing, gutters, culverts, automobile bodies
Hot-dip galvanizing	Hot dip	35–115 (1.4–4.6)	Interior or exterior: nearly all shapes and sizes, ranging from nails, nuts, and bolts to large structural assemblies



Atmosphere	Description
Heavy industrial atmospheres	These contain general industrial emissions such as sulfurous gases, corrosive mists, and fumes released from chemical plants and refineries. The most aggressive conditions are often found in places of intense industrial activity where the coating is frequently wetted by rain, snow, and other forms of condensation. In these areas, sulfur compounds can combine with atmospheric moisture to convert the normally adherent and insoluble zinc carbonates into zinc sulfite and zinc sulfate. These sulfur compounds are water soluble and adhere poorly to the zinc surface. They are removed by rain with relative ease, exposing a fresh zinc surface to additional corrosion. In general, zinc dissipates more when exposed to this type of environment than any other atmospheric environment. Still, the steel corrodes far more slowly in this type of environment when protected by zinc than when just bare steel is used.
Moderately industrial atmospheres	These environments are similar to those of heavy industrial atmospheric environments but, from the standpoint of corrosion, are not quite as aggressive. The amount of emissions in the air may be somewhat lower than that of heavy industrial environments, and/or the type of emissions may be less aggressive. Most city or urban area atmospheres are classified as moderately industrial.
Suburban atmospheres	These atmospheres are generally less corrosive than moderately industrial areas and, as the term suggests, are found in the largely residential, perimeter communities of urban or city areas.
Temperate marine atmospheres	The length of service life of the galvanized coating in marine environments is influenced by proximity to the coastline and prevailing wind direction and intensity. In marine air, chlorides from sea spray can react with the normally protective, initial corrosion products to form soluble zinc chlorides. When these chlorides are washed away, fresh zinc is exposed to corrosion. Nevertheless, temperate marine atmospheres are usually less corrosive than suburban atmospheres.
Tropical marine atmospheres	These environments are similar to temperate marine atmospheres except they are found in warmer climates. Possibly because many tropical areas are found relatively far removed from heavy industrial or even moderately industrial areas, tropical marine climates tend to be somewhat less corrosive than temperate marine climates.
Rural atmospheres	These are usually the least aggressive of the six atmospheric types. This is primarily due to the relatively low level of sulfur and other emissions found in such environments.

Fig. 11 Service life (time to 5% rusting of steel surface) versus thickness of hot dip galvanized (zinc) coating for selected atmospheres

activity, magnesium is widely used as sacrificial anodes for cathodic protection in waters and soils (refer to Chapter 10). However, the electrochemical activity of magnesium also makes it very susceptible to galvanic corrosion (see discussion in next section, "Galvanic Corrosion").

The high strength-to-weight ratio of magnesium-base alloys makes them attractive for aircraft, automobiles, and electronic and computer applications. Magnesium alloy helicopter parts and other critical components used in hostile environments require coating of all exposed surfaces. In less hostile environments, magnesium alloys can be used with no protective treatment.

Magnesium is rapidly attacked by all mineral acids, with the exception of HF and pure $HCrO_4$. In HF, a protective magnesium fluoride film is formed. Magnesium shows good resistance to alkalis and organic solvents. Chloride solutions are particularly corrosive to magnesium and can lead to SCC.

Galvanic Corrosion. Insufficient attention to galvanic corrosion has been one of the major obstacles to the growth of structural applications of magnesium alloys. Serious galvanic problems occur mainly in wet saline environments. Prevention of galvanic damage requires consideration of a combination of measures including these:

- Design to prevent access and entrapment of salt water at the dissimilar-metal junction
- Selection of the most compatible dissimilar metals
- Introduction of high resistance into the metallic portion of the circuit through insulators or into the electrolytic portion of the circuit by increasing the length of the path the electrolytic current must follow
- Protective coating of the full assembly

Table 14 rates the relative compatibility of various metals with two wrought magnesium alloys, AZ31B (Mg-3Al-1Zn) and AZ61A (Mg-6.5Al-0.95Zn).

Lead and Lead Alloys

Lead has a successful service record in exposure to the atmosphere and to water. Underground, thousands of kilometers of lead-sheathed cable and lead pipe give reliable long-term performance. In the chemical industry, lead is used in the corrosion resistant equipment necessary for handling many chemicals.

The corrosion rate of lead is usually under anodic control because, generally, the most important determinants are the solubility and other

physical characteristics of the corrosion products formed at anodic sites. Most of these products are relatively insoluble lead salts that are deposited on the lead surface as impervious films, which tend to stifle further attack. The formation of such insoluble protective films is responsible for the high resistance of lead to corrosion by H_2SO_4, H_2CrO_4, and H_3PO_4.

In general, anything that damages the protective film increases the corrosion rate of lead. Conversely, factors that help create or strengthen the film reduce the corrosion rate. Therefore, the life of the lead-protected equipment can be extended, for example, by washing it with film-forming aqueous solutions containing sulfates, carbonates, or silicates. This procedure is suggested for protecting lead when it will be in contact with corrosives that do not form protective films.

In most environments, lead is cathodic to steel, aluminum, zinc, cadmium, and magnesium and thus will accelerate the corrosion of these metals. With titanium and passivated stainless steels, lead is the anode of the cell and suffers accelerated attack.

Corrosion in Water. Distilled water free of oxygen and CO_2 does not attack lead. The corrosion behavior of lead in distilled water containing dissolved CO_2 and oxygen depends on CO_2 concentration.

In general, the corrosion rate in natural and domestic waters depends on the degree of water hardness. Calcium and magnesium salts in the water, if present in at least moderate amounts (>125 ppm), form films on lead that adequately protect it against corrosive attack. Silicate salts present in the water increase both the hardness and the protective value of the film. In contrast, nitrate and chloride ions either interfere with the formation of the protective film or penetrate it; thus, they increase corrosion.

Atmospheric Corrosion. In most of its forms, lead exhibits consistent durability in all types of atmospheric exposure, including

Table 14 Relative effects of various metals on galvanic corrrosion of magnesium alloys AZ31B and AZ61A exposed at the 24.4 and 244 m (80 and 800 ft) stations, Kure Beach, NC

Group 1 (least effect)	**Group 4**
Aluminum alloy 5052	Zinc-plated steel
Aluminum alloy 5056	Cadmium-plated steel
Aluminum alloy 6061	**Group 5 (greatest effect)**
Group 2	Low-carbon steel
Aluminum alloy 6063	Stainless steel
Alclad alloy 7075	Monel
Aluminum alloy 3003	Titanium
Aluminum alloy 7075	Lead
Group 3	Copper
Alclad alloy 2024	Brass
Aluminum alloy 2017	
Aluminum alloy 2024	
Zinc	

industrial, rural, and marine types. Antimonial lead, such as UNS L52760 (Pb-2.75Sb-0.2Sn-0.18As-0.075Cu), exhibits approximately the same corrosion rate in atmospheric environments as chemical lead (99.9% commercial-purity lead). However, the greater hardness, strength, and resistance to creep of antimonial lead often make it more desirable for use in specific chemical and architectural applications.

Corrosion in Underground Ducts. Lead is used extensively in the form of sheathing for power and communications cables because of its excellent resistance to corrosion in a wide variety of soil conditions. Cables are either buried directly in the ground or installed in ducts or conduits. Sheathing on cable installed in continuous concrete or asbestos cement ducts in concrete tunnels under waterways was found to be severely corroded. Analysis of water samples from these locations revealed that the corrosion had resulted from the presence of up to 1000 ppm of hydroxides.

Stray currents, as well as minor earth currents, can cause severe corrosion of lead pipe or lead cable sheathing. Stray currents cause corrosion at the point where they leave the metal. Sources of stray currents include electric railway systems, grounded electric direct-current power, electric welders, cathodic protection systems, and electroplating plants. Other factors that can initiate the corrosion of lead sheathing include contact with acetic acid (in wooden ducts), microorganisms, and corroded steel-tape armor.

Tin and Tin-Base Alloys

Tin is a soft, brilliant white, low-melting-point metal that is most widely known and characterized in the form of coating for steel, commonly referred to as tinplate. Because of its low strength, the pure metal is not regarded as a structural material and is rarely used in monolithic form. Rather, the metal is most frequently used to coat other metals and in alloys to impart corrosion resistance, enhance appearance, or improve solderability. It also finds wide use in tin-base soft solders and bearing alloys and in copper-base bronzes.

Corrosion Resistance. Tin reacts with both strong acids and strong alkalis, but it is relatively resistant to near-neutral solutions. Oxygen greatly accelerates corrosion in aqueous solutions. In general with mineral acids, the rate of attack increases with the temperature and concentration. Dilute solutions of weak alkalis have little effect on tin, but strong alkalis are corrosive even in cold dilute solutions. Salts with an acid reaction attack tin in the presence of oxidizers or air. Tin resists de-

mineralized waters, but it is slightly attacked near the waterline by hard tap waters.

Zirconium and Zirconium-Base Alloys

Zirconium is a reactive metal and depends on a passive film for corrosion resistance. Zirconium is very resistant to corrosive attack in most mineral and organic acids, strong alkalis, saline solutions, and some molten salts. It is not attacked by oxidizing media unless halides are present. Zirconium is not resistant to HF, ferric chloride ($FeCl_3$), cupric chloride ($CuCl_2$), aqua regia, concentrated H_2SO_4, and wet chloride gas.

The most prevalent use of zirconium, zirconium-hafnium alloys, and zirconium-hafnium-niobium alloys has been in the chemical processing industry for handling hot H_2SO_4. Zirconium and its alloys have excellent resistance to H_2SO_4 up to 50% concentration at temperatures to boiling and above. From 50 to 65% concentration, resistance is generally excellent at elevated temperatures, but the passive film is a less effective barrier. Experience has shown that oxidizing species in more than 50% H_2SO_4 can encourage selective attack. In concentrated H_2SO_4 above 70%, the corrosion rate of zirconium increases rapidly with increasing concentration.

Tantalum

Tantalum is one of the most versatile corrosion resistant metals. It combines the inertness of glass with the strength and ductility of low-carbon steel and has a much higher heat-transfer capability than glass. The relatively high cost of tantalum has been a limiting factor in its use, but where corrosion resistance is important, the economics are changing. Fabrication techniques that apply thin linings of tantalum to chemical-processing components result in equipment that has the acid corrosion resistance provided by tantalum, but at a much lower cost than an all-tantalum construction.

Corrosion of Tantalum in Specific Media. Because tantalum exhibits excellent corrosion resistance to a wide range of media at different concentrations and temperatures, one of its primary applications is as a construction material in the chemical processing industry. The outstanding corrosion resistance and inertness of tantalum are attributed to a very thin, impervious, protective oxide film that forms upon exposure of the metal to slightly anodic or oxidizing conditions.

The chemical properties of tantalum are similar to those of glass. Like glass, tantalum is immune to attack by almost all acids except HF. Tantalum is not attacked by H_2SO_4, HNO_3, HCl, aqua regia, perchloric acid ($HClO_4$), chorine, bromine, hydrobromine acid (HBr) or any of the bromides, H_3PO_4 when free of the F^- ion, nitric oxides, chlorine oxides, hypochlorous acid (HClO), organic acids, and hydrogen peroxide (H_2O_2) at ordinary temperatures. It is attacked, even at room temperature, by strong alkalis, HF, and free sulfur trioxide (SO_3) (as in fuming H_2SO_4).

Hydrogen Embrittlement, Galvanic Effects, and Cathodic Protection of Tantalum. Failures due to hydrogen embrittlement have occurred in some severe aqueous acid media in chemical industry applications where tantalum was, or became, electrically coupled to a less noble metal, such as low-carbon steel. Under these conditions, tantalum became the cathode in the galvanic cell thus created.

Because of the presence of stray currents, tantalum may become a cathode in the system and consequently may absorb and become embrittled by atomic hydrogen in the electrolytic (galvanic) cell. Stray currents can result from induction from adjacent lines, leakages, variable ground voltages, and other sources. Although stray voltages may be transient, absorbed hydrogen is cumulative in its effect, eventually producing hydrogen embrittlement.

Several methods have been used or proposed to reduce hydrogen embrittlement of tantalum:

- Complete electrical insulation of tantalum from all metals in the system
- Addition of a selected oxidizing agent to the solution
- Coupling of the tantalum surface to a noble metal
- Anodization of the tantalum

Niobium and Niobium-Base Alloys

Niobium and niobium-base alloys are used in several corrosion-resistant applications, principally rocket and jet engines, nuclear reactors, sodium vapor highway lighting, and chemical processing equipment. Niobium has many of the same properties of tantalum, its sister metal, but only one-half the density. A common property of niobium is the interaction with the reactive elements hydrogen, oxygen, nitrogen, and carbon at temperatures above 300 °C (570 °F). These reactions cause severe embrittlement. Consequently, at elevated temperatures, the metal must be protectively coated or used in vacuum or inert atmospheres. Niobium resists a variety of corrosive environments, including

concentrated mineral acids, organic acids, liquid metals (particularly sodium and lithium), metal vapors, and molten salts.

Niobium, like other reactive metals, derives its corrosion resistance from a readily formed, adherent, passive oxide film. The corrosion properties of niobium are similar to those of tantalum, but niobium is less resistant in aggressive media, such as hot concentrated mineral acids. Like tantalum, niobium is susceptible to hydrogen embrittlement if cathodically polarized by either galvanic coupling or impressed potential. In addition to being very stable, the anodic niobium oxide film has a high dielectric constant and a high breakdown potential. These properties, coupled with good electrical conductivity, have led to the use of niobium as a substrate for platinum-group metals in impressed-current cathodic protection anodes.

Cobalt-Base Alloys

As a group, the cobalt-base alloys may be generally described as wear resistant, corrosion resistant, and heat resistant (strong even at high temperatures). The single largest use for cobalt alloys is in the area of wear-resistant components/applications. Hardfacing (weld overlay) alloys are commonly used in such applications. These are cobalt-chromium-tungsten alloys (commonly referred to as Stellites) that protect surfaces in nuclear power and chemical processing applications. The use of such alloys stems from their outstanding resistance to wear, erosion-corrosion, cavitation damage, and, to a lesser extent, oxidation/corrosion. In heat resistant applications, cobalt is more widely used as an alloying element in nickel-base alloys with cobalt tonnages in excess of those used in cobalt-base heat resistant alloys.

Corrosion resistant cobalt alloys contain nickel, chromium, and molybdenum alloying additions. Molybdenum additions in these alloys (in preference to tungsten) impart a greater degree of resistance to a variety of aqueous media. Cobalt-chromium-nickel-molybdenum alloys are biocompatible and are widely used for the fabrication of various devices that are surgically implanted in the body, for example, hip and knee replacements. Cobalt-base implant alloys combine mechanical strength with corrosion and wear resistance.

Polymers

Polymers provide an increasing number of materials that can be used for corrosion protection. They are used as protective coatings and linings and for structural applications. Polymeric materials often compete

favorably with metals in terms of initial cost, structural properties, and service life.

Types of Polymers

Three classes of polymers are thermoplastics, thermosets, and reinforced plastics.

Thermoplastics soften when heated (and eventually liquify) and harden when cooled, processes that are totally reversible and may be repeated. Their processing characteristics are analogous to those of paraffin wax, which is heated until it softens and liquifies, poured into a mold, and allowed to cool. The wax takes the shape of the mold. If reheated, the wax can be molded into a different shape.

Examples of thermoplastic polymers are polyvinyl chloride, polyethylene, and nylon. Parts (e.g., pipes and fittings) are typically produced by extrusion or injection molding.

Thermosets are cured, set, and hardened, usually by heating, into a permanent shape. The polymerization reaction is an irreversible reaction known as cross linking. Once set, a thermosetting plastic cannot be remelted. The processing characteristics of thermosets are analogous to those of concrete. Once the slurry consisting of cement, aggregate, and water hardens, it cannot return to its original semisolid state.

Examples of thermoset polymers are acrylics, epoxies, and polyesters. They are often used for coatings and adhesives and can be used alone as structural materials.

Fiber-reinforced plastics (FRPs) are composites of fibers and either thermoplastic or thermoset polymers. These materials can compete with metals in terms of strength. Glass fibers are commonly used for reinforcement, and panels, pipes, and tanks are typical product forms.

Properties of Polymers

Typical properties of thermoplastics and thermosets are compared in Fig. 12. The glass transition temperature, T_g, defines a temperature

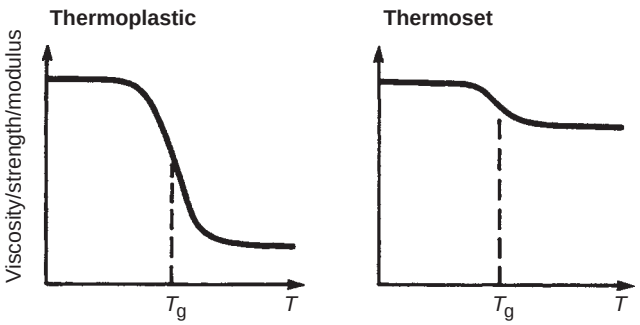


Fig. 12 Typical properties of thermoplastics and thermosets.

above which marked changes in physical properties are observed. For a thermoplastic polymer, viscosity, strength, and tensile modulus decrease sharply and to low values above T_g. These polymers are formed above T_g; their service use is limited to temperatures below T_g. For thermosets, the decrease in properties is clearly observed, but the degradation of properties is not so drastic as that for the thermoplastics. Generally, the thermosets provide higher chemical resistance and higher use temperatures than thermoplastics.

High-strength plastics, ranging from short glass fiber-reinforced thermoplastics for injection molding to 70% continuous carbon fiber-reinforced advanced composites, are used for aircraft structural components, auto body parts, appliances, and other products. Unreinforced engineering plastics have tensile strengths on the order of one-third to one-half those of low-carbon steels. Unreinforced engineering thermoplastics—so called because of their considerably better properties compared with commodity plastics—typically have tensile strengths ranging from 55 to 103 MPa (8 to 15 ksi).The workhorse of engineering plastics, unreinforced nylon 6/6, has a tensile strength of about 83 MPa (12 ksi).

Incorporating reinforcements in thermoplastics and thermosets dramatically increases strength. Short glass fibers at a 30% loading (by weight) boost the tensile strength of engineering plastics by an approximate factor of two; carbon fibers increase strength even further.

On the high end of the composite materials properties spectrum lie advanced composites—most commonly, graphite/epoxy laminates consisting of 60% (by volume) of continuous reinforcing fibers. Reinforced with a high-modulus graphite fiber, a unidirectional laminate typically has a tensile modulus of approximately 200 GPa (29,000 ksi) and a tensile strength of 1138 MPa (165 ksi); a high-strength graphite fiber reinforcement produces a modulus of 138 GPa (20,000 ksi) and a tensile strength of 1552 MPa (225 ksi). In addition to graphite and carbon, reinforcing fibers for advanced composites include boron, S-glass, aramid, and hybrids of these. Properties of selected glass fiber-reinforced composites and several metals are presented in Table 15.

The fiber-reinforced composites are lighter than steel. They show a range of tensile strengths but have limited elongations compared with steel. The tensile moduli are lower than those of steels. An advantage of these composites is that stiffness and strength can be built-in where required through the use of multidirectional laminates.

Environmental Degradation of Polymers

The environments of concern for polymers differ in general from those of concern for metals. Environmental factors that can affect polymers include:

Table 15 Properties of selected glass and fiber-reinforced composites

Properties of several metals are included for comparison.

Material(a)	Reinforcement, wt%	Specific gravity	Tensile strength		Tensile modulus		Compressive strength		Flexural strength		Flexural modulus		Elongation, %	Notched Izod impact toughness	
			MPa	ksi	GPA	10^6 psi	MPa	ksi	MPa	ksi	GPa	10^6 psi		J	ft · lbf
Composite molded polyester BMC	22	1.82	41.4	6.0	12.07	1.75	137.9	20	88.3	12.8	10.89	1.58	0.5	5.79	4.26
Injection molded polyester BMC	22	1.82	33.51	4.86	10.55	1.53	…	…	87.22	12.65	9.93	1.44	0.5	3.92	2.89
Composite molded polyester SMC	50	2.0	158.6	23.0	15.65	2.27	220.6	32.0	310.3	45.0	13.8	2.0	1.7	26.3	19.4
Composite molded polyester SMC	30	1.85	82.7	12.0	11.7	1.7	165.5	24.0	179.3	26.0	11.0	1.6	1.0	21.7	16.0
Composite molded polyester SMC	20	1.78	36.5	5.3	11.7	1.7	158.6	23.0	110.3	16.0	9.7	1.4	0.4	11.1	8.2
Polyester pultrusions	55	1.69	206.9	30.0	17.2	2.5	206.9	30.0	206.9	30.0	11.0	1.6	…	34.0	25.0
Filament-wound epoxy	80	2.08	551.6	80.0	27.6	4.0	310.3	45.0	690.0	100.0	34.5	5.0	…	61.1	45.0
Milled glass RRIM PUR	13	1.07	19.3	2.8	…	…	…	…	…	…	0.255–0.365	0.037–0.053	140	…	…
Flake glass RRIM PUR	23	1.17	30.4	4.41	…	…	…	…	…	…	1.03	0.15	38.9	2.9	2.1
Polyester, spray-up/lay-up	30	1.37	86.2	12.5	6.9	1 .0	151.7	22.0	193.1	28.0	5.17	0.75	1.3	17.7–20.4	13–15
Polyester, woven roving (lay-up)	50	1.64	255.1	37.0	15.5	2.25	186.2	27.0	317.2	46.0	15.5	2.25	1.6	44.8	33.0
Cold-rolled HSLA steel(b)	…	7.75	448.2	65.0	206.9	30.0	448.2	65.0	…	…	…	…	22.0	…	…
Cold-rolled low-carbon steel	…	7.86	331.0	48.0	206.9	30.0	331.0	48.0	…	…	…	…	37.0	…	…
Stainless steel(c)	…	8.03	551.6	80.0	193.1	28.0	551.6	80.0	…	…	…	…	40.0	…	…
Wrought aluminum(d)	…	2.74	337.9	49.0	70.3	10.2	337.9	49.0	…	…	…	…	23.0	…	…
Die-cast aluminum(e)	…	2.82	331.0	48.0	71.0	10.3	331.0	48.0	…	…	…	…	2.5	…	…
Die-cast magnesium(f)	…	1.83	227.5	33.0	44.8	6 .5	227.5	33.0	…	…	…	…	3.0	…	…
Die-cast zinc(g)	…	6.59	282.7	41.0	75.2	10.9	282.7	41.0	…	…	…	…	10.0	…	…

(a) BMC, bulk molding compound; SMC, sheet molding compound; RRIM PUR, reaction injection molded polyurethane. (b) ASTM A 606. (c) SAE 1008. (d) AA 2036. (e) ASTM B 85. (f) ASTM AZ91B. (g) ASTM AG40A. Property data courtesy of Owens-Corning Fiberglass Corp.

- Moisture and humidity
- Elevated temperature
- Impact load and creep
- Ultraviolet exposure
- Solvents
- Chemicals

The most common forms of environmental degradation in polymers are swelling, dissolution, and bond rupture. Often the environmental resistances of plastics and metals are complementary; for example, metals are resistant to organic solvents that attack plastics. Plastics are resistant to many acids that attack metals.

Some plastics such as nylon absorb moisture, which can substantially affect the mechanical properties as well as the dimensions of a part. When chemicals are present, a range of resistance is demonstrated, and no two plastics behave in exactly the same manner or resist the chemicals to the same degree. However, several plastics and composites can perform in very corrosive chemical environments where metals would corrode rapidly. A prime example is polytetrafluoroethylene (PTFE), one of the most inert substances known to man. Similarly, newer thermoplastics such as aromatic polyester liquid crystals, polyketones, and polyphenylene sulfide provide excellent chemical resistance, even at elevated temperatures. Their ability to be molded by thermoplastic processes, design versatility, and potential for parts consolidation are their prime advantages over corrosion resistant metals.

In general, because plastics are organic materials, they can be dissolved or attacked by chemical substances, notably organic solvents. How well a plastic withstands solvents has been linked to its polymeric structure, including degree of crystallinity, bond strength, and type of bonding. Crystalline engineering thermoplastics, such as PTFE and nylon, often have superior chemical resistance compared with that of amorphous types, such as polycarbonate.

Depending on both the nature of the chemical and the type of polymer, a plastic can dissolve in, chemically react with, or absorb a chemical agent. In the presence of certain chemicals and under the influence of stress, plastics can fail by gradual cracking. Known as environmental stress cracking, this phenomenon does not occur in the unstressed state. Detergents and oils can cause this type of failure in polyethylenes. Similarly, zinc chloride formed from road salt reacting with zinc parts has caused failure in under-the-hood nylon automobile components.

A basic knowledge of how a polymer reacts in the presence of chemical reagents or solvents is necessary in the materials selection process. To design or select a material for use in a particular environment, performance must be quantifiable. Dimensional changes from swelling,

Table 16 Chemical resistance of engineering plastics

Material	Resistant to	Attacked by
Acetals	Organic solvents; aliphatic, aromatic, and chlorinated hydrocarbons	Strong acids, alkalis, and oxidizing agents
Epoxies	Organic solvents; weak acids and alkalis	Some epoxies are attacked by strong alkalis; most, by strong acids.
Melamines	Organic solvents; weak alkalis and acids	Strong alkalis and acids
Nylons 6 and 6/6	Hydrocarbons; esters; ketones; alkalis	Mineral acids; phenols; cresols
Nylons 11 and 12	Oil; grease; petroleum chemicals; organic solvents	Phenols; strong oxidizers; mineral and organic acids
Phenolics	Those with high glass reinforcement resist organic solvents, hydrocarbons, weak acids, and cleaning fluids; chemically resistant grades withstand strong nonoxidizing acids	Strong alkalis and oxidizing acids
Polyamide-imides	Most acids and organic solvents	Strong bases
Polycarbonates	Weak organic and inorganic acids; oxidizing and reducing agents; aliphatic hydrocarbons	Aromatic and chlorinated hydrocarbons; alkalis, amines; esters
Aromatic polyester LCPs(a)	Most solvents and corrosive chemicals; polar and unpolar solvents; MEK; ethylacetate; hydrocarbons; trichloroethylene; acetic acid; caustic; bleach; detergents	…
PBT(b) and PET(c) thermoplastic polyesters	Alcohols; oils; petroleum; esters; ketones; aliphatic hydrocarbons; weak acids and bases	Low-molecular-weight ketones; strong acids and bases
Unsaturated polyesters	Organic solvents; acids; weak alkalis	Depending on type, can be attacked by strong alkalis
Polyetherether-ketone	Most inorganic and organic chemicals	Only known solvent is concentrated sulfuric acid.
Polyetherimides	Mineral acids; weak bases and hydrocarbons; fluorinated solvents and refrigerants	Chlorinated hydrocarbons
Thermoplastic polyamides	Most organic solvents; dilute acids and bases; oils	…
Modified polyphenylene oxide	Strong acids and bases; detergents	Aromatic and chlorinated hydrocarbons
Polyphenylene sulfide	All solvents at temperatures up to 205 °C (400 °F); strong oxidizing inorganic acids	…
Polysulfones	Aliphatic hydrocarbons; inorganic acids; alkalis	Aromatic hydrocarbons; esters; ketones; chlorinated hydrocarbons
Polytetrafluoroethylene	The most inert plastic; resists practically all solvents, acids and bases, oils, etc. Related polymers perform similarly.	…
Silicones	Acids; weak alkalis	Strong alkalis; some organic solvents
Ureas	Organic solvents; oils; greases	Concentrated acids and alkalis
Vinyl esters	Acids and alkalis at temperatures up to 120 °C (250 °F)	…

(a) Liquid crystal polymers. (b) Polybutylene terephthalates. (c) Polyethylene terephthalates

weight loss, and effects on mechanical and physical properties must be evaluated. Because plastics are viscoelastic, the long-term effects of both time and temperature must be considered. The chemical resistance of several engineering plastics is presented in Table 16. Data for retention of tensile strength for several engineering plastics after chemical exposure in a variety of environments are presented in Table 17.

Chemically resistant plastics and composites are used in the chemical, petroleum, and metals-processing industries. Fluoroplastics, such as PTFE, long used as tank liners and in pumps, are also used. Carbon fiber-reinforced plastics are used in components for magnetic-drive pumps because of their resistance to hot acids at 60% concentrations. Hot sheet stamping has been used to produce disk components for butterfly valves. Engineering plastics find use in valve, gears, and pressure vessels.

Table 17 Percent retention of tensile strength for several engineering plastics after chemical exposure

24 h exposure at 95 °C (200 °F).

	Retention of tensile strength, %				
Chemical media	**PPS**	**Nylon 6/6**	**PC**	**PSO**	**Modified PPO**
Acids					
37% hydrochloric	100	0	0	100	100
30% sulfuric	100	0	100	100	100
Glacial acetic	98	0	67	91	78
Bases					
28% ammonium hydroxide	100	85	0	100	100
30% sodium hydroxide	100	89	7	100	100
N-butylamine	49	91	0	0	0
Aniline	96	85	0	0	0
Hydrocarbons					
Cyclohexane	100	90	75	99	0
Toluene	98	76	0	0	0
Diesel fuel	100	87	100	100	36
Gasoline	100	80	99	100	0
Organic solvents					
Chloroform	87	57	0	0	0
Chlorobenzene	100	73	0	0	0
Ethylene chlorine	72	65	0	0	0
Butyl alcohol	100	87	94	100	84
Cyclohexanol	100	84	74	95	27
Phenol	100	0	0	0	0
Methyl ethyl ketone	100	87	0	0	0
Ethyl acetate	100	89	0	0	0

PPS, polyphenylene sulfide. PC, polycarbonate. PSO, polysulfone. PPO, polyphenylene oxide

Ceramics

The ceramics encompass a number of types of materials, including oxides, carbides, nitrides, concrete, brick, glass and fused silica, enamel, and stoneware. These materials are generally characterized by their high corrosion resistance, high-temperature capabilities, good erosion and abrasion resistance, poor impact resistance, and poor toughness. Table 18 lists typical applications for ceramics.

Corrosion is often thought of as the oxidation of metals such as iron, but ceramics also corrode or react with their environment. Concrete, for example, generally is very stable, but it contains calcium hydroxide and calcium aluminate, which are attacked by sulfates (e.g., calcium sulfate,

Table 18 Typical applications for ceramics

Material	**Application**
Concrete	Tanks, linings, paving, pipe, structural
Glass	Sulfuric acid, valves, lines, tank linings
Graphite	Hydrochloric acid, hydrofluoric acid
Enamel	Coating on plumbing fixtures and appliances
Tungsten carbide	Wear and corrosion: pumps, shafts, bearings
Silicon carbide	Wear and corrosion: pump sleeves, shafts, bearings

often present in ground water) and by strong acids. Tungsten carbide, usually highly resistant to corrosion, is destroyed in less than a week of contact with concentrated H_2SO_4. Alumina corrodes in concentrated alkalis, concentrated H_3PO_4, and other concentrated acids. Glass corrodes in HF and concentrated alkalis. Carbon is attacked by strong oxidizers.

Concrete is used underground to protect steel structures and pipes. Concrete structures in turn are often reinforced by steel rods (rebar). When concrete sets, it generates alkalis that produce a protective film over the steel surface. The structure of concrete is porous, however, and allows water to penetrate. When chlorides are in the water and reach the steel in concrete, corrosion can result in spalling and cracking of concrete, a phenomenon often seen on bridges and in parking garages.

Glass resists many chemicals, including detergents and acids, but is attacked by HF and concentrated alkalis. Glass may crack when the temperature changes rapidly and also is susceptible to fracture from impact. Glass liners can be broken even when not impacted directly.

Enamels are highly resistant to corrosion and are used to protect many steel and cast iron substrates. Enamels are comprised of silicate and borosilicate glass, with the addition of fluxes to promote adhesion. For applications in contact with acids, a smaller amount of flux is used. Chemical equipment requires an enamel with a higher percentage of borosilicate glass.

The composition of the enamel is adjusted so that its coefficient of thermal expansion closely matches that of the underlying metal. At least two coats of enamel are applied. The first coat contains cobalt or nickel oxides (for coating steel) or lead oxide (for coating cast iron) to aid adhesion.

Steels used in enamelware require a low carbon content, as the carbon may react with the molten oxides in the enamel to form a gas, which in turn causes blistering of the enamel. Alloyed steels may be used, such as those containing titanium. The titanium combines with the carbon, nitrogen, and oxygen to produce inert compounds, thus preventing the formation of gases.

High-temperature corrosion resistance is attained with silicide coatings. A thin layer of fused silicide is applied to metals (e.g., niobium alloys). However, the silicide coating is brittle and susceptible to chipping. Another high-temperature coating consists of a borosilicate glass matrix reinforced with iron and nickel powders. The iron and nickel impart toughness to the composite.

Chromium oxide is another corrosion-resistant ceramic. It has the ability to bond to glass and is capable of repairing fractured glass linings of chemical tanks. It also resists erosion and abrasion. Other oxides include aluminum oxide and zirconium oxide. These oxides are resis-

Table 19 Corrosion test results for several ceramics in liquids.

125 to 300 h of submersive testing, continuously stirred.

Concentrated reagent, wt%	Temperature °C	Temperature °F	Corrosive weight loss(a), mg/cm^2 per year: Si/SiC composites (12% Si)	Tungsten carbide (6% Co)	Aluminum oxide (99%)	Silicon carbide (no free Si)
98% H_2SO_4	100	212	55.0	>1000	65.0	1.8
50% NaOH	100	212	>1000	5.0	75.0	2.5
53% HF	25	77	7.9	8.0	20.0	<0.2
85% H_3PO_4	100	212	8.8	55.0	>1000	<0.2
70% HNO_3	100	212	0.5	>1000	7.0	<0.2
45% KOH	100	212	>1000	3.0	60.0	<0.2
25% HCl	70	158	0.9	85.0	72.0	<0.2
10% HF + 57% HNO_3	25	77	>1000	>1000	16.0	<0.2

(a) Corrosion weight loss guidelines are >1000 mg/cm^2 per year, completely destroyed within days; 100 to 999 mg/cm^2 per year, not recommended for service greater than 1 month; 50 to 100 mg/cm^2 per year, not recommended for service greater than 1 year; 10 to 49 mg/cm^2 per year, caution recommended based on the specific application; 0.3 to 9.9 mg/cm^2 per year, recommended for long-term service; <0.2 mg/cm^2 per year, recommended for long-term service; no corrosion, other than as a result of surface cleaning, was evident.

tant to a variety of chemicals, but are not recommended for long-term exposure to strong acids or alkalis.

Tungsten carbide is widely used in wear applications. It resists strong bases, such as NaOH and KOH, even at higher temperatures. However, strong acids, such as H_2SO_4 and HNO_3, attack the cobalt and nickel binders in tungsten carbide, weakening its structure.

Silicon carbide resists both strong acids and strong bases. It is virtually unaffected by HF, HCl, and KOH, having a corrosive weight loss of less than 0.2 mg/cm^2 per year (0.00005 oz/in.^{2} per year).

Corrosion resistance of ceramics can be screened in laboratory tests. Results for several ceramics in a variety of environments are shown in Table 19. Corrosion testing was performed by submersing the test material in a chemical bath. The bath was stirred continuously for the duration of exposure, often 100 to 300 h. Weights before and after testing were compared to determine weight loss, and the surface was examined. The strength of the test material was compared with that of nonsubmersed parts.

Other Nonmetallic Materials

Rubber (Ref 1)

Natural and synthetic rubbers are widely used as linings for the protection of steel tanks and pipes. Both natural and synthetic rubbers can be divided into soft rubbers, semihard rubbers, and hard rubbers. Soft rubbers contain 0.1% sulfur and have a hardness in the range of 40 to 80 international rubber hardness degree (IRHD) or a durometer A hardness of 30 to 75. Semihard rubber contains 13 to 20% sulfur and has a durometer A hardness of 35 to 60. Hard rubber contains 25 to 31%

sulfur and has a hardness of durometer D 60 to 85. In general, both semi-hard and hard rubbers are more resistant than soft rubbers to all organic and inorganic acids, caustic solutions, aliphatic hydrocarbons, and chlorine gas. Characteristics of some common soft rubber lining materials are reviewed subsequently.

Natural (NR) or Synthetic Polyisoprene (IR). Linings based on these rubbers are resistant to most inorganic chemicals with the exception of strong oxidizing agents. The resistance of these rubbers to organic chemicals is limited. They are satisfactory with alcohols and other polar organic chemicals. They should not be used in the presence of aliphatic, aromatic hydrocarbons, halogenated hydrocarbons, and mineral oils. Soft compounds (40 to 50 IRHD or durometer A 30 to 50) based on these rubbers have excellent resistance to abrasion and erosion. The service temperature range is about –30 to about 100 °C (–20 to 212 °F).

Polybutadiene (BR) and Styrene-butadiene (SBR) Copolymer. These materials can be used either singly or in blended form with natural rubber and have similar properties to natural rubber.

Polychloroprene (CR). Compounds made from CR possess greater resistance than NR to ozone and sunlight and also have resistance to some oils. They should not, however, be used in conjunction with halogenated or aromatic hydrocarbons. Suitably compounded grades of CR can be used in the temperature range of – 20 to 70 °C (–5 to 160 °F).

Butyl rubber (IIR) is a copolymer of isobutylene and isoprene. Butyl rubber has better resistance to oxidizing acids than NR or CR rubbers. Butyl rubber has a low permeability to gases and lower water absorption than other soft rubber compounds. Butyl rubber is not suitable for use with chlorine and other halogens, mineral oils, halogenated, or aromatic hydrocarbons. The service temperature range is about –30 to about 95 °C (–20 to 205 °F).

Nitrile rubbers (NBR) are copolymers of acrylonitrile and butadiene. Use in large-scale lining operations has been limited to occasions where oil resistance is required. Polymers that contain the higher ratios of acrylonitrile to butadiene are particularly resistant to swelling by mineral oils and fuels; similarly, gas impermeability is increased. Nitrile rubber should not be used with phenols, ketones, strong acetic acid, and most aromatic hydrocarbons. The useful temperature range is about –20 to about 105 °C (–5 to 220 °F).

Chlorosulfonated Polyethylene Rubber (CSM). This is a synthetic rubber with excellent resistance to ozone and oxidizing chemicals and good abrasion resistance. It can be compounded for very good resistance to oxidizing chemicals such as sodium hypochlorite solutions, to sulfuric acid and to sulfuric acid saturated with chlorine. It has good resistance to most oils, lubricants, and aliphatic hydrocarbons, but it is unsuitable for use with esters and ketones. The useful temperature

range is about –10 to about 110 °C (15 to 230 °F). This material is used on a limited scale for lining.

Ethylenepropylene rubbers (EPR and EPDM) are available as copolymers and terpolymers but are only used on a limited scale for linings. Their properties are very similar to those of butyl rubber. Selected compounds have very good resistance to water and steam at temperatures up to 100 °C (212 °F), but they may crack if highly stressed.

Fluoro rubbers (FPM) have excellent resistance to a very wide range of chemicals, but their use as linings is limited to small ancillary equipment. The notable exceptions in their chemical resistance are low-weight, polar organic chemicals, for example, methyl alcohol, ketones, amines, and anhydrous ammonia. Many grades are unsatisfactory for use with high-pressure steam. The service temperature range is about –30 to about 100 °C (–20 to 212 °F).

Carbon and Graphite

Carbon and graphite are quite inert and have the added advantages of good electrical conductivity and heat transfer (for heat exchangers). Their main disadvantage is fragility. Graphite is used in many applications involving HF and HCl as well as for impressed-current anodes in cathodic protection systems.

Woods

Cypress, pine, and redwood are the woods most often used for corrosion applications. Cooling tower internals, filter press parts, structural members, barrels, and tanks often are made of wood. Wooden tanks are sometimes less expensive than other types. One disadvantage is that they must be kept wet at all times, or the staves with shrink, warp, and leak. Wood generally is limited to applications involving water and dilute chemicals, because chemical and biological attack can pose problems.

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CHAPTER 7

Corrosion Control by Proper Design

THE DESIGN PROCESS is the first and most important step in corrosion control. Major savings in operating costs are possible by anticipating corrosion problems so as to provide proper design for equipment before assembly or construction begins.

Design can never be absolute. There will often be a tendency for compromise based on cost and the availability of materials and resources. For example, one designer might recognize a potential corrosion hazard and plan for early replacement or more regular maintenance. Such design options may be relatively inexpensive. Designers might have little experience with regard to corrosion and the subtleties of material fabrication and assembly. In these cases, incorrect decisions can be extremely costly.

A designer is seldom a corrosion engineer; therefore, it is necessary to convey a basic knowledge of corrosion to the designer. This information must relate to the total design requirements. In some cases, the process conditions might not be known with sufficient exactness to permit the optimal technical design decision.

It is important to be aware of design details that can lead to early deterioration. These fine details of design, often compounded by human error, account for many significant failures. Therefore, corrosion engineering design must be an integral part of the total design, which in turn includes aspects ranging from appraisal of the design concept to inspection and quality control in installation and operation. In addition, it cannot be overemphasized that poor design may render corrosion-resistant materials susceptible to premature corrosion.

The results of a survey of chemical-process plants (Ref 1) showed that design faults ranked highest (58%) as the causes for failure. Of almost equal ranking was the incorrect application of protective treatments (55%), followed by categories that demonstrated a lack of knowledge about the operating conditions (52%), lack of process control (35%), and a lack of awareness that there was actually a corrosion risk (25%).

Ideally, designers would call for some corrosion assessment *prior* to preparing the detailed engineering design. Typically, schemes would permit some form of evaluation with respect to both function and the necessary action, for example, from the proposal-to-production planning stages. In the practical "real" world, however, communication of "agreed" reasons for failures may not always reach the designer. Indeed, communication to contractors, who are closest to the application, is even poorer. Studies have shown that, while management is always informed of the reasons for failure in the chemical-processing industry, site personnel are informed only 77% of the time, designers 55%, material suppliers 37%, and contractors only 11% of the time (Ref 1).

Design as a Process

For many people, the word *design* brings to mind an actual product. However, when corrosion control is the objective, it is useful to think of design as a process rather than an actual product. When thought of in this way, it becomes apparent that many people forming a "design team" should be involved. It is only through successful integration of the efforts of each specialized member of this team that a successful final design can be produced.

The Design Team

Many people participate in or affect the design process. The roles of the mechanical or civil engineer, materials specialist, corrosion engineer, and coating specialist are fairly well understood. There are, however, others, such as accountants, planners, estimators, draftsmen, and contract specialists who can also affect the overall design. Operating and maintenance personnel, too, should often by included in the design team, but their valuable input is frequently not utilized. Whatever the composition of the design team, each member must be able to effectively provide some input. Each member must, therefore, be able to communicate continuously and effectively with the others. This communication requires that each member of the team understand the basics of the other members' jobs.

The corrosion engineer is one person who should be involved in the entire design process from beginning to end to oversee all of the aspects of the design that can affect the corrosion performance of the system. If corrosion control is only considered late in the design process, or worse yet, after the design is completed, efficient corrosion control can seldom be achieved.

Steps in the Design Process

The design process for corrosion control can be broken down into four effective steps.

Defining the Desired Component Function. This step is carried out by answering several basic questions: What is the function to be carried out by the component? How is this function to be accomplished? What are the required properties, and how are these properties ranked with respect to priority?

Defining the Service Environment. This definition includes the chemical composition, temperature, velocity, stresses of the environment, etc. The normal operating or service conditions are commonly well defined. However, it is just as important to consider the environment during start-up and shutdown and during possible upset conditions. It is during these "nonnormal" periods that many corrosion problems initiate and result in unanticipated failures. Conditions during outages should also be defined in this step of the design process.

Materials Selection, Fabrication Procedures, and Process Details. This step is an iterative process, and often many trade-offs are required among the materials properties and process options. The goal is to meet all of the mandatory objectives of the design function. Once the materials and process details have been determined, clear and concise specifications must be prepared to ensure that the materials and fabrication procedures will be followed. More detailed information on material selection criteria can be found in Chapter 8.

Inspection and Follow-up Monitoring. Inspection for quality assurance and follow-up monitoring are required in order to ensure that the designed and planned corrosion protection strategy is implemented and adequate for the service. Follow-up monitoring allows the effectiveness of a corrosion control program to be assessed and can guide any necessary adjustments and alterations.

General Considerations in Corrosion-Control Design

A major goal of corrosion-control strategy during the design process is to avoid trouble spots, either through minimization of the number of potential locations for corrosion or elimination of trouble spots by

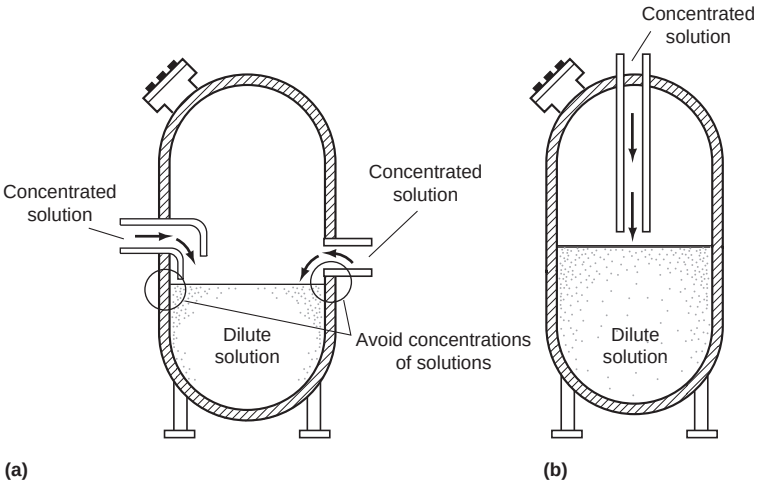


Fig. 1 Poor (a) and good (b) designs for vessels used for mixing concentrated and dilute solutions. Poor design causes concentration and uneven mixing of incoming chemicals along the vessel wall (circled areas). Good design allows concentrated solutions to mix away from vessel walls.

redesign. Designs that tend to concentrate corrosive media in a small area should be avoided. For example, tank inlets should be designed such that concentrated solutions are mixed and diluted upon introduction (Fig. 1). Otherwise, localized pockets of concentrated solutions can cause excessive corrosion.

Poor design of heaters can create similar problems, such as those that cause hot spots and thus accelerate corrosion. Heaters should be centrally located (Fig. 2). If a tank is to be heated externally, heaters should be distributed over as large a surface area as possible, and circulation of the corrosive medium should be encouraged, if possible.

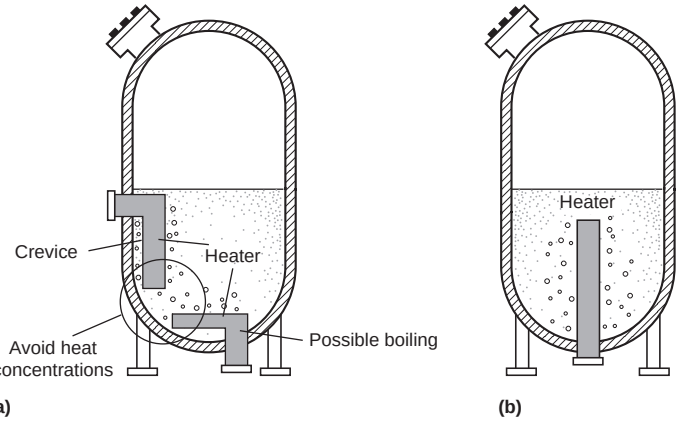


Fig. 2 Poor (a) and good (b) designs for heating of solutions. Poor design creates hot spots (circled area) that can induce boiling under the heater at the bottom of the vessel walls. Good design avoids hot spots and pockets in which small volumes of liquid can become trapped between the heater and the vessel wall.

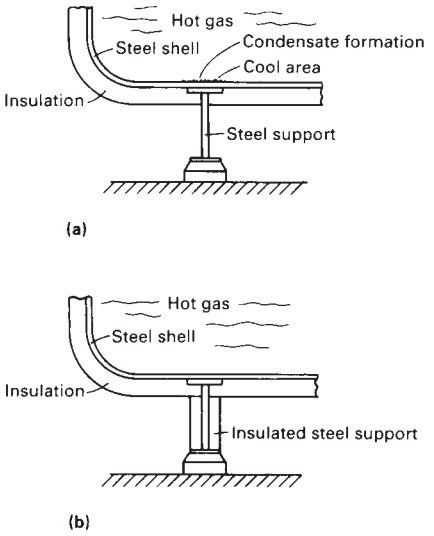


Fig. 3 Design to prevent localized cooling. In the poor design (a), the uninsulated steel support conducts heat, which causes a cool area on the steel shell. In (b), the steel support is insulated to prevent temperature decrease

Hot gases that are not corrosive to steel can form corrosive condensates on the cold portions of a poorly insulated unit. Proper design or insulation can prevent such localized cooling (Fig. 3). Conversely, vapors from noncorrosive liquids can cause attack; exhausts and overflows should be designed to prevent hot vapor pockets (Fig. 4). In general, the open ends of inlets, outlets, and tubes in heat exchangers should be flush with tank walls or tubesheets to avoid buildup of harmful corrodents, sludges, and deposits (Fig. 5). This is also true of tank bottom and drainage designs (Fig. 6).

Tanks and tank supports should be designed to prevent or minimize corrosion due to spills and overflows (Fig. 7). A tank support structure

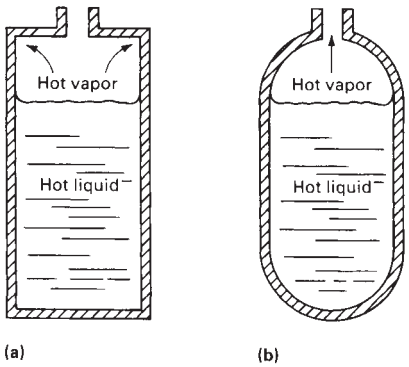


Fig. 4 Poor (a) and good (b) designs for vessels holding both liquid and vapor phases. Sharp corners and protruding outlet end in (a) allow hot gases to become trapped in the vapor space. This is avoided in (b) by using rounded corners and mounting the vessel outlet pipe flush.

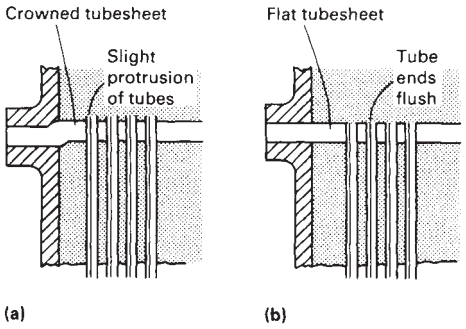


Fig. 5 Poor (a) and good (b) designs for tube/tubesheet assemblies. Crowned tubesheet and protruding tubes in (a) allow buildup of corrosive deposits; in (b), tubesheet is flat and tubes are mounted flush.

may not be as corrosive resistant as the tank itself, but it is a very important part of the unit and should not be made vulnerable to spilled corrodents.

Designs that increase turbulence or result in excessive flow rates should be avoided where erosion-corrosion may be a problem (Fig. 8). Gaskets in flanges should fit properly, intrusions in a flow stream should be avoided, and elbows should be given a generous radii. Finally, crevices should be avoided. Where crevices cannot be avoided, they should be sealed by welding, soldering, or by the use of caulking compounds or sealants.

Designing and planning for maintenance and repair of corrosion is also an essential consideration. It is not always possible or most economical to eliminate corrosion, but an efficient maintenance and repair program can result in considerably reduced corrosion costs. An important feature in this regard is accessibility to parts and structures.

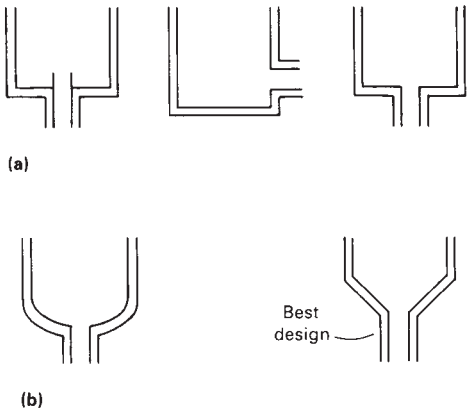


Fig. 6 Examples of poor (a) and good (b) designs for drainage, corners, and other dead spaces in vessels. Sharp corners, and other dead spaces in vessels. Sharp corners and protruding outlet pipes in (a) can cause buildup of corrosive deposits and crevice corrosion; these design features are avoided in (b).

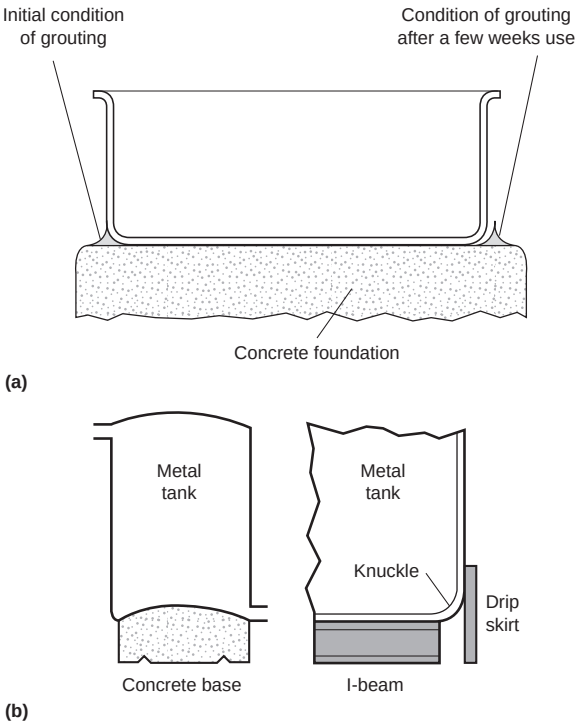


Fig. 7 Design for preventing external corrosion from spills and overflows. (a) Poor design. (b) Good designs

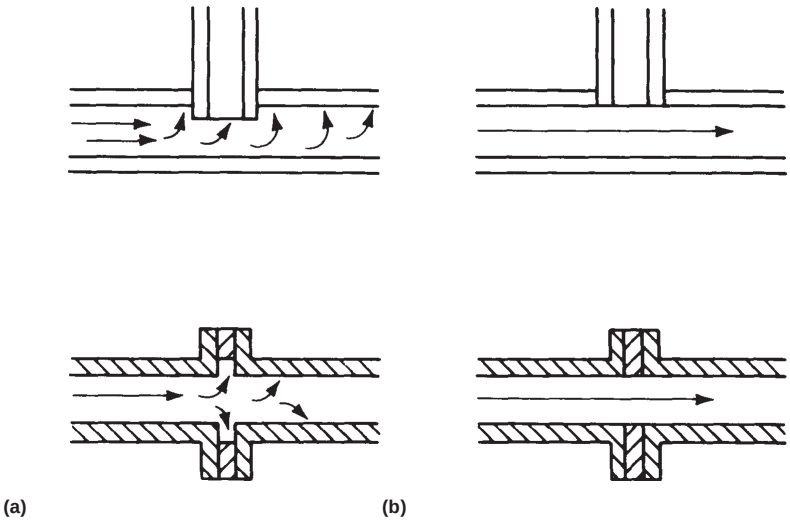


Fig. 8 Designs for preventing excessive turbulence. (a) Poor designs (both top and bottom figures). (b) Good designs (both top and bottom figures)

Design Details that Accelerate Corrosion

Details that must be considered when attempting to control corrosion by design include the following:

- Plant/site location
- Plant environment
- Component/assembly shape (joints, flanges, crevices, deposits, and liquid containment and entrapment)
- Movement (flowing fluids, parts moving in fluid)
- Compatibility (galvanic considerations regarding metals with metals and metals with other materials)
- Insulation (poor design can lead to severe localized corrosion of carbon steel and stress-corrosion cracking, SCC, of stainless steels)
- Stress (residual stress from fabrication or operating stresses, such as static, variable, or alternating)
- Surfaces (design details related to cleaning or coating)

Location. Exposure to winds and airborne particulates can lead to deterioration of structures. Designs that leave structures exposed to the elements should be carefully reviewed because atmospheric corrosion is significantly affected by temperature, relative humidity, rainfall, and pollutants. Also important are the season and location of on-site fabrication, assembly, and painting. Codes of practice must be adapted to the location and the season.

Plant Environment. One factor that is occasionally overlooked is the surrounding environment. For example, the instrument tubing at a new facility, built at an existing chemical plant in West Virginia, consisted of a combination of copper (C12200) tubing and yellow brass (C27000) fittings. However, within a few weeks, the fittings had failed by stress-corrosion cracking (SCC). The new building was located near, and downwind of, another facility that occasionally vented small amounts of nitric oxide (NO) to the atmosphere (Ref 2).

Tests later showed that brass samples would fail by SCC if exposed to the source of NO emissions. An expensive shutdown was necessary to replace all of the instrument tubing and fittings with stainless steel.

Similar failures of brass heat exchangers have occurred as a result of proximity to sources of ammonia (NH_3). In one case, cooling tower water became contaminated with a few parts per million of NH_3 when an ammonium-manufacturing plant was built nearby. In another case, the admiralty brass (C44400) heat-exchanger tubing in a large air compressor stress cracked in cold-worked areas after it was installed about 30 m (100 ft) from a building in which laboratory reagents, including ammonium hydroxide (NH_4OH) and nitric acid (HNO_3), were bottled.

Shape. Geometrical form is basic to design. The objective is to minimize or avoid situations that worsen corrosion. These situations can range from stagnation (e.g., retained fluids and/or solids or contaminated water used for hydrotesting) to sustained fluid flow (e.g., erosion/cavitation in components moving in or contacted by fluids, as well as splashing or droplet impingement).

Common examples of stagnation include nondraining structures, dead ends, poorly located components, and poor assembly or maintenance practices (Fig. 9). General problems include localized corrosion associated with differential aeration (oxygen concentration cells), crevice corrosion, and deposit corrosion.

Movement. Fluid movement need not be excessive to damage a material. Much depends on the nature of the fluid and the hardness of the material. A geometric shape can create a sustained delivery of fluid or can locally disturb a laminar stream and lead to turbulence. Replaceable baffle plates or deflectors are beneficial where circumstances permit. The use of such parts eliminates the problem of impingement damage to the structurally significant component.

Careful fabrication and inspection should eliminate or reduce poor profiles (e.g., welds, rivets, bolts), rubbing surfaces (e.g., wear, fretting), and galvanic effects due to the assembly of incompatible components. Figure 10 shows typical situations in which geometric details influence flow.

Compatibility. In plant environments, it is often necessary to use different materials in close proximity. Sometimes, components that were designed in isolation can end up in direct contact in the plant (Fig. 11). In such instances, the ideals of a total design concept become especially apparent but usually in hindsight. Direct contact of dissimilar metals introduces the possibility of galvanic corrosion, and small anodic (corroding) areas should be avoided wherever this contact is apparent.

Galvanic corrosion resulting from metallurgical sources is well documented. Problems such as weld decay and sensitization generally can be avoided by material selection or suitable fabrication techniques (discussions of sensitization can be found in Chapters 6 and 8). Less frequent instances of localized attack occur because of end-grain attack (discussion follows) and stray-current effects, which can render designs ineffective. Stray-current effects are common on underground cast iron or steel pipelines that are located close to electrical supply lines. Stray-current corrosion is further discussed in Chapter 5.

Designers, when aware of compatibility effects, need to exercise their ingenuity to minimize the conditions that most favor galvanic corrosion. Table 1 provides some relevant parameters in this context.

The most common design details relating to galvanic corrosion include jointed assemblies (Fig. 11). Where dissimilar metals are to be

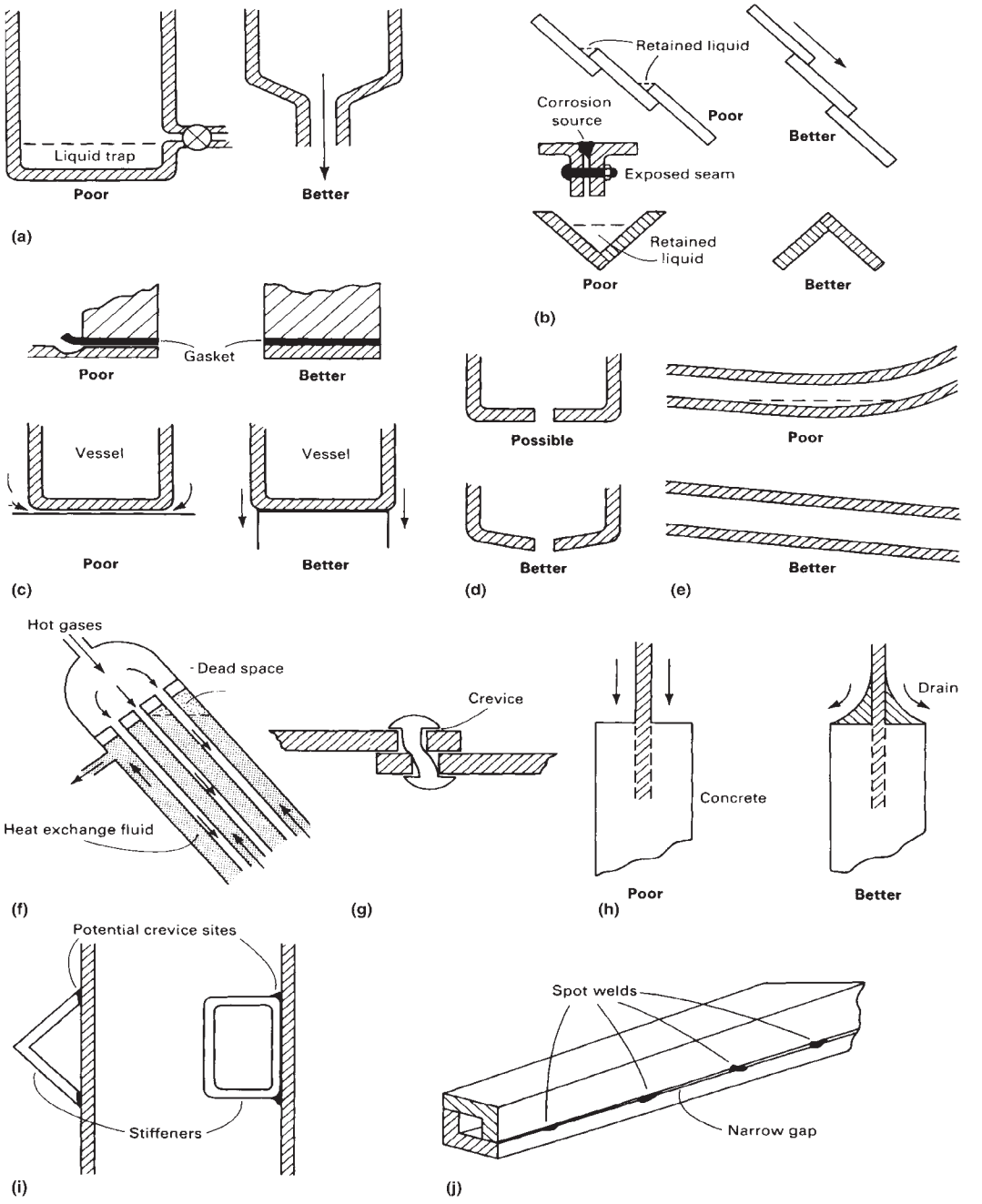


Fig. 9 Examples of how design and assembly can affect localized corrosion by creating crevices and traps where corrosive liquids can accumulate. (a) Storage containers or vessels should allow complete drainage; otherwise, corrosive species can concentrate in bottom vessel, and debris may accumulate if the vessel is open to the atmosphere. (b) Structural members should be designed to avoid retention of liquids; L-shaped sections should be used with the open side down, and exposed seams should be avoided. (c) Incorrect trimming or poor design of seals and gaskets can create crevice sites. (d) Drain valves should be designed with sloping bottoms to avoid pitting of the base of the valve. (e) Nonhorizontal tubing can leave pools of liquid at shutdown. (f) to (j) Examples of poor assembly that can lead to premature corrosion problems. (f) Nonvertical assembly of heat exchanger permits a dead space that may result in overheating if very hot gases are involved. (g) Load shift in loose assembly distorts the fastener, which creates a crevice and may result in a loose fitting that can contribute to vibration, fretting, and wear. (h) Structural supports should allow good drainage; use of a slope at the bottom of the member allows liquid to run off, rather than impinging directly on the concrete support. (i) Continuous welding is necessary for horizontal stiffeners to prevent the formation of traps and crevices. (j) Square sections formed from two L-shaped members require continuous welding to seal out the external environment.

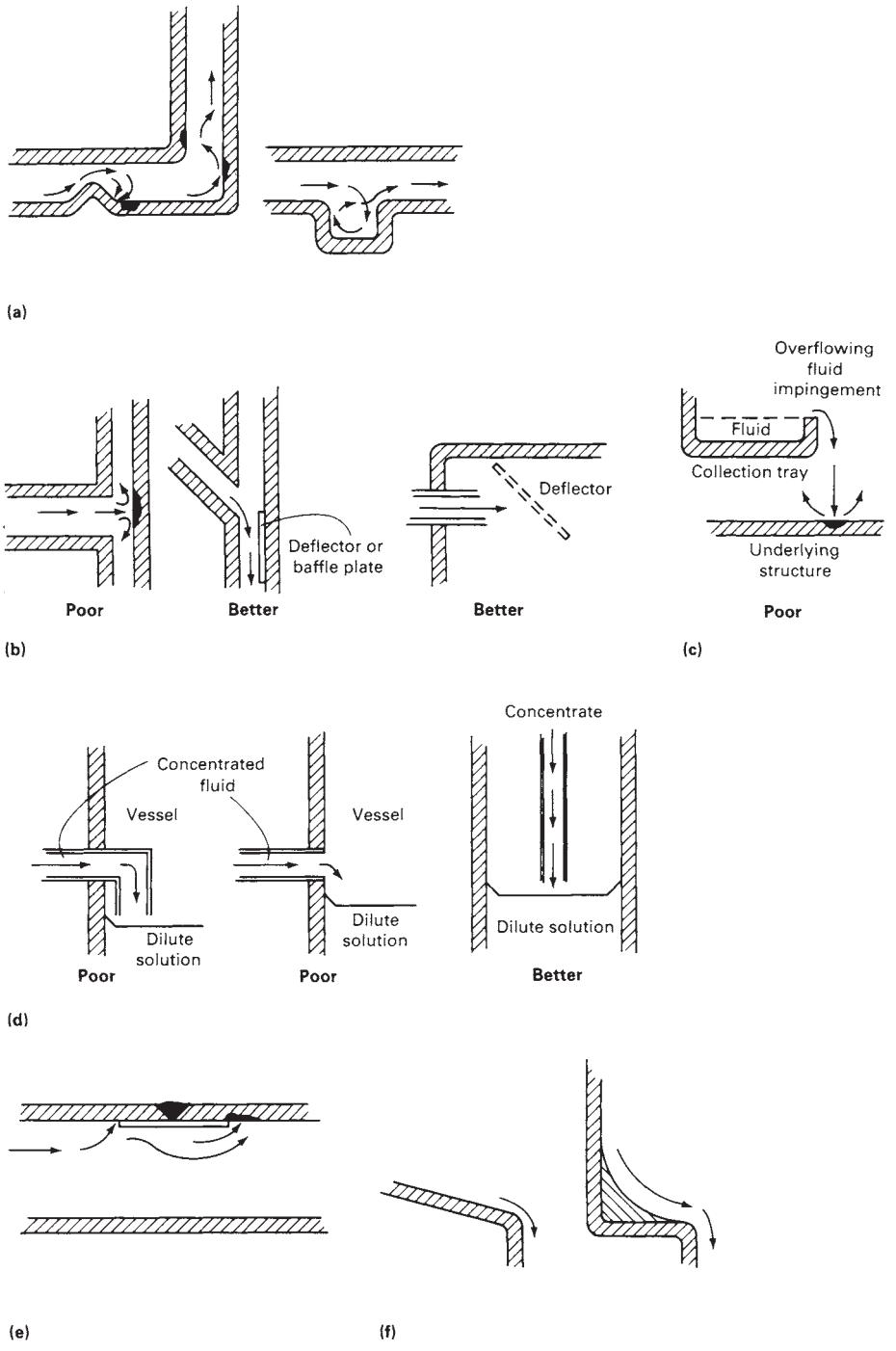


Fig. 10 Effect of design features on flow. (a) Disturbances to flow can create turbulence and cause impingement damage. (b) Direct impingement should be avoided; deflectors or baffle plates can be beneficial. (c) Impingement from fluid overflowing from a collection tray can be avoided by relocating the structure, by increasing the depth of the tray, or by using a deflector. (d) Splashing of concentrated fluid on container walls should be avoided. (e) Weld backing plates or rings can create local turbulence and crevices. (f) Slopes or modified profiles should be provided to permit flow and minimize fluid retention.

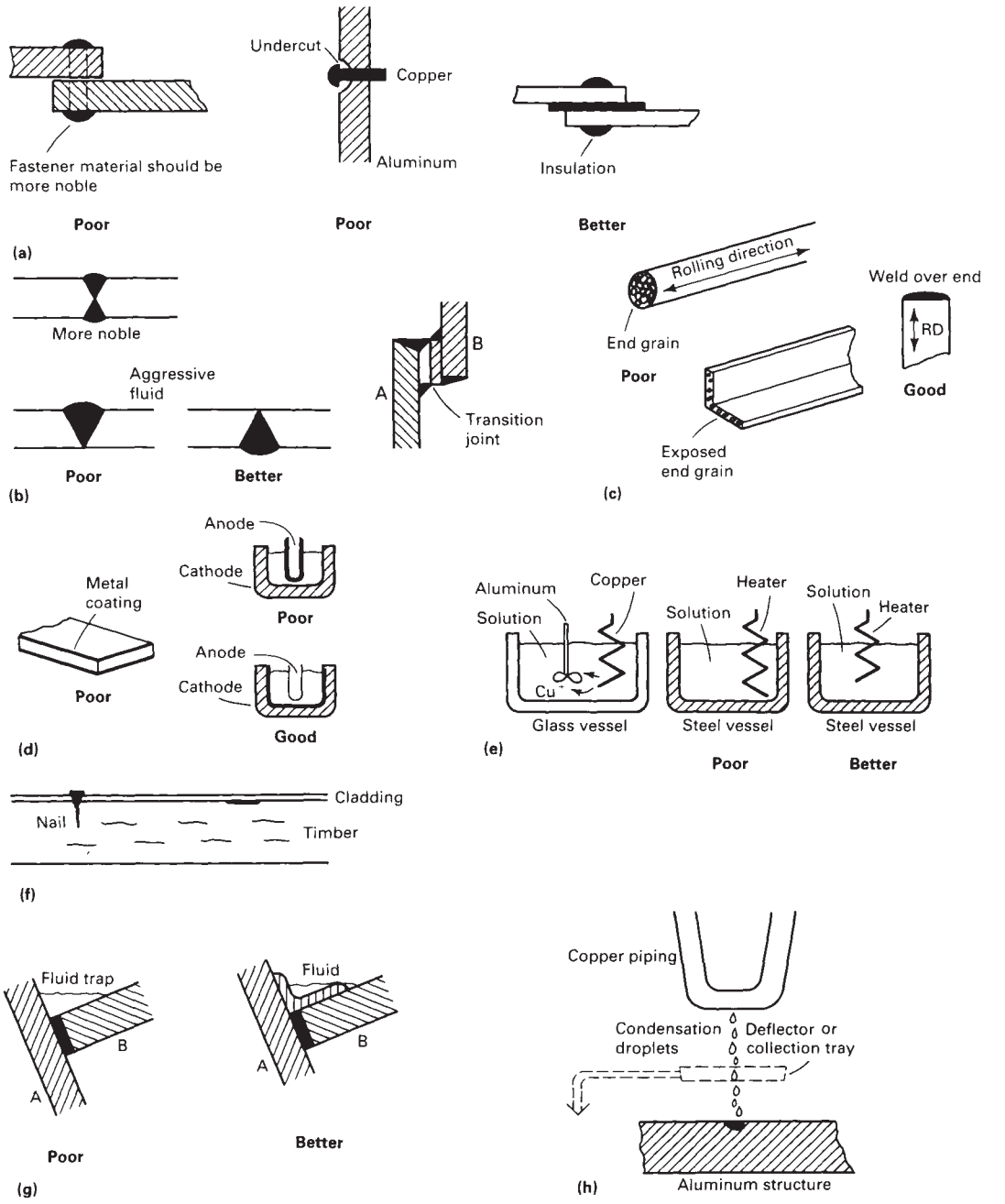


Fig. 11 Design details that can affect galvanic corrosion. (a) Fasteners should be more noble than the components being fastened; undercuts should be avoided, and insulating washers should be used. (b) Weld filler metals should also be more noble than base metals. Transitions joints can be used when a galvanic couple is anticipated at the design stage, and weld beads should be properly oriented to minimize galvanic effects. (c) Local damage can result from cuts across heavily worked areas. End grains should not be left exposed. (d) Galvanic corrosion is possible if a coated component is cut. When necessary, the cathodic component of a couple should be coated. (e) Ion transfer through a fluid can result in galvanic attack of less noble metals. In the example shown at left, Cu^+ ions from the copper heater coil could deposit on the aluminum stirrer. A nonmetallic stirrer may be necessary. At right, the distance from a metal container to a heater coil should be increased to minimize ion transfer. (f) Wood with copper preservatives can be corrosive to certain nails, especially those with nobility different from that of copper. Aluminum cladding may also be at risk. (g) Contact of two metals through a fluid trap can be avoided by using an extended seal, mastic, or a coating. (h) Condensation droplets from copper piping can impinge on an underlying aluminum structure; such contact can be avoided by the use of collection trays or deflectors.

Table 1 Galvanic corrosion sources and design considerations

Source	Design considerations
Metallurgical sources (both within the metal and for relative contact between dissimilar metals)	Difference in potential of dissimilar materials; distance apart; relative areas of anode and cathode; geometry (fluid retention); mechanical factors (for example, cold work, plastic deformation, sensitization)
Environmental sources	Conductivity and resistivity of fluid; changes in temperature; velocity and direction of fluid flow; aeration; ambient environment (seasonal changes, etc.); trace contamination of ionic species (for example, heavy metal ions, chlorine, ammonia, etc.)
Miscellaneous sources	Stray currents; conductive paths; composites (for example, concrete rebars)

used, some consideration should be given to compatible materials known to have similar potentials (a discussion of galvanic corrosion can be found in Chapter 4). Care should be exercised in that galvanic series are limited and refer to specific environments. The confusion of terminology can also be problematic; such terms as mild steel, stainless steel, Hastelloy, and Inconel are too vague and do not provide sufficient assurance about material performance in a corrosive environment.

Where noncompatible materials are to be joined, it is necessary to use a more noble metal in a joint (Fig. 11). Effective insulation can be useful if it does not introduce crevice corrosion possibilities. Some difficulties arise in the use of adhesives, which may not be sealants.

The relative surface areas of anodic and cathodic surfaces should not be underestimated because instances of corrosion failure may result from a combination of galvanic and crevice attack. Corrosion in a small anodic zone can be several hundred times greater than that in similar bimetallic components of similar area. Anodic components may on occasion be overdesigned (thicker) to allow for the anticipated corrosion loss. In other cases, easy replacement is a cost-effective option, given an awareness by the designer of such information.

Where metallic coatings are used, there is always a risk of galvanic corrosion, especially along the cut edges. Rounded profiles and effective sealants or coatings can be beneficial. Transition joints can be introduced when different metals will be in close proximity. These and other situations are illustrated in Fig. 11. Another aspect is the coating of the cathodic material for corrosion control. Ineffective painting of an anode in an assembly can significantly reduce the desired service lifetime because local defects will effectively multiply the risk of anodic sites and localized corrosion.

Less obvious examples of galvanic corrosion occur when ion transfer results in the deposition of active and noncompatible deposits on a metal surface. For example, an aluminum stirrer plate used in water was extensively pitted because the water bath was heated by a copper heater coil (Fig. 11e). The pits resulted from deposition of copper ions from

Table 2 Summary of insulation materials properties

Property	Calcium silicate	Glass fiber	Mineral wool	Cellular glass	Pearlite-Silicate
Water absorption, vol%	90	92	85–93	0.2	0.4
Compressive strength, psi	150	varies	10	100	90–110
Water vapor transmission	Very high	Very high	Very high	0	0
Capillarity	Will wick	Will wick	Will wick	None	None
Hygroscopicity, vol%	10–14	2	2.5	None	None

Source: Ref 3

the heater element. Another example of deposition corrosion is rain runoff from copper roof flashing, causing corrosion of aluminum gutters.

Insulation represents another area for potential corrosion attack, although most problems arise because of poor installation. Insulation types and properties vary considerably (Table 2), and expert advice from suppliers is recommended. The most common corrosion problems include crevice corrosion (where insulation and/or adhesives are tightly held against a metal surface, for example, when straps or ties are too tight) and pitting corrosion (where moisture condenses on the metal, usually because the insulation barrier was too thin or was improperly installed). Figure 12 shows some typical examples in which design and installation procedures could have been improved. Other problems occur when insulation is torn or joints are misaligned or incorrectly sealed with duct tape or similar bandaging, none of which is recommended by insulation suppliers.

Wet-dry cycling has been known to lead to concentration effects (e.g., chloride ions from calcium-silicate insulation). There have been reported instances of chloride SCC in certain stainless steel pipes and vessels, or pitting of these and other materials, such as aluminum, when contacted by insulation. The early instances of SCC failure were mainly attributable to high chloride levels (500–1500 ppm) associated with asbestos-type materials. The chloride levels have been significantly reduced in recent years to a level that is not expected to cause SCC. Standards are now available, as are tests, to evaluate insulation materials (Ref 4–6).

Table 3 summarizes the possible methods of preventing SCC of stainless steels under thermal insulation. As can be seen, application of a suitable protective (barrier) coating system is generally the most economical method, although other methods, such as the design of an external weather barrier installation, may be practical under certain circumstances.

Stress. From a general design philosophy, environments that promote metal dissolution can be considered more damaging if stresses are also involved. In such circumstances, materials can fail catastrophically and unexpectedly. Safety and health may also be significantly affected.

A classic example of chloride SCC occurred in a type 304 (UNS S30400) stainless steel vessel (Fig. 13). The stress-corrosion cracks extended radially over the area where a new flanged outlet was welded into the vessel. Residual stresses (from flame cutting) and the fluids in-

side the vessel (acidic with chlorides) were sufficient to cause this failure in a matter of weeks.

Figure 14 shows examples of using design detail to minimize stress. Perfection is rarely attained in general practice, and some compromise on materials limitation, both chemical and mechanical, is necessary. Mechanical loads can contribute to corrosion, and corrosion (as a corrosive environment) can initiate or trigger mechanical failure. Designs that introduce local stress concentrations directly or as a consequence of fabrication should be carefully considered.

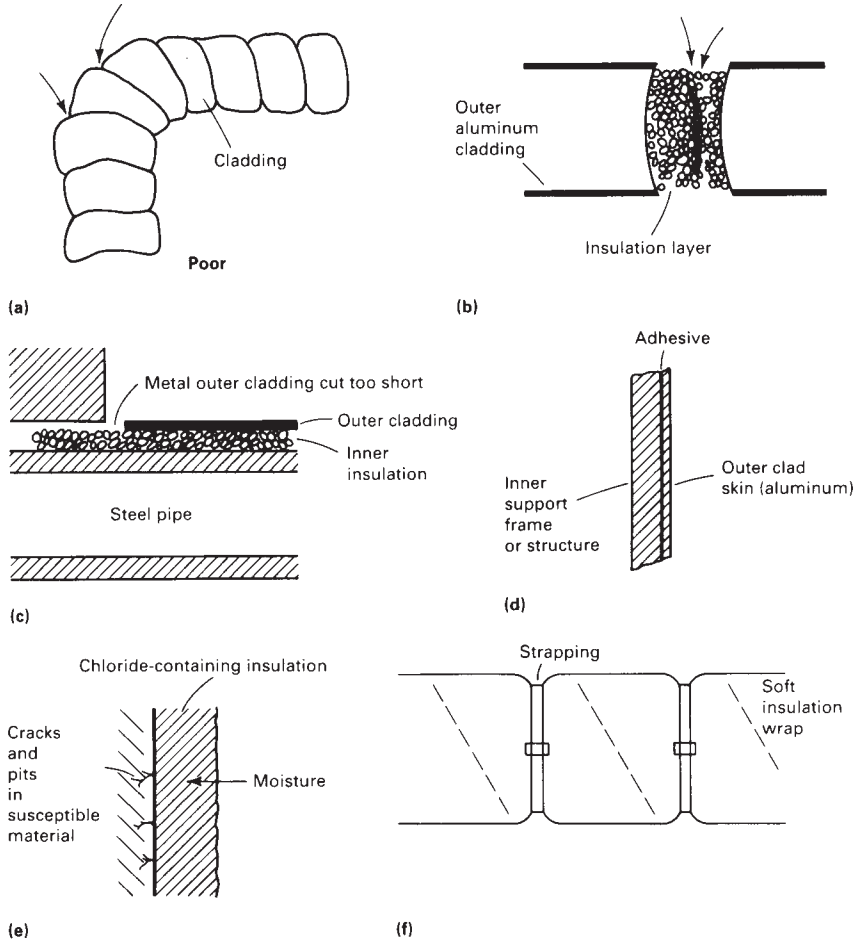


Fig. 12 Corrosion problems associated with improper use of insulation and cladding. (a) Incorrect overlap in lobster-back cladding does not allow fluid runoff. (b) Poor installation left a gap in the insulation that allows easy access to the elements. (c) Outer metal cladding was cut too short, leaving a gap with the inner insulation exposed. (d) Poor or noncontinuous contact of adhesives can lead to a crevice or capillary entry of fluid; also, adhesives might not have sealing properties. (e) Insufficient insulation can allow water to enter; chloride in some insulation can result in pitting or SCC of susceptible materials. (f) Overtightened strapping can damage the insulation layer.

Of particular importance in design are stress levels for the selected material, such as the influence of tensile, compressive, or shear stressing; alternating stresses; vibration or shock loading; service temperatures (thermal stressing); fatigue; and wear (fretting, friction). Profiles and shapes contribute to SCC, especially if material selection dictates

Table 3 Guidelines for preventing SCC of stainless steels under thermal insulation

Causative agent	Preventative method	Comments	Evaluation
Austenitic stainless steels	Change to SCC-resistant alloy	Stainless steel alloys with >30% Ni and the duplex stainless alloys are alternative choices but cost considerably more and might not be readily available	Extra cost compared to other preventive methods makes this an unwise choice
Tensile stress	Thermal treatment (anneal or stress relieve)	Annealing at 1065 °C (1950 °F), followed by water quenching, will distort and scale equipment severely.	Generally not practical for piping and vessels; can be used for small individual components
		Stress relieving at 955 °C (1750 °F) and slow cooling will sensitize the grain structure and cause some warpage and scaling. Note: A stress-relieved vessel or pipe will be subjected to tensile stresses in assembly and under operating conditions. Can override the thermal treatment	
	Shot peen	Shot peening converts the surface stresses to compressive stress and is a proven SCC preventative method. It is a delicate process requiring specific skills and experience. Can be costly or difficult to apply in the field	Should be considered but can be more costly and difficult to obtain than other prevention methods
Chlorides	Remove or eliminate Cl^- ion	Because of their widespread occurrence, highly soluble chloride salts are difficult to avoid or keep off of equipment.	Not practical
	Apply barrier coating to stainless steel	Use a protective coating on the stainless steel surface can prevent Cl^- contact with the alloy	This is a practical and proven preventative method
		Wrap stainless steel with aluminum foil, which serves as both a barrier coating and cathodic protection anode.	Being used with success. Extended life of the aluminum has not been determined
Water	Improve waterproofing to prevent water entry	No type of coating, cementing, or wrapping of insulation can keep air and water from entering the insulation system, except for constructing an external pressure shell. Note: The application and maintenance of a weather barrier is important to good insulation performance and should have a high maintenance priority.	Not practical to expect a wrap or coating to keep water out
	Apply barrier coating to stainless steel	A carefully selected protective coating can provide long-term protection for stainless steel equipment	This is a practical and proven preventive method.
		Use of aluminum foil wrap as above. Note: Use of inorganic zinc primer or paint system is not safe due to the possibility of liquid-metal embrittlement upon subsequent welding or exposure to extreme heat.	Limited use, but with success

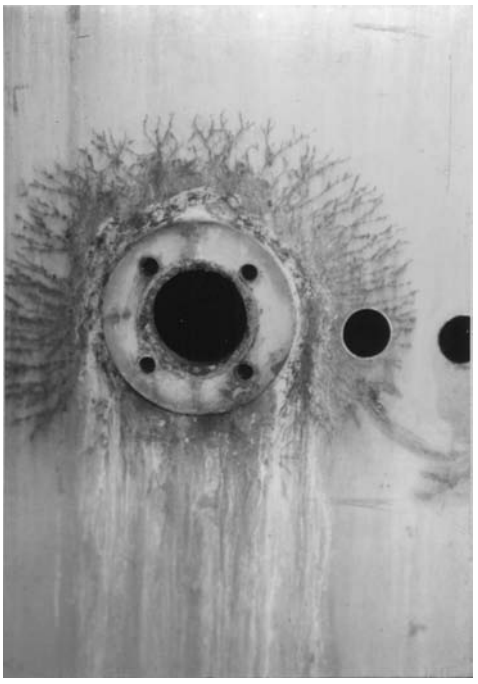


Fig. 13 Chloride SCC in a type 304 stainless-steel vessel after a new flange connection was welded into place

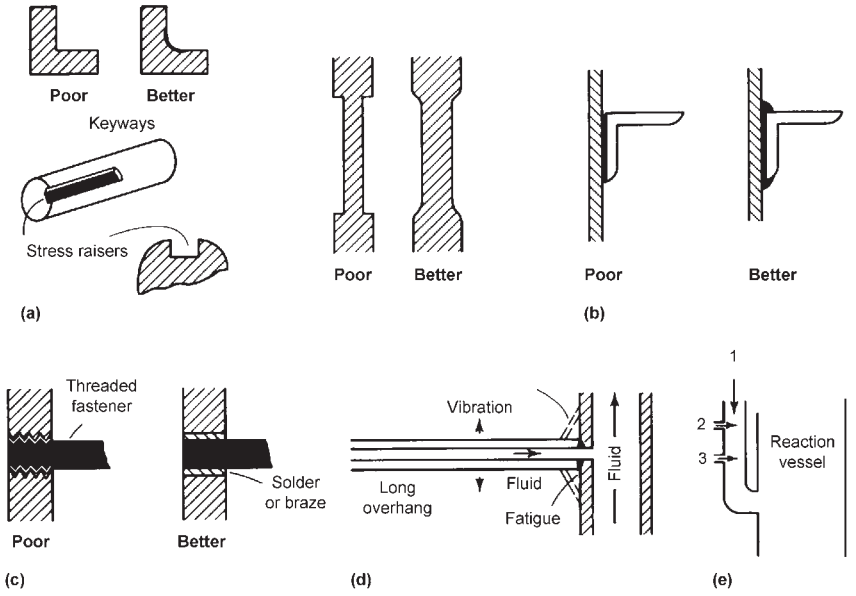


Fig. 14 Design details that can minimize local stress concentrations. (a) Corners should be given a generous radius. (b) Welds should be continuous to minimize sharp contours. (c) Sharp profiles can be avoided by using alternative fastening systems. (d) Too long an overhang without a support can lead to fatigue at the junction. Flexible hose can help alleviate this situation. (e) Side-supply pipework might be too rigid to sustain thermal shock from a recurring sequence that involves (1) air under pressure, (2) steam, and (3) cold water.

the use of materials that are susceptible to failure by SCC, hydrogen embrittlement, or corrosion fatigue.

Material selection is especially important wherever critical components are used. Also important is the need for correct procedures at all stages of operation, including fabrication, transport, storage, startup, shutdown, and normal operation.

Surfaces. Corrosion is a surface phenomenon, and the effects of poorly prepared surfaces, rough textures, and complex shapes and profiles can be expected to be deleterious. Figure 15 shows some examples in which design details could have considerably reduced the onset of corrosive damage resulting from ineffective cleaning or painting.

Designs should provide for surfaces that are free from deposits; access to remove retained soluble salts before painting; free-draining assemblies; proper handling of components to minimize distortion, scratches, and dents; and properly located components relative to adjacent equipment (to avoid carryover and spillages). Other recommended procedures for coating constructional materials are shown in Fig. 16.

In one instance, neglect and poor (or no) maintenance caused localized pitting on the underside of a type 304 stainless steel vessel lid that was exposed to high humidity, steam, and chloride vapors. Access in this example was possible but not used. Common engineering structural steelwork requires regular preventative maintenance, and restricted access makes this impossible. Figure 15 shows situations in which surface cleaning and/or painting is difficult or impossible. Condensation in critical areas can also contribute to corrosion. Typical structures susceptible to this phenomenon include automobile exhaust systems and chimneys or exhausts from high-temperature plants, such as boilers, kilns, furnaces, or incinerators.

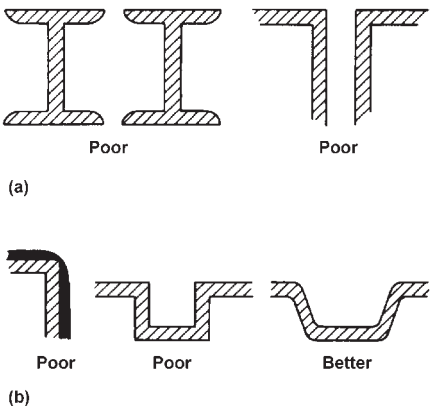


Fig. 15 Effects of design on effectiveness of cleaning or painting. (a) Poor access in some structures makes surface preparation and painting difficult; access to the types of areas shown should be maintained at a minimum of 45 mm (1¾ in.), or one-third of the height of the structure. (b) Sharp corners and profiles should be avoided if the structure is to be painted or coated.

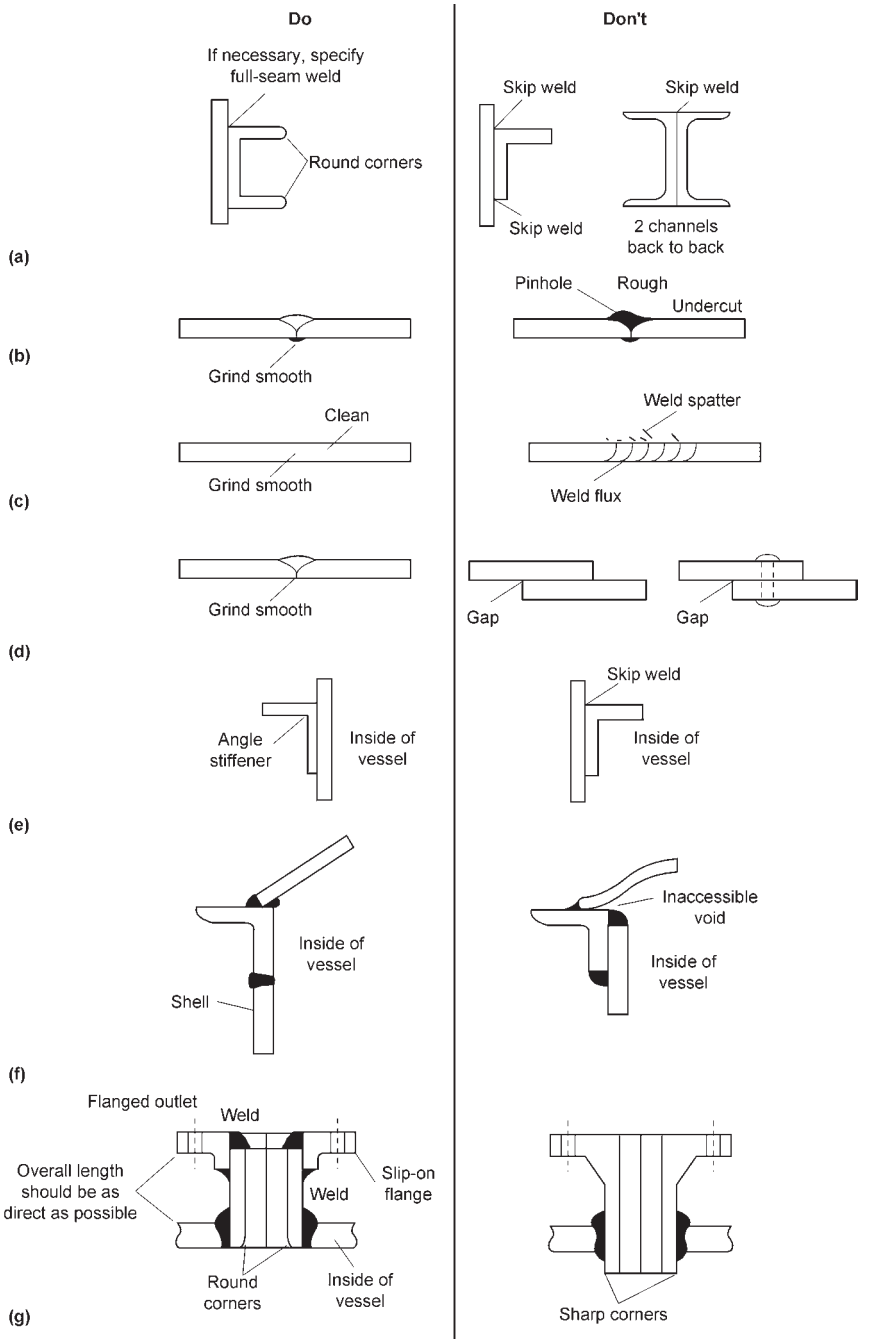


Fig. 16 Suggestions for steel construction to be coated. (a) Avoid pockets or crevices that do not drain or cannot be cleaned or coated properly. (b) Joints should be continuous and solidly welded. (c) Remove weld spatter. (d) Use butt welds rather than lap welds or rivet joints. (e) Keep stiffeners to outside of tank or vessel. (f) Eliminate crevice (void) at roof-to-shell interface in nonpressure vessel. (g) Outlets should be flanged or pad type, not threaded. Where pressure limits allow, slip-on flanges are preferred, because the inside surface of the attaching weld is readily available for radiusing and grinding.

Painting and surface coating techniques have advanced in recent years and have provided sophisticated products that require careful mixing and application. Maintenance procedures frequently require field application where some control (use of trained inspectors) is essential, as in offshore oil and gas rigs. Inspection codes and procedures are available, and total design should incorporate these wherever possible. In critical areas, design for online monitoring and inspection will also be important. The human factor in maintenance procedures is often questionable. Adequate training and motivation are of primary importance in ensuring that design details are appreciated and implemented.

Design Solutions for Specific Forms of Corrosion

Crevice corrosion, galvanic corrosion, erosion-corrosion, and stress-corrosion cracking are the types of corrosion most amenable to control by proper design. Procedures the designer can follow to prevent these forms of corrosion are briefly reviewed in this section.

Crevice Corrosion. From a design standpoint, the solution is simple and important: Avoid crevices whenever possible. A careful study of design can detect crevices, which often can be avoided entirely or at least minimized. The following corrective measures may be used to avoid crevice corrosion (Ref 8):

- Specify that crevices be welded shut.
- Improve the fit of parts.
- Specify that the crevices be filled with a plastic or an elastomer or other nonporous materials.
- Change the design to entirely eliminate the crevice.
- Specify double-butt or double-lap weld joints when practical and possible (Fig. 17).
- When single-butt joints must be used for critical pipelines, consider using consumable or removable inserts.
- For corrosive environments, specify continuous welds instead of skip welding (Fig. 18).
- Be especially careful when designing tank supports (especially for aluminum or stainless steel tanks) to assure as few crevices as possible.
- Seal weld tubes to tube sheets when practical. If seal welding cannot be specified, make sure that the tube installation procedure will result in a tight fit of tubes to tube sheet.
- In critical rotating equipment, where crevices cannot be eliminated, open the crevices enough so that they will circulate the solution, thus avoiding crevice corrosion problems.

- Do not specify that any material that absorbs water be placed next to metals or alloys.

Figure 9 also illustrates design solutions to crevice corrosion.

Galvanic Corrosion. If galvanic corrosion is a problem, the following remedial measures can be taken:

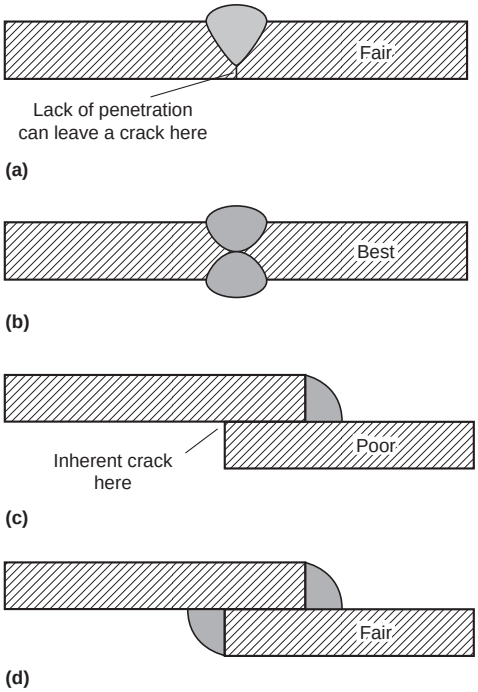


Fig. 17 Effect of weld geometry on crevice corrosion susceptibility. (a) Single-butt weld. (b) Double-butt weld (preferred geometry). (c) Lap weld, single fillet. (d) Lap weld, double fillet

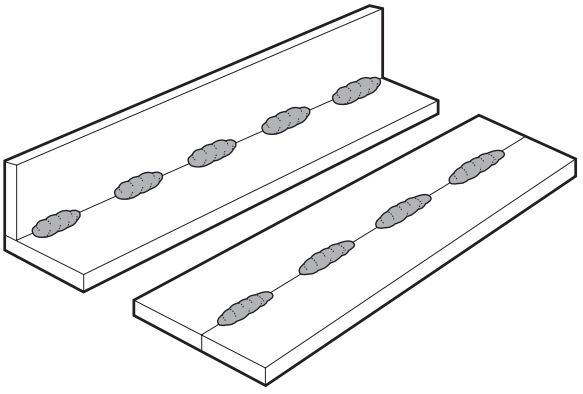


Fig. 18 Intermittent or skip welds like those shown above constitute poor design in corrosive service because of the inherent crevice.

- Use galvanic series tables to select suitable material couples.
- Avoid unfavorable area effect; that is, if the anode is large, and the cathode is small, the corrosion rate of the less corrosion-resistant material (anode) will not be high. On the other hand, if the anode is small, and the cathode is large, substantial corrosion will occur at the anode (refer to Fig. 11a).
- Insulate, that is, break the circuit between the two metals (Fig. 19). Make sure the contact is not restored in service (e.g., by solid corrosion products).
- When specifying that paint be used to insulate one member of a couple from the other, never specify painting the anode only. Either paint both the anode and the cathode or just the cathode.
- Put a third metal in contact with both of the metals in question. This third metal is chosen to be active to both the others so that it corrodes rather than the structure. This type of corrosion prevention— cathodic protection—is discussed in Chapter 10.

Erosion-corrosion is related to the environment and design. It usually increases with increasing velocity of the corrodent. Impingement and turbulence of the stream are also harmful. Process streams containing hard, solid particles (e.g., slurries) are most likely to cause problems, and hard solids should be filtered from the stream if practical.

In piping systems, erosion-corrosion can be reduced by increasing the pipe diameter, which decreases velocity and turbulence. The streamlining of bends is useful in minimizing the effects of impingement. Baffles can also be used to decrease the harmful effects of impingement. Inlet pipes should not be directed onto the vessel walls if it can be avoided. Flared tubing can be used to reduce problems at the inlet tubes in a tube bundle.

Since erosion-corrosion is a form of localized corrosion, it is useful to design the areas known to be susceptible to attack in a way that they can be replaced with minimum effort.

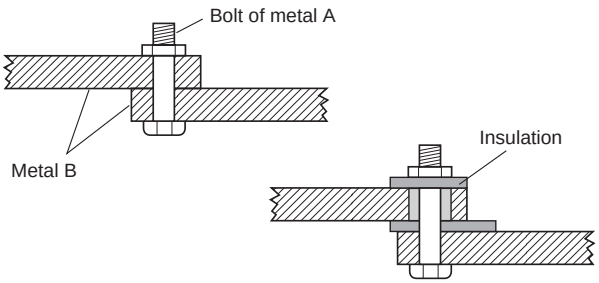


Fig. 19 Use of installation to avoid galvanic corrosion

In the special case of cavitation damage, the use of smooth surfaces is beneficial because these surfaces reduce the number of sites for bubble formation.

Stress-Corrosion Cracking. Design can influence SCC in several ways. Poor design may help produce the necessary environmental conditions (e.g., in a crevice) and may also be responsible for high stresses. From the stress point of view, a general rule is to avoid (or remove by stress relieving) high localized stresses whenever possible.

Tensile stresses are generally considered necessary for cracking, but of course, a system with compressive stresses on it will also have tensile stresses. These stresses might not be at the surface in contact with the corrodent and so might not be damaging. The introduction of compressive stresses is sometimes used to minimize stress-corrosion cracking (e.g., shot-peening or rolling threads on fasteners instead of machining them). In cases where hydrogen is involved in the cracking, having a surface under compression is less comforting because hydrogen can diffuse through the compressively stressed layers to regions in tension.

Stresses introduced by poor design also include those resulting from poor construction and fabrication and practices—that is, the use of the wrong size fittings made to fit by brute force. Deformation due to explosive bonding may also have to be considered when this technique is used.

Surface finishes can influence resistance to SCC. Machining and grinding operations may be detrimental if they do any of the following:

- Roughen the surface and so produce stress raisers
- Increase residual surface stress
- Introduce microcracks
- Produce deleterious metallurgical changes at the surface

Generally, a smooth, clean, stress-free surface will increase the resistance to cracking. This increased resistance, however, is often insufficient, and money can easily be wasted when it could have been put toward an alternative material that eventually has to be used.

End-Grain Attack. An unusual form of localized corrosion known as end-grain attack has occurred in chemical-processing plants with such specific metal/fluid combinations as austenitic stainless steels in hot nitric acid (HNO_3) and organic acids, and plain carbon steels in decanoic acid.

When certain forms of these metals (for example, plates, threaded rods, or pipe nozzle ends) are cut normal to the rolling direction, the ends of nonmetallic inclusions at the cut edges are attacked by the process fluid, resulting in small diameter but deep pits. The solution is to seal the cut edge with a layer of weld metal that is equal to the base

metal in composition (see Fig. 11c). An example of end-grain attack of type 316 stainless steel is shown in Fig. 20.

Corrosion Allowance

Corrosion allowance (CA) is commonly used for steel parts subject to uniform corrosion. The wall thickness is made greater than necessary for structural integrity, with the additional thickness serving as a CA.

In the chemical processing industry, engineers routinely specify a CA for carbon steel and low-alloy steel vessels and tanks. It is unusual that

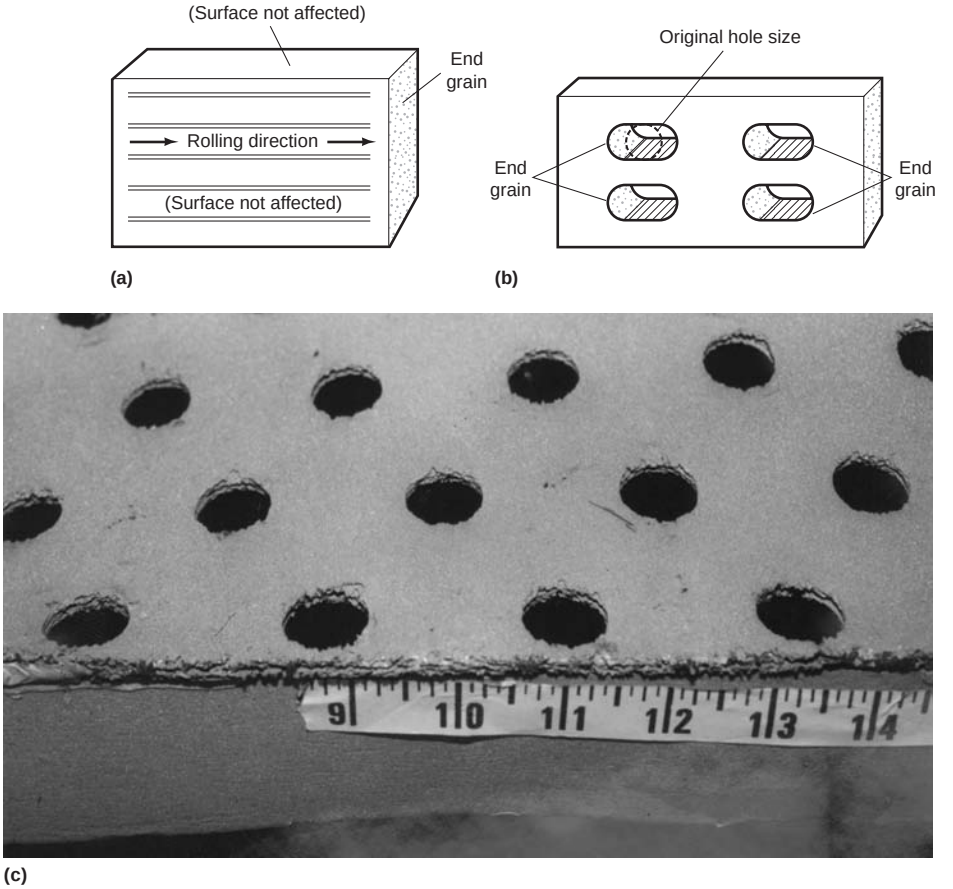


Fig. 20 End-grain attack (corrosion) or wrought stainless steel products. (a) Schematic of a stainless steel plate showing long lines of inclusions and stringers. (b) Elongation of holes in stainless steel plate at exposed end grain. In this particular case, the corrodent attacked the exposed end grain, leaving the rest of the interior surface of the hold relatively untouched. (c) End-grain corrosion along cut edges and punched holes in a reactor tray made from type 316 stainless steel

anything less than 3 mm (⅛ in.) CA is specified for such items, although subsequent analysis and experience often show that in many instances, this added thickness is excessive. Such excess CA is a waste of material and money (Ref 9).

Many engineers might be surprised at the actual weight of metal that is specified and provided in vessels as corrosion allowance. For example, when 3 mm (⅛ in.) CA is specified for carbon steel vessels, the weight of the shell and head corrosion allowance amounts to:

- 13,830 lb for a tower of 6 ft diameter and 140 ft shell length
- 1,810 lb for a drum of 6 ft diameter and 15 ft shell length
- 1,040 lb for an exchanger of 30 in. diameter and 20 ft tube length

So, a unit with 10 such towers, 30 such drums, and 45 such exchangers represents 240,000 lb of corrosion allowance. If all 240,000 lb of CA are really needed to permit each item to last its expected life, then the money is well spent. However, if, in this unit, only 25% of the area actually needed a 3 mm (⅛ in.) CA, and if 50% of the area could have been adequately protected with a 1/16 in CA, and if the remaining 25% of the area could reasonably have had zero CA, then a saving of half the CA weight, or 120,000 lb, could have been made with a corresponding fabricated metal cost savings of more than $250,000. Corrosion experience and reasonable estimates of expected plant life can sometimes result in lower specified CAs and provide extra savings.

Design Considerations for Using Weathering Steels

Many of the design details described earlier are applicable to the use of weathering steels, which are used extensively in buildings and bridges for resistance to atmospheric corrosion. In this class of materials (typified by ASTM specifications A 588 for buildings and A 709 for bridges), small amounts of alloying elements—typically nickel, chromium, and copper—are added to the steel. Under certain fairly specific situations, these alloying elements are incorporated into the oxide layer that forms on the steel, leading to the formation of a dense, more protective oxide. This oxide then serves as a barrier to further penetration of moisture and effectively acts almost as a “self-painted” coating, lessening the need for any other coating protection.

Although such behavior is valuable, it must be recognized that it will be observed only under certain circumstances. Interestingly, the improvement is generally best in an industrially polluted environment; less improvement is noted in environments containing chloride, for example, marine environments. Also, the film or patina must undergo repeated wetting and drying to develop. Any use of this type of steel in

a structure in which this type of exposure is not available will not allow development of the protection. In this context, it is vital to adhere to good corrosion-resistant design techniques when using weathering steels to ensure that the steel performs adequately. Any design or fabrication detail that incorporates crevices, improperly bolted connections, and so on, will lead to behavior in which weathering steels exhibit no advantage over other steels (see, for example, Fig. 21). Examples of problems related to the use of weathering steels will be discussed next.

Failures Involving Corrosion of Structural Steel

In general, failures related to the corrosion of conventional structural steel (that which has been painted or otherwise protected) are rare. Cases do exist in which excessive humidity or chloride-laden water has contacted the metal. The use of weathering steels, however, has caused significant problems, particularly where the necessary design features and environment have not been carefully considered during selection of the material. Two examples of problems involving weathering steels will be discussed.

Example 1: Weathering Steel Corrosion in a Stadium. A large sports stadium situated about 300 m (1000 ft) from the ocean was built with weathering steel in the major structural members. The steel was used not only for the exposed portions of the structure but also beneath the stands. Significant corrosion and rust flaking were noted on this steel at several locations:

- Underneath the stands, where air circulation was poor and no standard wetting/drying could be anticipated (Fig. 22)
- At sheltered locations on the exterior, again, where standard wetting/drying was not possible

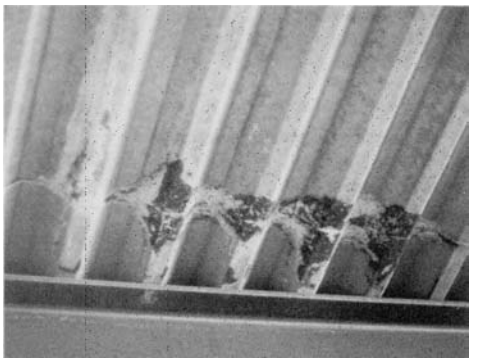


Fig. 21 Corroded weathering steel formwork on the ceiling of a parking garage. The seams in this corrugated structure act as condensation traps and lead to wet atmospheric corrosion.

- At joint details, where the important concepts of removal of crevices and pockets to retain water had not been practiced in the design of joints for the structure (Fig. 23)

The major problem associated with this structure was the amount of corrosion occurring on the structural steel beneath the stands. Although the loads in these structures were determined to be low, it was apparent that corrosion protection would be necessary. A series of tests was



Fig. 22 Heavy buildup of corrosion scale on weathering steel structural members in conditions of poor air circulation, high humidity, and no wetting/drying

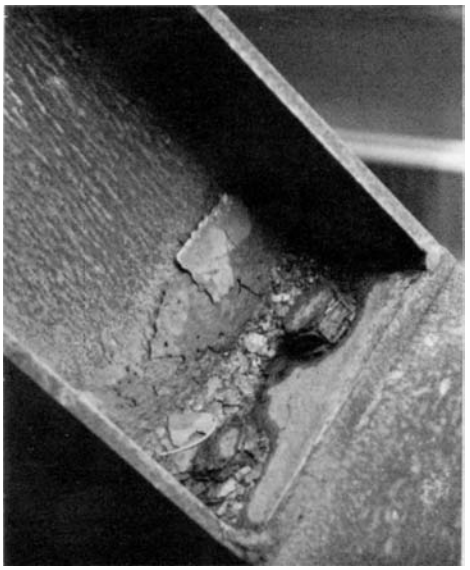


Fig. 23 Heavy corrosion scale buildup on structural members of weathering steel at a packet where water could collect and stand

conducted to determine the optimal coating protocol, including surface preparation, type of coating, thickness, and number of coats.

This example serves to point out the important factors to be considered by the designer when weathering steel is selected. In particular, the protective patina can be developed adequately only with exposure to weather. Furthermore, marine environments are not conducive to the formation of such a patina, which apparently develops best in an industrial environment with relatively high sulfur levels in the atmosphere.

Example 2: Corrosion of Weathering Steel in a Hotel Parking Garage. A hotel parking garage in the Northeast was constructed with weathering steel in the columns and beams, along with conventional reinforced concrete slabs placed as the decks. The hotel and garage were situated in an area that experienced considerable amounts of snow and freezing temperatures. Deicing salt was commonly applied to roadways adjacent to the structure and was also probably applied to the reinforced concrete slabs themselves. Severe deterioration was noted in the weathering steel beams and columns, particularly those adjacent to leakage points of water, and in expansion joints. This corrosion was caused by contact with the deicing salt-laden water, effectively destroying any patina that might have been expected to develop on the steel and leading to the production of voluminous, nonprotective oxides.

The failure in this case was caused by a lack of appreciation of the environment to which the weathering steel was to be exposed. Possible solutions to the problem include the use of coatings on the steel to protect it from further contact with chloride-laden water and the correction of water paths that lead to contact with the deicing salt. The sheltered locations of most of the steel, however, would not allow effective patina development. Prohibiting the use of chloride deicing salt on the garage decks would probably reduce the problem somewhat, although pickup of deicing salt from roadways and track-in into the garage is a perpetually deleterious condition that is unavoidable.

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CHAPTER **8**

Corrosion Control by Materials Selection

SELECTION of the optimal material of construction for any component can be a big money saver, but the selection process is *usually* not straightforward. If the material is not sufficiently corrosion resistant, its premature failure can result in a costly forced shutdown or outage. On the other hand, a material with a needlessly high corrosion resistance is usually more expensive than the optimal material. Hence, the challenge of materials selection is to achieve adequate performance at the lowest possible cost.

Corrosion resistance is not the only property to be considered in making materials selections, but it is of major importance in many industries, such as the chemical processing or pulp and paper industries. Eventual choice of material is the result of several compromises. For example, the technical appraisal of any alloy will generally be a compromise between corrosion resistance and some other properties, such as strength and weldability. In addition, the final selection will be a compromise between technical performance and economic factors.

In specifying a material, the selection process usually necessitates listing the requirements, selecting and evaluating candidate materials, and choosing the most economical material (often based on life-cycle costs, not initial costs). Typical requirements and some of the procedures involved in making a selection are given in Table 1. Some of the many factors that must be considered when determining the corrosion performance of a given material are listed in Table 2.

Frequently, a mistake is made by ignoring the factors in Table 1 and considering properties and material cost only. This approach does not

Table 1 Checklist for materials selection

Requirements to be met

Properties (corrosion, mechanical, physical, appearance)
Fabrication (ability to be formed, welded, machined, etc.)
Compatibility with existing equipment or fluids
Maintainability
Specification coverage
Availability of design data
Experience base with this or similar materials

Selection considerations

Expected total life or plant or process
Estimated service life of material
Reliability (safety and economic consequences of failure)
Availability and delivery time
Need for further testing
Material costs
Fabrication costs
Maintenance and inspection costs
Return or investment analysis

Table 2 Information necessary for estimating corrosion performance

Corrodent variables

Environment type (marine, industrial, internal fluid, etc.)
Main constituents (identity and amount)
Impurities (identify and amount)
Temperature
pH
Degree of aeration
Velocity or agitation
Pressure
Estimated range of each variable

Mechanism of reaction with fluids

Auto ignition (spontaneous ignition of material with fluid)
Impact ignition (ignition brought about by shock or impact within fluid)
Catalytic reaction (catalytic decomposition of fluid)
Material degradation (this includes such phenomena as chemical attack, corrosion, galvanic corrosion, stress corrosion, hydrogen embrittlement, and crack growth acceleration with metals and includes embrittlement, abnormal swelling, leaching of plasticizers, etc., with nonmetallic materials)
Fluid degradation (reactions in which the physical or chemical characteristics of the fluid are altered)

Type of loading

Type of stress and load levels (e.g., tensile, compressive, shear, and biaxial)
Cyclic stress (fatigue)
Creep, long-term stress, and creep rupture
Relative motion (sliding, rotating)/friction
Crack growth/impact toughness/fracture behavior
Thermal cycling, thermal stability, and thermal fatigue

Type of application

What is function of part or equipment?
What effect will uniform corrosion have on serviceability? Are size change, appearance, or corrosion product a problem?
What effect will localized corrosion have on usefulness?
Will there be stresses present? Is SCC a possibility?
Is design compatible with the corrosion characteristics of the material?
What is the desired service life?

Experience

Has material been used in an identical situation? What were the specific results? If equipment is still in operation, has it been inspected?
Has material been used in a similar situation? What was the performance, and specifically, what are the differences in the old and new situation?
Was there any pilot-plant experience?
Are there any plant corrosion-test data?
Have laboratory corrosion tests been run?
What literature or database information is available?

always lead to the most economical selection. For example, a process stream may require an agitator that is simply a 1.2 m (4 ft.) length of 50 mm (2 in.) diameter bar and an intricately machined valve part. The material cost will be a large percentage of the total cost of the agitator, which includes machining expenses but a much smaller percentage of the valve part. Also, the allowable corrosion rate for the stirrer will probably be much higher than for the complex valve part. Either of these factors could result in the agitator being made from two different materials for economic reasons even though the corrosion would be the same for both.

In this instance, a likely solution would be to use an inexpensive, less-corrosion-resistant carbon steel for the agitator and replace it annually. On the other hand, the valve part might be designed for a 10 year life by using a more expensive stainless steel with better corrosion resistance. (It might be implied from this discussion that the more expensive an alloy, the better is its corrosion resistance and vice versa. This is, of course, not always true.)

Construction of a new plant, or modification or repairs in an existing facility, can also influence materials selection. For a new plant, the selection procedure should begin as soon as possible—before the design is finalized. The optimal design for corrosion resistance will often vary with the material used. Also, the increasing availability of higher-strength materials might make it possible to design smaller sections. This can be beneficial by reducing costs, and in some cases, by reducing weight and/or bulk. Additional information on design considerations can be found in Chapter 7.

In a repair application, there is usually less opportunity for redesign, and the principal decision factors will often be delivery time, ease of fabrication in the field, and length of service required for the repair. It is also advisable to make an estimate of the remaining life of the equipment so that the repair is not overdesigned in terms of the corrosion allowance.

Elements of the Materials Selection Process

In this section, the various steps that might be included in a materials selection process are examined. It should be noted, however, that there is no universally accepted materials selection process. Each industry has its own unique requirements that influence or alter the selection process. For example, in the aircraft and aerospace industries, materials that exhibit high strength-to-weight ratios are preferred, particularly for structural frames. These materials include aluminum and titanium alloys and nonmetallic materials, such as composite materials (reinforced plastics) or graphite. The high density of corrosion-resistant alloys used

in other industries—stainless steels and high-nickel alloys—would preclude their use. Despite the varying requirements from industry to industry, the following elements can serve as a good starting point in many applications.

Review of Operating Conditions. The first step in the materials selection process is a thorough review of the corrosive environment and equipment operating conditions. This review requires input from knowledgeable process engineers. Precise definition of the chemical environment, including the presence of trace compounds, is vital. For example, the nickel-molybdenum alloy Hastelloy B-2 (UNS N10665) is highly resistant to hydrochloric acid (HCl) up to the atmospheric boiling point. However, the presence of small quantities of oxidizing metal ions, such as ferric ion (Fe^{3+}), will result in severe corrosion. Other operating conditions that require definition, especially for equipment used in the chemical-processing industry, include temperatures, pressures, flow rates, liquid versus gaseous phases, aqueous versus anhydrous phases, continuous versus intermittent operation, media used for cooling or heating, external versus internal environment, and product purity.

Abnormal or upset conditions are often overlooked during the selection process. For example, plain carbon steel may be the optimal choice for vessels and piping that must contain noncorrosive hydrocarbon gases, such as ethylene, under pressure at normal temperatures. However, the cooling effect that occurs during venting to the atmosphere, for whatever reason, can lower the temperature of vessels, piping, and relief valves to below the ductile-to-brittle transition point and result in a catastrophic brittle fracture. Thus, the selection of special steels, qualified by impact testing at the lowest expected temperature, would be appropriate.

Review of Design. Next, the type and design of the equipment and its various components should be considered, along with size, complexity, and critically in service. Selecting a material for a simple storage tank generally does not require the same attention and effort as choosing the material of construction for a highly sophisticated chemical process reactor. This is especially true when considering critical, unique pieces of equipment in large, single-train, continuous process plants in which a failure would shut down the entire operation. In this case, great effort is expended to select the optimal material for safe, low-maintenance service.

The materials used to join the components into an assembly will require as much attention as the component materials themselves. Many bolted agitator assemblies in reactors, as well as riveted wheels in centrifugal compressors, have failed catastrophically because the bolts or rivets did not have adequate strength or corrosion resistance.

When welding is the joining method, the materials engineer is challenged to ensure that the welds are as corrosion resistant as the base

metals. Generally, the weld metal must equal the base metal in chemical composition and must be virtually free of surface defects, such as porosity, slag inclusions, incomplete penetration, or lack of fusion, for long maintenance-free service. The challenge is even greater when dissimilar-metal welds are required. Improper selection might allow local attack due to weld metal dilution or might allow hydrogen-assisted cracking due to hard heat-affected zones (HAZs).

Selection of Candidate Materials. Once the chemical environment, operating conditions, and type and design of the equipment have been defined, consideration of materials of construction is in order. Occasionally, the selection is based on reliable, pertinent past experience, and as such, is well defined. More often, however, selection is anything but straightforward for a number of reasons, such as complex chemical environments and stringent code requirements.

The list of materials to choose from is large and continues to increase. Ferrous and nonferrous metals and alloys, thermoplastics, reinforced thermosetting plastics (RTP), nonmetallic linings, glass, carbon and graphite, catalyzed resin coatings and ceramics are among the various materials available. Many materials will be immediately excluded because of service conditions, that is, pressures too high for RTP, temperatures too high for nonmetallic linings and coatings such as rubber or epoxy resins, environment too aggressive for carbon steel, and so on. Remaining choices can still be great in number.

It is always desirable to minimize the list of materials to allow in-depth evaluation. In other instances, the initial list may be exceptionally small because of limited knowledge about the operating conditions or the complex chemical environment. A search of data sources should follow in either instance. These data sources include handbooks, conference proceedings, literature compilations/searches, and expert systems. The latter are computer programs, developed by corrosion experts, that contain information based on engineering expertise, operating plant experience, and laboratory test data. Such systems are designed to solve problems, make predictions, suggest possible treatments, and offer materials and corrosion advice with a degree of accuracy equaling that of their human counterparts.

One example of such an expert system is the COR•SUR program developed by NACE International (formerly the National Association of Corrosion Engineers) and the National Institute for Standards and Technology (NIST). With this software, the user can find data on the corrosion behavior of metals and nonmetals in comprehensive tables or graphs that evaluate a material performance (corrosion rates) with respect to the concentration and temperature of a specified environment.

Another useful expert system is the CHEM•COR program, which was developed by the Materials Technology Institute (of the Chemical Process Industry) (MTI) in collaboration with NACE, NIST, and the

Nickel Development Institute (NiDI). This interactive advisory system guides the user through the "what ifs" and helps in the selection of materials to use in shipping, handling, and storage of hazardous chemicals. It makes recommendations for materials selection based on service type, environment, and the presence of possible contaminants and contaminant concentration.

Users of these expert systems do not have to be corrosion experts. The systems intended for use by technically knowledgeable people without specialized materials training, who need to make materials selection decisions. Users might include process engineers, mechanical engineers, production supervisors, maintenance supervisors, or materials and corrosion engineers.

Experience and data generated in-house often serve as the most reliable bases for materials selection. Ideally, this base is coupled with outside experience, when available, from materials vendors and equipment fabricators to complete this initial screening process. Contacts with clients referred by vendors should not be overlooked for added experience.

At this point, the list of candidate materials should be narrowed to a reasonable number for in-depth evaluation. Final selections should not be based solely on the above data sources because, in most cases, the data provided are sufficient for the complete characterization of an environment or a set of conditions.

Evaluation of Materials. The in-depth evaluation of each candidate material should begin with a thorough understanding of the product forms available, along with the ease of fabrication by standard methods. For example, it would be wasteful of time and money to evaluate an Fe-14.5Si alloy for anything but a cast component such as a pump casing or valve body. The alloy is unavailable in any other form. Because of its poor weldability, this alloy should also be ruled out for applications involving welding.

Corrosion testing in representative environments is generally the next step. The extent of the investigation (and determination of test conditions) depends on such factors as the following:

- Degree of uncertainty after available information has been considered
- The consequences of making a less-than-optimal selection
- The time available for evaluation

Laboratory testing of candidate materials is common and in some cases may be the only means available for final determination. Wherever possible, the actual process fluids should be used. Otherwise, mixtures simulating the actual environment must be selected. There is considerable risk in using the latter because undefined constituents can have a significant effect on the performance of a particular material.

Depending on the application, weighed and measured coupons of candidate materials are exposed to the corrosive fluids under a variety of conditions ranging from simple static immersion at a controlled temperature to complex testing under combined heat transfer and velocity conditions. Guidance for conducting laboratory corrosion tests is available in Chapter 11. After exposure for a specified length of time (generally a minimum of one week), the coupons are, in the case of metals and alloys, cleaned and reweighed, and a corrosion rate is calculated based on weight loss and exposed surface area. The rate is commonly and expressed in millimeters of penetration per year or inches or mils (1 mil = 0.001 in.) of penetration per year.

In addition, coupons are examined under a microscope for evidence of local attack, such as pitting, crevice corrosion, and exfoliation. Special coupons, such as galvanic couples, welded, and stressed coupons, are often exposed to determine if other forms of corrosion may occur on certain metals and alloys. These coupons may require metallographic examination for evidence of dealloying (parting), SCC, intergranular corrosion, and other corrosion phenomena.

Nonmetallic materials, such as thermoplastics, coatings, reinforced thermosetting resins, elastomers, and ceramics, are also evaluated in laboratory tests, but the criteria are different from those used for metals. First, exposure time must generally be longer (often a minimum of one to three months) before significant changes occur. Exposure times of six months to one year are common. Also, corrosion rate calculations based on weight loss and surface area are not applicable in most cases. Of more importance are changes in weight, volume, hardness, strength, elasticity, and appearance before and after exposure.

If possible, candidate materials should be tested under conditions more like the final application rather than in laboratory glassware, that is, in a semiworks or pilot operation or in full-scale equipment. Generally, the results are more reliable because test coupons are integrated into the process and are exposed to the same conditions as the actual equipment. Because of nonuniform conditions (flows, compositions) within process equipment, coupon locations should be carefully selected.

Reliability is further enhanced when it is possible to test full-size components fabricated from candidate materials:

- Flanged sections of selected alloys and/or nonmetallics installed in a pipeline
- Experimental alloy impellers in pumps for corrosion and cavitation studies
- Tubing installed in a full-size operating or miniature test heat exchanger to evaluate materials with optimum resistance to corrosion under heat transfer conditions

- Paddles of candidate materials bolted to a reactor agitator for erosion-corrosion studies

The primary disadvantages of this method of testing are the cost of fabrication, installation, removal, and evaluation; the downtime resulting from equipment being taken out of service and dismantled for evaluation; and the fact that a test component could fail prematurely and cause a unit shutdown and/or equipment damage.

Specifications. At this point, all candidate materials have been thoroughly evaluated (along with the economics, to be discussed later), and the materials of construction have been selected for the particular application. Clear and concise specifications must now be prepared to ensure that the material is obtained as ordered and that it meets all the requirements of the application. Perhaps the best known and most widely used specifications are the standards of ASTM. Thousands of specifications for virtually all metal and nonmetal materials of construction are covered in 15 sections encompassing 65 volumes.

Similar standards in countries other than the United States include DIN (Germany), BS (Great Britain), AFNOR (France), UNI (Italy), NBN (Belgium), and JIS (Japan). Other materials specifications that are well known but are more limited in application are those of SAE International (formerly the Society of Automotive Engineers) and its Aerospace Materials Specifications (AMS), the American Welding Society (AWS), and the American Petroleum Institute (API), and the American National Standards Institute (ANSI). Military, federal, and NASA specifications also often exist for materials of concern.

Fabrication requirements must also be spelled out in detail to avoid mistakes that could shorten the life of the equipment and to satisfy the requirements of state and federal regulatory agencies and insurance companies. The American Society of Mechanical Engineers (ASME) code governs the fabrication of equipment for the chemical, power, and nuclear industries, and the API code governs the fabrication of equipment for the refining industry. Piping for these industries is generally fabricated per applicable ANSI codes. In these codes, allowable stresses for design calculations have been determined for virtually all metals and alloys that might be selected for corrosive (and noncorrosive) service. Where welding is the primary joining method, welding procedures and welders must be qualified before fabrication begins. Testing and quality assurance requirements, such as radiography, hydrostatic testing, and ultrasonic inspection, are also covered in the codes and are specified where applicable to ensure compliance.

The fabricator is generally required to provide detailed drawings that list dimensions, tolerances, all pertinent materials specifications, fabrication and welding details, and testing and quality

assurance requirements for review. Prefabrication meetings are held for final review of all drawings and details so that the customer and vendor are in agreement. Thus, problems or errors that could lead to costly delays in fabrication or failures in service can be detected early and corrected.

Money spent on inspection and monitoring during equipment fabrication/erection to ensure compliance with specifications is repaid by trouble-free startup and operation of the fabricated assembly. In some cases, every component of an assembly must be tested to avoid excessive corrosion and/or premature failure. For example, an additional quality check of a vessel fabricated from AISI type 316L stainless steel for hot acetic acid service might be to test every plate, flange, nozzle, weld, and so on, for the presence of molybdenum by using a chemical spot test method. The absence of molybdenum, which might indicate the mistaken use of a different stainless steel, such as type 304L, would result in accelerated corrosion in this service. Another example is the testing of every component (including weld metal) of a heat exchanger fabricated from chromium-molybdenum steels for hot high-pressure hydrogen service to avoid the possibility of catastrophic failure by hydrogen attack. The use of portable x-ray fluorescence analyzers for this type of quality assurance testing of critical service components has become quite popular in recent years.

Operation of a portable x-ray analyzer is simple. The instrument consists of two units: a handheld probe and a small display box. The probe "snout" is placed on the metal material to be identified, for example, a fitting or piece of piping. This procedure opens the radiation-protected door, exposing the surface of the material to a gamma ray beam.

The atoms of the various elements in the metal sample become energized through the loss of an orbital electron. The atoms then revert to their normal electron state by recapturing an electron and emitting x-radiation of specific energy.

A detector in the probe detects the x-rays by energy levels, and a microprocessor converts the x-ray information into alloy identification information. Commonly, the instrument compares the spectrum of the material to be identified with spectra stored in the memory of the instrument and determines which stored spectrum gives the best fit. Alloy identification is displayed on the module box. The measurement time for *alloy sorting* is very fast, in seconds.

Examples of alloy sorting are as follows:

- Type 304 (UNS S30400) stainless steel or type 316 (UNS S31600)
- Alloy C-276 (UNS N10276) or alloy 825 (UNS N08825)
- Carbon steel or low-alloy types

These analyzers cannot measure carbon content and, therefore, cannot distinguish low-carbon type 316L (UNS S32603) stainless steel from type 316 (UNS S31608) with greater than 0.03% carbon.

Follow-up Monitoring. Once built, installed, and commissioned in service, the equipment, piping, reactor, heat exchanger, and so on should be monitored by the materials engineer to confirm the selection of materials of construction and all other requirements for the intended application. Frequent shutdowns for thorough inspections (visually and with the aid of applicable nondestructive examination methods) and periodic evaluation of corrosion coupons exposed at key locations in the equipment represent both the ideal and most difficult monitoring techniques to achieve. In actual practice, equipment is generally kept onstream continuously for long periods of time between shutdowns, so onstream monitoring techniques must also be used.

In the petroleum industry, the internal corrosion in oil and gas production operations is often monitored with hydrogen probes. These instruments measure hydrogen created by corrosion reactions. A portion of the hydrogen penetrates the vessel or pipeline wall, and the rest of the hydrogen is dissolved in the process fluid or released as gas bubbles. Hydrogen probes measure hydrogen permeation and provide information on the rate of corrosion.

Other onstream corrosion-monitoring techniques that are used in petroleum and chemical industries include the following:

- Electrical resistance and linear polarization methods. The former determines corrosion trends with time, and the latter determines an instantaneous corrosion rate.
- Ultrasonic thickness measurement. This is a useful monitoring tool, especially when baseline readings are taken at selected locations before the equipment is placed in service. The inspection locations can be changed if erosion or corrosion areas are localized.

With these methods, the materials engineer is able to determine the adequacy of the materials selection and to predict the remaining life so that replacements and/or repairs can be scheduled well in advance of failure. The corrosion test methods discussed above can also be used to evaluate alternate materials that might be more cost effective at the time of replacement of the vessel or a component. More detailed information on corrosion testing and monitoring can be found in Chapter 11.

Final Materials Selection. Criteria for making the final materials selection will include judgments about each of the following:

- Initial costs. How much money can be spent now?
- Maintenance costs. How frequently will the equipment need to be inspected for corrosion damage?

- Repair costs. Can the equipment be repaired easily and quickly? Can damage be detected before it becomes extensive? Will major components have to be replaced if damage occurs?

In each instance, estimates can be stated in dollars. Cost of lost production is also a factor, but this is usually best handled in the establishment of acceptable risk in the initial project evaluation strategy.

Although a review of corrosion economic calculations is beyond the scope of this chapter, literature is available that addresses the economic methods to prevent and control corrosion. NACE report 3C194, "Economics of Corrosion," takes into account the various costs listed above and evaluates them in light of the time value of money and the effect of taxes and depreciation. The principles and terminology of "engineering economy" and their application to a number of generic corrosion-related problems are also described in "Corrosion Economic Calculations" in *Corrosion,* Volume 13 of the *ASM Handbook.*

Materials Considerations

Adding to the complexity of the selection process is the fact that there are literally thousands of materials to choose from. Since World War II, the demand for more efficient and less costly products has increased dramatically, and the need for materials that are stronger, lighter, and/or more resistant to corrosion, wear, and heat has promoted tremendous advances in materials science.

The three primary classes of materials used for engineering applications are metals (and alloys), polymers, and ceramics. These classes of materials are used as single elements or in combination as coatings, composites, or other hybrid structures. Regardless of how a material is classified, in order to be successfully used, it must meet a combination of needs, including corrosion resistance, strength, stiffness, fabricability, cost, and availability (refer to Tables 1 and 2). Often these needs conflict, and the overall materials selection process is one requiring cooperation between design team members, rigorous materials analysis and, ultimately, trade-offs.

General Material Considerations. The complexity associated with material requirements is illustrated by the case history of a battery. Fig. 1 shows the processes and disciplines associated with the design and performance of a battery, including electrochemistry, chemical engineering, chemistry, mechanical engineering, and metallurgy. These, in turn, can be further broken down into such categories as cell design, electrolytes, energy conversion, and plating. It is apparent from Fig. 1 that corrosion, although a necessary consideration, is but one of a large

number of interrelated factors, all of which must work in conjunction in order for a battery to perform suitably.

A cutaway diagram of an alkaline cell battery is shown in Fig. 2, identifying the materials used for its construction and function. The outer containment is provided by a steel can covered with a metallized plastic-film label. The anode consists of powdered zinc metal surrounding a brass current collector. The cathode is manganese dioxide and carbon. Polymers and nonwoven fabrics are used for seals.

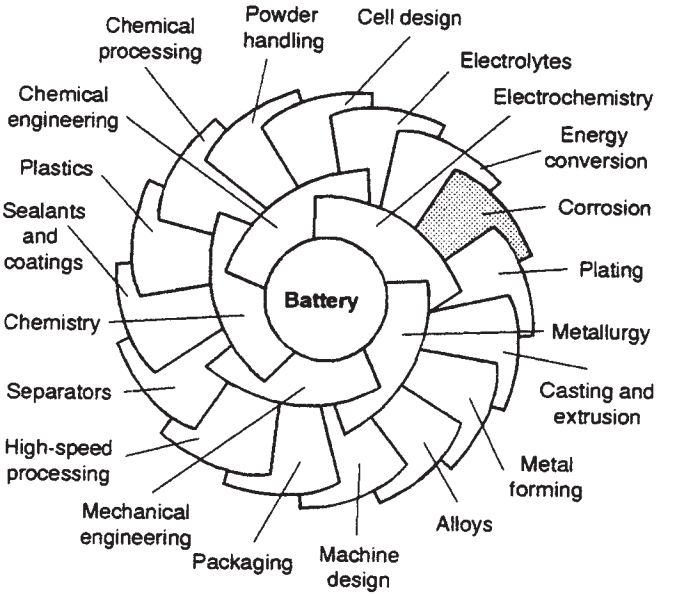


Fig. 1 Processes, materials, and engineering disciplines involved in manufacturing a battery

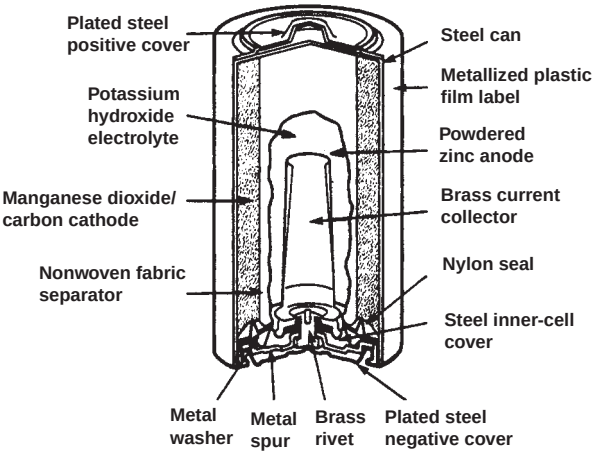


Fig. 2 Cross-sectional view of a cylindrical alkaline battery showing the various materials used

A major consideration regarding the performance, cost, and compatibility of materials in this case is the many interfaces within the battery, which are shown schematically in Fig. 3. The anode interfaces with the electrolyte, negative collector, and separator. The cathode interfaces with the electrolyte, positive collector, and separator. What may, at first glance, appear to be a fairly simple device is, in fact, a quite intricate and complex system. When one looks at the individual components and the many requirements placed on each, this complexity is more readily appreciated.

Cost Considerations. During the materials selection process, relative costs are always a concern. In the development of cost comparison information, it is important that materials be compared on the basis of similar size, product form, and so forth. Often, the installed cost will vary considerably from costs based simply on bulk amounts of the materials. Presentation of cost comparisons on a per-unit weight versus a per-unit linear measure of volume can greatly influence the relative cost of any given material.

Other factors that have a bearing on the relative cost of materials are the complexity of a part and the number of assemblies required. A simple part used in the application where few are required can be made from materials that are not as readily fabricated or as amenable to mass production, in contrast to applications requiring parts of highly complex shape or many assemblies. These latter factors affect the selection of manufacturing processes and procedures, which, in turn, affects material selection. In addition to the stated technical factors, changes in market, industry, and political climate can greatly affect the relative costs and ranking of materials.

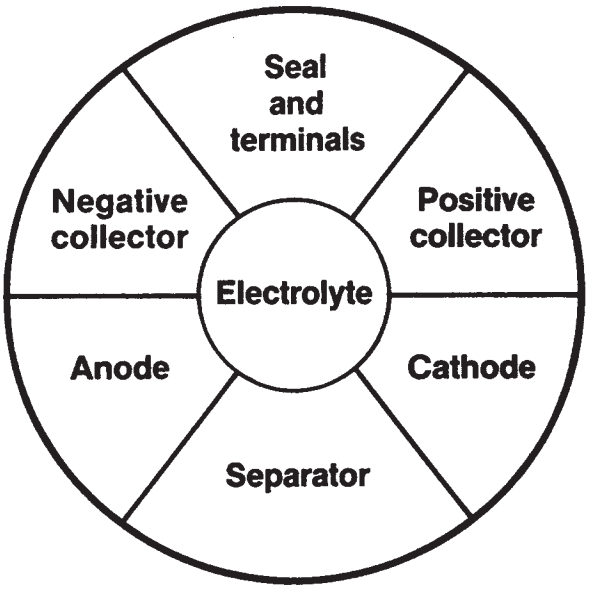


Fig. 3 Interfaces within a battery

The relative costs of installed piping systems produced from various materials are presented in Table 3. The effects of the complexity and diameter of the piping system are shown using a schedule 40 (7.1 mm or 0.280 in.) carbon steel piping system as the reference point, assigned a relative cost value of 1.00. Fiberglass-reinforced plastics are favored for more complex and larger-diameter piping systems. Stainless steel piping systems of the same thickness (i.e., schedule 40) are considerably more expensive than carbon steel piping. However, if a thinner-wall stainless steel piping system can be substituted, the cost differential may be greatly reduced. Compare the cost for schedule 5 (2.8 mm, or 0.109 in.) type 304 stainless steel with that of the schedule 40 carbon steel piping system. This substitution would be justifiable if a significant thickness of the carbon steel was for a corrosion allowance, which would not be required for the stainless steel.

The relative costs of a series of materials can be examined by following a given column in Table 3. For example, for a 150 mm (6 in.) diameter

Table 3 Relative costs of installed piping systems of various materials based on a reference point of 1.00 for Schedule 40 carbon steel piping

	150 m (500 ft) complex piping system		300 m (1000 ft) straight-pipe piping system	
Piping material	50 mm (2 in.)	150 mm (6 in.)	50 mm (2 in.)	150 mm (6 in.)
Carbon steel, Sch. 40	1.00	1.00	1.00	1.00
Fiberglass-reinforced vinylester	1.01	0.87	1.32	0.99
Fiberglass-reinforced polyester	1.32	0.84	1.35	0.97
Glass pipe	1.37	1.39	0.90	1.05
Aluminum, Sch. 40	1.48	1.44	1.24	1.11
304 stainless steel, Sch. 5	1.49	1.76	1.43	1.36
Polyvinylidene chloride-lined steel	1.53	1.43	1.23	1.23
Polypropylene-lined steel	1.60	1.49	1.02	1.06
Rubber-lined steel, Sch. 40	1.64	1.53	1.07	1.08
316 stainless steel, Sch. 5	1.68	1.93	1.55	1.86
304 stainless steel, Sch. 40	1.86	2.67	1.81	2.52
Polyvinylidene fluoride-lined steel	2.07	2.16	1.52	1.77
316 stainless steel, Sch. 40	2.13	3.18	2.19	3.11
Alloy 20, Sch. 5	2.14	2.96	2.41	3.61
FEP-lined steel	2.21	2.64	1.63	2.39
PFA-lined steel	2.45	3.03	1.83	2.73
Armored glass pipe	2.47	2.74	1.74	2.38
PTFE-lined steel	2.62	2.78	2.14	2.70
Ni-Cu Alloy 400, Sch. 5	2.63	2.95	2.28	2.47
Nickel 200, Sch. 5	2.69	3.71	2.32	2.65
Alloy 20, Sch. 40	2.87	4.68	2.41	5.55
Ni-Cu Alloy 400, Sch. 40	3.17	4.95	3.17	4.33
Ni-Cr Alloy 600, Sch. 5	3.23	4.81	3.18	3.85
Titanium, Sch. 5	3.45	3.75	2.90	3.76
Nickel 200, Sch. 40	3.68	5.85	3.48	4.89
Titanium, Sch. 40	4.19	6.31	3.69	6.73
Ni-Cr Alloy 600, Sch. 40	4.32	6.55	3.91	5.62
Glass-lined steel, Sch. 40	4.48	3.41	3.35	3.38
Ni-Cr-Mo Alloy C-276, Sch. 5	4.50	4.63	4.38	5.58
Zirconium, Sch. 5	4.64	5.74	4.06	6.04
Ni-Mo alloy B, Sch. 5	4.79	4.94	4.63	5.93
Zirconium, Sch. 40	5.79	7.79	5.89	9.59
Ni-Cr-Mo Alloy C-276, Sch. 40	6.23	6.84	7.23	9.74
Ni-Mo Alloy B, Sch. 40	6.59	7.68	7.73	10.64
Tantalum-lined steel, Sch. 5	7.73	9.10	8.65	12.13
Tantalum-lined steel, Sch. 40	10.08	17.46	11.30	23.27

FEP, fluorinated ethylene propylene polymer; PFA, pefluoro (alkoxy-alkane) copolymer; PTFE, polytetrafluoroethylene; Sch., schedule. Source: Ref 1

by 300 m (1000 ft) straight-run piping system, carbon steel has a relative cost of 1.00, compared with 0.97 for fiber-reinforced polyester, 2.52 for type 304 stainless steel at the same thickness, 3.76 for titanium at the same thickness, and 23.27 for tantalum-lined steel.

Installed costs of corrosion-resistant 150 mm (6 in.) outside diameter (OD) piping are given in Table 4 and Fig. 4. The piping system used to generate the data was a 124 m (406 ft) long process piping arrangement typical of those found in a chemical plant. It contains twenty-one 90° ells, four 45° ells, and 15 tees. A detailed presentation of cost summaries is presented in Table 4 and includes:

- Pipe and fitting costs
- Equipment costs, which cover applicable rental costs for welders, cranes and other equipment, pipe hangers, filler metal or adhesive, wire brushes, cleaning gear, and fasteners.
- Painting costs for carbon steel and lined piping
- Total material costs (the sum of the previous four cost-related items)
- Shop fabrication costs

Table 4 Summary of costs for 150 mm (6 in.) OD corrosion-resistant piping for chemical processing plant based on a reference point (cost ratio) of 1.00 for type 316L Schedule 5S. See text for a description of individual costs.

Material	Pipe, $	Fittings, $	Equipment, $	Painting, $	Total material, $	Shop, $	Field erection, h	Installed cost, $	Cost ratio
Metallic									
Carbon steel, Sch. 40	4,990	1,145	1,630	5,700	13,465	6,384	432	34,696	0.51
Type 304L, Sch. 5S	3,865	4,831	3,730	3,200	15,626	16,420	950	65,296	0.96
Type 304L, Sch. 10S	4,572	5,797	3,830	3,200	17,399	18,400	935	68,524	1.00
Type 316L, Sch. 5S	5,367	6,337	3,730	3,200	18,634	16,420	950	68,304	1.00
Type 316L, Sch. 10S	6,403	7,638	3,830	3,200	21,071	18,400	935	72,196	1.06
Type 317L, Sch. 125	4,815	6,825	3,465	3,200	18,305	11,125	865	59,705	0.87
Type 317L, Sch. 5S	8,079	11,123	3,830	3,200	26,232	16,900	975	77,257	1.13
20Cr-25Ni-4.5Mo, Sch. 125	8,250	10,862	3,980	3,200	26,292	15,900	910	74,042	1.08
20Cr-25Ni-4.5Mo, Sch. 5S	13,481	17,887	4,705	3,200	39,273	18,400	1,095	95,998	1.41
20Cr-25Ni-6Mo, Sch. 125	14,648	11,380	4,000	3,200	33,228	16,050	920	81,478	1.19
20Cr-25Ni-6Mo, Sch. 5S	24,575	22,950	4,740	3,200	55,465	18,565	1,105	112,705	1.65
Alloy G, Sch. 125	30,803	40,940	4,050	3,200	78,993	18,700	950	130,943	1.92
Alloy G, Sch. 5S	51,680	68,364	4,795	3,200	128,039	21,325	1,250	193,114	2.83
Nonmetallic									
PVC, Sch. 40	1,072	2,992	1,200	3,200	8,464	…	425	23,339	0.34(a)
PVC, Sch. 80	2,826	3,114	1,250	3,200	10,390	…	475	27,015	0.40(a)
RTRP, 150 psi	4,182	8,563	1,000	3,200	16,945	…	245	25,520	0.37(a)
Lined									
Rubber, 150 psi	22,183	10,350	5,940	5,700	44,173	7,980	1,920	119,353	1.75(b)
SL, 150 psi	26,813	16,760	6,950	5,700	56,223	…	2,205	133,398	1.95(b)
PPL, 150 psi	14,381	14,285	5,940	5,700	40,306	…	1,920	107,506	1.57(b)
PVDF, 150 psi	29,845	23,140	5,940	5,700	64,625	…	1,920	131,825	1.93(b)
PTFE, 150 psi	64,540	32,315	6,950	5,700	109,505	…	2,205	186,680	2.73(b)

PVC, polyvinyl chloride; RTRP, reinforced thermosetting resin pipe; SL, polyvinylidene chloride-lined carbon steel; PPL, polypropylene-lined carbon steel; PVDF, polyvinylidene fluoride-lined carbon steel; PTFE, polytetrafluorethylene-lined carbon steel; Sch., schedule. (a) Installed cost of PVC and RTRP piping varies substantially, depending on whether press fits are allowed, and safeguarding and anti-vibration measures are required. (b) Adjustments necessary to compensate for reduced flow area can significantly increase the cost of lined pipe and alter the cost ratio accordingly. Source: Ref 2

- Field erection costs (calculated on a field erection rate of $35 per hour)
- Installed costs (the sum of the dollar values under total material costs, shop fabrication costs, and field erection costs)

Type 316L Schedule (Sch.) 5S stainless steel is the cost base (i.e., cost ratio = 1). The costs of all the other materials are expressed as a multiple of the cost of type 316L Sch. 5S (see Table 4 and Fig. 4b).

While these examples of installed piping costs are quite useful in the materials selection process, they do not represent the value of all costs associated with each candidate material over the *total life cycle* of the system. Such a calculation takes into account the expected service life, the installed cost, including removal of failed materials, and annual operation and maintenance costs. Often, the biggest unknown in the calculation is the anticipated service life, especially in equipment with little or no service experience. Only when service life calculations are entered into the equation can cost considerations be truly understood and the correct material selected.

Materials Properties Considerations. The physical properties of materials vary widely, as illustrated in Table 5. The density, modulus of elasticity, tensile strength, and thermal conductivity of carbon steel,

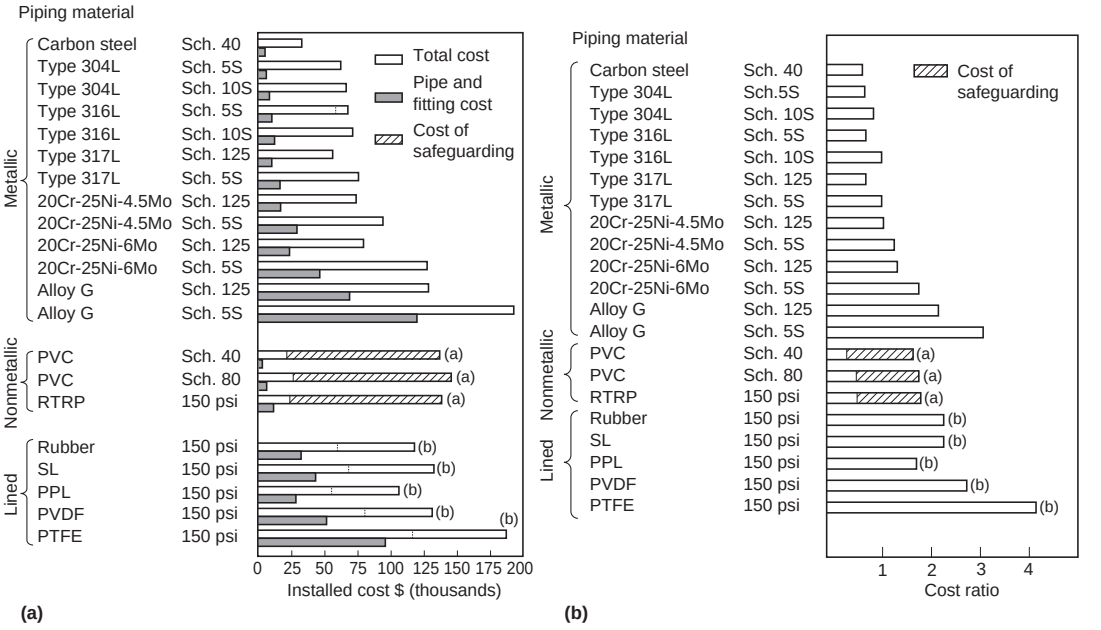


Fig. 4 Summary of (a) total costs and (b) cost ratio (based on type 316L Sch. 5S = 1.00) for 150 mm (6 in.) OD corrosion-resistant piping for a chemical processing plant. Safeguarding costs associated with nonmetallic piping include engineering design features such as insulation, shock protection, and armor or double containment. See Table 4 for an explanation of the abbreviations, footnotes (a) and (b) within the figure, and the source of these data.

Table 5 Comparative properties of steel, commercial-purity aluminum, and fiber-reinforced plastics (FRP)

Property	Carbon steel(a)	Aluminum (99% min Al)(b)	FRP
Density, g/cm^3	7.86	2.71	1.95
Modulus of elasticity, GPa (10^6 psi)	210 (30)	70 (10)	5–11 (0.7–1.6)
Tensile strength, MPa (ksi)	460 (67)	75 (11)	84–140 (12–20)
Thermal conductivity, W/m · K	4	20	0.02

(a) Typical values for a medium-carbon steel in the annealed condition. (b) Sheet in annealed condition

aluminum, and fiber-reinforced plastic are compared. The densities of aluminum and fiber-reinforced plastic are lower than that of carbon steel by factors of 2.8 and 4, respectively. Compared to carbon steel, the modulus of elasticity of aluminum is lower by a factor of 3, and that of fiber-reinforced plastic is lower by a factor of 20 or more. Smaller differences are observed for other materials properties. For any desired property, values for metals and nonmetals can vary over several orders of magnitude. Once again, the challenge of the materials selection process is to provide the required properties for a given service application.

In nearly all cases, the number of materials available for a given application begins with an originally successful version of a material that can be subsequently modified to maximize its properties. Property modification, however, is often a trade-off, as described in the following example.

The family of alloys based on 18% Cr and 8% Ni—the workhorse of the austenitic stainless steel family—is shown in Fig. 5. The composition of this highly successful austenitic stainless steel was modified to enhance its corrosion resistance by increasing the chromium and nickel concentrations or by increasing the chromium, nickel, and molybdenum concentrations. Pitting resistance is increased by adding molybdenum, and machinability is increased by adding sulfur. However, the addition of sulfur lowers corrosion resistance—an example of a trade-off in alloy design. To control sensitization of 18Cr-8Ni stainless steel, either the carbon content is reduced or small amounts of titanium or niobium (columbium) are added. As further described in Chapter 6, there are many other variations of the 18Cr-8Ni compositions where other properties are improved.

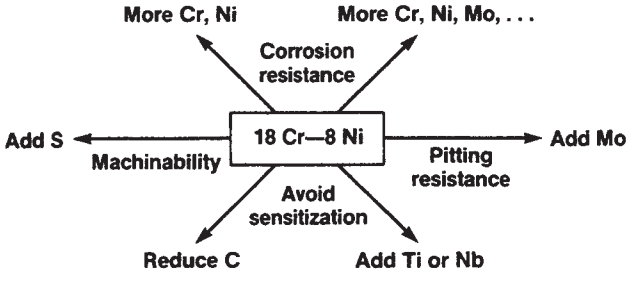


Fig. 5 Alloying modifications to 18Cr-8Ni stainless steel to enhance specific properties

Processing and Fabrication Considerations. Materials must be fabricated and joined into useful forms, a fact that must be considered in the materials selection process. Steel is useful because it can be readily formed into a desired shape and retain that shape while maintaining mechanical strength and toughness. Some of the most corrosion-resistant materials cannot be readily formed and joined. This drawback results in special design and fabrication requirements and some limitations in cases where these materials must be used for their corrosion resistance. An example of a material of this type is tantalum, which requires special handling and fabrication procedures.

Materials processing and fabrication requirements must be an integral part of the materials selection process. As an example, consider the effect of welds on material performance. Welds can affect the corrosion performance of a material for several reasons:

- Geometric irregularities at welds
- Compositional variations from the base material across the weld
- Microstructural variations in the metal adjacent to the weld and in the weld metal itself
- Residual stresses associated with the weld caused by varying thermal expansion and different thermal histories across the weld

The complexity of a weld on a plate is shown schematically in Fig. 6. The three general areas associated with a weld are the weld nugget itself; a HAZ, that is, the base metal adjacent to the weld nugget; and the unaffected base metal well away from the weld nugget. The HAZ can be further broken down into several areas. The weld nugget has been exposed to temperatures above the melting point of the alloy whereas the

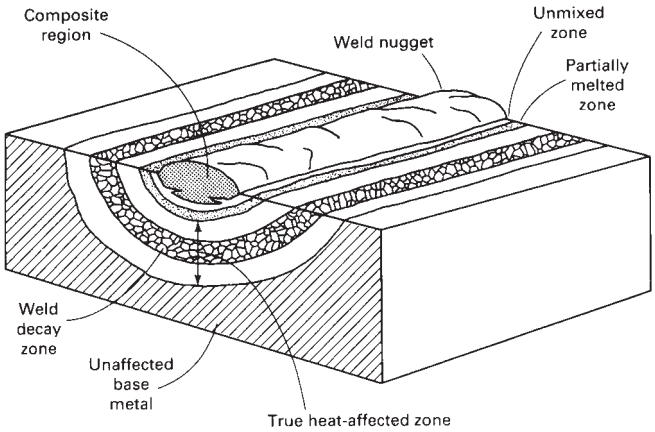


Fig. 6 Schematic diagram of components of weldment in austenitic stainless steel

unaffected base metal has experienced little or no increase in temperature from the welding process. The base material between these two zones has undergone a variety of time/temperature combinations at elevated temperatures. These time/temperature cycles can result in microstructural changes and lead to the formation of regions highly susceptible to corrosion.

A classic example of how welds affect corrosion resistance is the sensitization of a fine band of material in the HAZ of some stainless steel weldments. This sensitized region is designated by the weld decay zone shown in Fig. 6. This narrow band of material is highly susceptible to intergranular corrosion, whereas the material on either side of the decay zone is essentially unattacked in many environments. As stated earlier, sensitization can be avoided by selecting lower carbon content stainless grades (<0.03% C, [e.g., type 304L]) or stabilized grades such as type 321, which contains titanium, or type 347, which contains niobium.

Welds have been briefly discussed here to illustrate the effect of manufacturing processes on corrosion resistance. Other manufacturing and assembly features must also be considered when evaluating the corrosion resistance of final assemblies. Take, for example, the introduction of nickel-chromium-molybdenum alloys for tubing in oil and gas wells. Examples include Alloy C-276 (UNS N10276) and Alloy 825 (UNS N08025). In order to meet the strength requirements of downhole tubulars, these corrosion-resistant alloys (CRAs) had to be cold worked (they were normally used in the annealed condition). Unfortunately, the higher strength due to cold working made these alloys susceptible to environmentally assisted cracking, namely, stress-corrosion and hydrogen embrittlement. As a result, these alloys had to undergo extensive corrosion evaluation programs to demonstrate suitability for service. A flowchart of the qualification process for CRAs is shown in Fig. 7. Such testing led to tighter control of alloy composition and processing to maximize corrosion resistance and helped to define acceptable CRA/environment combinations. Although the initial costs associated with using CRAs versus low-alloy steels are much higher, their use ultimately led to economic savings because costly replacements of failed low-alloy steel tubing could be avoided. In addition, increased gas and oil flow rates were possible by taking advantage of the lower friction of an uncorroded CRA tubing surface.

Selecting Materials to Avoid or Minimize Corrosion

The three interrelated factors that drive materials selection for corrosion control are the corrosivity of the environment, the corrosion resistance of the material, and the acceptable rate of attack. This relationship

can be demonstrated by the hypothetical situation shown in Fig. 8. In this case, an acceptable failure-rate or rate-of-attack curve has been defined as a function of the corrosivity of the environment on the vertical axis and the corrosion resistance or the material on the horizontal axis. For a given corrosivity, the dashed lines intersecting the rate-of-attack curve define the boundary between acceptable and unacceptable materials. Those materials to the left of this boundary have insufficient corrosion resistance and will fail, whereas those materials to the right of this boundary have sufficient corrosion resistance and will provide adequate service. In the example shown, plain (uncoated) steel, galvanized steel, and stainless steels would be to the left of acceptable boundary, and nickel alloys and titanium would have sufficient corrosion resistance for this application.

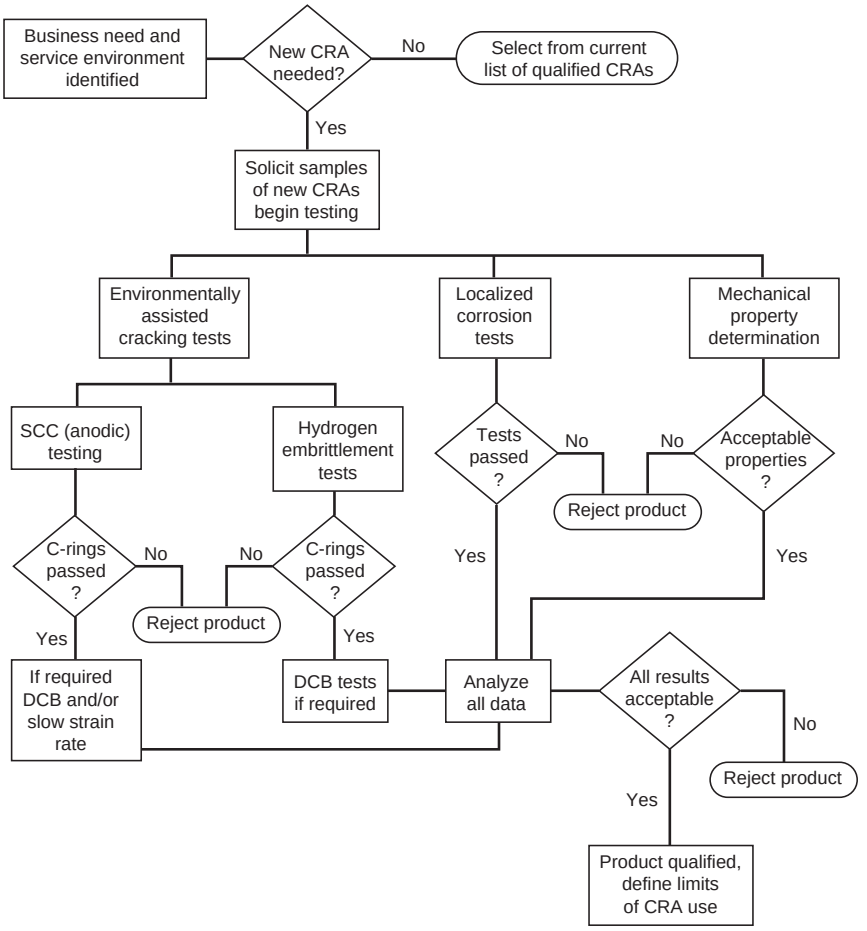


Fig. 7 Flowchart of the qualification process for nickel-based corrosion-resistant alloys (CRAs) used as tubing in the oil and gas industries. DCB, double-cantilever beam

In practice, it is not always possible to identify the acceptable failure-rate curve specifically. Some relative rate of attack must be defined. The more inexact is the definition of the corrosivity of the environment, the expected failure rate, or the rate-of-attack dependency, the more conservative must be the materials selection.

The relationship among corrosivity, rate of attack, and corrosion resistance is shown for materials selection in cooling waters in Table 6. As the corrosivity of the water type increases from fresh water to corrosive fresh water up to polluted seawater, the corrosion resistance of materials to handle these cooling waters must also increase. For fresh waters, steel, copper, and aluminum alloys are acceptable. For polluted seawater, highly corrosion-resistant ferritic stainless steels or titanium alloys are recommended.

This point is again illustrated by the recommended acceptable galvanic couples in atmospheric exposure, fresh water exposure, or seawater exposure. As the corrosivity of the environment increases, the list of acceptable galvanic couples becomes more restrictive. In atmospheric

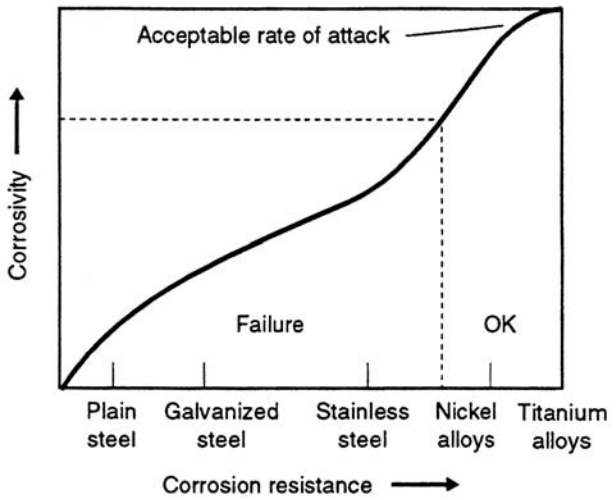


Fig. 8 Boundary between acceptable (right of the curve) and unacceptable (left of the curve) materials

Table 6 Materials selection for use in cooling waters

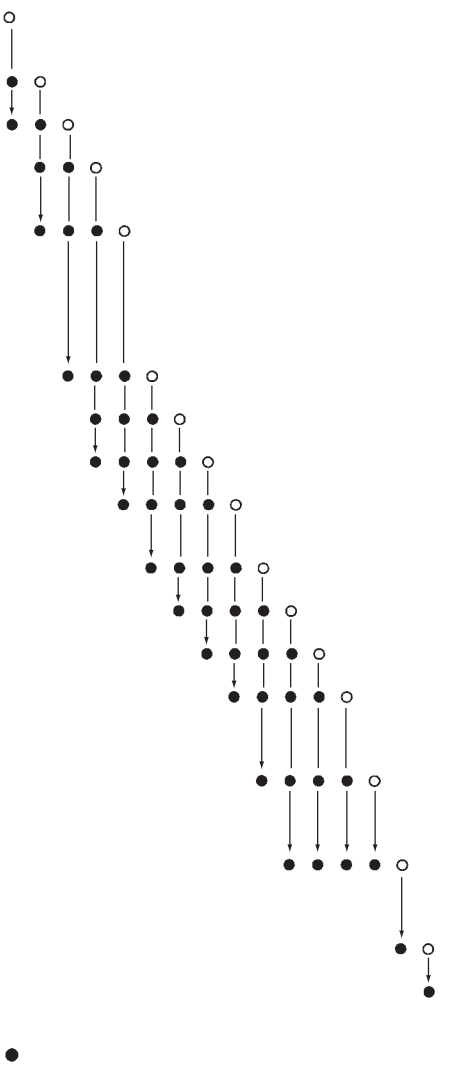
Water type(a)	Minimum alloy selection
Fresh water	Steel
	Copper
	Aluminum
Corrosive fresh water	Copper (admiralty)
Brackish water and seawater (low to moderate velocity)	70Cu-30Ni, 90Cu-10Ni
Pure and polluted seawater (high velocity)	Stainless steel (type 316)
	Ferritic molybdenum stainless steels (Fe-Cr-Mo)
	Titanium
Polluted seawater (low velocity)	Ferritic molybdenum stainless steels (Fe-Cr-Mo)
	Titanium

(a) Listed in order of increasing corrosivity

corrosion, galvanic couples between aluminum, cadmium, iron, steel, lead, and tin are not expected to yield severe detrimental effects under most conditions. In fresh water or seawater service, however, the list of acceptable couples with aluminum is shortened to aluminum, aluminum alloys, and cadmium (Table 7).

Table 7 Metals and alloys compatible in dissimilar-metal couples

Group number	Metallurgical category	emf, V	Anodic index(a), V	Compatible couples(b)
1	Gold, solid and plated; gold- platinum alloys; wrought platinum	+0.15	0	
2	Rhodium plated on silver-plated copper	+0.05	0.10	
3	Silver, solid or plated; high-silver alloys	0	0.15	
4	Nickel, solid or plated; monel metal, high-nickel-copper alloys	–0.15	0.30	
5	Copper, solid or plated; low brasses or bronzes; silver solder; German silvery high copper-nickel alloys; nickel-chromium alloys; austenitic corrosion-resistant steels	–0.20	0.35	
6	Commercial yellow brasses and bronzes	–0.25	0.40	
7	High brasses and bronzes; naval brass; Muntz metal	–0.30	0.45	
8	18% Cr type corrosion-resistant steels	–0.35	0.50	
9	Chromium plated; tin plated; 12% Cr type corrosion-resistant steels	–0.45	0.60	
10	Tin-plate; ternplate; tin-lead solder	–0.50	0.65	
11	Lead, solid or plated; high-lead alloys	–0.55	0.70	
12	Aluminum, wrought alloys of the 2000 series	–0.60	0.75	
13	Iron, wrought, gray or malleable; plain carbon and low-alloy steels; Armco iron	–0.70	0.85	
14	Aluminum, wrought alloys other than 2000 series aluminum, cast alloys of the silicon type	–0.75	0.90	
15	Aluminum, cast alloys other than silicon type; cadmium, plated and chromated	–0.80	0.95	
16	Hot-dip-zinc plate; galvanized steel	–1.05	1.20	
17	Zinc, wrought; zinc-base die-casting alloys; zinc plated	–1.10	1.25	
18	Magnesium and magnesium-base alloys, cast or wrought	–1.60	1.75	



(a) Anodic index is the absolute value of the potential difference between the most noble (cathodic) metals listed and the metal or alloy in question. For example, the emf of gold (group 1) is +0.15 V, and the emf of wrought 2000-series aluminum alloys (group 12) is –0.60 V. Thus, the anodic index of wrought 2000-series aluminum alloys is 0.75 V. (b) "Compatible" means the potential difference of the metals in question, which are connected by lines, is not more than 0.25 V. An open circle indicates the most cathodic members of a series; a closed circle indicates an anodic member. Arrows indicate the anodic direction.

General Corrosion

Of the many forms of corrosion, general, or uniform, corrosion is the easiest to evaluate and monitor. Materials selection is usually straightforward. If a material shows only general attack, a low corrosion rate, and negligible contamination of the process fluid and if all other factors, such as cost, availability, and ease of fabrication are favorable, then that is the material of choice. An acceptable corrosion rate for a relatively low-cost material such as plain carbon steel is about 0.25 mm/year (10 mils/year) or less. At this rate and with proper design and adequate corrosion allowance, a carbon steel vessel will provide many years of low-maintenance service.

For more costly materials, such as the austenitic (300 series) stainless steels and the copper- and nickel-base alloys, a maximum corrosion rate of 0.1 mm/year (4 mils/year) is generally acceptable. However, a word of caution is in order. One should never assume, without proper evaluation, that the higher the alloy, the better the corrosion resistance in a given environment. A good example is seawater, which corrodes plain carbon steel fairly uniformly at a rate of 0.1 to 0.2 mm/year (4 to 8 mils/year) but severely pits certain austenitic stainless steels.

At times, nonmetallic coatings and linings ranging in thickness from a few tenths to several millimeters are applied to prolong the life of low-cost alloys such as plain carbon steels in environments that cause general corrosion. The thin-film coatings that are widely used include baked phenolics, catalyzed cross-linked epoxy-phenolics, and catalyzed coal tar-epoxy resins (guidelines for coating selection can be found in Chapter 9). It is advisable not to use thin-film coatings in services where the base metal corrosion rate exceeds 0.5 mm/year (20 mils/year), because corrosion is often accelerated at holidays (for example, pinholes) in the coating. Thick-film linings include glass, fiber- or flake-reinforced furan, polyester and epoxy resins, hot-applied coal tar enamels, and various elastomers, such as natural rubber.

A special case for materials selection under general corrosion conditions is that of contamination of the process fluid by even trace amounts of corrosion products. In this case, product purity, rather than corrosion rate, is the prime consideration. One example is storage of 93% sulfuric acid (H_2SO_4) in plain carbon steel at ambient temperature. The general corrosion rate is 0.25 mm/year (10 mils/year) or less, but traces of iron impart a color that is objectionable in many applications. Therefore, thin-film baked phenolic coatings are used on carbon steel to minimize or eliminate iron contamination. In the same way, thin-film epoxy-coated carbon steel or solid or clad austenitic stainless steels are used to maintain the purity of adipic acid for various food and synthetic fiber applications.

Effects of Alloying on Corrosion Resistance. To understand how alloying helps to minimize general corrosion, some of the thermodynamic and electrochemical "tools" that were described in Chapter 3 (e.g., Pourbaix diagrams and anodic polarization curves) are discussed here. From a thermodynamic viewpoint, there is no question that materials can often be selected that can withstand even highly aggressive solutions. For instance, the noble metals (e.g., gold, silver, platinum) are resistant to most concentrated acids. These metals, however, are hardly materials of widespread use, and for most engineering materials, general corrosion protection is achieved by the presence of a surface film or oxide that has very limited solubility in the environment. Thus, material choices have to be based on the specific environment under consideration.

Alloying is generally needed for engineering-strength purposes, and knowledge of corrosion mechanisms can facilitate the selection of alloys that also have adequate corrosion resistance. For instance, based solely on examination of the Pourbaix diagram, nickel and its alloys are normally a good choice for use in alkaline environments given the

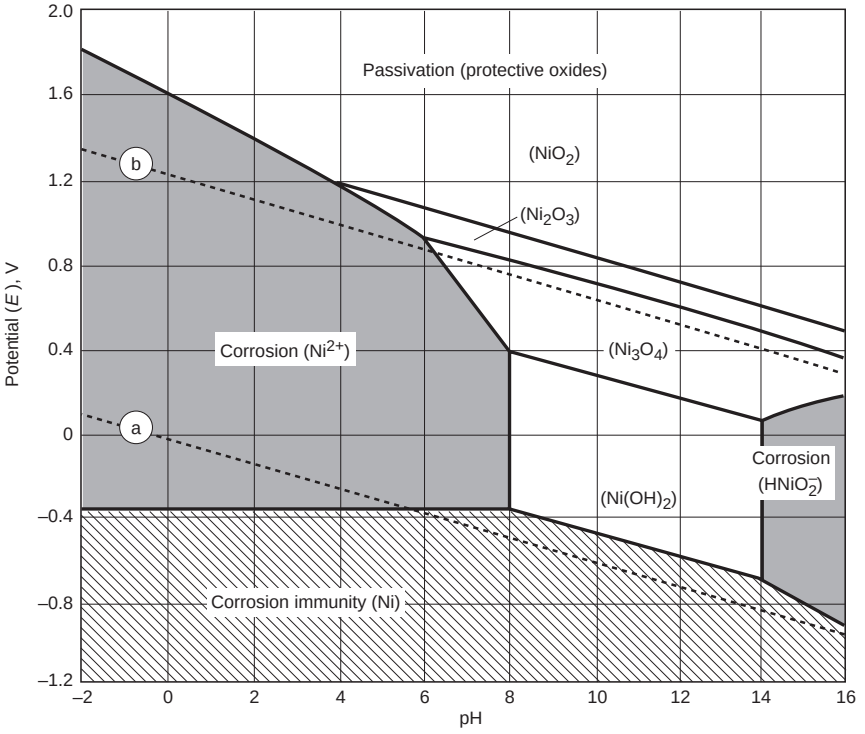


Fig. 9 Pourbaix diagram for the nickel-water system, indicating the *E*/pH regions of thermodynamic stability of various dissolved and solid species and the regions of "corrosion immunity," "passivation," and "active corrosion." Dashed lines show the equilibrium potentials for the (a) H_2/H_2O and (b) O_2/H_2O systems

fact that this metal has a relatively small stability region for the dissolved $HNiO_2^-$ anion in high-pH solutions; hence, the use of nickel electrodes in alkaline batteries (Fig. 9). Conversely, aluminum and its alloys would *not* be good candidates for alkaline environments given the fact that the usefulness of aluminum is normally limited to the pH range of 4 to ~8.5 (Fig. 10).

The general corrosion resistance of many alloys is increased by elements that enhance the passivation region on the Pourbaix diagram due to the formation of mixed surface oxides:

Base metal	Alloying element	Alloy
Fe	Cr	400-series ferritic stainless steels (11–23% Cr)
Fe	Cr, Ni	300-series austenitic stainless steels (16–26% Cr, 6–22% Ni)
Ni	Cr	Alloy 600 (16% Cr, 0.2% Cu, 8% Fe) Nimonic 75 (20% Cr)
Ni	Mo, Cr	Hastelloy B (28% Mo, 6% Fe, 1.5% Cr) Hastelloy C (17% Mo, 5% Fe, 15% Cr), Hastelloy C-22 (13.5% Mo, 4% Fe, 21% Cr) Hastelloy C-276 (16% Mo, 6% Fe, 15% Cr)
Ni	Si	Hastelloy D (10% Si, 3% Cu)
Ti	Mo, Ta, Al	3–6% Al, 2.5–4% V
Zn	Al	35–50% Al
Co	Cr	Vitallium and Stellite orthopedic inserts

The increase in the corrosion resistance associated with alloying may be indicated by the Pourbaix diagrams for the major elements in the alloy. For instance, the superposition of the Cr_2O_3 stability domains onto the Pourbaix diagram for iron-water (Fig. 11) or the MoO_4 and Cr_2O_3 stability domains onto the Pourbaix diagram for nickel-water (Fig. 12) indicate that, in both instances, the "passivation" domains are reinforced in neutral/alkaline environments and are increased in acidic environments. This behavior gives some rationale for the corrosion resistance improvement observed in, for instance, the ferritic and austenitic stainless steels and in the nickel-chromium and nickel-chromium-molybdenum alloys.

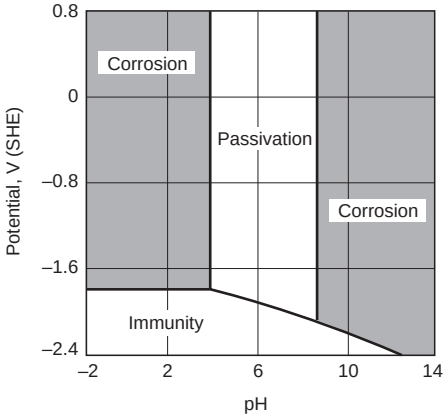


Fig. 10 Pourbaix diagram for aluminum-water

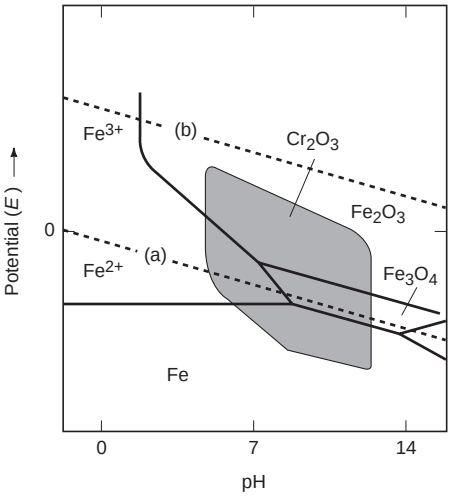


Fig. 11 Superposition of the Cr_2O_3 stability regions (shaded) on the iron-water Pourbaix diagram, to illustrate the *E*/pH regions where chromium alloying might confer added corrosion resistance. Dashed lines show the equilibrium potentials for (a) H_2/H_2O and (b) O_2/H_2O.

It should be emphasized that such material-design analysis based on thermodynamic considerations does not give a direct prediction of the corrosion rates. However, when considering the anodic polarization curves for iron and iron-chromium alloys in deaerated sulfuric acid (Fig. 13a), it is not surprising that, at low overpotentials, the dissolution rate increases with increasing polarization, followed by a decrease at a potential associated with the formation of a protective "passivating" film (Fig. 13b). The marked decrease in corrosion rate is due to the chromium alloying and the resultant formation of a

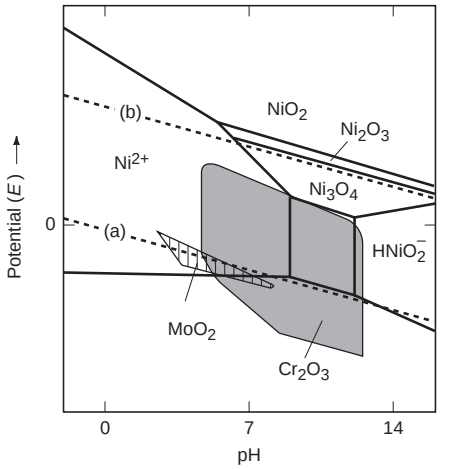


Fig. 12 Superposition of the MoO_4 and Cr_2O_3 stability regions (shaded) on the nickel-water Pourbaix diagram to illustrate the thermodynamic reason for the improved corrosion resistance of various nickel alloys in neutral and acid environments

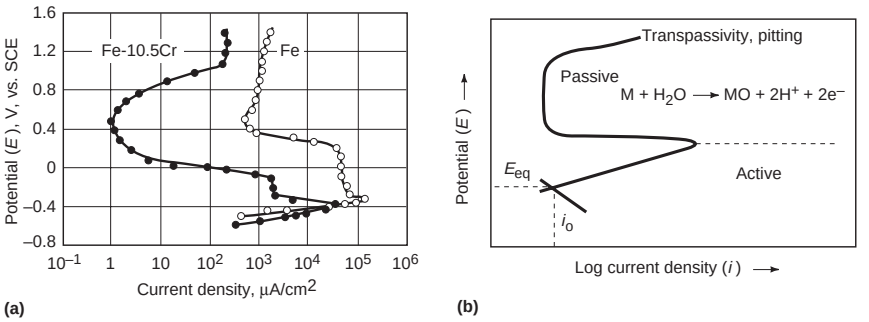


Fig. 13 Effects of alloying and polarization behavior. (a) The potentiostatic anodic polarization of pure iron and iron-chromium alloy in sulfuric acid. (b) Active-to-passive transitions due to the formation of surface oxide. This curve is typical of stainless steels, e.g., the curve on the left-hand side in (a).

low-solubility iron-chromium oxide. Similar polarization curves for nickel-base alloys in deaerated sulfuric acid are shown in Fig. 14 to illustrate the combined effects of different alloying additions. As would be expected from Fig. 12, molybdenum has only a mild effect

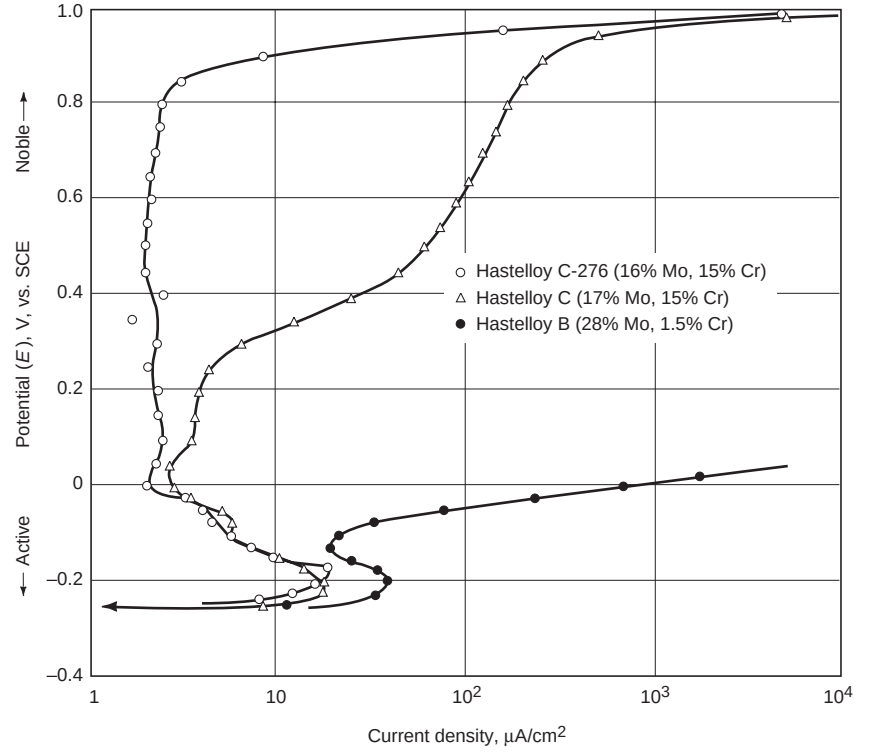


Fig. 14 Evans diagram showing the comparison of potentiostatic anodic polarization of nickel alloys in H_2SO_4 at ambient temperature. See text for details on the effects of alloying additions on corrosion behavior.

on the passivation characteristics in acidic conditions, and, hence, alloying nickel primarily with molybdenum in Hastelloy B does not significantly reduce the dissolution kinetics under these particular environmental conditions. However, Fig. 12 also indicates that the passivation domain for nickel is considerably increased in acidic environments by further alloying with chromium, and the effect of this observation is reflected in Fig. 14 by the vastly reduced oxidation rates for the chromium-containing Hastelloy C family of alloys. Thus, under deaerated acid conditions, where the corrosion potential will be about –0.250 V (versus the standard calomel electrode, or SCE) in Fig. 14, there is little difference in corrosion current densities (~10 $\mu A/cm^2$) between the three alloys. Under aerated or oxidizing acid conditions, however, when the corrosion potential will be at more positive potentials, there is a considerable benefit in choosing the chromium-containing (and more expensive) Hastelloy C grades. The combination of the high molybdenum and chromium alloying contents also confers enhanced corrosion resistance in environments other than oxidizing acids. For instance, the increased general (and pitting) resistance of the molybdenum- and chromium-containing nickel-base alloys allow their satisfactory long-term use in desalination plant and seawater heat exchangers.

Localized Corrosion

Although general corrosion is relatively easy to evaluate and monitor, localized corrosion in such forms as pitting, crevice corrosion, and SCC is at the opposite end of the scale, and materials selection is difficult. Localized corrosion is insidious and often results in failure or even total destruction of equipment without warning.

All metals and alloy systems are susceptible to most forms of localized corrosion by specific environments. For example, carbon or alloy steel pipelines will pit in aggressive soils because of local concentrations of corrosive compounds, differential aeration cells, corrosion bacteria, stray dc currents, or other conditions, and these pipelines generally require a combination of nonmetallic coatings and cathodic protection for long life. Also, holidays in mill scale left on plain carbon steels are sites for pitting because the mill scale is cathodic to the steel surface exposed at the holiday (Fig. 15). For this reason, it is advisable to remove all mill scale by sandblasting or gritblasting before exposing plain carbon steels to corrosive environments.

Emphasis in the remainder of this section is on pitting corrosion, which is the most common form of localized corrosion, and crevice corrosion, which presents both metallurgical and design challenges. Information (including materials selection guidelines) on the other forms of

localized corrosion—intergranular, dealloying, SCC, erosion-corrosion, etc.—can be found in Chapters 4 and 6.

Pitting Corrosion. Aqueous solutions of chlorides, particularly oxidizing acid salts, such as ferritic and cupric chlorides, will cause pitting of a number of ferrous and nonferrous metals and alloys under a variety of conditions. The ferritic (400 series) and austenitic stainless steels are very susceptible to chloride pitting (as well as to crevice corrosion and SCC, which are discussed later in this section). Molybdenum as an alloying element is beneficial, so molybdenum-containing stainless steels, such as types 316 and 317, are more resistant than the nonmolybdenum alloys. However, most chloride environments require alloys containing greater amounts of chromium and molybdenum, such as Hastelloy alloy G-3 (UNS N06985), Inconel alloy 625 (UNS N06625), and Hastelloy C-22 (UNS N06022), for optimal performance. Exceptions are titanium and its alloys, which show exceptional resistance to aqueous chloride environments (including the oxidizing acid chlorides), and copper, copper-nickel, and nickel-copper alloys, which are widely used in marine applications.

Other noteworthy combinations of metals and corrosive fluids to avoid when selecting materials because of pitting tendencies include the following:

- Aluminum and aluminum alloys in electrolytes containing ions of such heavy metals as lead, copper, iron, and mercury
- Plain carbon and low-alloy steels in waters containing dissolved oxygen or in waters and soils infected with sulfate-reducing bacteria
- Austenitic stainless steel weldments exposed to stagnant natural waters, particularly U.S. Gulf Coast well waters, which are infected with iron- and/or manganese-oxidizing bacteria.

Crevice corrosion can occur not only at metal/metal crevices, such as weld backing rings, but also at metal/nonmetallic crevices, such as asbestos-gasketed pipe flanges or under deposits. In some fabricated assemblies, it is possible and cost effective to avoid crevices by careful design. For example, crevice corrosion occurred behind a weld backing

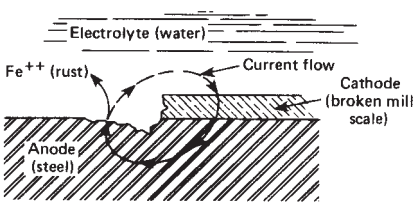


Fig. 15 Mill scale forming a corrosion cell on steel. The resulting electrochemical action will corrode (pit) the steel without affecting the mill scale.

strip at the closing seam in a type 304L stainless steel reactor handling hot nitric acid (HNO_3). A small amount of corrosion by stagnant acid in the crevice created hexavalent chromium ions (Cr^{6+}), which caused accelerated attack; other exposed surfaces in the vessel were unaffected. The closing seam could have been welded from both sides or from one side with a consumable insert ring, which would have avoided the problem. Similar attack has occurred in stainless shell and tube heat exchangers at the rolled tube-to-tubesheet joints and has been solved by seal welding the joints with appropriate weld filler metal and process.

However, in many cases, crevices are either too costly or impossible to design out of a system, so careful selection of materials is the answer. Titanium is susceptible to crevice corrosion in hot seawater and other hot aqueous chloride environments. Therefore, for a flanged and gasketed piping system in these fluids, commercially pure titanium grade 55 (UNS R50550) may be acceptable for piping, but flanges will require the more crevice attack resistant grade 7 (UNS R52400), which contains 0.15% (nominal) Pd, or grade 12 (UNS R53400), which contains small amounts of molybdenum and nickel. This is more cost effective than selecting the more expensive alloys for the piping as well. Another approach that has been successfully used in these fluids is installation of nickel-impregnated gaskets with grade 55 titanium flanges.

The austenitic stainless steels are susceptible to crevice corrosion in media other than HNO_3 solutions. For example, type 304L stainless steel exhibits borderline passivity in hot acetic acid solutions, particularly in crevices. Accordingly, the materials engineer will specify the more crevice corrosion resistant type 316L stainless steel where crevices cannot be avoided, such as piping and vessel flanges, or for the entire fabricated assembly because the cost differential between materials in this case may be negligible.

Selecting Nonmetallics. Nonmetallic materials of construction are widely used where temperatures, pressures, and stresses are not limiting and in such media as aqueous chloride solutions, which cause localized corrosion of metals and alloys. Examples in which lower-cost nonmetallic constructions are selected over expensive high alloys include the following:

- Rubber-lined steel for water treatment ion exchange resin beds, which must be periodically regenerated with salt brine or dilute mineral acids or caustic solutions
- Glass-lined steel for reaction vessels in chlorinated hydrocarbon service
- Acid-proof brick and membrane-lined steel for higher temperature, and solid RTP polyester and vinyl-ester construction for lower temperature, flue gas and chlorine neutralization scrubbers

Evaluation and Final Selection. It should be apparent that an in-depth evaluation of candidate materials for environments that can cause localized corrosion is imperative in order to select the optimal material of construction. In particular, corrosion test coupons should reflect the final fabricated component—that is, include crevices and weldments where applicable—and should be examined critically under the microscope for evidence of local attack. In cases in which the more common 300- and 400-series stainless steels fall short, the newer ferritics, such as 26Cr-1Mo (UNS S44627) and 27Cr-3Mo-2Ni (UNS S44660), and the duplex ferritic-austenitic alloys, such as 26Cr-1.5Ni-4.5Mo (UNS S32900) and 26Cr-5Ni-2Cu-3.3Mo (UNS S32550), should be evaluated as potentially lower-cost alternatives to higher alloys. Finally proven nonmetallic materials (for example, the RTPs), used either as linings for lower-cost metals (such as plain carbon steel) or for solid construction, should not be overlooked.

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CHAPTER **9**

Corrosion Control by Protective Coatings and Inhibitors

COATINGS are the most commonly used method for combating corrosion. Organic coatings (paints and plastic or rubber linings), metallic coatings, and nonmetallic inorganic coatings (conversion coatings, cements, ceramics, and glasses) are used in applications requiring corrosion protection. These materials can be used individually or in multiple layers to provide protection and other functions required of the coating or lining. The coatings applied to substrates often are multifunctional, providing corrosion control, an aesthetic surface appearance, abrasion and impact resistance, electrical insulation, and/or other important properties.

Coatings and linings may protect substrates by three basic mechanisms:

- Barrier protection
- Chemical inhibition
- Galvanic (sacrificial) protection

Barrier protection is achieved when coatings completely isolate the substrate from the environment. Chemical inhibition is achieved by the addition of inhibitive pigments to paints. Sacrificial protection is achieved by coating the substrate with a more active metal. This results in the substrate becoming the cathode in the corrosion cell. Galvanized

steel, which is comprised of a thin layer of metallic zinc over a steel substrate, is an example of a sacrificial coating.

An inhibitor is a chemical substance that, when added in a small concentrations to an environment, effectively decreases the corrosion rate. In many cases, the role of inhibitors is to form a surface coating from one to several molecular layers thick that serves as a barrier. As indicated above, inhibitors are also incorporated into paint formulations.

Organic Coatings and Linings

Corrosion protection by organic coatings and linings is accomplished through either a barrier function or an inhibitive function. (Note: The general terms *organic coating* and *paint* are essentially interchangeable and are used to designate certain coatings having an organic base.) The barrier function is achieved by blocking the entrance of moisture, ionic species, or gaseous species into the reactive substrate by means of a coating.

The inhibitive function is achieved by modification of the aqueous environment as it moves through, or is in contact with, the coating. Some organic coating systems include more active metal particles, and some sacrificial protection is provided; however, this is a secondary feature of these metal-filled organic coating systems. The purpose of the organic coating and lining is to promote, enhance, and maintain a passive or protective layer on the reactive metal substrate.

A coating system often is composed of multiple layers or multiple components within layers. The system can comprise a metal surface treatment, for example, a phosphate conversion coating, a primer, and a top coat. A desirable coating system provides chemical resistance, low moisture permeability, adhesion, flexibility and impact resistance, ease of application, durability, and affordability. Specific applications may require other coating properties as well. For example, in underground applications, resistance to cathodic disbonding is required for compatibility with cathodic protection systems. In addition, resistance to soil stresses may be required. In atmospheric corrosion, resistance to ultraviolet degradation, bacteria, and fungi is sometimes an important consideration.

The coating process can be broken down into the following steps:

- Design and selection
- Surface preparation
- Application
- Inspection and quality assurance

Design and Selection of a Coating System

Design Considerations. The selection of the proper corrosion-resistant coating system depends on a number of factors and should be addressed during the design stage. Accessibility for surface preparation and application of protective coatings is of critical importance. Edges and corners on component details should be smooth and rounded. Sharp edges can result in thin spots in the coating or exposed metal substrate (Fig. 1). Figure 2 shows the presence of a poorly coated area at a sharp internal corner. The coating of dissimilar metals is shown in Fig. 3; both

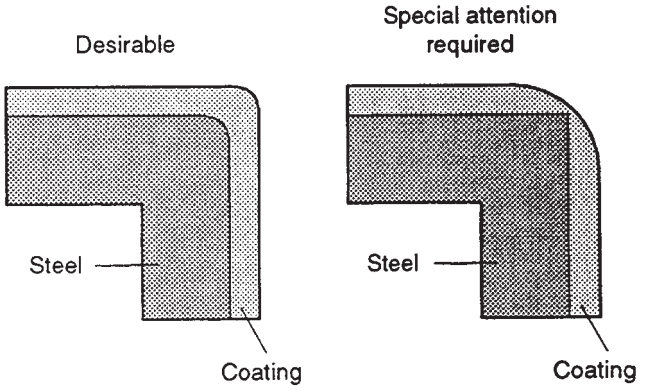


Fig. 1 Thin spot resulting from coating sharp exterior corners

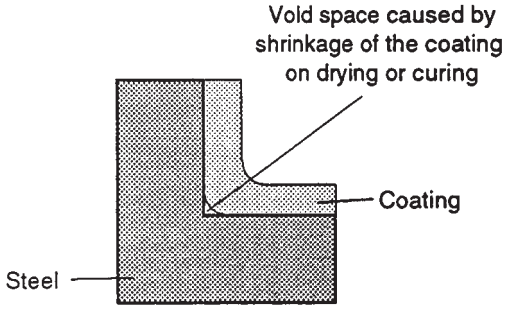


Fig. 2 Poorly coated area at a sharp interior corner

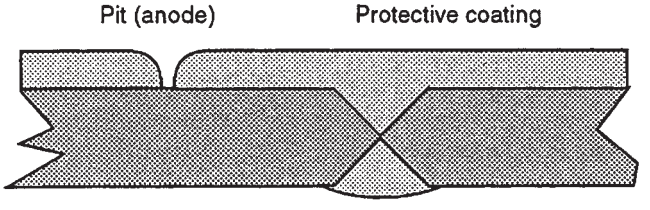


Fig. 3 Coating of dissimilar metals. See text for discussion.

the active member of the couple (steel) and the more noble member of the couple (alloy or cathode) have been coated. Although the more noble metal in the dissimilar metal structure may have sufficient corrosion resistance in the environment, it is still good practice to coat it. If the noble metal is left uncoated and a small flaw exists somewhere in the coated steel, a highly unfavorable anode-to-cathode area ratio will result, and the unexposed noble component will have a detrimental effect on the small area of exposed steel. The more important considerations in the selection of a proper corrosion-resistant coating are discussed briefly in the following section.

Environmental Resistance. The coating system should be resistant to the chemical, thermal, and moisture conditions expected to be encountered in service.

Appearance. In high-visibility areas (e.g., water tanks, railroad cars, and appliances), color, gloss, and a pleasing appearance may be very important.

Safety. Because some coatings contain toxic pigments and solvents, future removal and disposal problems should be considered. Coatings with volatile and explosive solvents may be dangerous in enclosed, poorly ventilated spaces. More detailed information on environmental, health, and safety considerations can be found later in this Chapter.

Surface Preparation. Blast cleaning may be prohibited in some operations or near electrical and hydraulic machinery.

Skill of the Labor Force. Certain coating systems require more application expertise than others. Generally, inorganic zincs, vinyl-esters, polyesters, vinyls, and chlorinated rubbers are less tolerant of improper application than some of the other coating systems.

Substrate to be Coated. Coating systems for aluminum, lead, or copper may differ from those for ferrous metals.

Available Equipment. The more resistant coating systems generally require spray application over a blast-cleaned surface. For some polyester and vinyl-esters, the use of multicomponent spray equipment may be required.

Design Life. If a structure is intended to have a long service life, the use of a more highly resistant coating system may be justified.

Cost. Generally speaking, the applied cost of a more resistant coating system is greater than the applied cost of a less resistant system.

Accessibility for Future Repair. If future repair will be difficult or expensive, a longer-life coating system should be specified.

Consequences of Coating Failure. If a coating failure will be disastrous, such as in tanks holding highly corrosive chemicals or in nuclear power plants where peeling or disbonding of coatings may clog sumps and screens, a more resistant coating system should be selected.

Specifications. Each of the factors previously listed will, to varying degrees, directly influence the selection of a coating system to protect a metal in a given environment. Once the choice is made, it is usually

necessary to prepare appropriate specifications that describe in detail the surfaces to be painted and protected. In addition, the surface preparation and coating application details should be delineated. Minimum requirements dictate that the thickness of each coat and the total coating thickness be specified; the surface profile of a blast-cleaned surface, the interval between application of coats, and other factors (such as inspecting for holidays and pinholes and testing for adhesion) should also be specified.

Specifications and industrial guidance have been developed by the Steel Structures Painting Council (SSPC). These specifications are used for industrial applications. A second source of standardization data and guidance is that found in the Department of Defense publications. The standardization documents include military handbooks that reference federal and military specifications. All these federal and military documents are listed in the Department of Defense Index of Specifications and Standards (DoDISS). ASTM issues consensus standards on paint constituents and the testing of paints; however, these standards currently do not cover paints as supplied by industrial producers or vendors. Other specifications and guidance are available from NACE International and the American Society of Naval Architects. Most of the documents are available in various libraries throughout the United States.

Surface Preparation

The selection of the coating material to be used to protect a given metal from an environment usually determines the surface preparation required. Zinc-rich coatings, for example, almost always require blast cleaning, while some alkyd and oil-base coating systems can be applied over rust, mill scale, or a poorly cleaned surface.

In addition to being cleaned, the surface must be roughened to provide for a mechanical bond of the paint to the substrate. This is usually accomplished by abrasive blasting. It is important that the surface roughness be carefully controlled according to the coating system being applied.

The roughness or surface profile influences adhesion. As a rule, greater roughness results in greater adhesion, although excessive roughness can result in high spots or peaks that are not adequately covered. As a general rule, most mineral abrasive blast-cleaning materials impart a profile or roughness ranging from 13 to 100 μm (0.5 to 4 mils), depending on particle size and impact velocity. Metallic grits may have deeper profiles, approaching 178 μm (7 mils) or more. When sized properly, however, metallic shot and grit will usually impart profiles within the 50 to 115 μm (2 to 4.5 mils) range. Such surface roughnesses are suitable for most coating systems.

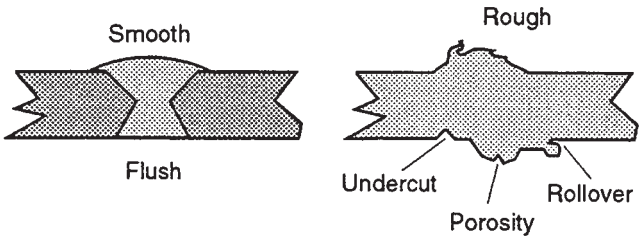


Fig. 4 Comparison of a smooth contour (as-welded or ground) versus a difficult-to-coat rough weld

Cleanliness is essential in the preparation of a surface that will receive protective coatings. Paint applied over rust, dirt, or oil will bond poorly (or not at all) to the substrate, and early paint failures will usually result. A clean surface is free of such contaminants as rust, dirt and dust, salts, oil and grease, old paint, and mill scale.

Other areas of surface preparation must also be addressed. Coatings will generally not cover weld spatter properly. Sharp edges cause paint to draw thin because of surface tension effects and should be eliminated by grinding. Inside corners provide a collection site for excess paint and/or abrasive and should be filled. Crevices and pits should be filled with weld metal, if necessary, and smoothed.

Two forms of surface roughness that must be removed prior to painting are rough welds and laminations. Figure 4 schematically compares a rough weld to a smooth weld. The sharp edges and protrusions of the rough weld will result in flaws in the coating and subsequent breakdown. Laminations or slivers are surface imperfections resulting from the steel fabrication process. A lamination is shown schematically in Fig. 5. The sharp point will protrude through a protective coating and provide a site for corrosion and coating breakdown.

Methods of Surface Preparation. A variety of surface preparation methods are available, including the following:

- Solvent or chemical washing
- Steam cleaning

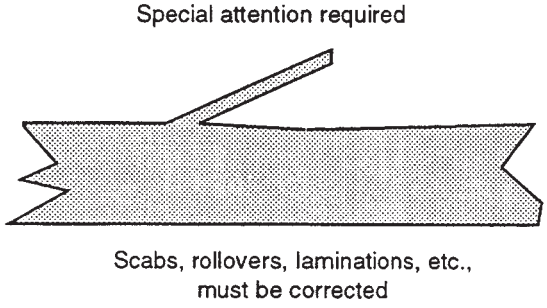


Fig. 5 Schematic of a difficult-to-coat lamination

- Hand tool cleaning
- Power tool cleaning
- Water blasting
- Abrasive blast cleaning

Table 1 lists the uses and applicable standards for these cleaning methods. More detailed information can be found in various SSPC publications and specifications and in *Surface Engineering,* Vol 5, of the *ASM Handbook*.

Inspection and Quality Assurance

To obtain the desired protection of a metal substrate from a coating system, it is important not only to choose the proper coating materials, but also to ensure that they are properly applied. On most jobs, such assurance is provided by a reputable paint company or contractor. On many other jobs, surveillance by plant personnel or thorough inspection by independent third-party organizations is advisable. In all cases, the rudiments of quality are the same:

- Proper masking and protection of surfaces not to be blast cleaned or painted
- Removal of rust scale, and contaminants and suitable roughening of the surface
- Testing to verify proper cleanliness and surface quality, for example, a water-break test or ultraviolet inspection can detect residual oils, etc.
- Application of the specified coating system to the proper thickness
- Observation of application parameters, such as minimum and maximum temperatures, interval between coats, and coating thickness
- Verification of proper hardening or cure of the coating
- Testing to ensure that defects such as pinholes, skips, or holidays are minimized or avoided
- Testing for adhesion, color, gloss, and other parameters that may affect the appearance or protective capability of the coating

Coating inspection requires training, expertise, and familiarity with various instruments. Inspector training courses are available, and verification of inspectors is available from some training organizations. For example, both NACE International and the National Institute of Accreditation and Certification certify coating inspectors.

Inspection often begins with a prejob conference, at which time the ground rules are set. When the work begins, however, the inspector is responsible for witnessing, verifying, inspecting, and documenting the

Table 1 Steel Structure Painting Council (SSPC) designations of surface preparation methods for painted coatings

SSPC designation	Method of surface preparation	NACE designation	Equipment and materials	Remarks
SP1	Solvent cleaning	…	Mineral spirits, chlorinated solvents, coal tar solvents, using tack rags or dip tanks	For the removal of grease, oil, or other soluble materials before removing mill scale, rust, and coatings by other methods. Alkaline cleaners saponify oils and greases, but these cleaners must be neutralized with 0.1 wt% chromic acid, sodium dichromate, or potassium dichromate
SP2	Hand tool cleaning	…	Hand scrapers	Hand tool cleaning should be limited to removing loose materials for maintenance and normal atmospheric exposure; coatings with good wetting properties are brush applied
SP3	Power tool cleaning	…	Power wire brushes, grinders, sanders, impact tools, needle guns	For the removal of loose rust, loose mill scale, and loose paint by power tool chipping, descaling, sanding, wire brushing, and grinding without excessive roughing that causes ridges, burrs, or burnishing. Used when primer is to be brush applied.
SP4	Flame cleaning	(a)	…	Removal of contaminants by high-velocity oxyacetylene flame burners. Usually followed by wire brushing
SP5	White metal blast	1	Abrasive blasting	Removal of 100% of oil, grease, dirt, rust, mill scale, and paint. Cleaning rate 9.3 m^2/h (100 ft^2/h), using 7.94 mm ($\frac{5}{16}$ in.) nozzle with 690 kPa (100 psig) at nozzle. Because of atmospheric contamination, maintaining this degree of cleanliness before primer application is difficult
SP6	Commercial blast	3	Abrasive blasting	Removal of 67% of oil, grease, dirt, rust, mill scale, and paint. Cleaning rate of 34 m^2/h (370 ft^2/h), using 7.94 mm ($\frac{5}{16}$ in.) nozzle with 690 kPa (100 psig) at nozzle. Used for general-purpose blast cleaning to remove all detrimental matter from the surface, but leaves staining from rust or mill scale
SP7	Brush-off blast cleaning	4	Abrasive blasting	All loose mill scale and rust are removed, with tight mill scale, paint and minor amounts of rust and other foreign matter remaining. The remaining rust is an integral part of the surface. This level of surface preparation is used for mild exposure and is suitable where a temperature change of less than 11 °C/h (20 °F/h) can be anticipated. Cleaning rate of 81 m^2/h (870 ft^2/h) using 7.94 mm ($\frac{5}{16}$ in.) nozzle
SP8	Pickling	…	Hydrochloric acid, sulfuric acid with inhibitors, or phosphoric acid with a final phosphate treatment	A shop method of surface preparation for removal of rust and mill scale from structural shapes, beams, and plates where there are few pockets or crevices to trap acid. Excess acid must be rinsed off with water, and painting is required as soon as possible to prevent recontamination of the surface
SP9	Weathering	(b)	…	Although mill scale is weathered away, this process is detrimental because surface contamination is more difficult to remove when weathered
SP10	Near-white blast	2	Abrasive blasting	Removal of 95% of oil, grease, dirt, rust, mill scale, and paint. A cost savings of 25% can be realized on average where this level of cleanliness can be tolerated. Shadows, streaks, or discolorations are distributed over the surface but are not concentrated in any area or particular spot. Cleaning rate 16 m^2/h (175 ft^2/h) using a 7.94 mm ($\frac{5}{16}$ in.) nozzle and 690 kPa (100 psig) at nozzle
	Water blasting	…	Inhibited water at pressures of 6900 to 69,000 kPa (1000 to 10,000 psig) used	Removal is slow and the degree of cleaning must be specified. High pressures may cause damage to substrate or structures
SP11	Power tool cleaning to bare metal	…	Same as SP3	Removal of all mill scale, rust, old paint, and oil, exposing bare metal. The resulting surface must be roughened as necessary to obtain a 25 μm (1 mil) surface profile

(a) Discontinued as of January 1982. (b) Discontinued in 1971

coating procedures at various inspection points. If feasible, these inspection points should include the following:

- Initial surface preparation inspection
- Measurement of ambient conditions
- Evaluation of compressed air cleanliness and surface preparation equipment
- Determination of surface preparation, cleanliness, and profile
- Witnessing coating mixing and thinning
- Inspection of application equipment
- Inspection of coating applications
- Determination of wet-film thickness
- Determination of dry-film thickness
- Evaluation of cleanliness between coats
- Pinhole and holiday testing
- Evaluation of adhesion and cure

A brief review of each of the above inspection sequences can be found in *Corrosion,* Vol 13, of the *ASM Handbook* (pages 417 to 418).

Causes of Paint Defects. Although all paints eventually fail by weathering, premature failure of coatings is generally due to either improper preparation of the paint or substrate surface or lack of control of processing variables. Table 2 lists a variety of paint failures along with their causes and remedies. Figure 6 illustrates a number of common coating defects.

Coating and Lining Materials

Paints or linings that act as protective film to isolate the substrate from the environment exist in a number of different forms. Sheet linings, commonly of the vinyl or vinylidene chloride family, are one such type of coating that can be either adhered to the surface to be protected or suspended as a bag within a tank, for example, to provide protection. Hot-applied organisols, or plastisols, again usually of the vinyl family, can also be applied to a surface, typically by dipping or flow coating, to provide a protective film.

Powder coatings are being increasingly used to protect concrete-reinforcing rod, as pipeline coatings, and as coating materials in the original equipment manufacturing markets. Fine powders produced from high molecular weight resins of the thermoplastic vinyl and fluorinated hydrocarbon families or from thermoset resins of the epoxy and polyester families are applied to the surface to be protected by either electrostatic spray or fluidized-bed deposition. The metal being protected is usually preheated at the time of application, and after

Table 2 Paint-failure causes and remedies

Failure	Description	Cause	Remedy
Sags	Also called runs or curtains. Excess flow of paint (Fig. 6a)	Spray gun too close to work, too much thinner, too much paint, or surface too hard or glossy to hold paint	Before cure, brush out excess paint, and modify spray conditions. After cure, sand and apply another coat.
Orange peel	Hills, valleys in paint resembling skin of orange (Fig. 6b)	Paint too viscous, gun too close to surface, solvent evaporated too fast, or air pressure too low for proper atomization	Before cure, brush out excess paint, and modify spray conditions. After cure, sand and apply another coat.
Overspray	Also called dry spray. Dry, flat, pebbly surface	Particles reaching surface not wet enough to level because of too-rapid solvent evaporation, gun too far from surface, or paint particles falling outside spray pattern	Before cure, remove by dry brushing followed by solvent wiping. After cure, sand and apply another coat.
Cobwebbing	Thin, stringy paint with spiderweb-like particles	Solvent evaporating too rapidly; most common with fast evaporating lacquers, such as vinyls and chlorinated rubbers	Use slower evaporating solvent, or apply when cooler. After cure, sand and apply another coat.
Cratering	Also called pitting. Small, uniform indentations in film	Air pockets trapped in wet film during spraying	Sand or blast to smooth finish, and apply additional coats.
Fish eyes	Separation or pulling apart of wet film to expose underlying finish or substrates	Application over oil, dirt, silicone, or incompatible coating	Sand or blast to remove; brush apply a fresh coat plus topcoat.
Blushing	Flat finish with milky appearance	Moisture condensation in high humidity with fast evaporating or unbalanced thinner in spray application	Sand or blast to remove; respray with retarder added to thinner.
Uneven gloss	Nonuniform sheen, shiny spots	Nonuniform film thickness, moisture in film, temperature change during curing, or paint applied over soft or wet undercoat	Allow to dry and apply another finish coat under acceptable conditions for moisture and humidity.
Fading	Color changes or irregularities	Ultraviolet light degradation or moisture behind paint film	Repaint and avoid possible sources of moisture.
Wrinkling	Rough, crinkled surface (Fig. 6c)	Surface skinning over uncured paint because of too much thickness and/or too warm weather, especially with oil-based paints	Scrape off wrinkles and apply thinner coat; avoid intense sunlight.
Blistering	Small to large broken or unbroken bubbles	Solvent entrapment; oil, moisture, or salt-contaminated surfaces; or cathodic disbonding	Blowers in enclosed areas accelerate solvent release; adequately clean surface of contamination. Maintain proper levels of cathodic protection.
Pinholing	Tiny, deep holes exposing substrate	Insufficient paint spray atomization, coarse atomization, or settle pigment	If uncured, brush out and apply additional coat. If cured, apply additional coat.
Pinpoint rusting	Rusting at pinholes or holidays	Pinholing or too high a steel surface profile for coating thickness	Use holiday detector for early detection of pinholes; apply additional coats after mechanical or blast cleaning.
Checking	Narrow breaks, usually short, in topcoat that expose undercoat (Fig. 6d)	Limited paint flexibility, too thick a coat, or application at too high a temperature	Sand (or mechanically remove checked coat) and apply another coat.
Cracking	Deep cracks in paint that expose substrate (Fig. 6e)	Paint shrinkage, limited flexibility, excessive thickness (especially zinc-rich paints), or application/curing at too high a temperature	Sand, blast, or mechanically remove total paint, and apply new coat.
Undercutting	Blistering and/or peeling of paint where exposed steel is rusting	Corrosion products formed where steel is exposed, undermining and lifting paint.	Detect defects early with holiday detector and correct; use inhibitive pigments in primer.
Dirt under paint	Peeling; dirt dried in paint film	Contaminated surface, spray, or work area	Sand, blast, or mechanically remove paint, and recoat.
Delamination	Peeling from undercoat or substrate	Separation/lifting of paint from chalky substrate or smooth, poor-bonded undercoat	Sand or mechanically remove all loose paint; clean and roughen smooth surface, and recoat.
Irregular surface deterioration	Deterioration at edges, corners, crevices, channels, etc.	Difficult to coat surfaces or configurations that permit collection of moisture, salt, and dirt	Round edges, fillet weld seams and crevices; avoid configurations that permit collection of contaminants; provide drainage.
Abrasion damage	Mechanical damage	Physical damage by abrasion (also impact)	Provide fendering protection; spot repair and use more abrasion or impact-resistant coatings.
Fouling damage	Penetration or peeling by action of marine fouling organisms	Barnacles, etc., penetrating soft coatings (e.g., coal tar); weight of fouling peeling poorly bonded paint	Remove and replace damaged paint with a tougher or more adherent paint; use antifouling paints for fouling control.
Mudcracking	Deep, irregular cracks as with dried mud (Fig. 6f)	A relatively inflexible coating applied too thickly (especially common with inorganic zincs)	Remove coating and abrasively blast steel before reapplying at lesser thickness; sanding/mechanical cleaning can be acceptable on older substrates.

Source: Ref 1

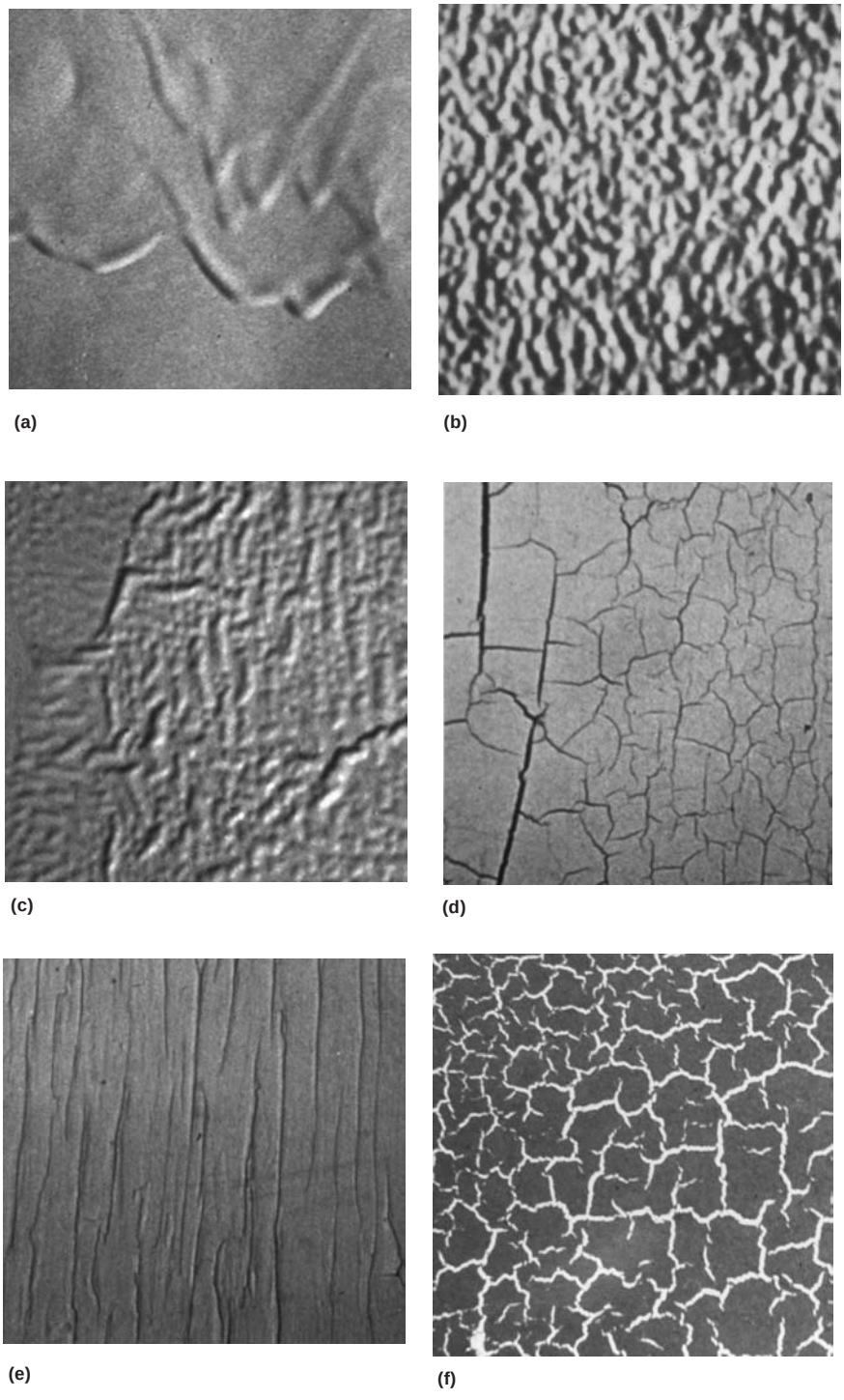


Fig. 6 Examples of common paint defects. (a) Sags. (b) Orange peel. (c) Wrinkling. (d) Checking. (e) Cracking. (f) Mudcracking. Table 2 provides a general description of these defects as well as their causes and remedies. Courtesy of J. Lederer, Department of the Navy, Port Hueneme, CA

application it is reheated to an elevated temperature (generally from 150 to 315 °C, or 300 to 600 °F). The specific time/temperature baking schedule depends on the metal temperature at the time of application and the type of powder being applied.

Alternatively, some coating systems are characterized by the application method used. For example, for coil-coated metal sheet (commonly steel or galvanized steel), very specialized high-speed roller application equipment is used to coat the sheet steel as it is unwound from a coil. The paint used in the coil-coating process can be of virtually any generic type, although alkyds, polyesters, epoxies, and zinc-rich epoxy coatings are the most prevalent.

Certain lining materials, such as hand lay-up fiberglass-reinforced plastics, are also used to protect steel from corrosion. Such coating systems usually consist of an epoxy primer applied to a blast-cleaned steel surface, followed by one or more polyester gel coats, with one or more layers of a fiberglass veil or woven roving mat laid within the gel coats as reinforcement. The system is then sealed with a layer of the polyester gel coat (a semiclear, 100% solids resin coat). Similarly, rubber linings are used to protect against corrosion. There are various types of rubbers, but they can generally be categorized as prevulcanized or postvulcanized (vulcanized after application). Similarly, rubbers (or elastomers) can be formulated with different hardnesses and chemical resistances. Commonly, a rubber lining is a composite of two or three different types of rubbers adhered to each other and to the surface. The environmental resistance of some common rubber lining materials is summarized in Table 3. An excellent source of information on rubber linings can be found in MTI Manual No. 7, *Practical Guide to the Use of Elastomeric Linings,* published by the Materials Technology Institute (MTI) of the Chemical Process In-

Table 3 Environmental resistance of common rubber lining materials

Common name	ASTM D 1418 designation	Resistance to(a): Ozone	Oxidation	Water	Alkalies	Aliphatic	Aromatic	Halogenated	Alcohol	Acids	Permeability to gases
Butadiene rubber	BR	P	G	E	F-G	P	P	P	G	F-G	Low
Natural rubber, isoprene rubber	NR, IR	P	G	E	F-G	P	P	P	G	F-G	Low
Chloroprene rubber	CR	VG	VG	G	E	G	F	P	G	F-E	Low-medium
Styrene-butadiene rubber	SBR	P	G	E	F-G	P	P	P	G	F-G	Low
Acrylontrile-butadiene (nitrile) rubber	NBR	P	F-G	E	F-G	E	G	P	VG	E	Very low
Isobutylene-isoprene (butyl) rubber	IIR	E	E	E	E	F	F-G	P	VG	G-E	Very low
Ethylene-propylene (-diene) rubber	EPM, EPDM	O	E	E	G-E	P-G	P	P-F	P-G	F-E	Medium
Silicone rubber	VMQ	E	E	E	P-F	P-G	P-G	F	F	G-VG	High
Fluoroelastomer	FKM	O	O	VG	F-G	E	E	G	VG	F-E	Low

(a) O, outstanding; E, excellent; VG, very good; G, good; F, fair; P, poor

dustries, Inc. This guide provides practical information pertaining to liner material selection, design criteria, application of linings, vulcanization methods, and inspection and acceptance testing. The MTI manual is also available from NACE International.

Paints. Despite the importance of the coatings and linings discussed above, the most commonly used organic materials for corrosion protection in atmospheric or immersion service are the liquid-applied (usually by brush, roller, or spray) coating and lining materials, that is, paints. Liquid-applied organic coatings have four basic components: a resin, a solvent, pigments, and other miscellaneous compounds, The resins, often called binders, are identified by their generic type, as indicated in Table 4. These are based on the organic compound structure that makes up the resin. The solvent can be either water or an organic solvent. Increasing environmental regulations are limiting the use of organic solvent-base systems. The pigments are added for such functions as rust inhibition, decreased permeability, to provide color, or to increase resistance to ultraviolet or weathering conditions. Typical pigments include zinc phosphate, zinc molybdate, zinc phosphorus silicate, zinc chromate, and strontium chromate. Miscellaneous compounds added include dryers, flow-control and gloss-control agents, and suspension agents. Although the resin or organic binder of the coating material is most influential in determining the resistance and properties of the paint, the type and amount of pigments, solvents, and additives will dramatically influence the application properties and protective capability of the coating system. Furthermore, hybridized systems can be formulated that are crosses between the categories. For example, an acrylic monomer or prepolymer can be incorporated with virtually any other generic type of resin to produce a product with properties that are a compromise between the acrylic and the original polymer. In many cases, this is advantageous, as in the mixing of vinyls and acrylics or the heat-curing of alkyds and acrylics. In other cases, such as with an epoxy, acrylic modification can be a detriment. Table 4 lists the advantages and limitations of the principal coating resins.

The rate of the base metal corrosion where liquid-applied coatings are used should not exceed approximately 1.3 mm/year (50 mpy). For corrosion rates above this, both in atmospheric and immersion service, or where catastrophic failure is of concern, paints should generally not be used. For more severe corrosion applications, alternative corrosion prevention measures such as the use of more corrosion resistant alloys, sheet or rubber coatings and linings, fiberglass lay-ups, and metallic coatings and claddings should be considered.

Information Sources. A wealth of literature and technical expertise is available for guidance in the selection and relative comparison of various organic systems. A good place to start is to review the selected references on organic coatings found at the conclusion of this Chapter.

Table 4 Advantages and limitations of the principal coating resins

Resin type	Advantages	Limitations	Comments
Acrylic (solvent based)	Excellent light and ultraviolet stability, gloss, and color retention. Good chemical resistance and excellent atmospheric weathering resistance. Resistant to chemical fumes and occasional mild chemical splash and spillage. Minimal chalking and little if any darkening upon prolonged exposure to ultraviolet light	Not suitable for water immersion or any substantial acid or alkaline chemical exposure. Used principally as topcoats over epoxies in atmospheric service environments	Used predominately where light stability, color, and gloss retention are of primary importance. With cross-linking, greater chemical resistance can be achieved. Cross-linked acrylics are the most common automotive finish.
Acrylic (water based)	Good light and color stability. Less gloss than solvent acrylics. Moisture and chemical resistance approaching that of solvent acrylics. Ease of application and cleanup. Good compatibility as topcoat over most other generic types	Must be stored above freezing. Does not penetrate chalky surfaces. Exterior weather and chemical resistance not as good as solvent-based or oil-based coatings. Not suitable for immersion service	Ease of application and cleanup. No toxic solvents, low VOC (a) levels. Complies with air pollution restrictions. Good concrete and masonry sealers, because breathing film allows passage of water vapor. Can be used as a wood paint (primer-topcoat system), or preferably as a topcoat over an oil-based primer on a wood substrate. Most common water-based emulsion coating
Alkyds	Good resistance to atmospheric weathering and moderate chemical fumes; not resistant to chemical splash and spillage. Long oil alkyds have good penetration but are slow drying; short oil alkyds are fast drying. Temperature resistant to 105 °C (225 °F)	Not chemically resistant; not suitable for application over alkaline surfaces, such as fresh concrete or for water immersion	Long oil alkyds make excellent primers for rusted and pitted steel and wooden surfaces. Corrosion resistance is adequate for mild chemical fumes that predominate in many industrial areas. Widely used as interior and exterior industrial and marine finishes
Asphalt pitch	Good water resistance and ultraviolet stability. Will not crack or degrade in sunlight. Nontoxic and suitable for exposure to food products. Resistant to mineral salts and alkalies to 30% concentration	Black color only. Poor resistance to hydrocarbon solvents, oils, fats, and some organic solvents. Do not have the moisture resistance of coal tars. Can embrittle after prolonged exposure to dry environments or temperatures above 150 °C (300 °F) and can soften and flow at temperatures as low as 40 °C (100 °F)	Often used as a relatively inexpensive coating in atmospheric service, where coal tars cannot be used. Relatively inexpensive. Most common use is as a pavement sealer or roof coating.
Chlorinated rubber	Low moisture permeability and excellent resistance to water. Resistant to strong acids, alkalis, bleaches, soaps and detergents, mineral oils, mold, and mildew. Good abrasion resistance	Redissolved in strong solvents. Degraded by heat (95 °C, or 200 °F, dry; 60 °C, or 140 °F, wet) and ultraviolet light but can be stabilized to improve these properties. Can be difficult to spray, especially in hot weather	Fire resistant, odorless, tasteless, and nontoxic. Quick drying with excellent adhesion to concrete and steel. Used in concrete and masonry paints, swimming pool coatings, industrial coatings, marine finishes. Might not comply with VOC regulations. More common in Europe as an industrial coating
Coal tar pitch	Excellent water resistance (greater than for all other types of coatings); good resistance to acids, alkalis, and mineral, animal, and vegetable oils	Unless cross-linked with another resin, is thermoplastic and flows at temperatures of 40 °C (100 °F) or less. Hardens and embrittles in cold weather. Black color only. Alligators and cracks on prolonged sunlight exposure, although still protective.	Used as moisture resistant coatings in immersion and underground service. Widely used as pipeline exterior and interior coatings below grade. Pitch emulsions used as pavement sealers. Relatively inexpensive
Epoxy-amine	Excellent resistance to alkalis, most organic and inorganic acids, water, and aqueous salt solutions. Good solvent-resistance and resistance to oxidizing agents as long as not continually wetted. Amine adducts have slightly less chemical and moisture resistance.	Harder and less flexible than other epoxies and intolerant of moisture during application. Coating will chalk on exposure to ultraviolet light. Strong solvents can lift coatings. Temperature resistance: 105 °C (225 °F) wet; 90 °C (190 °F) dry. Will not cure below 5 °C (40 °F); should be topcoated within 72 h to avoid intercoat delamination. Maximum properties require curing time of about 7 days. Needs induction time to prevent amine blush	Good chemical and weather resistance. Excellent adhesion to steel and concrete. Widely used in maintenance coatings and tank linings. High-build epoxy mastic formulations available with greater flexibility, less resistance

(continued)

Table 4 (continued)

Resin type	Advantages	Limitations	Comments
Epoxy coal tar	Excellent resistance to saltwater and freshwater immersion. Very good acid and alkali resistance. Solvent resistance is good, although immersion in strong solvents can leach the coal tar.	Embrittles on exposure to cold or ultraviolet light. Cold weather abrasion resistance is poor. Should be topcoated within 48 h to avoid intercoat adhesion problems. Will not cure below 10 °C (50 °F). Black or dark colors only. Temperature resistance: 105 °C (225 °F) dry; 65 °C (150 °F) wet	Good water resistance. Thickness to 0.25 mm (10 mils) per coat. Can be applied to bare steel or concrete without a primer. Low cost per unit coverage
Epoxy (novolac)	Excellent solvent, chemical heat, and moisture resistance; better than other epoxy types	Less flexible than amine and polyamide epoxies. Temperature resistance 260 °C (500 °F) and 69 MPa (10,000 psi). More costly than other epoxies.	Used as lining in deep wells, flue gas desulfurization, and high-temperature, high-abrasion service. Used as tank linings for methanol and ethanol modified fuels
Epoxy (polyamide)	Superior to amine-cured epoxies for water resistance. Excellent adhesion, gloss, hardness impact, and abrasion resistance. More flexible and tougher than amine-cured epoxies. Temperature resistance: 105 °C (225 °F) dry; 65 °C (150 °F) wet	Cross-linking does not occur below 5 °C (40 °F). Maximum resistances generally require 7 day cure at 20 °C (70 °F). Slightly lower chemical resistance than amine-cured epoxies	Easier to apply and to topcoat. More flexible and moisture resistant than amine-cured epoxies. Excellent adhesion over steel and concrete. A widely used industrial and marine maintenance coating. Some formulations can be applied to wet or underwater surfaces.
Fluoropolymer	Hard, smooth, tough, flexible coatings with good color retention and high heat resistance. Very good moisture and weathering resistance	Can have poor adhesion to many surfaces. Needs specialized primers; expensive. Applied in thin coats 36 μm (1.5 mils) maximum. Temperature resistance 260 °C (500 °F)	Used as a coil-coating for exterior metal wall and roof sheets. Used as vessel liners and as duct and fan coatings, and nonstick cookware. Has use as automotive and aircraft coating
Phenolics	Greatest solvent resistance of all organic coatings described. Excellent resistance to aliphatic and aromatic hydrocarbons, alcohols, esters, ethers, ketones, and chlorinated solvents. Wet temperature resistance at 95 °C (200 °F). Odorless, tasteless, and nontoxic; suitable for food use	Must be baked at a metal temperature ranging from 175 to 230 °C (350 to 450 °F). Coating must be applied in a thin film (approximately 0.025 mm, or 1 mil) and partially baked between coats. Multiple thin coats are necessary to allow water from the condensation reaction to be removed. Cured coating is difficult to patch due to extreme solvent resistance. Poor resistance to alkalis and strong oxidants	A brown color results upon baking, which can be used to indicate the degree of cross-linking. Widely used as tank lining for alcohol storage and fermentation and other food products. Used for hot water immersion service. Can be modified with epoxies and other resins to enhance water, chemical, and heat resistance
Polyester/ vinyl ester	Thick film (40+ mils, 1000+ μm). Lining with excellent abrasion and acid resistance, good alkali and moisture resistance. Temperature resistance to 120 °C (250 °F)	Softened by organic solvents and alkalis. Requires deep blast cleaning anchor profile (100 μm, 4+ mils). Often reinforced with fiberglass veil or mat	Vinyl esters have better temperature and chemical resistance than polyesters. Used as tank linings in chemical and waste water facilities as linings in flue gas desulfurization service. Polyesters are used as fillers and coatings for boats.
Polyurethane (aliphatic)	Noted for their chemically excellent gloss, color, and ultraviolet light resistance. Properties vary widely, depending on the polyol co-reactant. Generally, chemical and moisture resistances are similar to those of polyamide-cured epoxies and abrasion resistance is usually excellent.	Most common are acrylic polyol types that have excellent weatherability but lesser chemical and moisture resistance than the more expensive polyester polyol types. Apply in thin film 36 μm (1.5 mils). Because of the versatility of the isocyanate reaction, wide diversity exists in specific coating properties. Exposure to the isocyanate should be minimized to avoid sensitivity that may result in an asthmatic-like breathing condition upon continued exposure. Carbon dioxide is released upon exposure to humidity, which can result in gasing or bubbling of the coating in humid conditions. Aromatic urethanes can darken or yellow upon exposure to ultraviolet radiation.	Widely used as glossy light-fast topcoats on many exterior structures in corrosive structures in corrosive environments. They are relatively expensive but extremely durable. The isocyanate can be combined with other generic materials to enhance chemical, moisture, low-temperature, and abrasion resistance. Use as a topcoat over epoxy coating to prevent chalking

(continued)

(a) VOC, volatile organic compound. Source: Kenneth B. Tator, KTA-Tator, Inc.

Table 4 (continued)

Resin type	Advantages	Limitations	Comments
Polyurethane (aromatic)	Excellent adhesion, hardness abrasion, and chemical resistance. Fast cure, even at temperatures below freezing. Better adhesion, moisture, and chemical resistance than aliphatic polyurethanes. Applies in thicker coat than aliphatic types.	Same humidity and isocyante sensitivity concerns, as aliphatic polyurethanes will darken upon ultraviolet light radiation (sunlight)	Most common type is single package moisture cured. Usually topcoated with aliphatic polyurethanes in exterior environments
Silicone	Resist temperatures to 540 °C (1000 °F) or with lesser amounts incorporated in alkyd resins to provide greater moisture, heat, and chemical resistance and higher gloss than conventional alkyd.	High temperature types must cure at 325 °C (450 °F). These types are applied at thickness of max 36 μm (1.5 mils). Alkyd modifications resist dry heat to 205 °C (400 °F) but are more expensive than conventional alkyds. If topcoated, adhesion problems possible	High heat types used as metal chimney exterior coatings, and for hot pipe, duct, and fan coatings. Alkyd modification provides a cost-effective upgrade to coatings. Used as coatings. Used as coatings for tanks and steel work
Vinyls	Insoluble in oils, greases, aliphatic hydrocarbons, and alcohols. Resistant to water and salt solutions. Not attacked at room temperature by inorganic acids and alkalis. Fire resistant; good abrasion resistance	Strong polar solvents redissolve the vinyl. Initial adhesion poor. Relatively low thickness (0.04 to 0.05 mm, or 1.5 to 2 mils) per coat. Some types will not adhere to bare steel without primer. Pinholes in dried film are more prevalent than in other coating types.	Tough and flexible, low toxicity, tasteless, colorless, fire resistant. Used in potable water tanks and sanitary equipment; widely used industrial coating. Might not comply with VOC regulations.
Zinc-rich inorganic	Provides excellent long-term protection against corrosion pitting in neutral and near-neutral atmospheric (and some immersion) services. Abrasion resistance is excellent, and dry heat resistance exceeds 370 °C (700 °F). Water-base inorganic silicates are available for confined spaces and VOC compliance.	Inorganic nature necessitates thorough blast-cleaning surface preparation and results in difficulty when topoating with organic topcoats. Zinc dust is reactive outside the pH range of 5 to 10, and topcoating is necessary in chemical fume environments. Somewhat difficult to apply; can mudcrack at thicknesses in excess of 0.13 mm (5 mils). Sensitive to humidity levels for curing	Solvent-based ethyl silicate zinc-rich requires atmospheric moisture to cure and are most common types. Water-based zinc-rich needs low humidities to dry/cure and is VOC compliant. Widely used as a primer on bridges, offshore structures, and steel in the building and chemical-processing industries. Used as a weldable preconstruction primer in the automotive and shipbuilding industries. Use eliminates pitting corrosion.
Zinc-rich organic	Galvanic protection afforded by the zinc content with chemical and moisture resistance similar to that of the organic binder. Should be topcoated in chemical environments with a pH outside the range of 5 to 10. More tolerant of surface preparation and topcoating than inorganic zinc-rich coatings	Generally lower service performance than for inorganic zinc-rich coatings, but ease of applications and surface preparation tolerance make them increasingly popular	Widely used in Europe and Far East, while inorganic zinc-rich coatings are more common in North America. Organic binder can be closely tailored to topcoats (for example, epoxy topcoats over epoxy-zinc-rich coatings) for a more compatible system. Organic zinc-rich coatings are often used to repair galvanized or inorganic zinc-rich coatings.

(a) VOC, volatile organic compound. Source: Kenneth B. Tator, KTA-Tator, Inc.

Another valuable source is the "The Paint and Coatings Cost and Selection Guide," which is updated every two years and published in the journal *Materials Performance*. This guide is designed to help coatings engineers, specifiers, and users to identify suitable paint and protective coating systems for specific industrial environments, to calculate approximate installation costs and service life, and to determine the most cost-effective systems. Costs for both new construction and maintenance painting are reviewed, including the effect of maintenance sequences on long-term costs and system performance. Published through NACE International since 1979, this guide is the collaborative effort of

major manufacturers of protective coatings, steel fabricators, painting contractors, users, NACE, SSPC, and coating consultants.

Another useful source for comparing generic resin types is *Generic Coating Types: An Introduction to Industrial Maintenance Coating Materials*, published by SSPC in 1996. In addition to reviewing the characteristics of important coating resins, it includes both a "Coatings Directory" and a "Coatings Company Profiles" section. More than 3200 protective materials for steel and concrete are listed in the directory, which is intended to help users of coatings and linings identify sources for the products they need. The company profiles section is an alphabetical listing of more than 200 companies that produce organic coatings. Addresses, telephone numbers, key contacts, and generic listings of coating types for each company are provided.

*Environmental, Health, and Safety Considerations**

Legislation concerning worker health and safety and environmental protection has had a dramatic impact on the organic coatings industry. Increased regulation on federal, state, and local levels has affected every aspect of coatings removal and application. Many coating formulations have been changed as a result of legislation restricting the release of volatile organic compounds (VOCs). As coatings containing an organic solvent dry, the solvent evaporates into the atmosphere. Virtually all the VOCs that comprise the organic solvent portion of coatings react in sunlight to form ozone, an air pollutant. As a result, there are increasing restrictions on the VOC content in coatings. In addition, restrictions regarding the use of toxic pigments, such as lead, cadmium, and arsenic have also been imposed.

Abrasive blast media manufacturers have also been influenced by the potential presence of toxic or regulated materials (i.e., silica, arsenic, etc.) in the abrasive media itself, regardless of the removed coatings. Facility owners and contractors alike have felt increased legislative requirements for protection of the environment (i.e., air, soil, and water), the public, and workers, as well as requirements relative to the proper disposal of all waste generated on the project. This section presents a brief review of the major regulatory impacts experienced by the coatings industry from September 1987 to July 1999.

Worker Health and Safety Regulations. The most sweeping regulatory impact during this period has been due to the federal requirements established by the Occupational Safety and Health Administration (OSHA) under 29 CFR 1926.62, Interim Final Rule—Lead Exposure in Construction, which became effective 3 June 1993. The development of the Interim Final Rule was mandated by Congress through Title X

*This section was prepared by Alison B. Kaelin, Environmental, Health, and Safety Group, KTA-Tator, Inc.

of the Housing and Community Development Act of 1992. The OSHA Lead Standard requires employers to perform airborne assessments of employee exposures when any lead is present, in order to determine the applicability of the balance of the standard's requirements. The airborne exposure assessments are compared to the action level and permissible exposure levels (PEL) for lead. The action level refers to an airborne concentration of 30 μg of lead per cubic meter of air (30 $\mu g/m^3$) calculated as an 8 h time-weighted average (TWA) exposure. Airborne lead concentrations in excess of the action level trigger the implementation of exposure assessment, medical surveillance, employee information and training, signs/regulated areas, and record-keeping requirements. The employer is also required to assure that no employee is exposed to lead at concentrations in excess of the PEL or 50 μg of lead per cubic meter of air (50 $\mu g/m^3$) as an 8 h TWA exposure. Employers must institute engineering and work practice controls to the extent feasible to reduce exposures to as low as achievable, preferably below the PEL. A hierarchy of controls is followed to reduce employee exposure below the PEL. The hierarchy includes engineering controls (e.g., ventilation or alternative removal method), work-practice controls, respiratory protective equipment, written compliance plans, and job site inspections.

OSHA has issued similar regulations for cadmium (29 CFR 1926.1127) and inorganic arsenic (29 CFR 1926.1118). Combined, these regulations have substantively influenced the coating removal industry by introducing the concepts of containment and ventilation, initial and periodic medical surveillance, worker training, and nontraditional paint removal methodologies.

OSHA has also issued or revised a number of construction regulations (29 CFR 1926) addressing fall protection, scaffolding, and aerial lifts, which significantly alter how access and working platforms are installed and maintained for field operations. Most recently, in 1998, OSHA revised its respiratory protection standards for both the general (29 CFR 1910.134) and construction (29 CFR 1926.103) industries. The revisions directly impact both the removal and application of coatings. The revised standard requires more thorough assessment of potential inhalation hazards such as paints and solvents, increased engineering controls, and formal oversight of the implementation of respiratory protection programs.

Environmental regulations have continued to impact the coatings industry in the areas of formulation, coatings removal, and waste disposal. The Environmental Protection Agency (EPA) issued final regulations (40 CFR 59) to control VOC emissions from architectural coating in August, 1998. This regulation limits the VOC content for over 61 categories of architectural coatings. It also requires manufacturers and importers to include VOC limits on labels and to provide recommenda-

tions regarding thinning. The rule also requires notification and record keeping. The following is an excerpt from Table 1 of Subpart D—Volatile Organic Compound Content Limits for Architectural Coatings.

Coating category	Maximum VOC content	
	g/L	lb/gal
Concrete protective coatings	400	3.3
Industrial maintenance coatings	450	3.8
Thermoplastic rubber coatings and mastics	550	4.6
Repair and maintenance thermoplastic coatings	650	5.4
Traffic marking coatings	150	1.3
Zone marking coatings	450	3.8
Rust preventative coatings	400	3.3

Environmental regulations effecting the removal of coating have not changed appreciably since the 1970s; enforcement, however, has increased in some areas of the country. More and more owners and specification writers are invoking environmental protection criteria as part of project specifications. For example, the Clean Air Act (40 CFR 50-99), the Clean Water Act (40 CFR 136-149), and the Comprehensive Environmental Response, Compensation and Liability Act (40 CFR 305-307) have all been in effect since the late 1970s. Each of these regulations prohibits impact on the air, soil, and water. Compliance with these and other regulatory requirements (e.g., OSHA lead standard and EPA hazardous waste regulations) applicable to the coatings removal industry has resulted in the use of sophisticated containment and ventilation systems to contain debris generated during surface preparation processes, as well as the advent of less dusty methods of coating removal such as water jetting, chemical stripping, and vacuum-shrouded power tool cleaning.

Environmental regulations addressing the disposal of waste resulting from industrial painting projects continue to change. The Resource Conservation and Recovery Act (RCRA) (40 CFR 260-268) addresses the disposal of hazardous wastes. These regulations impact the coatings industry, both in the waste resulting from the removal of coatings and in the disposal of excess coating and spent solvent wastes. All wastes resulting from a painting project must be classified under RCRA and disposed of appropriately. Additionally, 40 CFR 268, Land Disposal Restrictions (published in 1990) prohibit the land disposal of any hazardous waste. This requires treatments of lead-containing wastes prior to disposal to stabilize the lead.

In summary, the promulgation of a variety of legislation continues to have a substantial impact on the industrial maintenance painting industry. To its credit, the coating industry, including facility owners, coatings manufacturers, suppliers, consultants and contractors, continue to respond to these challenges by modifying existing processes, improving training and safety practices, and developing new products and technologies to meet the changing regulatory climate.

Metallic Coatings

Metals, and in some cases their alloys, can be applied to almost all other metals and alloys by using the following methods:

- Electroplating
- Electroless plating
- Hot dipping
- Thermal spraying
- Cladding
- Pack cementation
- Vapor deposition
- Ion implantation
- Laser processing

Thicknesses range from less than 1 μm (0.04 mil) for ion implanted surfaces to more than 6 mm (¼ in.) for clad metal surfaces.

The two classes of metallic coatings are noble (cathodic) coatings and sacrificial (anodic) coatings. A noble metal coating is more corrosion resistant than the substrate, and it provides protection when it is a pore-free barrier coating. A sacrificial coating is more active than the substrate, and it provides protection first as a barrier and secondly as a sacrificial coating; that is, the coating cathodically protects the substrate at exposed edges and pits (holes) through the system. The differences between noble and sacrificial coatings are further described below in the section describing electroplating.

Metallic coatings are used extensively for the protection of steel. In order to appreciate the wide variety of applicable metallic coatings, one needs only to consider the types of precoated sheet steel for automotive body and chassis parts (Table 5). These coatings can be applied to either one side or both sides of the part.

Electroplated Coatings

Electroplating is the electrodeposition of an adherent metallic coating upon an electrode for the purpose of securing a surface with properties or dimensions different from those of the base metal. Electrodeposits are applied to metal substrates for decoration, protection, corrosion resistance, chemical inertness, wear resistance, buildup of substrate dimensions, electrical properties, magnetic properties, solderability, reflectance, and reduction of friction. Electrodeposited coatings are sometimes applied for two or more reasons. For example, decorative and protective plating are combined in such applications as chromium-plated steel automobile bumpers, trim items made of zinc die casting or

steel, trim items on large and small appliances, costume jewelry, electronic circuits, piano strings, construction and architectural hardware, plumbing fittings, electrical contacts, plastic items, and magnetic memory devices.

The ability to be both decorative and protective to substrates distinguishes electrodeposited coatings from metallic coatings applied by hot

Table 5 Coatings for automotive sheet steels

Steel coating	Description	Typical applications
Hot-dipped zinc coated (regular and minimized spangle)	Made on continuous hot-dip galvanizing lines and supplied in coils and cut lengths. Includes regular and minimized spangle in a wide range of coating designations (ASTM A 653/A 653M) and is available in extra-smooth finish	Rocker panels, wheelhouse inner and outer panels, cowl top panels, luggage compartment floor pans, bumper reinforcements, body structure inner reinforcements, floor pans
Hot-dipped zinc coated (fully alloyed zinc-iron coated)	Hot-dipped zinc coated product, heat treated or wiped to produce a fully alloyed zinc-iron coating	Body rails, cross members, light truck box beds
Hot-dipped zinc coated (differentially zinc coated)	Hot-dipped zinc coated product, with different specified coating weights on opposite sheet surfaces, significantly lighter on one surface. Both surfaces are zinc.	Cross members, hoods, fenders, door outer panels, quarter panels, wheelhouses, various underbody components
Hot-dipped zinc coated (differentially zinc-iron coated)	Same as coating listed above except the coating on the lighter surface is heat treated or wiped to produce a fully alloyed zinc-iron coating	Fenders, door outer panels, quarter panels, hoods, floor pans, door inner panels, dash panels
Hot-dipped zinc coated one side	Continuous hot-dipped zinc coating one side; zinc-free, cold-rolled steel surface on the other for superior paintability	Fenders, door outer panels, quarter panels, deck lids, lower back panels, roofs, hoods
Electrolytic zinc flash coated	Continuously flash electroplated with zinc, 30 to 60 g/m^2 total on both sides. Used when minimal corrosion resistance is required	Window guides, wiper blade frames, radio speaker baskets, head rest supports
Electroplated zinc coated	Continuously electroplated zinc. Two-side coatings can be equal or differential, to a practical minimum of 200 g/m^2 total coating. One-side product has a standard cold-rolled surface for superior paintability	Exposed and unexposed body panels
Electroplated iron-zinc alloy coated	Produced by the simultaneous electroplating of zinc and iron to form an alloy coating. One- and two-side coatings can be produced on an equal basis or differentially coated	Exposed and unexposed body panels
Electroplated zinc-nickel alloy coated	Produced by the simultaneous electroplating of zinc and nickel to form an alloy coating. Two-side coatings can be produced on an equal basis or differentially coated	Exposed and unexposed body panels
Aluminum coated	Continuous hot-dip coat, cold-rolled sheet steel. Surface properties equivalent to aluminum	Exhaust systems, catalytic converters, chassis components
Aluminum-zinc coated	Continuous hot-dip coat, cold-rolled sheet steel. Provides excellent corrosion resistance	Exhaust systems, air cleaner covers, core plugs, brake shields, floor pan covers
Zinc-aluminum/mischmetal coated	Produced by hot-dip coating on continuous lines. Provides maximum formability and excellent corrosion resistance	Fuel tank shields, fuel filter shields, motor housings, shock towers, and other deep drawn underbody parts
Long terne	Cold-rolled sheet, coated both sides with a lead-tin alloy by a continuous hot-dip process	Fuel tanks, fuel lines, brake lines, radiator and heater parts, air cleaners
Nickel terne	Cold-rolled sheet, electrolytically nickel flash plated, then coated both sides with a lead-tin alloy by continuous hot-dip process. Corrosion resistance superior to standard long terne	Fuel tanks, fuel lines, brake lines, radiator and heater parts, air cleaners
Tin coated	Cold-rolled sheet, coated with tin by a continuous electrolytic process	Oil filter and heater components
Zincrometal	Cold-rolled sheet. Base coat contains primarily chromium and zinc; top coat is a weldable zinc-rich primer for corrosion resistance. Generally applied to one side with the other side standard cold-rolled surface for superior paintability	Door inner and outer panels, fenders, quarter panels, hoods, deck lids, lift gate outers, lower back panels

Source: American Iron and Steel Institute

dipping or thermal spraying. Metallic luster, achieved by bright plating or by polishing after plating, lends a distinctive appearance not provided by other types of coatings. However, corrosion resistance is the primary reason for the use of electrodeposited coatings. Examples of this application include the following:

- Tin or chromium plating (via continuous electrodeposition) of steel strip for food packaging and other container uses
- Electrogalvanizing or zinc plating of steel strip, sheet, stampings, forgings, wire, and screw machine products
- Zinc and cadmium plating of fasteners and other hardware items
- Bright nickel-chromium plating of household appliances, interior auto hardware, and standing ashtrays
- Chromium plating of gun bores

Electrodeposits are used to enhance properties other than corrosion protection. For example, many fasteners are coated with a bright cadmium or zinc deposit supplemented with a clear or colored chromate conversion film. This results in coatings that are both protective and decorative. In addition, chromium is applied to the interior of gun barrels to provide lubricity and erosion resistance as well as corrosion protection.

Coatings applied by electrodeposition protect substrate metals in three ways. The first is cathodic protection of the substrate by sacrificial corrosion of the coating, as in the case of zinc and cadmium coatings on steel. The second protection mechanism is by barrier action, that is, by interposing a more corrosion resistant coating between the environment and a less corrosion resistant substrate. Examples of this are copper-nickel-chromium coating systems over steel and zinc alloy automotive parts. A third means of protection is environmental modification or control in combination with a nonimpervious barrier coating. An example of this type of protection is the electrolytic tinplate used in food packaging.

Active (Sacrificial) Coatings. Zinc and cadmium deposits will protect steel at pores and other discontinuities by cathodic protection. Zinc is electronegative to steel in potential when these metals are immersed in solutions of their own ions. Under the same conditions, cadmium is more noble than iron, but in actual service under several environmental influences, cadmium is anodic to iron. Figure 7 shows the galvanic protection offered by a zinc coating to a steel substrate.

Noble Coatings. Several metals commonly plated are electropositive to iron. These noble coatings on steel are therefore expected to act strictly as barriers to prevent corrosion of the steel substrate. For this to be successful, the coatings must be free of pores and flaws. It is very difficult to obtain impervious coatings of noble metals on steel or zinc alloys. Substantial metal thicknesses, usually 25 μm (1 mil) or more, are required.

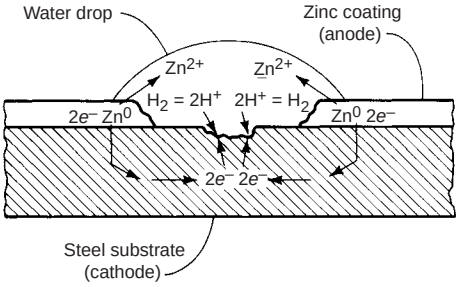


Fig. 7 Principles and mechanism of galvanic protection of a substrate by a coating. Galvanic protection of a steel substrate at a void in a zinc coating. Corrosion of the substrate is light and occurs at some distance from the zinc.

Coating Defects. Generally, electroplated coatings that are completely free of pores and other discontinuities are not commercially feasible. Pits eventually form at coating flaws, and the coating is penetrated. The resulting corrosion cell is shown in Fig. 8. The substrate exposed at the bottom of the resulting pit corrodes rapidly. A crater forms in the substrate, and because of the large area ratio between the more noble coating and the anodic crater, the crater becomes anodic, and high corrosion current density results. Electrons flow from the substrate to the coating as the steel dissolves. Hydrogen ions (H^+) in the moisture accept the electron and, with dissolved oxygen, form water at the noble metal surface near the void. Use of an intermediate coating that is less noble than a surface coating but more noble than the base metal can result in the mode of corrosion shown in Fig. 9. This would be typical of a costume jewelry item with a brass substrate, an intermediate nickel coating, and a tarnish-resistant gold top coat. It is also exemplified by nickel-chromium coating systems.

The durability of a plated coating system cannot always be accurately predicted by conventional analysis of the potentials shown in the electromotive force series or galvanic series. Much depends on environmental exposure and the oxidized films formed in pores and discontinuities of

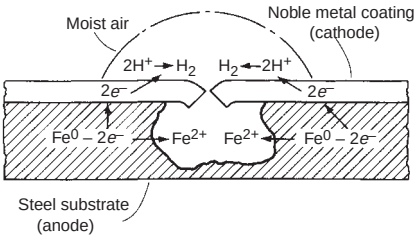


Fig. 8 Crater formation in a steel substrate beneath a void in a noble metal coating, for example, passive chromium or copper. Corrosion proceeds under the noble metal, the edges of which collapse into the corrosion pit.

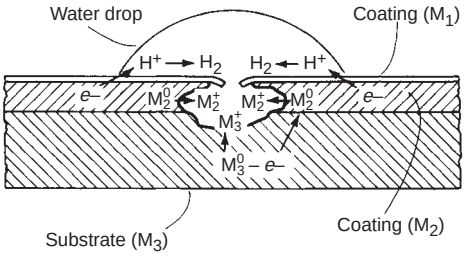


Fig. 9 Corrosion pit formation in a substrate beneath a void in a duplex noble metal coating. The top coating layer (M_1) is cathodic to the coating underlayer (M_2), which is in turn cathodic to the substrate (M_3). As in Fig. 8, the coating tends to collapse into the pit.

plated coatings. For example, lead-plated steel is quite durable, despite the fact that lead is more noble than iron. This is the case because a lead corrosion product develops in the pores (most likely lead sulfate, $PbSO_4$) and arrests the progress of corrosion.

Environmental Concerns. More stringent environmental regulations have also affected the plating industry. For example, OSHA has evaluated the health effects of cadmium on workers and has determined that exposure to respirable particles/fumes represents the most significant risk factor. Cadmium and its compounds are not readily absorbed through the skin, but they can be ingested. Inhaling cadmium or its compounds can directly cause lung cancer, and it also allows the toxic metal to enter the bloodstream. Once in the blood, cadmium readily accumulates in the kidneys, degrading their function. These health, safety, and environmental concerns are driving the reduction or elimination of cadmium for many applications. Cadmium replacement materials include vapor-deposited or electroplated aluminum, various zinc and zinc alloy electroplates, and tin-zinc electroplates.

Similarly, the use and emission of hexavalent chromium originating from chromium plating baths has come under increased scrutiny by various regulatory bodies due to adverse health and environmental effects. Potential replacements for chromium electroplates are electroless nickel and various high-velocity oxyfuel spray deposited coatings, for example, nickel-chromium-molybdenum (Ni-Cr-Mo), chromium carbide- nickel chromium (CrC-NiCr), and iron-nickel-chromium (Fe-Ni-Cr) alloy systems.

Electroless Nickel Plating

Electroless nickel coatings are produced by the autocatalytic chemical reduction of nickel ions from an aqueous solution. They do not require electrical current to be produced. Two types of electroless coatings are produced: nickel-phosphorus and nickel-boron alloy coatings. Both coating types are used in applications requiring a combination of corrosion and wear resistance.

Nickel-phosphorus alloy coatings are classified as either low phosphorus (1 to 4 wt% P), medium phosphorus (5 to 8% P), or high phosphorus (9 to 12% P). These amorphous barrier coatings provide excellent corrosion protection in a wide range of environments. The resistance to attack in neutral and acidic environments is increased as the phosphorus content is increased in the deposit. The reverse is true in alkaline corrosive environments. A practical guide to using Ni-P electroless nickel coatings can be found in the July 1990 issue of the journal *Materials Performance* (pages 65 to 70). Plating procedures, engineering properties, surface preparation recommendations, corrosion resistance, and specifications and quality control are reviewed. An application summary is also included.

The nickel-boron alloy coatings, which typically contain 5% boron, have outstanding resistance to wear and abrasion. These coatings, however, are not completely amorphous and have reduced resistance to corrosion; furthermore, they are much more expensive than nickel-phosphorus coatings.

Hot-Dip Coatings

Hot dipping is a process in which a protective coating is applied to a metal by immersing it in a molten bath of the coating metal. Hot-dip coatings can be used to protect a number of metals; those used to protect steel are most common.

Hot-dip coatings have a number of advantages, including the ability to coat recessed or difficult areas (such as corners and edges) with a standard minimum coating thickness, resistance to mechanical damage (because the coating is metallurgically bonded to the steel), and good resistance to corrosion in a number of environments. However, the process has two limiting factors. First, the coating must melt at a reasonably low temperature. Second, the base metal must not undergo undesirable property changes during the coating process.

Hot-dip coatings can be applied by continuous or batch processes. Materials such as steel sheet and wire can be hot dipped by continuously passing the steel through the molten metal bath. Continuous processing is highly automated and mechanized and is often associated with steel mill operations. Zinc, aluminum, and zinc-aluminum alloy hot-dip coatings are applied on steel. Materials that are batch processed are generally fabricated before hot dipping. Articles that can be hot dipped by the batch process range in size from large steel structural members to small items such as fasteners.

Zinc-Coated Steels. Hot-dip zinc-coated steel sheet, also called galvanized, is by far the most widely used coated steel product. About 85% of the hot-dip coated sheet produced in the United States is zinc coated. Because of its long history (galvanized steel has been in use for more

than 100 years), galvanized steel has been exposed to, and studied in, a wide range of corrosive environments.

Hot-dip zinc coatings for sheet are available in a broad range of coating thicknesses. For general purpose galvanized sheet, 19 μm (0.75 mil) per side is the usual coating thickness. Heavier coatings (up to 100 μm, or 4 mils) are used in applications requiring maximum corrosion resistance, such as highway drainage culverts.

Zinc coatings protect steel in three ways:

- Initially, a continuous film of zinc at the surface of steel serves as a barrier to separate the steel from the environment.
- At voids in the coating, such as scratches and cut edges, the zinc behaves as a sacrificial anode to provide galvanic protection.
- After anodic dissolution of the zinc metal, zinc hydroxide can precipitate at the cathodic areas of exposed steel, thus forming a secondary barrier.

Zinc-Iron Alloy Coatings. Also known as *galvanneal*, zinc-iron alloy coating produced by the thermal diffusion and alloying of a galvanized coating with a steel substrate was developed during the 1970s, primarily for painted applications. Today, galvanneal is used increasingly often by the automobile industry because of its improved paintability and spot weldability relative to pure hot-dip zinc of equal thickness. The iron content of the alloy surface is usually in the range of 9 to 12%.

Zinc-aluminum coatings include Zn-5Al and Zn-55Al alloys. The Zn-5Al coatings are more corrosion resistant than an equal-thickness galvanized coating when testing in accelerated laboratory tests or in severe marine environments. However, the same alloy coatings perform no better than pure zinc in moderate marine, industrial, and rural environments (Table 6).

The purpose of the Zn-55Al alloy coatings, also known as *galvalume*, is to combine the excellent long-term atmospheric corrosion resistance of aluminum with the sacrificial characteristics of galvanized material in a single coating. Atmospheric corrosion resistance of the Zn-55Al alloy coating is generally at least two to four times that of an equal thickness of galvanized coating, as evident in Fig. 10 and Table 6.

Aluminum-Coated Steels. Two types of aluminum coatings are produced. Type 2 is a thicker coating (typically 30 to 50 μm, or 1 to 2 mils) that is applied by dipping the steel in an unalloyed aluminum bath. This product is used for outdoor construction applications, such as roofing, culverts, and silos that require resistance to atmospheric corrosion and have limited formability requirements. The resistance of Type 2 coatings to atmospheric corrosion is shown in Fig. 10.

Table 6 Lifetimes of hot-dip zinc and zinc-alloy coatings

Environment	Years to first rust			
	Zn	Zn-4Al	Zn-7Al	Zn-55Al
Severe marine: 25 m from ocean, Kure Beach, NC	4	9	9	15
Moderate marine: 250 m from ocean, Kure Beach, NC	16	15	14	25
Rural: Saylorsburg, PA	14	14	14	25
Industrial: Bethlehem, PA	10	10	9	25

Type I aluminum coating is a thinner, aluminum-silicon alloy (5 to 11% Si) coating intended primarily for applications requiring formability and resistance to high temperatures, such as automobile exhaust components. Type I aluminum coatings are also applied to improve appearance.

Lead-tin alloy coatings are widely known as *terne coatings.* Generally, 3 to 15% Sn is added to the bath in order to facilitate wetting of the steel substrate. Terne-coated steel has a long history of use in automotive fuel tanks and tubing because of its excellent weldability, solderability, and formability. Moreover, the low corrosion rate of terne allows it to function primarily as a barrier coating without the evolution of corrosion products that might otherwise clog fuel and hydraulic systems.

Due to concerns about the effects of lead in the environment, work is now under way to find suitable replacement materials. Zinc alloy coatings (hot-dip zinc-iron or electroplated zinc-nickel) with an organic topcoat are among the most likely candidates.

Painting galvanized steel provides a more resistant product. Galvanized coatings, when used without further treatment, offer the most economical corrosion protection for steel in many environments. The galvanized coating makes an excellent base on which to apply a paint system. Painting of galvanized steel is desirable for aesthetics, as

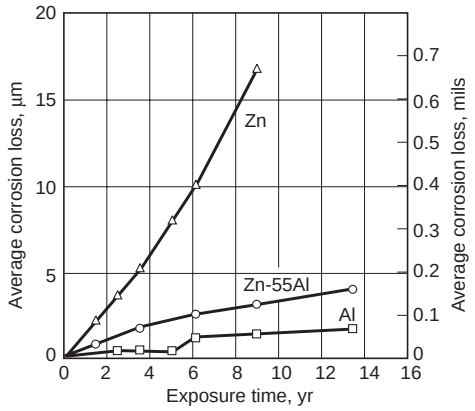


Fig. 10 Corrosion losses of hot-dip coatings in the industrial environment of Bethlehem, PA

camouflage, as warning or identification markings, to prevent bimetallic corrosion, or when the anticipated environment is particularly severe.

In corrosive atmospheres, a duplex system of galvanized steel with a paint top coat has several advantages that make it an excellent system for corrosion prevention:

- The life of the galvanized coating is extended by the paint coating
- The sacrificial and barrier properties of the zinc coating are used if a break occurs in the paint film
- Undercutting of damaged paint coatings, a major cause of failure of paints on steel, does not occur with a zinc substrate
- Surface preparation of a weathered zinc surface for maintenance painting is easier than that for rusted steel

The synergistic effects of galvanized and painted systems are shown in Fig. 11. When painted steel is exposed to the environment, rust forms at the steel/paint interface. Because rust occupies a volume several times that of the steel, the expansion resulting from rusting leads to rup-

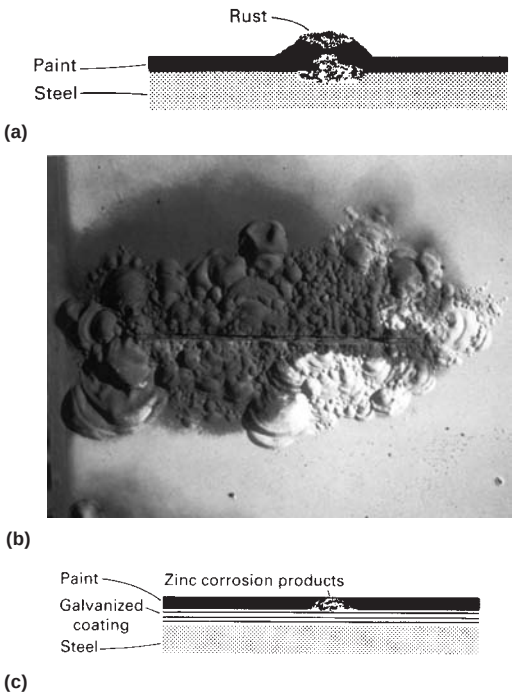


Fig. 11 Illustration of the mechanism of corrosion for painted steel and painted galvanized steel. (a) A void in the paint results in rusting of the steel, which undercuts the paint coating and results in further coating degradation. (b) Photograph showing blistering and/or peeling (undercutting) of paint where exposed steel is rusting. (c) A void in the coating of a painted galvanized steel is sealed with zinc corrosion products; this avoids the undercutting seen in (a) and (b) and prevents further deterioration of the painted coating. Photograph courtesy of J. Lederer, Department of the Navy, Port Hueneme, CA

ture of the steel/paint bond. Furthermore, rust is porous; it accumulates moisture and other reactants, and this increases the rate of attack on the steel. The result is undercutting, flaking, and blistering of the paint film, leading to failure of the paint coating. Zinc corrosion products occupy a volume only slightly greater (20 to 25%) than zinc; this reduces the expansive forces and conditions that lead to paint failure.

Thermal Spray Coatings

Thermal spraying comprises a group of processes in which finely divided molten metallic or nonmetallic material is sprayed onto a prepared substrate to form a coating. The sprayed material is originally in the form of wire or powder. As the coating materials are fed through the spray unit, they are heated to a molten or plastic state and propelled by a stream of compressed gas onto the substrate. As the particles strike the surface, they flatten and form thin platelets that conform and adhere to the irregularities of the prepared surface and to each other. They cool and accumulate, particle by particle, into a lamellar, castlike structure. The spray gun generates the necessary heat for melting through combustion of gases, electric arc, or a plasma.

The deposited structures of thermal spray coatings differ from those of the same material in the rough form because of the incremental nature of the coating buildup and because the coating composition is often affected by reaction with the process gases and the surrounding atmosphere while the materials are in the molten state. For example, where air or oxygen is used as the process gas, oxides or the material applied may be formed and become part of the coating. The bond between the sprayed coating and the substrate is generally mechanical, although newly developed high-velocity thermal spray processes can produce metallurgical bonds.

Thermal spray coatings, primarily zinc and aluminum, have been successfully used to combat corrosion in a wide range of applications (Table 7). Steel structures and components that have been zinc sprayed or aluminum sprayed include television towers, antennae, radar, bridges,

Table 7 Typical corrosion-resistant applications for thermal spraying

Application	Thermal spray materials
Pipe sections for saltwater pumps	Alloy 625 (Ni-22Cr-9Mo-5Fe-4Nb) or Al
Oil platform components	Al and Al alloys
Bridges	Zn, Zn-Al, or Al
Bridge fabrication shops	Zn, Zn-Al, or Al
Chemical and water storage tanks	Alloy 625, Al, Zn, and a high-Cr/Ni alloy
Power transmission poles	85% Zn-15% Al
Piping in power plant cooling towers	Al
Cooling water pump diffuser	Al
Concrete bridge structures	Zn or Zn-Al
Grandstands	Zn-Al
Ski lifts	Zn
Decorative hand rails	Zn

light poles, girders, ski lifts, and countless other similar structures. In addition, thermal spray coatings—primarily aluminum–offer years of protection in marine applications such as buoys and pylons. Aluminum spraying has been used in offshore oil rigs for wellhead assemblies, flare stacks, walkways, and other structural steel components.

Stainless steel, nickel-base alloys, and other corrosion resistant alloys applied by thermal spraying can also be effective against chemical corrosion for storage vessels, rolls, pumps, and other structures. The coatings must be properly sealed when using these alloys.

Clad Metals

Clad metals are bonded metal-to-metal laminar composite systems that can be fabricated by a number of processes. The principal cladding techniques include hot-roll bonding, cold-roll bonding, explosive bonding, and weld cladding, although centrifugal casting, adhesive bonding, extrusion, and hot isostatic pressing have also been used to produce clad metals. Clad metals can be provided in plate, sheet, tube, rod, and wire forms. Most engineering metals and alloys can be clad. Cladding combinations that have been commercially produced on a large scale are shown in Fig. 12. The cladding of steel with stainless steel, copper, nickel alloys, titanium, and tantalum has become increasingly popular in the chemical processing industries. Applications include pressure vessels, reactors, heat exchangers, and storage tanks.

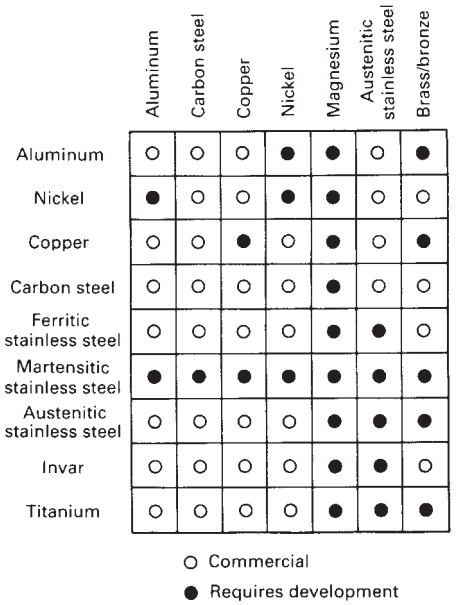


Fig. 12 High-volume commercially available clad metals

Clad metals provide a means of designing into a composite material specific properties that cannot be obtained in a single material. The early use of clad metals in the jewelry industry combined the aesthetics of precious metals with the low cost strength of base metals. These materials systems are currently being used for electrical and electronics applications, such as contacts and connectors with selectively clad (inlay) precious metals for low contact resistance and high reliability.

Clad metal systems designed for corrosion control can be categorized as follows:

- Noble metal clad systems
- Corrosion barrier systems
- Sacrificial metal systems
- Transition metal systems

Proper design is essential for providing maximum corrosion resistance with clad metals.

Noble metal clad systems are materials having a relatively inexpensive base metal covered with a corrosion resistant metal. Another group of commonly used noble metal clad metals uses aluminum as a substrate. For example, in stainless steel-clad aluminum truck bumpers, the stainless steel provides corrosion resistance, and the aluminum provides a high strength-to-weight ratio.

Corrosion Barrier Systems. The combination of two or more metals to form a corrosion barrier system is most widely used where perforation caused by corrosion must be avoided. This is shown schematically in Fig. 13. Low-carbon steel and stainless steel are susceptible to localized corrosion in chloride-containing environments and can perforate rapidly. When steel is clad with a stainless steel layer, the corrosion barrier mechanism prevents perforation. Localized corrosion of the stainless steel is prevented; the stainless steel is protected galvanically by

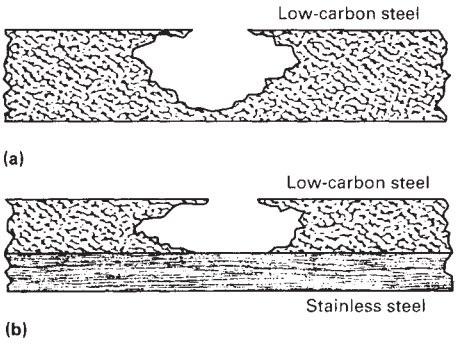


Fig. 13 Illustrations of the corrosion barrier principle. (a) Solid carbon steel. (b) Carbon steel clad with stainless steel

the sacrificial corrosion of the carbon steel in the metal laminate. Therefore, only a thin pore-free layer is required.

Sacrificial metals, such as magnesium, zinc, and aluminum, are in the active region of the galvanic series and are extensively used for corrosion protection. The single largest application for cold-roll bonded materials is stainless steel-clad aluminum for automotive trim. The stainless steel exterior surface provides corrosion resistance, high luster, and abrasion and dent resistance, and the aluminum on the inside provides sacrificial protection for the painted auto body steel and for the stainless steel.

The largest application for hot-roll bonded materials—alclad aluminum—also falls into this category. In this case, a more active aluminum alloy is bonded to a more noble aluminum alloy. In service, the outer clad layer of aluminum corrodes sacrificially and protects the more noble aluminum substrate.

Clad transition metal systems provide an interface between two incompatible metals. They not only reduce galvanic corrosion where dissimilar metals are joined, but they also allow welding techniques to be used when direct joining is not possible. Clad metals provide an ideal solution to the materials problem of dual environments. For example, in the application of small battery cans and caps, copper-clad, stainless steel-clad nickel (Cu/SS/Ni) is used where the external nickel layer provides atmospheric corrosion resistance and low contact resistance. The copper layer on the inside provides the electrode contact surface as well as compatible cell chemistry. The stainless steel layer provides strength and resistance to perforation corrosion.

Pack Cementation

The pack cementation aluminizing process is a proprietary process to improve the performance of steels in high-temperature corrosive environments. The process is performed in a pack consisting of aluminum powder, an inert filler (aluminum oxide), and an activator (halide salt), which is heated under an inert atmosphere in a retort (reactor). When the mixture is heated, the activator reacts with the aluminum to form volatile aluminum halides, which then diffuse through the pack in the gaseous state and react at the steel substrate surface, depositing the aluminum. Aluminum is diffused deeply into the steel. The complex aluminide intermetallic coatings formed during the process exhibit superior resistance to oxidation, carburization, and sulfidation. Table 8 provides a partial listing of commercial applications for the pack aluminizing process. Similar pack aluminizing and chromizing treatments can be carried out on other alloy substrates, for example, nickel-base alloys used for gas turbine components.

Vapor-Deposited Coatings

The vapor deposition processes fall into two major categories—physical vapor deposition (PVD) and chemical vapor deposition (CVD). The major vapor deposition processes are sputtering, evaporation, and ion plating (all of which are PVD processes) and CVD. These processes have one characteristic in common: the deposition species are transferred and deposited in the form of individual atoms or molecules.

Aluminum and aluminum alloys are among the most widely used vapor-deposited materials and are gradually replacing cadmium in many corrosion applications. Sputtered chromium and stainless steel are also making great inroads in corrosion applications. A promising material is titanium nitride—a hard, very stable, refractory material that has good lubricating characteristics and a pleasing gold appearance. It is widely used in wear applications, such as cutting tools, and in decorative applications.

Vapor-deposited coatings have the advantage that the film (if thick enough) is essentially pore-free and fully dense. Penetration by moisture and gases to the substrate is greatly reduced, if not eliminated. Despite this, the role played by CVD/PVD coatings in corrosion protection remains small because of the high costs of vapor deposition processes when compared to hot-dip coatings or electroplating.

Surface Modification

Surface modification is the alteration of the surface composition or structure by the use of high-energy or particle beams. Elements can be added to influence the surface characteristics of the substrate by the formation of alloys, metastable alloys or phases, or amorphous layers. Two different modification methods will be discussed. The first, ion

Table 8 Partial list of commercial applications of pack cementation aluminizing

Industry	Component	Typical materials aluminized
Hydrocarbon processing	Refinery heater tubes	2¼% Cr-1% Mo steel
	Ethylene pyrolysis furnace tubes	Incoloy 802
	Hydrodesulfurizer furnace tubes	2¼% Cr-1% Mo steel
	Delayed coker furnace tubes	9% Cr-1% Mo steel
	Catalyst reactor screens	347 stainless steel
	Catalyst reactor grating	Carbon steel
Sulfuric acid	Gas-to-gas heat exchanger tubes	Carbon steel
Industrial furnace components	Aluminum plant furnace parts	Carbon steel
	Heat treating pots	Carbon steel
	Structural members	High-nickel alloy steel
	Thermowells	Carbon and stainless steels
Steam power and cogeneration	Waterwell tubes	2¼% Cr-1% Mo steel
	Fluidized bed combustor tubes	2¼% Cr-1% Mo steel
	Waste heat boiler tubes	Carbon steel
	Economizer and air preheater tubes	2¼% Cr-1% Mo steel
	Superheater tubes	2¼%Cr-1% Mo steel
Flue gas scrubbers	NO_x/SO_x removal units	304 stainless steel
Chemical processing	Reactor vessels and tubing	304/316 stainless steel
Cement	Cooler grates	Cast, heat resistant stainless steels (e.g., HP or HK)

implantation, is the introduction of ionized species (usually elements—for example, Ti^+) into the substrate using kilovolt to megavolt ion accelerating potentials. The second method, laser processing, is high-power laser melting with or without mixing of materials precoated on the substrate, followed by rapid melt quenching.

Ion Implantation. Surface modification by ion implantation is a technique that was derived from the semiconductor industry. Ion implantation is reaching a stage of development in which specific advantages are being recognized and exploited for enhancing the corrosion and wear resistance of critical metal parts. For wear resistance, ion implantation has been used for the hardening and friction reduction of metal surfaces.

There are two approaches to using ion implantation for increasing the corrosion resistance of substrates. The first is to enhance passivation characteristics, and the second is to create novel materials. In the first approach, implantation creates a surface composition based on conventional metallurgical experience that reacts to form a passive layer. In the second approach, implantation creates a surface composition and structure that are difficult, impossible, or impractical to achieve by conventional metallurgy. It should be noted that to date, neither of these approaches has achieved commercial success.

Laser Processing. Lasers with continuous outputs of 0.5 to 10 kW can be used to modify the metallurgical structure of a surface and to tailor the surface properties without adversely affecting the bulk properties. The surface modification can take the following three forms. The first is transformation hardening, in which a surface is heated so that thermal diffusion and solid-state transformations can take place. The second is surface melting, which results in the refinement of the structure due to rapid quenching from the melt. The third is surface alloying, in which alloying elements are added to the melt pool to change the composition of the surface. The novel structures produced by laser surface melting and alloying can exhibit improved corrosion behavior.

Laser processing provides unique opportunities to produce corrosion resistant surface layers. High-performance surface layers can be designed while conserving scarce, expensive, or critical materials. However, the major limitation associated with laser processing are the compatibility of substrates with thermal conduction requirements and the current restriction to planar substrates.

Nonmetallic Inorganic Coatings

Nonmetallic inorganic coatings include ceramic coating materials, conversion coatings, and anodized coatings. The ceramic coatings most commonly used for corrosion applications are chemical-setting silicate

cement linings and porcelain enamels. Porcelain enamels are distinguished from other ceramic coatings by their predominantly vitreous (glassy) nature. Conversion coatings are formed by a chemical or electrochemical treatment of metals. The process results in the formation of complex protective coatings that consist of the surface metal (substrate) and compounds and components of the processing bath. Examples include phosphate conversion coatings and chromate conversion coatings. Anodizing is an electrolytic oxidation process in which the surface of a metal (usually aluminum, but also magnesium and titanium), when anodic, is converted to a coating having desirable protective, decorative, or other properties.

Concrete and Cementatious Coatings and Linings

Cementatious linings have become one of the most widely used construction materials in designing protective linings for industrial installations in which high temperatures, aggressive corrosive media, and complicated substrate geometry exist, such as floors, trenches, sumps, ducts, chimneys, and other air pollution control equipment. They are used in various industries, including power, steel and metalworking, chemical, pulp and paper, refinery, waste treatment, and mining.

Inorganic monolithic linings have proved themselves in these industries because of their chemical resistance to both high and low concentrations of strong acids and solvents, thermal insulation that protects the substrates from extremely high temperatures, temperature resistance to 870 °C (1600 °F), good compressive and flexural strength for environments in which stress and strain are factors, and abrasion resistance. Monolithic linings can be applied by cast or gunite (shotcreting) methods over old and new steel or concrete, as well as by brick and mortar masonry.

Certain disadvantages were encountered during the development of the acid-resistant silicate cements. The silicate cements were not resistant to alkalies, hydrofluoric acid (HF), and fluoride salts. The Na_2SiO_3 cements formed a growth salt when exposed to H_2SO_4 that put undue internal stresses on the structure of the material.

Inorganic monolithic linings also have a certain amount of permeability compared to organic surfacing materials. Over time, acid can penetrate the lining and eventually reach the surface of the substrate. The problem is now being combated by using a dual-lining system, which includes a chemically resistant elastomeric membrane applied to the surface of the substrate.

Dual Linings. In recent years, the trend toward using the superior technology of dual linings has emerged and is being recommended where corrosion problems occur. Figure 14 shows the design of a typical membrane/monolithic system in the chemical industry. Condensa-

tion occurs not only on the face of the acid-resistant lining, but it can also penetrate and condense on the substrate to be protected. Although acid-proof monolithic linings offer the proper chemical resistance, they are inherently inelastic, or brittle. In time, monolithic linings may tend to crack and absorb acids in acid gas condensate; therefore, it is advantageous to have a backup membrane. In many applications, the coefficient of thermal expansion of the monolithic lining may not match that of the substrate. Therefore, a flexible membrane will help accommodate stresses resulting from these differences in thermal expansion, as well as other mechanically induced stresses.

Porcelain Enamels

Porcelain enamels are glass coatings that are applied primarily to fabricated sheet steel, cast iron, or aluminum parts to improve appearance and to protect the metal surface. Porcelain enamels are distinguished from other ceramic coatings by their predominantly vitreous nature and the types of applications for which they are used, and they are distinguished from paint by their inorganic composition and the fusion of the coating matrix to the substrate metal. Porcelain enamels of all compositions are fired at 425 °C (800 °F) or above. Because they offer only barrier protection to the metal substrate, porcelain enamel coatings must be free from defects and coating discontinuities to provide optimum protection.

The most common applications of porcelain enamels include major appliances, water heater tanks, sanitary ware, and cookware. Porcelain enamels are also used in a wide variety of applications ranging from

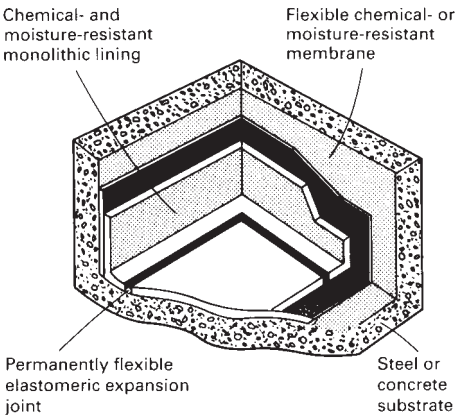


Fig. 14 Schematic of a chemical-resistant dual-lining system that provides double protection to the substrate in the form of a flexible membrane and a rigid surface layer. The flexible, corrosion-resistant membrane is applied in direct contact with steel or concrete substrates. It is then covered by the monolithic cement lining, which provides protection over a broad pH range as well as against high temperatures.

chemical processing vessels, heat exchangers, agricultural storage tanks, piping and pump components, and barbecue grills to architectural panels, signs, specially executed murals, and microcircuitry components.

Conversion Coatings

Phosphate coating is the treatment of iron, steel, galvanized steel, or aluminum with a dilute solution of phosphoric acid and other chemicals in which the surface of the metal, reacting chemically with the phosphoric acid media, is converted to an integral, mildly protective layer of insoluble crystalline phosphate. Phosphate conversion coatings are applied to various metal substrates to enhance corrosion resistance, increase paint or plating adhesion, or both. Other applications include the use of phosphate conversion coatings for their electrical insulating properties (for example, in electric motor laminations) and for lubricity (for example, to increase the formability of sheet metals). The basic types of phosphate coatings are the following:

- Iron phosphates—lightweight, amorphous phosphate coatings that do not contain significant amounts of divalent metal ions from solution. Coating weights range from 0.16 to 0.80 g/m^2 (15 to 75 mg/ft^2).
- Zinc phosphates—medium-weight, crystalline phosphate coatings that contain divalent metal ions from the solution and/or the metal surface. Coating weights range from 1.4 to 4.0 g/m^2 (130 to 370 mg/ft^2).
- Heavy phosphates (manganese phosphates)—heavy coatings that contain divalent metal ions from solution and from the metal surface. Coating weights range from 7.5 to 30 g/m^2 (700 to 2800 mg/ft^2).

There are two major categories for the uses of phosphate coatings: bare corrosion protection and painted corrosion protection. Bare phosphate means simply that the phosphate coating is not painted.

Because of the crystalline nature of zinc phosphates and manganese phosphates, these coatings can hold oils and waxes so well that the corrosion resistance of the metal is increased much more than is expected based on either the phosphate or the oil separately. Similarly, the phosphate coating holds paint physically.

The basic process in the formation of any phosphate coating is the precipitation of a divalent metal and phosphate ions (PO_4^{3-}) on a metal surface. Phosphate salts, particularly divalent metal salts, are soluble in acid solutions and insoluble in neutral and basic solutions. The phosphate baths are acidic enough to keep the ions in solution. When metal is exposed to the solution, the acid attacks the metal surface. Two changes occur in the solution directly adjacent to the metal surface. First, the

acid is neutralized and the pH rises. Second, the concentration of metal ions increases. Typical metals phosphated, such as steel or galvanized steel, will increase the concentration of iron or zinc ions, respectively, in this boundary layer between the metal surface and the bulk of solution.

The two methods of applying phosphate conversion coatings are spraying and immersion. In general, spray coating is less expensive, but immersion coating provides better quality. Immersion phosphating produces changes in the phosphate coating composition that result in better painted performance with some paint systems.

Chromate conversion coatings are formed by a chemical or an electrochemical treatment of metals or metallic coatings in solutions containing hexavalent chromium (Cr^{6+}) and, usually, other components. The process results in the formation of an amorphous protective coating composed of the substrate, complex chromium compounds, and other components of the processing bath.

Chromate conversion coatings are applied primarily to enhance bare or painted corrosion resistance, to improve the adhesion of paint or other organic finishes, and to provide the metallic surface with a decorative finish. Chromating processes are widely used to finish aluminum, zinc, steel, magnesium, cadmium, copper, tin, nickel, silver, and other substrates. Chromate conversion coatings are most frequently applied by immersion or spray coating, but other methods of application, such as brushing, roll coatings, dip and squeegee, electrostatic spraying, or anodic deposition, are used in special cases.

The disposal of spent solutions and rinse waters requires waste treatment. Hexavalent chromium must be reduced to Cr^{3+} before neutralizing and precipitation. Sodium pyrosulfite ($Na_2S_2O_5$) is usually used as the reducing agent in smaller operations, while for larger plants, sulfur dioxide (SO_2) is preferred for economic reasons.

Wastewater treatment sludges from chromating operations are considered hazardous waste. As a result, the use and disposal of chromium and chromium compounds have received much regulatory attention because of the toxicity of chromium and indications that it is a cancer-causing agent. As has been described for other coating methods, for example, cadmium and chromium plating, alternatives to chromate conversion coatings are being sought. Unfortunately, there are currently no drop-in substitutes to chromate conversion coatings that adequately match their corrosion resistance, paint adhesion, etc.

Possible elimination of chromate conversion coatings due to regulatory restrictions is particularly troublesome for the aircraft industry. In applying the coating to the entire aircraft aluminum structure, the subsequent rinse process can generate large quantities of chromium-containing wastes. The challenges of adequately maintaining aging aircraft will help drive the search for effective chromate substitutes.

Aluminum Anodizing

Aluminum anodizing is an electrochemical method of converting aluminum into aluminum oxide (Al_2O_3) at the surface of the item being coated. It is accomplished by making the workpiece the anode while suspended in a suitable electrolytic cell. Although several metals can be anodized, including aluminum, titanium, and magnesium, only aluminum anodizing has found widespread use in industry. Anodizing increases corrosion resistance and paint adhesion, permits subsequent plating, improves adhesive bonding, and provides a lustrous decorative appearance.

Because a wide variety of coating properties can be produced through variations in the process, anodizing is used in almost every industry in which aluminum can be used. The broadest classification of anodizing treatments is according to the acid electrolyte used. Various acids have been used to produce anodic coatings, but the most common ones in current use are sulfuric (H_2SO_4) and chromic (CrO_3) acids. Although CrO_3 anodizing is standardized, there are two main types of H_2SO_4 anodizing. The first is a room-temperature H_2SO_4 process termed conventional anodizing, and the second is a low-temperature H_2SO_4 process termed hardcoat anodizing.

Because all of the anodic processes produce porous Al_2O_3 coatings, it is often desirable to seal the coating to close these pores and to eliminate the path between the aluminum and the environment. Sealing involves immersing the coating in hot water; this hydrates the Al_2O_3 and causes the coating to swell in order to close the pores, forming $Al_2O_3 \cdot 3H_2O$. Conventional sealing is generally done at a minimum temperature of 95 °C (200 °F) for not less than 15 min. There are also several proprietary nickel-base sealing agents available that are said to produce sealing at a low temperature through catalytic action. Chromic and sulfuric anodizes are almost always sealed. However, because sealing softens the coating somewhat, hardcoat anodize is usually not sealed unless criteria other than hardness are of maximum importance in the finished coating.

Inhibitors

An inhibitor is a chemical substance or combination of substances that, when present in the environment, prevents or reduces corrosion without significant reaction with the components of the environment. Inhibitors find major use in closed environment systems that have good circulation, so that an adequate and controlled concentration of inhibitor is ensured. Such conditions can be met, for instance, in cooling water recirculating systems, oil production, oil refining, and acid pickling of steel components. One of the more

recognizable applications for inhibitors is in antifreeze for automobile radiators.

The application of inhibitors must be viewed with caution by the user because inhibitors may afford excellent protection for one metal in a specific system but can aggravate corrosion for other metals in the same system. Since many closed systems contain a variety of metals and alloys, this fact should be remembered. Many companies or divisions of companies specialize in this method of corrosion control and are willing to provide technical support for specific applications.

Inhibitors can be organic or inorganic compounds, and they are usually dissolved in aqueous environments. Some of the most effective inorganic inhibitors are chromates, nitrites, silicates, carbonates, phosphates, and arsenates. (It should be noted that environmental concerns have significantly impacted the use of chromates.) The organic inhibitors are many and include amines, heterocyclic nitrogen compounds, sulfur compounds (such as thioethers, thioalcohols, thioamides, thiourea, and hydrazine), some natural compounds (such as glue or proteins), and mixtures of two or more compounds.

Types of Inhibitors

Various types of inhibitors commonly used include the following:

- Anodic
- Cathodic
- Ohmic
- Precipitation
- Vapor phase

The protection afforded by these inhibitor types can result from several different mechanisms: the presence of adsorbed films, the formation of

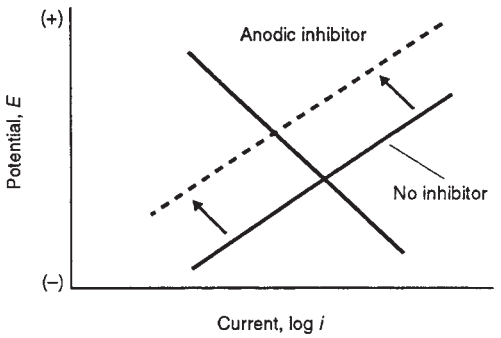


Fig. 15 Anodic and cathodic polarization curves showing the effect of an anodic inhibitor

bulky precipitates, or the promotion of passivity of the metal to be protected.

Anodic (passivating) inhibitors function by selectively covering anodic sites on the metal surface. This effect is shown using mixed-potential diagrams for the anodic and cathodic reaction kinetics in Fig. 15. The addition of an inhibitor on the potential versus log current density diagram promotes a shift of the anodic polarization curve from the solid line to the dashed line, with little or no effect on the cathodic polarization curve. The net effect is an increase in the corrosion potential and a decrease in the corrosion rate. Anodic inhibitors are considered dangerous, because insufficient concentrations can lead to accelerated localized attack at unprotected sites. Generally, a critical concentration for anodic inhibitors must be maintained. Typical anodic inhibitors include oxidizing chemicals, such as chromates, nitrites, and nitrates, and nonoxidizing chemicals, such as phosphates, tungstates, and molybdates. The nonoxidizing chemicals require the presence of other oxidizing species (e.g., oxygen) in the environment to be effective.

Cathodic inhibitors reduce corrosion by slowing the reduction reaction rate of the electrochemical corrosion cell. This is done by blocking the cathodic sites by precipitation. For example, calcium, magnesium, and zinc ions will precipitate hydroxides on cathodic sites as the local environment becomes more alkaline due to the reduction reaction at these sites. As the pH increases, hydroxide precipitation occurs. Cathodic inhibitors are effective when they slow down the cathodic reaction rate. Arsenic, bismuth, and antimony, which are referred to as *cathodic poisons,* reduce the hydrogen reduction reaction rate and, thus, lower the overall corrosion rate. Other cathodic inhibitors remove reducible species from the environment. Removal of oxygen from the corrosive environment will significantly decrease the corrosion rate. This can be done through (a) the use of oxygen scavengers, such as sodium sulfite and hydrazine, which react with the oxygen and remove it from the solution; (b) vacuum deaeration; or (c) boiling to lower the dissolved oxygen concentrations.

Ohmic inhibitors, also referred to as general filming inhibitors, reduce the corrosion rate by decreasing the mobility of ionic species between anodes and cathodes on the corroding metal surface. By decreasing the ionic conductivity of the solution, the corrosion rate is reduced. These inhibitors function through strong adsorption to the metal surface. Ohmic inhibitors include amines, which are cationic, and sulfonates, which are anionic.

Precipitation inhibitors promote the formation of a bulky precipitation film over the entire surface. Silicates and phosphates are examples of such inhibitors.

Vapor-phase inhibitors are chemical compounds that have relatively high vapor pressures and that adsorb on metal surfaces. Once

adsorbed, they can either neutralize moisture, promote the formation of passive films, or protect through the formation of a general film on the surface. Most vapor-phase inhibitors provide protection by multiple means. A caution is that vapor-phase inhibitors are metal specific, and, used with the wrong metal, they can lead to accelerated attack. The protection is most effective in closed spaces with little ventilation. A common practice is to include a small porous packet containing a vapor-phase inhibitor and a desiccant within the packaging material for electronic and other delicate equipment during shipment. The desiccant removes water from the environment and lowers the likelihood of condensation, while the vapor-phase inhibitor adsorbs on metal surfaces and protects them in the event of condensation.

Biocides

Microbiologically induced corrosion (MIC) is brought on by the presence of bacteria or other microbes in the environment (see Chapter 5, "Types of Corrosive Environments"). Corrosion induced by bacteria is a recognized problem in the gas and oil industries, pipelines, municipal sewage treatment systems, the pulp and paper industry, and a variety of industrial applications. Sulfate-reducing bacteria can convert noncorrosive water into highly corrosive water through the conversion of sulfate to sulfide. Other microorganisms can also increase the corrosivity of the environment by a variety of mechanisms.

Chemical treatment to control MIC is an option, but it is not straightforward. The treatment must be done with care and be compatible with the materials of the system, other water-treatment chemicals, and the surrounding environment. Biocides are chemicals that kill or control microorganisms. A list of biocides used in cooling

Table 9 Biocides used in cooling water systems

Microbiocide	Effectiveness(a)			Comments
	Bacteria	Fungi	Algae	
Chlorine	E	S	G	Oxidizing; reacts with $-NH_2$ groups; effective at neutral pH; loses effectiveness at high pH. Use concentration: 0.1–0.2 mg/L continuous free residual; 0.5–1.0 mg/L intermittent free residual
Chlorine dioxide	E	G	G	Oxidizing; pH insensitive; can be used in presence of $-NH_2$ groups. Use concentration: 0.1–1 mg/L intermittent free residual
Bromine	E	S	E	Oxidizing; substitute for Cl_2 and ClO_2; effective over broad pH range. Use concentration: 0.5–0.1 mg/L continuous free residual; 0.2–0.4 mg/L intermittent free residual
Organo-bromide (DBNPA)	E	NA	S	Nonoxidizing; pH range 6–8.5. Use concentration: 0.5–24 mg/L intermittent feed
Methylene bisthiocyanate	E	S	S	Nonoxidizing; hydrolyzes above pH 8. Use concentration: 1.5–8 mg/L intermittent feed
Isothiazolinone	E	G	E	Nonoxidizing; pH insensitive; deactivated by HS^- and $-NH_2$ groups. Use concentration: 0.9–13 mg/L intermittent feed
Quaternary ammonium salts	E	G	E	Nonoxidizing; tendency to foam; surface active; ineffective in highly oil-fouled or organic-fouled systems. Use concentration: 8–35 mg/L intermittent feed
Organo-tin/quaternary ammonium salts	E	G	E	Nonoxidizing; tendency to foam; functions best in alkaline pH. Use concentration: 7–50 mg/L
Glutaraldehyde	E	E	E	Nonoxidizing; deactivated by $-NH_2$ groups; effective over a broad pH range. Use concentration: 10–75 mg/L intermittent feed

(a) E, excellent; G, good; S, slight; NA, not applicable

water systems is presented in Table 9. These chemicals are either surface-active chemicals or non-surface-active species such as chlorine dioxide, chlorine, and sodium hypochlorite. Because of the potential for rapid multiplication when favorable conditions are restored, organisms that survive under deposits or in crevices or corrosion pits can be difficult to eliminate. The chemicals that provide effective MIC control may also increase the susceptibility of the materials of construction to other forms of corrosion, such as pitting and stress-corrosion cracking.

Application of Inhibitors

The delivery application or delivery and replenishment of inhibitors to the metal surface to be protected is a critical part of an effective inhibitor program. Inhibitor application techniques include continuous injection, batch treatment, and the incorporation of inhibitors into protective coatings or primers. The latter method provides protection by allowing the inhibitor to leach from the protective coating or primer into the environment as it comes into contact with the metal surface.

Water-treatment chemicals and inhibitor packages often are combinations of chemicals used in the overall inhibitor program, including inhibitors, wetting agents, and defoaming agents. The appropriate application technique is determined based on analysis of the system to be protected.

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CHAPTER **10**

Corrosion Control by Cathodic and Anodic Protection

BOTH CATHODIC AND ANODIC PROTECTION METHODS involve modification of a metals potential. In these methods, the potential of the metal to be protected is shifted, either by the application of a direct current from a power supply or by galvanic action from the connection of dissimilar metals. The potential can be shifted into a region of immunity or into a region of passivity for the metal. Shifting the potential to more reducing or more negative potentials favors immunity of the metal and is referred to as cathodic protection. Shifting the metal to more oxidizing conditions or more positive potentials within a region of passivity is referred to as anodic protection.

Cathodic Protection

Cathodic protection is a technique that can be applied to structures that are exposed to a continuous bulk electrolyte (i.e., structures that are immersed in water, buried in the soil, or encased in concrete). The method has been used for more than 175 years and is applicable to virtually all metals, although it is primarily used for steel. Common applications include protection from soil corrosion (e.g., underground pipelines) and marine corrosion (pipelines, ship hulls, and offshore drilling

platforms). Frequently, cathodic protection is used in conjunction with organic coatings.

How Cathodic Protection Works

Cathodic protection is defined as the reduction or elimination of corrosion by making the metal a cathode by means of an impressed current or attachments to a sacrificial (galvanic) anode. This method is described here with reference to a buried steel structure. Figure 1 is a schematic of an operating corrosion cell on a buried steel pipe. Under freely corroding conditions, an area on the steel surface becomes an anode, and another area becomes a cathode. The potential difference between the anode and cathode gives rise to a corrosion current flowing from the anode into the soil. The corrosion current enters the steel structure from the soil at the cathode, and the circuit is completed by current flow through the steel by electronic conductivity from the cathode to the anode. A result of this operating corrosion cell is metal loss in the form of general corrosion or pitting corrosion at the anodic areas.

A schematic of a cathodic protection system is shown in Fig. 2. The concept of cathodic protection is to overcome the detrimental corrosion current in the corrosion cell by imposing a current to the steel structure over its entire area. When current enters the steel over its entire area, no areas can operate as localized anodes, and corrosion is stopped. The system shown in Fig. 2 utilizes a power supply and a buried anode in the soil to make the cathodic protection circuit. Current is forced to flow from the buried anode to the buried steel structure by the power supply. In practice, the current capacity of the power supply and the size and distribution of the cathodic protection anodes are designed to provide uniform current distribution over the entire structure to be protected.

The concept of cathodic protection is related to potential-pH (Pourbaix) diagrams and electrochemical polarization curves as shown in Fig. 3 and described in Chapter 3. Under freely corroding conditions,

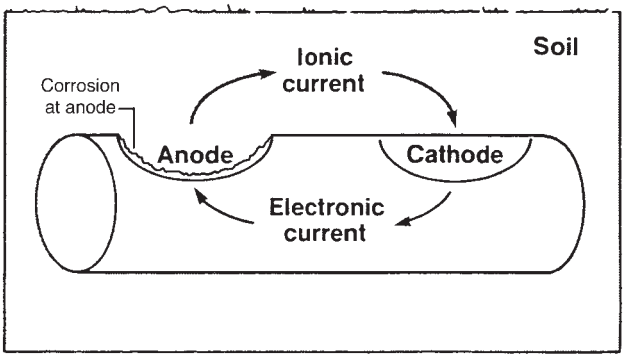


Fig. 1 Schematic of a corrosion cell operating on a steel pipe buried in the soil

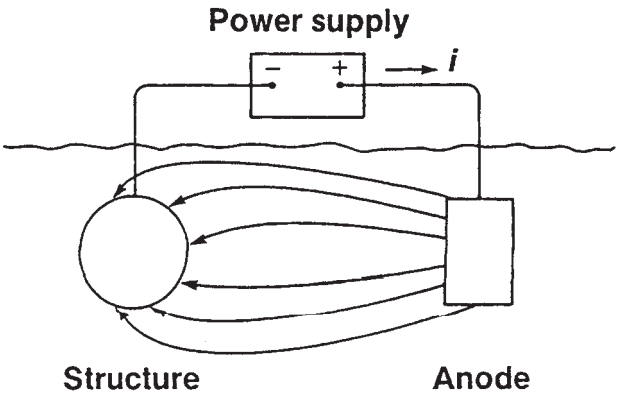


Fig. 2 Schematic of an impressed-current cathodic protection system

the metal in the electrolyte has a potential and pH combination in the active region as indicated by the X in the diagram. In this region, soluble corrosion products are the stable species, and the prediction of the potential-pH diagram is that the metal will corrode. The concept of cathodic protection is to shift the potential from the active region to more reducing (negative) values in the immune region. Corrosion is thus prevented. An electrochemical polarization curve for an active/passive metal is shown in the diagram to the right in Fig. 3. The freely corroding metal is at a potential in the active range, and corrosion is observed. The application of cathodic protection shifts the potential below the original corrosion potential and into the region designated by the crosshatched area along the polarization curve. The current at the intersection with the crosshatched area indicates the magnitude of cathodic protection current required to maintain the metal at the desired protection potential. The location of the immune region on the potential-pH diagram and the shape and magnitude of currents on the polarization curve are a function of the metal/electrolyte combination.

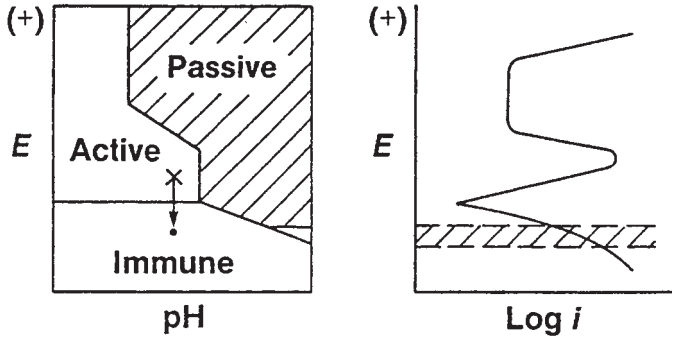


Fig. 3 The concept of cathodic protection related to a potential-pH diagram (left) and to electrochemical polarization curves (right)

Types of Cathodic Protection

There are two types of cathodic protection systems. Sacrificial cathodic protection uses galvanic action in a beneficial manner to provide the current to the structure to be protected. An impressed-current cathodic protection system uses a power supply to provide the current to the structure to be protected. Design and installation of both types of systems should be conducted by consulting companies that specialize in cathodic corrosion control.

A sacrificial cathodic protection system uses a more active metal than that used in the structure to be protected to supply the current needed to stop corrosion. The more active metal is called a sacrificial anode. Coupling two dissimilar metals in the same environment can lead to accelerated corrosion of the more active metal and protection of the less active (more noble) one. Although galvanic corrosion is generally considered a nuisance, it can be used to advantage as a control method (Fig. 4a).

Sacrificial (galvanic) protection is often used in preference to impressed-current techniques when the current requirements are low and the electrolyte has relatively low resistivity (less than about 10,000 $\Omega \cdot$ cm). Clearly, it has an advantage when there is no source of electrical power and when a completely underground system is desired. Capital investment will generally be lower, particularly for smaller installations, and it is often the most economical method for short-life protection, although this is not its only application. Routine replacement of anodes must also be considered.

Impressed-Current Systems. Figure 4(b) shows an impressed-current system used to protect a pipeline. The buried anode(s) and the pipeline are both connected to an electrical rectifier, which supplies direct current to the buried electrodes (anodes and protected cathode) of the system. Unlike sacrificial anodes, impressed-current anodes

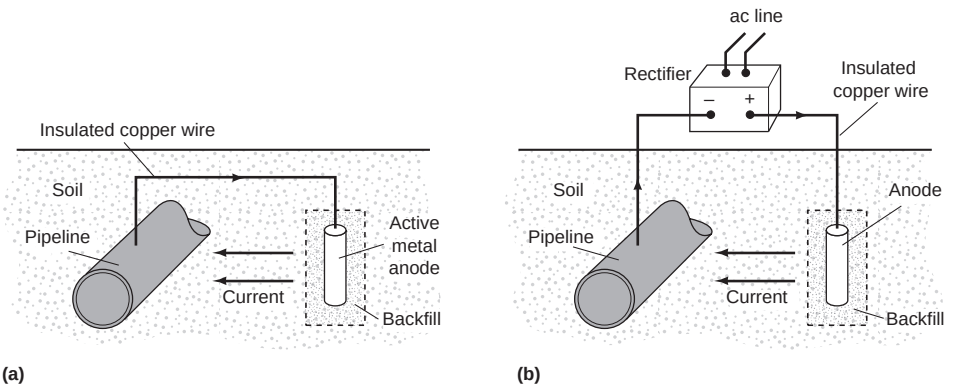


Fig. 4 Cathodic protection for underground pipe. (a) Sacrificial or galvanic anode. (b) Impressed-current anode

need not be naturally anodic to steel and, in fact, seldom are. Most impressed-current anodes are made from nonconsumable electrode materials that are naturally cathodic to steel. If these electrodes were wired directly to a structure, they would act as cathodes and would cause accelerated corrosion of the structure they are intended to protect. The direct current (dc) source reverses the natural polarity and allows the materials to act as anodes. Instead of corrosion of the anodes, some other oxidation reaction, that is, oxygen or chlorine evaluation, occurs at the anodes, and the anodes are not consumed.

The most common source of electricity for impressed-current systems is a local power utility. Power normally involves the dc rectifier arrangement shown in Fig. 4(b). Remote locations can use solar cells (Fig. 5), thermoelectric current sources, special fuel-driven electric generators, or even windmills.

Impressed-current systems are preferred when current requirements and electrolyte resistivity are high. These systems require an inexpensive source of electrical power, are well suited to long-time operation and large structures, and can be automatically controlled. Automatic control reduces maintenance and operating costs.

Anode Materials

Different requirements for sacrificial anodes and impressed-current anodes lead to the use of widely different materials for these applications.

Sacrificial Anodes. Requirements for sacrificial anodes include the following:

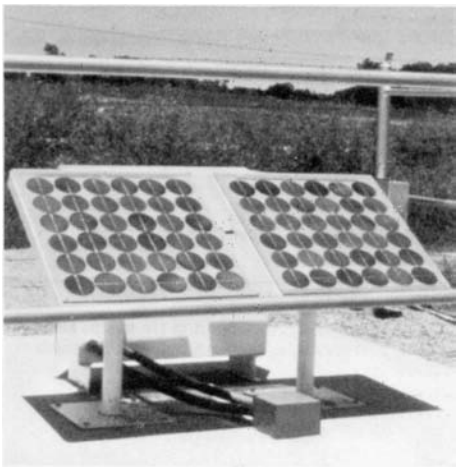


Fig. 5 Solar cells used to provide electricity for the cathodic protection of a buried pipeline

- The anode must be a metal that is more active (i.e., have a more negative corrosion potential) than the metal/steel to be protected. Commercial sacrificial anodes include magnesium, zinc, and aluminum.
- The potential difference between the freely corroding potential of the structure to be protected and the sacrificial anode must be large enough to provide the necessary cathodic protection current.
- The sacrificial anodes must be of sufficient size and have sufficient efficiency to provide the necessary useable life. Information on anode energy capabilities and consumption rates are available from manufacturers of sacrificial anodes.

Magnesium anodes are the only sacrificial anodes that are routinely specified for use in buried soil applications. Most magnesium anodes in the United States are supplied with a prepackaged bentonite clay backfill in a permeable cloth sack. This backfill ensures that the anode will have a conductive environment and will corrode reliably. The additional material is less expensive than the soil resistivity surveys that would be needed to determine if the backfill is necessary.

Some magnesium anodes have been used offshore in recent years in an attempt to polarize the structures to a protected potential faster than would occur if zinc or aluminum alloy anodes were used. Magnesium tends to corrode quite readily in salt water, and most designers avoid the use of magnesium for permanent long-term marine cathodic protection applications.

Zinc is used for cathodic protection in freshwater and marine water. Zinc is especially well suited for cathodic protection on ships that move between salt water and harbors in brackish rivers or estuaries. Figure 6 shows zinc anodes on the underside of a small fishing boat. Aluminum anodes would passivate in the harbors and might not work when they return to sea. Zinc anodes also are used to protect ballast tanks, heat

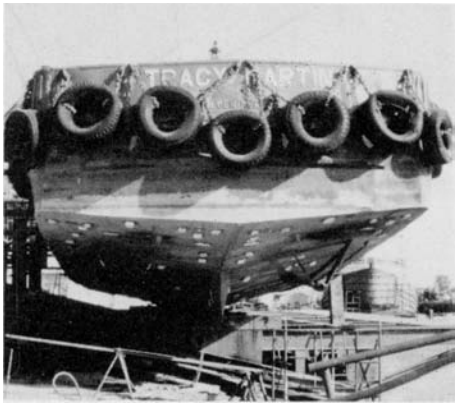


Fig. 6 Zinc anodes on the underside of a fishing boat

exchangers, and many mechanical components on ships, coastal power plants, and similar structures.

Aluminum anodes and, more recently, aluminum-zinc alloys, have become the preferred sacrificial anodes for offshore platform cathodic protection. This preference is because aluminum anodes demonstrate reliable long-term performance when compared with magnesium, which might be consumed before the platform has served its useful life. Aluminum also has better current/weight characteristics than zinc. Weight can be a major consideration for large offshore platforms.

The major disadvantage of aluminum for some applications, for example, the protection of painted ship hulls, is that aluminum is too corrosion resistant in many environments. Aluminum alloys will not corrode reliably onshore or in freshwaters. In marine environments, the chloride content of seawater depassivates some aluminum alloys and allows them to perform reliably as anode materials. Unfortunately, it is necessary to add mercury, antimony, indium, tin, or similar metals to the aluminum alloy to ensure that this depassivation occurs. Heavy-metal pollution concerns have led to bans on the use of mercury alloys in some locations.

Impressed current anodes must be corrosion resistant and otherwise durable in the environment in which they are used, and they must have low consumption rates when connected to a cathodic protection source. All materials used for impressed-current anodes are cathodic (more noble) than steel.

High-silicon cast iron (Fe-0.95C-0.75Mn-14.5Si-4.5Cr) is used for onshore cathodic protection applications and in other locations where abrasion resistance and other mechanical damage considerations are important.

Graphite anodes are extensively used for onshore pipeline cathodic protection applications in which they can be buried in multiple-anode ground beds (Fig. 7). Because of its brittle nature, graphite must be stored and handled carefully.

Polymeric anodes are used to mitigate the corrosion of reinforcing steel in salt-contaminated concrete. The system consists of a mesh of wirelike anodes, which are made of a conductive polymer electrode material coated onto copper conductors. Examples of polymer anodes are provided in the section “Applications of Cathodic Protection.”

Precious metals are used for impressed-current anodes because they are highly efficient electrodes and can handle much higher currents than anodes fabricated from other materials. Precious metal anodes are actually platinized titanium or niobium anodes; the platinum is either clad or electroplated on the substrate. Platinized anodes are used in marine work on ships, hulls, and for applications involving the interior parts of structures such as condenser water boxes, internal parts of pumps, certain pipeline interiors.

Lead alloy anodes, containing 2% silver, or 1% silver and 5% antimony, are used for cathodic protection systems in seawater. Lead alloy anodes should not be buried in the sea bottom or used in freshwater applications.

Oxide-metal composite anodes consist of a mixed ruthenium dioxide and titanium oxide coating sintered onto a commercially pure titanium substrate. These meshlike anodes also are used for protecting reinforcing steel in concrete.

Criteria for Cathodic Protection

An important aspect of cathodic protection is the means to monitor the effectiveness and the criteria for protection. The criteria for protection are addressed in NACE standard RP0169 (as revised): "Control of External Corrosion on Underground or Submerged Metallic Piping Systems." These criteria are updated and revised periodically, and the reader is guided to the most recent version of this standard for currently accepted practice. For steel protection, several criteria are described. The most commonly used criterion is that the steel structure to be protected be maintained at a potential more negative than –0.85 V-Cu/$CuSO_4$ (volts with respect to the copper-copper sulfate reference

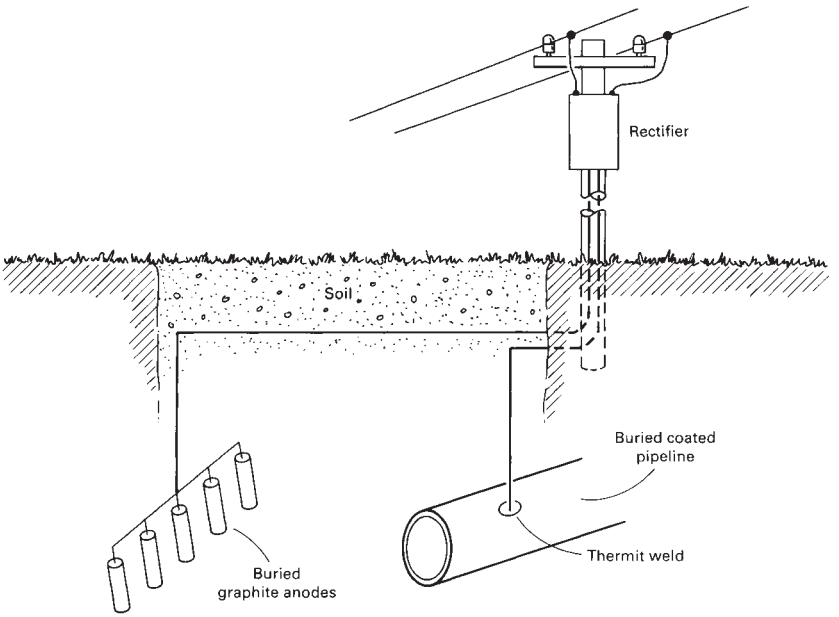


Fig. 7 Impressed-current cathodic protection of a buried pipeline using graphite anodes

electrode). Other criteria applied to the protection of steel include the following:

- Maintain a minimum negative shift of 300 mV (0.3 V) from the freely corroding potential
- Provide a minimum 100 mV shift on the polarization decay when cathodic protection is removed
- Measure protective cathodic currents to previously anodic sites on a structure by measuring earth currents

For metals other than steel, the general criterion for protection is based on a minimum level of potential shift in the negative direction from the freely corroding potential. In addition, test coupons can be applied to the structure to be protected and removed periodically to determine the level of protection and effectiveness of the cathodic protection system.

The amount of cathodic protection should be sufficient to reduce the corrosion rate to an acceptable range. Caution should be exercised to avoid overprotection. Overprotection results in the premature consumption of sacrificial anodes or excessive amounts of impressed-current demands. Moreover, the application of too much cathodic protection can result in damage to the structure to be protected as described in the following section.

Problems with Cathodic Protection

Cathodic protection is not without problems and limitations. Apart from the expense items, such as capital investment and maintenance costs, there are also some technical problems.

Effects of Stray Currents. One of the more serious problems associated with cathodic protection are the possible effects of stray currents on the corrosion of adjacent metal structures. For example, a cathodic protection system that is efficiently protecting pipeline A might increase the corrosion of neighboring pipeline B (Fig. 8a). This increase can lead to unexpected corrosion problems/failure, as well as undesirable legal ramifications. Redesign can sometimes eliminate stray current corrosion (Fig. 8b), but often the solution is not simple.

The use of deeply buried anodes can alleviate the problem when stray currents affect structures just below ground level. A survey of all other metal structures in the area is essential before installing cathodic protection. Such inspection also might reveal a source of protection from a neighboring system.

Effects of Chemical Reactions. Other problems associated with cathodic protection are related to the chemical reactions occurring at the surface of the protected structure because it is the cathode in the

circuit. For example, if the cathodic reaction is hydrogen reduction, the resulting hydrogen can have a deleterious effect. It can cause blistering of the metal or, if the metal is under stress, might cause cracking of the structure. The cathodic reaction can also create problems because of the resultant buildup of hydroxyl ions (increased alkalinity). This increased alkalinity can be harmful to an amphoteric metal such as aluminum. The alkaline environment breaks down the protective film on aluminum and can result in severe weight-loss corrosion.

Adverse Effects of Cathodic Protection on Coatings. The increased alkalinity of the surface of the structure being protected can also lead to the deterioration and/or failure of some coatings. Oil-based paints such as alkyds are particularly susceptible to damage by the alkalinity produced by cathodic protection systems. This damage can occur even under normal operation of the system.

Another problem is the disbonding of coatings due to the generation of hydrogen at the metal-coating interface where there is excessive protection current. If the amount of current applied is excessive, hydrogen can be generated on the surface of the structure being protected, which can cause disbondment (Fig. 9) and premature failure of the coatings used. If the cathodic protection system is properly designed and operated, however, the evolution of hydrogen can be prevented.

Other Variables Affecting Underground Structures. Many other problems are to be faced and solved in the application of cathodic protection to underground structures. Corrosivity of soils will change as does the degree of aeration and the resistivity (additional information on corrosion in soils can be found in Chapter 5). Bacterial effects also can change the corrosion potential. All of these factors influence corrosion

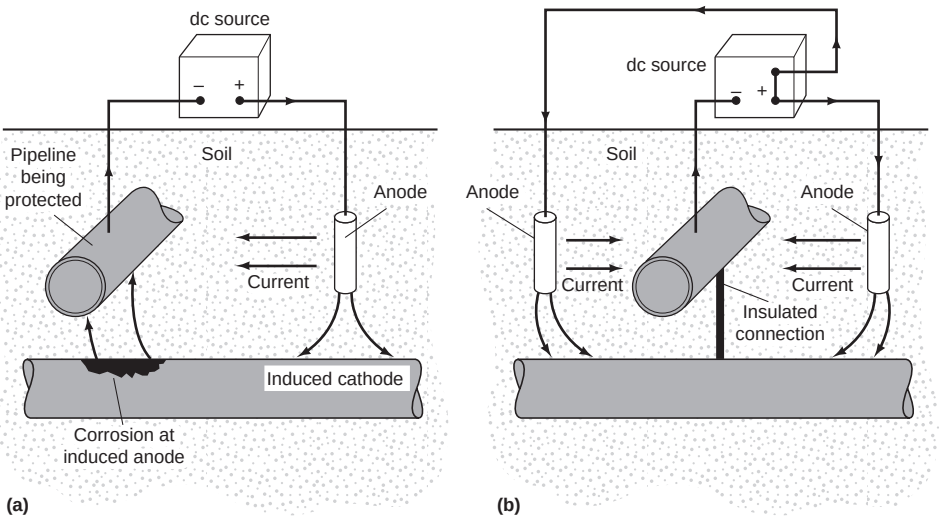


Fig. 8 Stray-current effects in underground pipelines. (a) Stray currents cause corrosion in neighboring pipeline. (b) Redesign minimizes stray-current effects.

so that along a pipeline there can be varying cathodic control requirements that have to be estimated from potential measurements, experience, etc.

Applications of Cathodic Protection

The applications of cathodic protection are quite diverse with respect to the corrosive environment in which it is applied, the industries in which it is applied, and the types of equipment and structures that are cathodically protected. Early applications included the protection of buried steel structures in soil, including steel pipes, tanks, and structural columns. The glass-lined steel tanks of domestic water heaters are typically protected by a magnesium rod inside the tank (Fig. 10). The magnesium anode provides sacrificial cathodic protection to any exposed steel within the tank. Several manufacturers provide water heaters with two different useful lives under warranty. The technical basis for the water heater with a longer useful life is that it has a larger amount of magnesium internally. The greater amount of magnesium provides sacrificial cathodic protection over a longer period of time.

Cathodic protection has been used for decades to protect structures in seawater. It is common practice to protect steel ship hulls by attaching zinc anodes to the steel structure. Zinc "bracelet" anodes are installed on pipelines immersed in seawater to provide sacrificial cathodic protection to the outer surfaces of the steel pipe (Fig. 11). Offshore structures

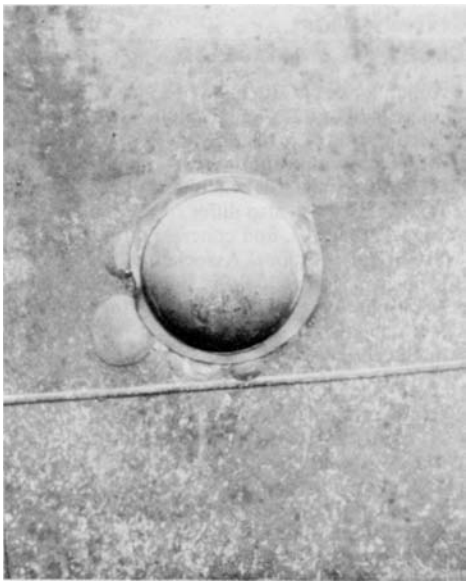


Fig. 9 Debonded organic coating near a high-silicon cast iron impressed-current anode on a navigational lock on the Tennessee River. The debonding of the coating was due to improper design and excessive protective current.

for gas and oil exploration, drilling, and production are commonly protected by the use of aluminum anodes on the steel structures. In seawater, the sacrificial aluminum anodes remain active and do not form passive films that would negate their effectiveness as sacrificial anodes.

Cathodic protection applications have evolved from this traditional base to a much broader variety of applications. These applications include the protection of the internal surfaces of process equipment in the chemical process and pulp and paper industries, the protection of water boxes and condenser tubesheets in the electric power industry, and the protection of steel reinforcing bars in concrete in highway bridges and parking garages.

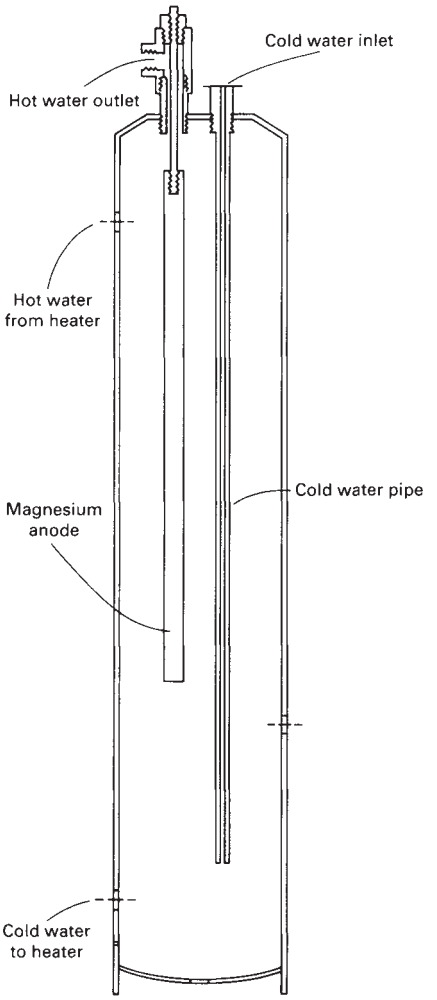


Fig. 10 Magnesium anode used to cathodically protect glass-lined steel water heater

Steel in contact with concrete is typically in a passive condition due to the buildup of a protective film on steel in the alkaline electrolyte within the concrete. In the presence of chloride ions in the electrolyte, the protective films on steel can break down, leading to severe corrosion of the steel. The result of the steel corrosion is that a higher volume corrosion product than the original steel is formed. This volume expansion results in tensile stresses within the concrete and subsequent spalling and cracking of the concrete. This damage can be a major problem where salt water is in contact with the concrete and permeates the concrete to the steel surface. The problem has been observed in northern regions where deicing salts are used on highway bridges and in parking garages. The problem also is detected in concrete in marine environments where contact with salt water directly or with airborne salt can result in chloride penetration into the concrete.

Cathodic protection can be used to effectively arrest the detrimental corrosion of steel in chloride-containing concrete. A schematic diagram of a cathodic protection system for steel and concrete is shown in Fig. 12.

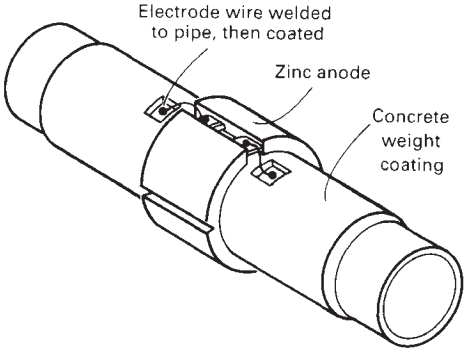


Fig. 11 Zinc "bracelet" anode at a joint in an offshore pipeline

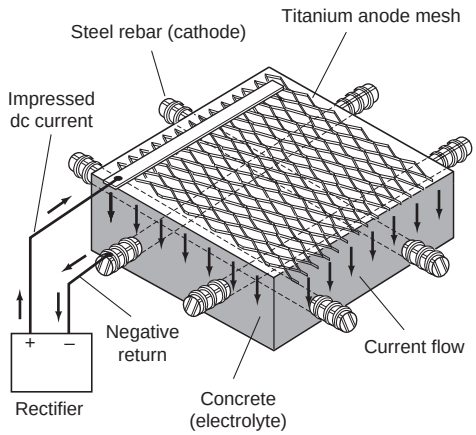
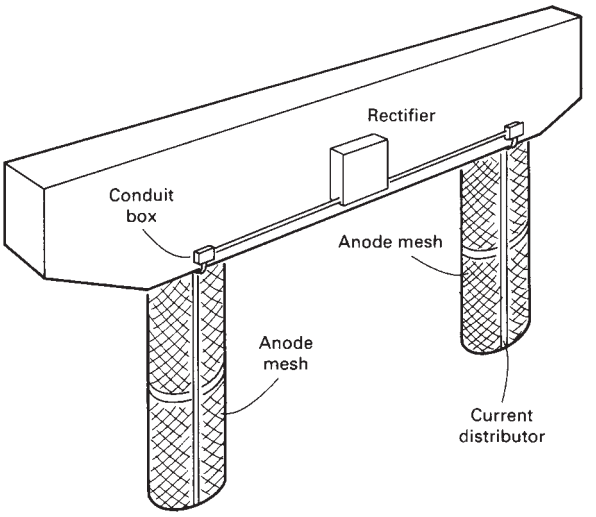


Fig. 12 Schematic of the cathodic protection of steel reinforcing bars in concrete. Arrows indicate current to the steel.

A dc power supply provides the protective cathodic protection current to an anode on the surface of the concrete. The protective current then moves through the concrete (as indicated by the arrows) to the steel structure to be protected. For effective protection, the steel piece to be protected must be in electrical contact, and a return current path must be provided to the power supply. The anode for these systems can be either oxide-coated titanium, conductive polymer cables, or conductive poly-



(a)



(b)

Fig. 13 Use of mixed oxide/titanium anode mesh for cathodic protection. (a) Sidewalk and barrier wall installation. (b) Installation of anode mesh on a bridge substructure.

meric paint systems. Installations of oxide-coated, expanded titanium mesh anodes on a sidewalk and a bridge substructure are shown in Fig. 13(a) and (b), respectively. The expanded titanium metal anodes are coated with a grouting material after application to the concrete structure. Figure 14 shows polymer mesh anodes used to protect reinforcing steel in bridge decks, parking garages, and other large structures. The anode mesh is placed on the surface of the reinforced concrete structure, covered with an overlay of Portland cement or polymer-modified concrete, and then connected to a low-voltage dc power source.

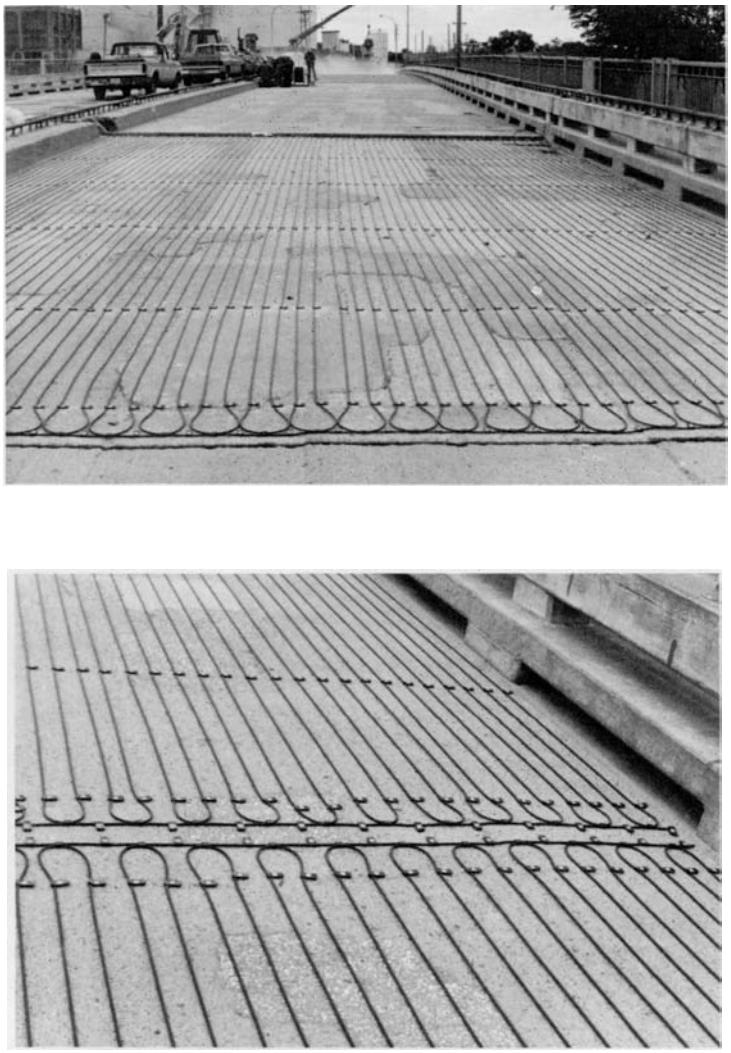


Fig. 14 Two views of polymer mesh anodes used to protect reinforcing steel in bridge decks, parking garages, and other large structural surfaces.

Anodic Protection

Anodic protection is the most recently developed of all the various corrosion control methods available. This method was first used in the field in the late 1950s. Anodic protection did not become commercially successful until the early 1970s, and it is currently used on a smaller scale than other corrosion control techniques.

Anodic protection is corrosion protection achieved by maintaining an active-passive metal or alloy in the passive region by an externally applied anodic current. The potential of the metal to be protected is made more positive (more oxidizing) to shift the conditions from a region of active corrosion to a region of passive behavior.

The Concept of Anodic Protection

The concept of anodic protection is related to a potential-pH diagram and to electrochemical polarization curves for an active-passive metal (Fig. 15). In the potential-pH diagram, the starting condition for the steel/electrolyte combination is indicated by the X in the active region. Through the application of an anodic protection current, the potential of the steel is raised from the active region into the passive region as shown by the arrow in the diagram. The corrosion rate of the steel is significantly reduced through the onset of passivity. Anodic protection with respect to the electrochemical polarization curve is also shown in Fig. 15 (right). The potential is increased to more oxidizing conditions and maintained in the region designated by the crosshatched area on the figure. Within this potential range, the corrosion rate of the steel is quite low, as indicated by the passive current within this range.

Anodic protection is effective only for metal/environment combinations where passivity is achievable and maintainable. If, for any

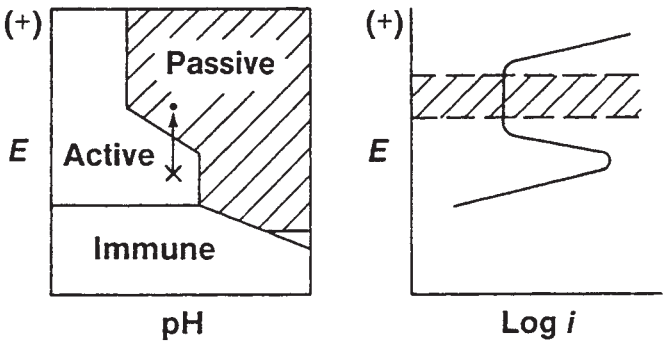


Fig. 15 Concept of anodic protection related to a potential-pH diagram (left) and to an electrochemical polarization curve (right)

reason, the passive film is damaged and breaks down, the application of anodic protection can result in greater damage than would be observed with no protection at all. This situation is shown schematically in Fig. 16 for a metal exhibiting active-passive behavior. The application of anodic protection is good if the passive film is developed, and a low current is achieved (Fig. 16). If the passive film breaks down, however, then no decrease in the current is observed, and the corrosion current follows the dashed path indicated on the diagram with increasing potential. In this latter case, the increase of potential for oxidizing values will accelerate the corrosion as indicated by the X marked "bad."

Equipment Required for Anodic Protection

Figure 17 shows a schematic of an anodic protection system for a storage vessel. One or more cathodes, a reference electrode, a potential sensing and controlling circuit, and a dc power supply are required for each anodic protection system. The vessel wall becomes the anode of the circuit by current forced between the cathode and the tank wall. The currents are controlled so that the potential of the wall with respect to the reference electrode is shifted and maintained in the passive region (Fig. 15).

The cathode should be a permanent-type electrode that is not dissolved by the solution or the current impressed between the vessel wall and electrode. Because the overall circuit resistance between cathode and vessel wall is proportional to the electrode surface area, it is advantageous to use large surface area electrodes. Metals that have

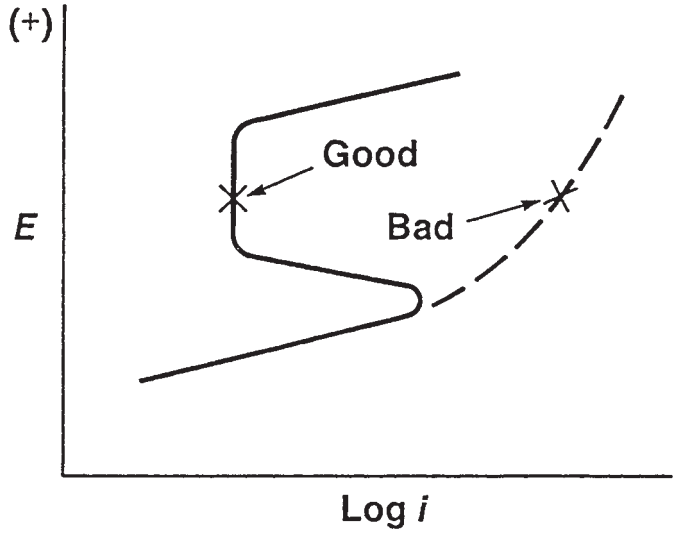


Fig. 16 Danger of anodic protection when a protective (passive) film is not realized

been used for cathodes in anodic protection systems, as well as the chemical environments in which they were used, include the following:

Metals	Environment
Platinum on brass	Various
Steel	Kraft digester liquid
Illium G	H_2SO_4 (78–105%)
Silicon cast iron	H_2SO_4 (89–105%)
Copper	Hydroxylamine sulfate
Stainless steel	Liquid fertilizers (nitrate solutions)
Nickel-plated steel	Chemical nickel-plating solutions
Hastelloy C	Liquid fertilizers (nitrate solutions), H_2SO_4, Kraft digester liquid

The electrode size is chosen to conform to the geometry of the vessel and to provide as large a surface area as possible. The location of the cathode is not a critical factor in simple geometries, such as storage vessels, but in heat exchangers, it is necessary to extend the electrode around the surface to be protected. Multiple cathodes can be used in parallel to distribute the current and to decrease the circuit resistance.

Reference electrodes must be used in anodic protection systems because the potential of the vessel wall as the anode must be controlled. The reference electrode must have an electrochemical potential that is constant with respect to time and that is minimally affected by changes in temperature and solution composition. Several reference electrodes have been used for anodic protection:

Electrode	Solutions
Calomel	H_2SO_4
Ag-AgCl	H_2SO_4, Kraft solutions, fertilizer solutions
Mo-MoO_3	Sodium carbonate solutions
Bismuth	NH_4OH
Type 316 stainless steel	Fertilizer solutions, oleum
Hg-$HgSO_4$	H_2SO_4, hydroxylamine sulfate
Pt-PtO	H_2SO_4

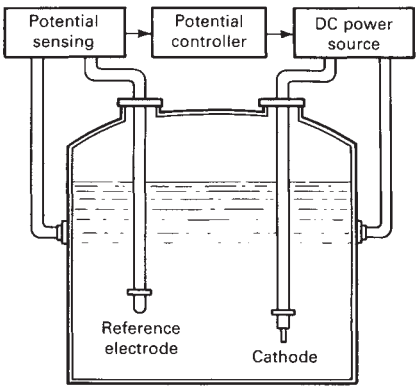


Fig. 17 Schematic of an anodic protection system

The reference electrode has been a source of many problems in anodic protection installations because of its more fragile nature with respect to the cathode.

Potential Control. As mentioned previously, the potential of the vessel wall with respect to the reference electrode must be controlled in anodic protection installations. The potential control circuit has two functions. First, the potential must be measured and compared with the desired preset value. Second, a control signal must then be sent to the power supply to force the direct current between the cathode and vessel wall. In early systems, this control function was done in an on-off method because of the high costs of electronic circuitry. The more sophisticated and extremely low-cost circuitry currently available has resulted in all systems having a continuous proportional-type control. The amount of current forced through the circuitry is that required to maintain the potential at the preset control point.

The dc power supplies have the identical design and requirements as the rectifiers for cathodic protection with one exception. Because of the nature of the active-passive behavior of the vessel, the currents required to maintain the potential of the vessel wall in the passive range can become very small. Some designs of dc power supplies must be specially modified to reduce the minimum amount of current put out of the power supply.

The packaging of these electronic components occasionally involves special requirements because most of the installations are made in chemical plants. Explosion-proof enclosures are sometimes required, and chemically resistant enclosures are necessary in other installations.

Applications of Anodic Protection

Anodic protection has been used for more than 30 years to protect hundreds of tanks containing sulfuric acid, as well as for many heat exchangers used for acid production. It has been used to lessen corrosion rates for storing 93 to 99% sulfuric acid. The intent is to minimize iron pickup, as well as to extend service life. If proper passivation is reached, the corrosion rate can be lowered significantly compared with having no anodic protection.

Anodic protection can be used to widen the range of temperatures where stainless steel can be used in sulfuric acid. The range of sulfuric acid concentration that can be handled by stainless steel can also be increased.

Anodic protection is also used to protect carbon and stainless steels against a wide range of other acidic and alkaline solutions. It has been used to protect mild steel in paper mill black acids, and spent alkylation acid, ammonia, ammonium nitrate with and without ammonium hydroxide,

and other fertilizer solutions. It has also been applied to titanium, aluminum, nickel, and their alloys.

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CHAPTER 11

Corrosion Testing and Monitoring

CORROSION TESTING AND MONITORING are powerful tools in the flight to control corrosion. Testing provides the necessary data for the evaluation and/or selection of existing, alternative, or new materials in various environments. Monitoring allows workers to follow the effectiveness of a corrosion-control system and provides early warning when damaging conditions arise.

It is beyond the scope of this chapter to present a detailed description of all corrosion tests and/or tests for specific forms of corrosion. Instead, a general overview of the major corrosion test categories is provided. More detailed information can be found in several excellent texts (including the selected references at the conclusion of this chapter) and in standards issued by ASTM, NACE International, the International Organization for Standardization (ISO), the Materials Technology Institute of the Chemical Process Industries (MTI), etc. A number of such standards are referenced throughout this chapter. Expertise in corrosion testing and monitoring is also available from companies that sell equipment, materials, and services; from consultants and technical associations; and from testing laboratories specializing in corrosion testing.

Classification of Corrosion Testing

There are three general categories of corrosion tests:

- Laboratory tests
- Pilot-plant tests
- Field tests

Laboratory corrosion tests are used to predict corrosion behavior when service history is lacking and time or budget constraints prohibit field testing. They can also be used as screening tests prior to field testing. Laboratory tests are particularly suited for quality control, materials selection, material and environment combinations, and the study of corrosion mechanisms. These tests range from simple immersion tests to various kinds of cabinet-controlled and autoclave-controlled environments to sophisticated electrochemical tests.

Most laboratory tests are accelerated (short-time) tests by design. The need for accelerated laboratory testing is shown graphically in Fig. 1. The typical time allowed for testing of candidate materials to support a materials selection process is measured in weeks and months—a relatively short period of time. By contrast, the desired useful lives of different equipment varies from approximately 7 to 10 years for automobiles, up to 1000 years (without appreciable leakage) in high-level nuclear waste containers. The goal of any accelerated laboratory test is to provide reliable information on the performance of candidate materials or coatings in service. The ranking of materials in accelerated tests should be the same as that which would be observed in service, and the relative life in the accelerated test should be translatable to the useful life in service. Establishing this reliable bridge between accelerated test data and expected performance life in service is a great challenge.

Typically, accelerated laboratory corrosion tests increase the severity of the environment by exposing the materials to more concentrated solutions, higher-temperature solutions, or increased periods of wetness. The environment used might simulate a humid tropical area, the salty air of a seaside area, a salted road in winter, or one of many others. Other accelerated tests measure a given behavior of the materials by electrochemical means, such as the pitting-breakdown potential in an anodic polarization test, and relate this property to corrosion performance in service. The danger associated with any laboratory test is that the accelerated condition will substantially change the mechanism of corrosion and, therefore, break all ties to reality and service performance.

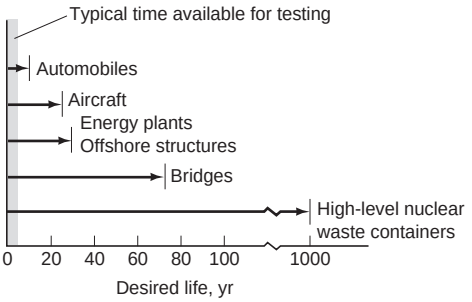


Fig. 1 Typical time available for testing, compared to desired life.

Pilot-plant tests are usually more desirable than laboratory tests, but they are also more expensive. Here the tests are made in a small-scale plant that essentially duplicates the intended large-scale operation. It is built so that design problems can be recognized and corrected, operators can be trained, and materials can be tested in authentic environmental conditions. Because a pilot plant is constantly being modified in order to determine optimum operating conditions, the solution temperature, velocities, and concentrations fluctuate more than they do in a full-scale operation. Although these fluctuating environmental conditions facilitate testing of materials under the worst possible conditions, careful and thorough record keeping of the specimen exposure history is required. Lack of accurate documentation of the specific conditions to which the specimens have been exposed can lead to erroneous results and/or assumptions regarding the suitability of a given material for a specific application. On the other hand, an advantage of a pilot plant is that equipment made of one material can be tested simultaneously with test coupons made of an alternative material.

Field testing, also referred to as simulated-service testing, is the most reliable predictor of corrosion behavior short of actual service experience. This includes exposures of either structural components, for example, welded pipes, or test specimens in outdoor environments that are representative of many general service situations. These so-called natural environments include exposures to the atmosphere, waters, and soil. Test materials are subjected to the cyclic effects of the weather, geographical influences, and bacteriological factors that cannot be realistically duplicated in the laboratory. Field tests normally range in duration from several months to many years. Some atmospheric tests of metals, for example, zinc-coated steels, have been conducted for more than 30 years.

This type of testing is important for such objectives as materials selection, predicting the probable service life of a product or structure, evaluating new commercial alloys and processes, and calibrating laboratory corrosion tests. The type of information sought determines the selection of test specimens and the methods of assessing the corrosion effects.

Purposes of Corrosion Tests

Corrosion tests are conducted in order to accomplish the following:

- Evaluation and selection of materials
- Obtaining reference or database information
- Determining quality-control and material acceptance requirements

- Monitoring corrosion-control programs
- Identifying research parameters and corrosion mechanisms

The type of approach, as well as its degree of complexity and formality, that is used to attain each of these objectives varies greatly. The approach can range from a screening or a one-shot test of a concept to a full-blown quality assurance program with complete certification of records and procedures using multiple test methods and analytical procedures.

To assist in the materials evaluation and selection process, corrosion tests are often conducted on candidate materials that are selected based on available data. Corrosion data that are specific to the application are developed then in the laboratory or the field.

Corrosion tests are also conducted in order to develop reference or database information that allows designers and engineers to categorize individual materials in terms of corrosion resistance and behavior, relative to those features in other available materials. The responsibility for generating this database on corrosion behavior often falls upon the alloy producers or developers of improved corrosion-control coatings or systems.

After an appropriate material is selected, it is common practice to require specific quality-control tests to determine material acceptability. These tests ensure customers and vendors that the ordered material meets its specifications and can be put into place.

Another good practice is to include a corrosion-monitoring program to follow the effectiveness of the overall corrosion-control program. If, for example, inhibitors are used to protect against corrosion, then coupons can be exposed throughout the system and inspected periodically to determine the effectiveness of the inhibitor treatment. On-line corrosion sensors and monitors can report the status of corrosion control and warn of a change in conditions that can be detrimental to equipment and facilities. In other cases, the corrosion sensors can directly initiate corrective action.

Finally, tests are conducted in the laboratory under controlled conditions in order to validate various corrosion mechanisms and models of corrosion behavior. Laboratory tests can be used to validate the results of a failure analysis. If the mode of failure and morphology of corrosion can be duplicated in the laboratory, then the conditions that resulted in service failure can be determined more definitively, and corrective actions can be specified.

Steps in a Corrosion Test Program

The logical steps to be taken when designing and conducting a corrosion test program are identified in this section.

Define the Test Objectives. What is to be learned by the test program? How will the data be used? How will the results be assimilated into the overall decision process? These questions are best developed and answered before the test program is initiated in order to obtain the most effective and efficient use of the test results.

Identify the Time and Cost/Budget Constraints. The timing of the corrosion tests must be compatible with the overall decision-making process. There are often trade-offs between the available time and money and the approach to the corrosion tests. These time and cost constraints can severely limit the options available in a corrosion test program. As the development cycle for products and processes is shortened, the time constraint on the corrosion test program becomes even more restrictive. The option of longer-term corrosion tests to aid in materials selection, for example, becomes impractical.

Select Test Methods and Procedures To Meet Program Objectives. The service conditions, candidate alloys, and possible corrosion failure modes for each type of material guide the selection of the appropriate test procedures of the materials evaluation. The staff, equipment, and facility requirements for those test procedures can then be determined. A decision can be made as to whether to conduct in-house corrosion tests or to contract them to others. Often, dedicated and specialized corrosion test equipment or analytical facilities are required for corrosion testing. One option is to develop the required technology and skills in house. Obviously, the degree of complexity, initial startup costs, and the frequency of use for the particular test procedure are important factors in this decision. Another option is to utilize facilities that are available for hire and have the resources to conduct almost any type of corrosion test.

Prepare Test Plan and Specimens. First, a detailed test plan that includes timing and cost information is developed. Next, test specimens are prepared and the necessary test equipment is assembled. Its availability is scheduled. The procurement of test materials and the desired configurations of test specimens can present a challenge. Various companies specialize in corrosion test specimen preparation, and they often stock a variety of materials used for corrosion tests in common shapes. In addition, materials suppliers are often cooperative and helpful in supplying samples for evaluations.

Perform the Testing. The next step is to carry out the test program as planned. Adjustments can be made along the way. The documentation of test conditions is required throughout the exposure. Standardized tests and practices should be chosen when available and applicable.

Evaluate the Specimens and the Environment. After the test exposures, the specimens are evaluated for the degree and morphology of corrosion attack. Useful information often can be gleaned by evaluating the environment after the test. A determination of the chemistry and

structure of the corrosion products and deposits on test specimens after exposure can be particularly informative.

Analyze the Results. The final step of corrosion test program involves analyzing the test results, documenting and reporting those results, and incorporating the results into the overall program.

Preparation and Cleaning of Test Specimens

The sampling of test materials and the preparation of test specimens are extremely important variables in corrosion testing, because corrosion behavior can be significantly influenced by variations in metallurgical structure and the condition of the metal surface. These factors are especially pertinent when various forms of localized corrosion are under evaluation in complex alloys. The uniformity of the metal sample should be checked in advance as part of the plan for preparation of the test specimens. Problems resulting from this cause are less likely to be encountered with pure metals and homogeneous alloys.

The primary consideration should be the use of test specimens that are truly representative of the specified material, that is, alloy, metallurgical condition, and product form, rather than specimens that are the most expedient for the investigation. For example, it might seem advantageous to obtain flat, uniform disk specimens by machining slices from an extruded rod rather than by shearing or stamping test coupons from rolled sheet (and avoiding residual stresses in the sheared edges). However, the corrosion behavior of the end-grain surfaces of the machined disks could be different from that of the rolled surface of the sheet product.

Surface preparation by various grinding or polishing methods and various chemical treatments can be a source of considerable variation in test results and must be controlled. As a general rule, the corrosion-testing standards contain specific recommendations regarding appropriate surface treatments, depending on the metal alloy system. Judicious use of proper or standardized surface treatments reduces variability in corrosion test results, as discussed in ASTM G 1, “Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.”

Using electropolishing as a surface-preparation method requires a note of caution. The electropolishing operation typically involves dissolution of the metal through an oxide film. Exposure to these conditions can result in films that remain on the surface and do not characterize the surface of a mill-produced product. This can seriously distort the

corrosion behavior that is observed, particularly for metals that depend on the integrity of passive films for their corrosion resistance.

Specimen Cleaning. After the test, specimens must be cleaned and evaluated. In order to determine the amount of corrosion damage, all nonprotective corrosion products should be removed, so that the amount of weight loss during the exposure can be measured. The goal is to remove all of these products without removing any of the underlying metal. The options for removing corrosion products include scraping with a rubber stopper or stiff-bristle brush, chemical descaling, and electrochemical descaling. The recommended descaling solutions for each material and alloy system are identified in the corrosion testing standards (e.g., ASTM G 1). Inhibited hydrochloric acid for example, is recommended for the removal of corrosion products from steel, because it dissolves any porous corrosion products without attacking the underlying steel surface to a significant degree.

Specific Types of Laboratory Tests

Excluding electrochemical tests, which are described later in this chapter, laboratory tests can be grouped into three categories:

- Wetting of the surface by condensing media in humid atmospheres (simulated atmosphere tests)
- Spraying of aggressive media (salt spray tests)
- Immersion into corrosive liquid (immersion tests)

Table 1 compares the characteristics of these laboratory corrosion tests.

Table 1 Laboratory corrosion tests

Test	Conditions	Information
Simulated atmospheres		
Condensed water climate test	Saturated water vapor	Behavior in humid environment
Condensed water alternating climate test	Water vapor + SO_2, temperature change	As in condensed water climate test, with polluted gas
Salt spray tests		
Salt spray test	NaCl solution	Ocean climate
Acetic acid salt spray test	NaCl + CH_3COOH	Salted roads
Copper-accelerated acetic acid salt spray test	As in acetic acid salt spray test	As in acetic acid salt spray test, but more aggressive
Immersion tests		
Artificial sweat test	…	Wearing of decorative parts
Immersion test	Solutions of HCl, HNO_3, etc.	Wearing of decorative parts, corrosion in aqueous media

Simulated Atmosphere Tests

Simulated atmosphere tests are performed in closed cabinets (humidity-temperature chambers) under a variety of conditions ranging in temperature from freezing to 65 °C (150 °F) and in relative humidity from 20 to 100% (Fig. 2). The standard test procedure is to dry the samples and visually inspect them after a certain period (cycle), after which the test is repeated several times.

The simple condensed water climate test consists of 24 h cycles performed in saturated water vapor at 40 °C (105 °F). The corrosion processes are accelerated by intensifying such factors as temperature, relative humidity, condensation of the moisture, and corrosive agents such as sulfur dioxide (SO_2), chlorides, ammonia, etc. This test is described in ISO standard 7384, "Corrosion Tests in Artificial Atmospheres." This standard applies to metals and alloys with and without permanent or temporary corrosion protection.

The condensed water alternating climate test consists of 24 h cycles of changing temperature conditions (e.g., water vapor plus 0.07 to 0.7 vol% SO_2 at 18 to 28 °C, or 64 to 82 °F, and 40% humidity, then 75 to 100 °C, or 166 to 212 °F, and 40% humidity). This test is described in ASTM G 87, "Standard Practice for Conducting Moist SO_2 Test."



Fig. 2 Chamber for testing materials under a variety of temperature and humidity conditions.

Moist air that contains SO_2 quickly produces easily visible corrosion on many metals in a form resembling that which occurs in industrial environments. It is therefore a test environment that is well suited to the detection of pores or other sources of weakness in protective coatings, as well as deficiencies in corrosion resistance associated with unsuitable alloy composition or treatments.

Other Standard Tests. ASTM G 60, "Method for Conducting Cyclic Humidity Tests," is a procedure used to observe the behavior of steels under test conditions that retard the formation of a protective type of rust. Some humidity tests are used for evaluating various nonmetallic materials of construction that are used in contact with metals, such as thermal insulation products and leather. Examples of humidity tests include the following:

- ASTM C 665, "Specification for Mineral Fiber Blanket Thermal Insulation for Light Frame Construction and Manufacturing Housing"
- ASTM C 739, "Specification of Cellulosic Fiber (Wood-Base) Loose-Fill Thermal Insulation"
- ASTM D 611, "Test Method for Corrosion Produced by Leather in Contact with Metal"

Salt-Spray Testing

Salt-spray tests have been used for more than 90 years as accelerated tests in order to determine the corrodibility of nonferrous and ferrous metals, as well as the degree of protection afforded by both inorganic and organic coatings on a metallic base. This procedure has been extensively discussed since its inception because of the reproducibility variances and the questionable correlation of results as related to the actual service performance. The primary objective of this type of test is to provide an easily applied and acceptable standard for comparing the performance of materials and coatings. Typical salt-spray cabinets are shown in Fig. 3.

The most commonly used and accepted salt-spray test methods in the United States are the various methods outlined in ASTM standard B 117, "Standard Method of Salt Spray (Fog) Testing," and G 85, "Standard Practice for Modified Salt Spray (Fog) Testing." Many government agencies and automotive companies have also written their own standards and procedures.

Applications. The salt-spray (fog) test has received its widest acceptance as a tool for evaluating the uniformity of thickness and degree of porosity of metallic and nonmetallic protective coatings. It has served this purpose with a great deal of success. The test is useful for evaluating different lots of the same product, once a standard

level of performance has been established, and it is especially helpful as a screening test for revealing a particularly inferior coating. In recent years, certain cyclic acidified salt-spray (fog) tests have been implemented to test the resistance of aluminum alloys to exfoliation corrosion. The salt-spray (fog) test is considered to be most useful as an accelerated laboratory corrosion test that simulates the effects of marine atmospheres on different metals, with or without protective coatings.

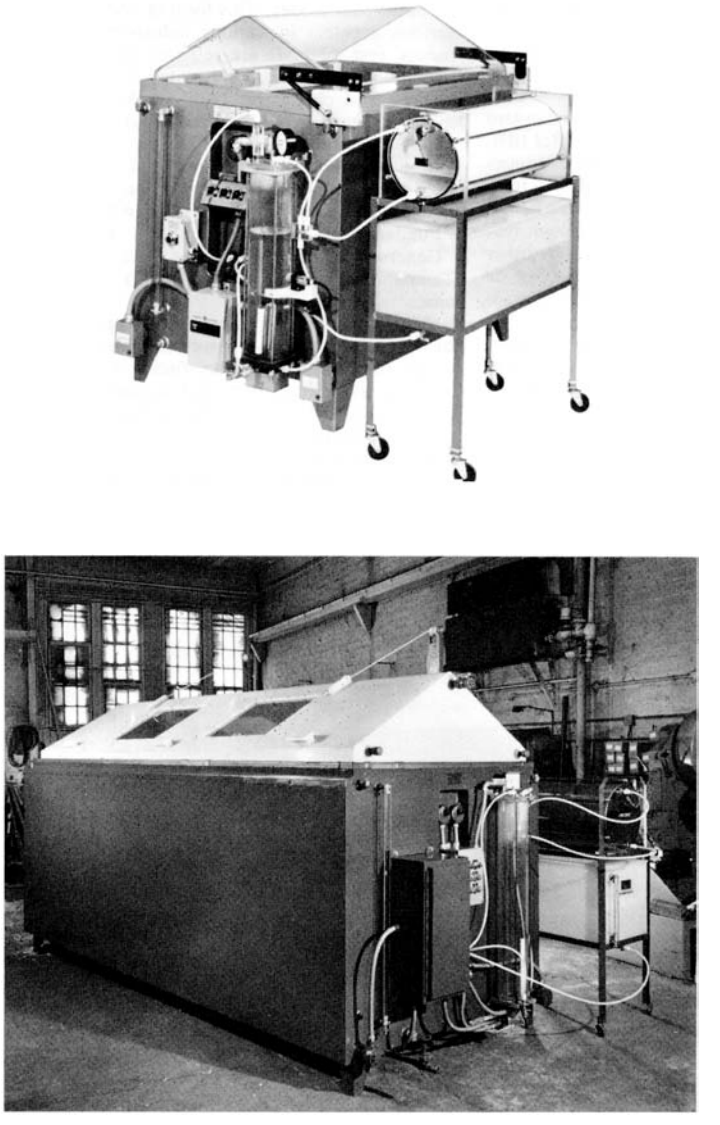


Fig. 3 Typical examples of top-opening salt spray cabinets with state-of-the-art features and pertinent accessories. Cabinets range in size from 0.25 to 4.5 m^3 (9 to 160 ft^3).

The neutral salt-spray (fog) test (ASTM B 117—Method 811.1 of Federal Test Method 151b) is perhaps the most commonly used salt spray test in existence for testing inorganic and organic coatings, especially where such tests are used for material or product specifications. The duration of this test can range from 8 to 3000 h, depending on the product type of coating. A 5% sodium chloride (NaCl) solution that does not contain more than 200 ppm total solids and with a pH range of 6.5 to 7.2 when atomized is used. The temperature of the salt spray cabinet is controlled to maintain 35 + 1.1 or –1.7 °C (95 + 2 or –3 °F) within the exposure zone of the closed cabinet.

The Acetic Acid-Salt Spray (Fog) Test (ASTM G 85, Annex A1; Former Method B 287) is also used for testing inorganic and organic coatings, but is particularly applicable to the study or testing of decorative chromium plate (nickel-chromium or copper-nickel-chromium) plating and cadmium plating on steel or zinc die-castings and for the evaluation of the quality of a product.

This test can be as brief as 16 h, although it normally ranges from 144 to 240 h or more. As in the neutral salt spray test, a 5% NaCl solution is used, but the solution is adjusted to a pH range of 3.1 to 3.3 by the addition of acetic acid, and again, the temperature of the salt spray cabinet is controlled to maintain 35 + 1.1 or –1.7 °C (95 + 2 or –3 °F) within the exposure zone of the closed cabinet.

The Copper-Accelerated Acetic Acid-Salt Spray (Fog) Test (CASS test), which is covered in ASTM B 368, is primarily used for the rapid testing of decorative copper-nickel-chromium or nickel-chromium plating on steel and zinc die-castings. It is also useful in the testing of anodized, chromated, or phosphated aluminum. The duration of this test ranges from 6 to 720 h. A 5% NaCl solution is used, with 1 g of copper II chloride ($CuCl_2$-$2H_2O$) added to each 3.8 L of salt solution. The solution is then adjusted to a pH range of 3.1 to 3.3 by adding acetic acid. The temperature of the CASS cabinet is controlled to maintain 49 + 1.1 or –1.7 °C (120 + 2 or –3 °F) within the exposure zone of the closed cabinet.

Other Standard Tests. Many new salt-spray test procedures have been developed in the past 30 years in order to achieve tests that are more closely aligned with specific applications. These modifications include a cyclic acidified salt-spray (fog) test (ASTM G 85, Annex A2), and acidified synthetic seawater-spray (fog) test (ASTM G 85, Annex A3: Former Method G 43), and a salt/sulfur dioxide (SO_2) spray (fog) test (ASTM G 85, Annex A4). The cyclic acidified salt spray (fog) test and the acidified synthetic seawater spray (fog) test are both primarily used for the production control of exfoliation-resistant heat treatments for various aluminum alloys. The salt/SO_2 spray (fog) test is mainly used to test for the exfoliation corrosion resistance of various aluminum alloys and a wide range of

nonferrous and ferrous materials and coatings, both inorganic and organic, when exposed to an SO_2-laden salt spray (fog).

ASTM D 2830, "Standard Guide for Testing Filiform Corrosion Resistance of Organic Coatings on Metal," describes three procedures for determining the susceptibility of organically coated metal substrates to the formation of filiform corrosion. In procedure A, scribed panels are subjected to a preliminary exposure in a salt spray cabinet (per ASTM B 117 as mentioned above) to initiate corrosion, rinsed, and placed in a humidity cabinet that operates at 25 ± 2 °C (77 ± 3 °F) and 85% relative humidity. In procedure B, which is based on ISO 4623, "Paints and Varnishes—Filiform Corrosion on Steel," scribed panels are either exposed to salt spray or dipped in a salt solution but not rinsed prior to being placed in the humidity cabinet. In procedure C, scribed specimens are exposed as in procedure A except the humidity cabinet is operated at 40 ± 2 °C (105 ± 3 °F). Depending on the test method selected, test periods range from as little as 4 h to as much as 6 weeks (refer to ASTM D 2803 for details).

Immersion Tests

Immersion tests can be divided into three types: total immersion, partial immersion, and alternate, or intermittent, immersion. The type of test selected is determined mostly by the environmental conditions that must be simulated. For example, if the equipment is immersed in service, then the test specimens should be immersed in the laboratory test; or if the exposure is alternating immersion and atmospheric exposure, then a cyclic exposure to wet/dry conditions should be used. Table 2 summarizes some of the more common forms of corrosion and the ap-

Table 2 Common forms of corrosion and laboratory immersion tests

Mode of attack	Evaluation tests	ASTM standard
General corrosion	Total immersion (atmospheric and autoclave)	G 31
	Multiphase (liquid, vapor, condensate, interface)	G 31
Stress-corrosion cracking	Boiling chloride U-bend	G 36
	Wick test	C 692
	Polythionic acid cracking	G 35
	3.5% sodium chloride	G 44
Pitting corrosion	Ferric chloride immersion	G 48
	Cyclic potentiodynamic polarization (hysteresis)	G 61
	Critical pitting/crevice temperature determination	G 48
	Seawater/marine exposure testing	G 78
	Surgical implant	F 746
	Critical pitting potential (potentiostatic)	G 5
Crevice corrosion	Multi-crevice washer/process solutions	G 48
Intergranular corrosion	Electrolytic oxalic acid screening	A 262
	Nitric acid (Huey test)	A 262
	Ferric sulfate-sulfuric acid (Streicher test)	A 262
	Copper sulfate-sulfuric acid	A 262
Dealloying (dezincification)	Total immersion testing for dealloying	G 31
Exfoliation (aluminum alloys)	Ammonium chloride-ammonium nitrate-ammonium tartrate-hydrogen peroxide (ASSET test)	G 66
	Sodium chloride-potassium nitrate-nitric acid (EXCO test)	G34
Galvanic corrosion	Dissimilar metal couple immersion	G 31

propriate immersion tests used to evaluate the susceptibility of a material to a specific mode of attack.

Total Immersion Tests. ASTM standard G 31, "Practice for Laboratory Immersion Corrosion Testing of Metals," and NACE standard method TM0169, "Laboratory Corrosion Testing of Metals," are general guides on how these tests may be performed. They also describe the following test variables that must be considered for proper interpretation of test results:

- Solution composition, temperature, aeration, volume, velocity, and waterline effects
- Specimen surface preparation
- Duration of test
- Method of cleaning specimens at conclusion of the exposure

For typical immersion tests, small specimens (e.g., 2.5 cm by 5 cm by 0.3 cm thickness) of the candidate material are exposed to the test solution, and the loss of weight of the material is measured for a given time period. Immersion testing remains as one of the best methods of screening and eliminating from further consideration those materials that should not be considered as useable materials.

Partial Immersion Tests. Laboratory tests conducted under conditions of partial immersion are of practical importance, because such conditions are commonly found in service. Tests conducted in three locations in a resin flask, as shown in Fig. 4, can be used to determine the relative susceptibility of a material to localized corrosion at the liquid line. Partial immersion conditions provide a very suitable accelerated test for metals such as aluminum alloys and others that develop concentrated attack at the liquid line (or splash zone, in certain equipment).

Alternate Immersion Tests. Alternate immersion refers to repeated immersion in and removal from a liquid corrosive. These conditions are of practical importance because they simulate, for example, the effects of the rise and fall of tidal waters and the movements of corrosive liquids in chemical plants. In addition, these conditions can provide a relatively rapid test for the effect of aqueous solutions, because a thin film of the solution, frequently renewed and almost saturated with oxygen, can be maintained on the test specimen during most of the exposure period, even when the shape of the specimen is complex.

To simulate service conditions, the specimens should be dry before reimmersion, because this has an important effect on the protective character of films on the metal. To achieve maximum corrosion, this drying should be done slowly to allow the corrosive film on the metal the maximum amount of time to act during immersion. In the interest of reproducibility, it is desirable to control the humidity and temperature of the atmosphere in order to endure a constant rate of drying in successive cycles.

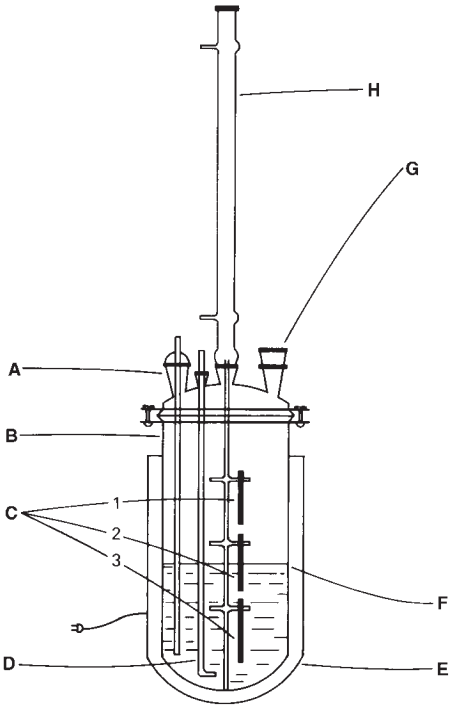


Fig. 4 Resin flask used to conduct simple immersion tests. A, thermowell; B, resin flask; C, specimens hung on supporting device (C-1, vapor phase; C-2,partial immersion; C-3, total immersion); D, air inlet; E, eating mantle; F, liquid interface; G, opening in flask for additional apparatus that may be required; H, reflux condenser

The usual methods of immersion involve:

- Placing specimens on a movable rack that is periodically lowered into a stationary tank containing the solution. A large apparatus of this type is shown in Fig. 5.
- Placing specimens on a hexagonal Ferris wheel arrangement that rotates every 10 min through 60° and thus passes the specimens through a stationary tank of solution.
- Placing specimens in a stationary tray that is open to the atmosphere and moving the solution by air pressure, a nonmetallic pump, or a gravity drain from a reservoir to the tray.

An important feature of each of these alternate immersion techniques is that the wet/dry cycle must be well controlled and reproducible.

Alternate Immersion in 3.5% Sodium Chloride (NaCl). The conditions of this test have gained the most widespread acceptance, particularly in the United States, are those described in ASTM G 44, "Standard Recommended Practice for Stress Corrosion Testing in 3.5% Sodium Chloride Solution." This practice utilizes a 1 h cycle, which

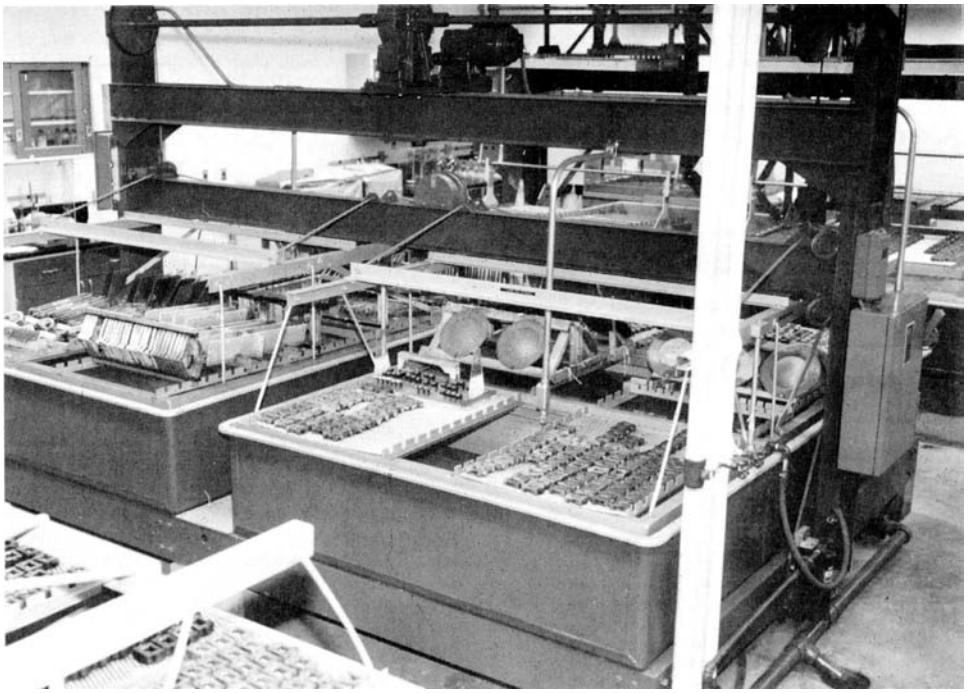


Fig. 5 Lift-type alternate-immersion apparatus. Specimens shown are in the emersion position, where they remain for 50 min. They are then lowered into the tanks of saltwater for 10 min to complete the 1 h cycle. Many shapes and sized of specimens can be tested in this large equipment.

includes a 10 min period of immersion in an aqueous solution of 3.5% NaCl or in substitute ocean water, followed by a 50 min emersion period. This 1 h cycle is continued 24 h/day for the test duration required for the particular test material. Aluminum and steel alloys are typically exposed from 10 to 90 days or more, depending on the resistance of the alloy to corrosion by saltwater. Although this alternate-immersion test is considered to be an accelerated test representative of certain natural conditions (particularly marine environments), it is not intended to relate to specialized chemical environments. A comparison of the stress-corrosion cracking (SCC) behavior of a variety of aluminum alloys in the ASTM G 44 test and in a severe seacoast atmosphere is shown in Table 3.

Field Tests

Examples of field tests are atmospheric exposure of a large number of specimens in racks at one or more geographical locations and similar tests in soils or seawater. Only corrosion testing in the atmosphere is discussed in this section. Information pertaining to testing in waters and

Table 3 Comparison of the SCC behavior of various aluminum alloys in the ASTM G 44 test and after 5 years in a seacoast atmosphere

3.2 mm (⅛ in.) diam short-transverse tension specimens obtained from 64 mm (2.5 in.) thick hot-rolled plate; nine replicate specimens per test stress

Alloy and temper	Applied stress			Number of failures		Time to first and median failure, days			
				ASTM	Seacoast	ASTM G 44(a)		Seacoast atmosphere(b)	
	MPa	ksi	% of yield strength	G 44(a)	atmosphere(b)	First	Median	First	Median
2024-T351	145	21	50	9	9	7	7	37	37
	87	12.6	30	9	9	7	7	37	37
2024-T851	295	42.8	75	8	8	37	65	37	266
	197	28.6	50	0	2	…	…	643	…
5456-H116	156	22.6	75	0	0	…	…	…	…
6061-T651	254	36.8	90	0	0	…	…	…	…
7050-T7651	227	32.9	50	0	0	…	…	…	…
	136	19.7	30	0	0	…	…	…	…
	91	13.2	20	0	0	…	…	…	…
7050-T7451	217	31.5	50	0	0	…	…	…	…
	130	18.9	30	0	0	…	…	…	…
	87	12.6	20	0	0	…	…	…	…
7075-T651	221	32	50	…	9	…	…	7	7
	154	22.3	35	9	9	7	7	7	15
	88	12.8	20	9	9	7	67	7	37
7075-T7651	300	43.5	75	8	6	69	77	709	1491
	200	29	50	0	1	…	…	1069	…
	120	17.4	30	…	0	…	…	…	…
7075-T7351	335	48.6	90	6	2	67	80	1866	…
	273	39.6	75	0	0	…	…	…	…
	183	26.5	50	…	0	…	…	…	…

(a) Alternate immersion in 3.5% sodium chloride solution for 84 days. (b) Point Judith, RI

soils can be found in the selected references listed at the conclusion of this chapter.

Atmospheric Tests

Atmospheric field tests evaluate the general corrosion behavior of a material or determine its resistance to solar radiation, coating discoloration, pitting, galvanic effects, loss of strength, stress-corrosion cracking, or other changes in physical properties. For example, alloy producers have used outdoor atmospheric exposure tests to evaluate the performance of new alloys in a variety of atmospheric conditions. Atmospheric corrosion testing has also been used to test both metallic and nonmetallic coatings to demonstrate their performance in atmospheric conditions. Manufacturers of items designed to be used in outdoor conditions sometimes expose components to various atmospheres to demonstrate their performance and develop data on the service life that may be expected. In some cases, atmospheric exposure programs are run to determine the corrosivity of specific atmospheres. This type of information can be helpful in selecting coatings or other corrosion protection systems to be used at specific sites.

Types of Atmospheres. Historically the severity of the environment has been indicated by designating the environment as rural, urban, industrial, or marine, or a combination of these.

A rural atmosphere is normally classified as one that does not contain chemical pollutants but does contain organic and inorganic dusts. Its principal corrodent is moisture and, of course, oxygen and carbon dioxide. Arid or tropical atmospheres are special cases of the rural environment because of their extreme relative humidities and condensations. The rural atmosphere is generally the least corrosive.

An urban atmosphere is similar to the rural environment in that it is away from the industrial complexes. Materials exposed in these areas are subjected to the normal precipitation patters and typical urban contaminants of SO_x and NO_x emitted by motor vehicles and home fuels.

An industrial atmosphere is typically identified with heavy industrial manufacturing facilities. These atmospheres can contain concentrations of sulfur dioxide, chlorides, phosphates, nitrates, or other specific industrial emissions. These emissions combine with precipitation or dew to form the liquid corrosive.

A marine atmosphere is laden with fine particles of sea salt carried by the winds and deposited on materials. The marine atmosphere is usually one of the more corrosive atmospheric environments. It has been shown that the amount of salt (chlorides) in the marine environment decreases with increasing distance from the ocean and is greatly influenced by wind direction and velocity.

Atmospheric Factors. The corrosion or degradation of materials in the atmosphere occurs naturally. The rate of degree of degradation varies for different materials and is influenced by several environmental factors. Many of these factors are natural in origin, but some result from man-made sources. Among the latter sources, which are known to affect atmospheric degradation of materials, are the SO_x and NO_x compounds produced as fossil fuel combustion by-products. These species can react with moisture in the atmosphere and result in acid deposition. Although considerable public attention is focused on the effects of acid deposition on our ecosystem, the potential damage to materials may represent the largest economic impact of acid deposition.

Some of the important factors that should be considered when conducting atmospheric tests are listed in Table 4. Table 5 lists the typical activity ranges of SO_x and Cl^- in the various environments. The relative corrosivity of different environments is compared in Table 6, which summarizes site comparisons for atmospheric-corrosion behavior of steel and zinc.

Materials to Be Exposed. Atmospheric-corrosion studies are usually carried out for a period of months and even years to ascertain the environmental effects on the degradation of the materials evaluated. Therefore, it is important to select standard or reference materials (control specimens or materials) that will be exposed alongside of the materials, alloys, or coating of interest. Control materials with a prior performance record in the exposure environment are extremely important for

comparison purposes and for monitoring site corrosivity. For example, ISO 9223, "Corrosion of Metals and Alloys Classification of the Corrosivity of Atmospheres," provides recommendations on low-carbon low-copper steel, commercial-purity aluminum, commercial-purity

Table 4 Environmental parameters suggested for consideration of their influence on the atmospheric degradation of materials

Wet deposition

pH
Conductivity
Cations: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^{2+}), potassium (K^{+}), ammonium (NH_4^{+}), and hydrogen (H^{+})
Anions: sulfates (SO_4^{2-}), nitrates (NO_3^{-}), and chlorides (Cl^{-})

Dry deposition

Sulfur dioxide (SO_2)
Nitrogen dioxide (NO_2), nitric acid (HNO_3)
Ammonia (NH_3)
Particulate matter, sulfates, nitrates

Meteorology

Wind speed
Wind direction
Relative humidity (dew point)
Temperature
Solar radiation
Rainfall volume and intensity

Others

Test specimen surface temperature
Time of wetness
Test specimen orientation

Note: Time of wetness and the quantity of SO_2 and chloride are the most important variables in determining atmospheric corrosion. Such factors as hydrogen sulfide, nitrogen compounds, and other specific pollutants may be significant at specific sites if sources of these pollutants are located nearby.

Table 5 Typical activity ranges of SO_x and chlorides measured in various atmospheres

These are average activity ranges measured over a 20–25 month period.

	Activity range, $mg/dm^2/day$	
Atmosphere	**SO_x**	**Cl^-**
Industrial	0.5–2	nil
Urban	0.5–4	nil
Rural (semi)	nil–2	nil
Marine	nil–0.5	25–150

Table 6 Relative corrosivity of atmospheres at different locations

Location	Type of atmosphere	Average weight loss of iron specimens in 1 year, mg/cm^2	Relative corrosivity
Khartoum, Sudan	Dry island (arid)	0.08	1
Singapore	Tropical/marine	0.69	9
State College, PA	Rural	1.90	25
Panama Canal Zone	Tropical/marine	2.28	31
Kure Beach, NC (250 m, or 800 ft, lot)	Marine	2.93	38
Kearny, NJ	Industrial	3.92	52
Pittsburgh, PA	Industrial	4.88	65
Frodingham, UK	Industrial	7.50	100
Daytona Beach, FL	Marine	10.34	138
Kure Beach, NC (25 m, or 80 ft, lot)	Marine	35.68	475

zinc, and commercial-purity copper as recommended control metals. The various reference materials selected by ISO for their exposure programs were chosen because they are representative engineering materials that are widely used and frequently employed in external exposures. The materials were also selected, for comparison purposes, because they have known performance records in various environments and documented corrosion behaviors to different atmospheric constituents. Site corrosivity varies occasionally and underscores the need for simultaneous exposure of test and reference materials.

The number of duplicate or replicate specimens depends on the exposure period and the number of scheduled removals. For visual observations, two specimens for each environment are usually sufficient. Specimens that have been removed and cleaned should not be reexposed, because reexposure would, in essence, be starting the exposure period at time zero again.

Test Specimens. Some of the more common atmospheric test specimens are listed in Table 7. These specimens are used to determine susceptibility to general corrosion, galvanic corrosion, and stress corrosion. Probably the most widely used specimen is a 100 by 150 mm (4 by 6 in.) flat panel. This type of panel is very suitable for mass loss measurements (general corrosion). It is also used for evaluating coatings and is convenient to handle.

Atmospheric stress corrosion tests are frequently run with U-bend specimens or two-point loaded specimens. U-bend specimens are used when the stress level is not a variable, but it is desired to determine if an alloy is susceptible to cracking. Two-point loaded specimens have the advantage of being held at points of low stress and at locations where a crevice will do the least damage. It is relatively simple to construct racks to hold two-point loaded specimens. A two-point loaded specimen can be designed to cover a wide range of maximum stresses. Other types of standard stress specimens may also be used, for example, direct

Table 7 Atmospheric test specimens

Type	Standards
Flat panel	
100 by 150 mm	ASTM G 50
100 by 200 mm	ASTM G 50
100 by 300 mm	ASTM G 50
Helix-wire	…
Stress-corrosion cracking	
Bent beam	ASTM G 39
C-ring	ASTM G 38
U-bend	ASTM G 30
Direct tension	ASTM G 49
Welded	ASTM G 58
Galvanic	
Plate on plate	ASTM G 104
Disk on disk	…
Wire on bolt	…
Coated specimen	ASTM D 1654
Fabricated items	…

tension specimens, C-ring specimens, and other bent beam configurations. Figure 6 shows four common atmospheric SCC test specimens.

Exposure Guidelines. Specimens are normally exposed on a test rack similar to that shown in Fig. 7. The rack is then attached to a frame or stand. Specimen sizes are normally 100 by 150 mm (4 by 6 in.) but can be any size necessary to evaluate the behavior of the material properly. The specimens should be isolated from each other and the exposure rack by some nonconductive material, for example, porcelain insulators.

The normal convention used for specimen orientation is as follows. Specimens exposed in the northern hemisphere normally face south, and specimens exposed in the southern hemisphere face north. Also, it is common practice to expose specimens facing the most corrosive direction if the exposure site is close to a source of corrodent, such as seawater or power plant stacks. The ASTM standard G 50, "Practice for

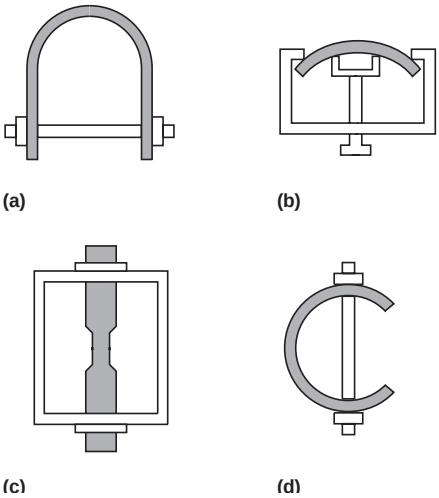


Fig. 6 Specimens for atmospheric stress-corrosion tests. (a) U-beam specimen. (b) Bent-beam specimen. (c) Direct tension specimen. (d) C-ring specimen

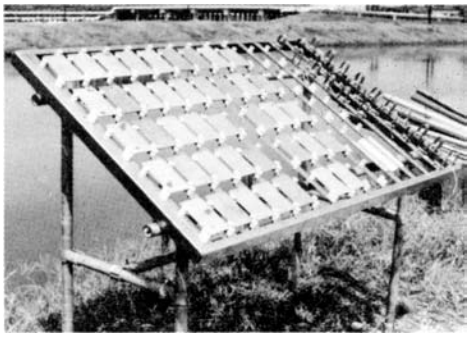


Fig. 7 Atmospheric-corrosion test rack

Conducting Atmospheric Corrosion Test on Metals," recommends that specimens be exposed on an angle of 30° to the horizontal (this angle has been established to be 45° in Europe). If maximum exposure to sunlight is desired, the specimens should be exposed at an angle equal to the latitude of the site.

Another type of exposure can be obtained with the dynamic (or mobile) test where test panels are mounted on vehicles to simulate the service conditions of cars or trucks. Vehicles are exposed to significant amounts of spray and splash from the road surface and, as a consequence, this environment is significantly different from that normally experienced in static (test rack) exposures. In some cases, panels have been mounted on the sides of trucks to allow a larger number of panels to be mounted in approximately the same type of environment. Panels mounted on automobiles are generally mounted in locations where they are not visible, although in some cases bumper-mounted panels have been used. Variability in dynamic tests is substantial, because no two vehicles see exactly the same environment. A similar situation exists for ocean-going vessels. The atmospheric corrosion that occurs on aircraft carriers, for example, is unique, because it incorporates both marine spray from the ocean and flue gases from the engines.

Evaluation of Results. A number of techniques are available for evaluating test panels and interpreting test results (Table 8) after exposure of test panels to the atmosphere. The most important step in atmospheric-corrosion testing is the documentation of results and observations for future reference and application. This reporting can take the form of internal company reports, technical papers, or presentations.

Table 8 Evaluation techniques for atmospheric-corrosion specimens

Technique	Value
Photographic documentation	Photographs of the specimens before and after cleaning give a permanent record of the performance of the material in the particular atmosphere.
Corrosion product analysis and surface deposits	Atmospheric-corrosion specimens usually have the corrosion product and airborne deposits on the surface at the time of removal. This adds a wealth of information on the observed behavior of the material.
Weight loss	For uniform corrosion, this is simple and can be converted to corrosion rate as g/m^2/day, mils per year, etc.
Pitting and localized corrosion	Yields information on the susceptibility of a material to localized attack. Pitting corrosion is often reported as average or maximum depth of attack and is usually measured with a dial depth gage or vernier microscope. Where possible, pitting data should be treated statistically with recognized methods covered in various standards. Weight loss data should not be used indiscriminately to calculate corrosion rates where the primary form of corrosion is localized.
Rust or rust stain	Data reveal the propensity of a material to rust and the degree of rust staining. Also, through cleaning procedures, it can be determined if the original appearance was retained.
Tensile test and other physical tests	Can often yield information on the atmospheric effect on the strength of materials, cracking behavior, etc.
Appearance	Effect of environment on appearance, color retention, etc.

In all cases, the author should attempt to outline the objectives of the work, the exposure details, and the conclusions of the exposure program.

Electrochemical Tests

Electrochemical test methods primarily focus on the control and measurement of the fundamental properties of electrochemical reactions. The electrochemical potential is equivalent to the driving force for reactions, and it determines the reactions that can occur at the anode and cathode in an electrochemical cell. The current is equivalent to the reaction rate in an operating corrosion cell. The greater the current, the greater the corrosion rate; that is, the polarization of an operating corrosion cell is due to activation polarization, concentration polarization, and ohmic polarization. The sum of all these resistance elements throughout the corrosion cell determines the resultant current for a given value of potential difference between the anode and cathode. Using electrochemical techniques, it is possible to control the potential at desired levels and to measure the resulting current. Similarly, the potential can be measured in operating cells when the current is controlled in operating cells. The resistance, or polarization, elements throughout the cell also can be measured. Knowing these fundamental properties gives great insight into the effects of material and environmental changes on corrosion behavior, as well as the mechanisms of corrosion.

Electrochemical Test Classification

The general classes of electrochemical measurements are the following:

- Potential
- Current
- Resistivity
- Polarization curves
- Linear polarization
- Frequency response (alternating-current impedance)

Potential, current, and resistance properties are measured either individually or collectively. The combined measurement of potential and current relationships for an operating corrosion cell over a wide range of oxidizing conditions results in polarization curves that describe the electrochemical reactions. The combined measurement of potential and current at potentials that are very close to the freely corroding potential of the system gives rise to linear polarization curves. Both of these com-

bined potential and current measurements have useful applications in corrosion control. Alternating-current (ac) impedance, or electrochemical impedance spectroscopy, is a method that determines the electrochemical response of a corrosion cell over a wide range of frequencies. The advantage of this method is that it can provide useful information on both the resistance and capacitance elements of the operating system. Although there are many types of electrochemical test measurements, they are all variations of the classifications listed above.

Reference Electrode

A stable and reliable reference electrode is a critical component of most electrochemical test methods. It is used with an electrometer to measure the electrochemical potential of a metal surface in a given environment. When a stable reference electrode is used, any changes in potential can be related to changes at the metal surface of interest. The requirements of a reference electrode are the following:

- A reproducible potential for the reference electrode itself
- A stable (unchanging) potential of the reference electrode
- A convenient and durable construction

Several reference electrode systems meet these requirements, and they are used in a broad range of electrochemical test techniques in laboratory and field applications. The selection of a particular reference electrode depends on the given application. Factors that influence selection are the required degrees of accuracy, durability, and ruggedness, and the properties of the specific corrosive environment.

The construction of a copper/copper sulfate reference electrode is shown in Fig. 8. The object is to provide a device that maintains a steady and reproducible potential. The reference electrode can then be used in conjunction with an electrometer or voltmeter to measure the potential of the metal surface of interest.

The stable potential for a copper/copper sulfate electrode is achieved by exposing a copper rod to a copper-sulfate solution with a fixed concentration of copper ions in solution. The copper-ion concentration is fixed by maintaining the solution at saturation with copper sulfate crystals. As long as copper sulfate crystals remain in contact with the solution, it is known that the copper ions in solution are at their solubility limit. The copper rod extends through the housing of the reference electrode and provides a point of attachment for a lead wire to the electrometer. A porous plug at the end of the copper/copper sulfate reference electrode provides for electrical contact with the corrosive environment, such as seawater or soil.

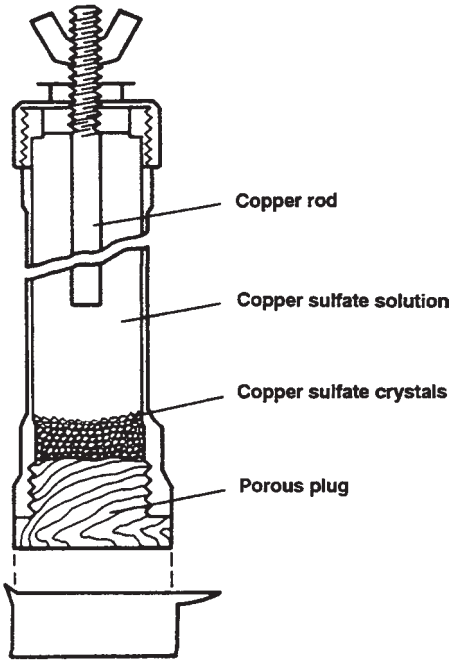


Fig. 8 A copper/copper sulfate reference electrode

The body of the reference electrode is made from a durable and impact-resistant polymeric material. A removable endcap is provided to protect the electrode when it is not in use. All reference electrodes have similar features, in that the stable reference potential is achieved by maintaining a metal surface in contact with an environment of controlled chemical composition. By fixing the concentration of species in the environment, the potential of the metal surface is fixed.

Standard reference electrodes that are identified in Table 9 include a standard hydrogen electrode, a silver/silver chloride electrode, a saturated calomel electrode, and a copper/copper sulfate electrode. The electrode reaction to fix the potential of the reference electrode is identified for each reference electrode. For the copper/copper sulfate electrode described above, the electrode reaction is copper in contact with saturated copper-sulfate solution, which fixes the copper-ion concentration in solution. For the standard hydrogen electrode, the electrode

Table 9 Standard reference electrodes

Name	Symbol	Electrode	Potential, V-SHE, at 25 °C (75 °F)
Standard hydrogen electrode	SHE	(Pt)[H_2 (a = 1)]/[H^+ (a = 1)]	0.000
1 *M* silver/silver chloride	…	Ag/AgCl/1 *M* KCl	+0.235
Saturated calomel electrode	SCE	Hg/Hg_2Cl_2/saturated KCl	+0.241
1 *M* calomel electrode	…	Hg/Hg_2Cl_2/1 *M* KCl	+0.280
0.1 *M* calomel electrode	…	Hg/Hg_2Cl_2/0.1 *M* KCl	+0.334
Copper/copper sulfate	$Cu/CuSO_4$	Cu/saturated $CuSO_4$	+0.30

reaction is that of the equilibrium between hydrogen ions in solution and hydrogen gas dissolved in the environment. The reaction occurs on an inert surface (in this case, platinum). The hydrogen-ion concentration is fixed at unit activity (*a*), and the hydrogen gas pressure is maintained at 0.1 MPa (1 atm) over that of the environment. For these conditions, the potential of the standard hydrogen electrode (SHE) is assigned a value of 0.000 V at 25 °C (75 °F). This standard reference value of zero for the potential scale has been set and accepted by international consensus. The potential of all other standard reference electrodes, and any measurements made with respect to any other reference electrodes, can then be converted to the saturated hydrogen electrode scale.

The values of standard reference electrodes with respect to the SHE are also presented in Table 9. For example, the copper/copper sulfate reference electrode has a value of +0.30 V, with respect to the SHE. Thus, any measurement made with respect to copper/copper sulfate would be converted to SHE by adding +0.30 to the measured value. When reporting any potential measurements, it is essential to identify the reference electrode with which the measurements were made.

Types of Electrochemical Measurements

The electrochemical measurements to be described include potential measurement, resistance measurement, current measurement, and polarization measurements.

Potential Measurement. The setup for measuring electrochemical potential is shown in Fig. 9. A voltmeter or an electrometer is connected to a reference electrode and to a working electrode or metal specimen in the environment of interest. The potential of the working electrode surface is then measured with respect to the reference electrode. The

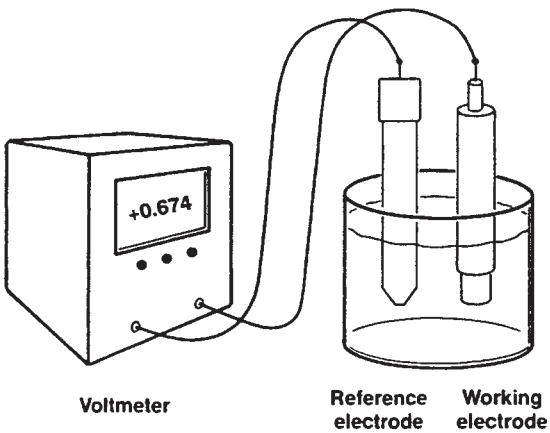


Fig. 9 Schematic of a potential measurement. Source: NACE International

internal resistance, or impedance, of the electrometer should be quite high in order to avoid changing the potential of the working electrode during the potential measurement. A high-resistance voltmeter allows only an extremely small current (essentially insignificant) to pass through the measuring circuit.

Although the working electrode in Fig. 9 is shown as a small test specimen, the potential could be established with an operating piece of equipment either directly or by making electrical contact with the metal surface of the equipment and then immersing a reference electrode in the solution in contact with the equipment and connecting a voltmeter. For test specimens, it is common practice to thread and tap the metal specimen so that a rod can be inserted into it for electrical connection to the voltmeter lead. The lead and connecting rod are insulated from the test environment either by compression gasket seals and insulating tubes or by masking off the environment with nonconducting polymeric coatings.

With a stable reference electrode, the potential measurements can be used to monitor changes in potential that are due to changes that occur at the metal surface or in the environment during the test time period. Potential measurements can be related to the regions of metal stability and reactivity in order to predict whether the metal will be immune, passive, or active under the operating conditions.

Resistance Measurements. The resistivity or, conversely, the conductivity of the environment can greatly affect corrosion behavior. The lower the resistance or greater the conductivity, the more readily corrosion current can flow between anodes and cathodes. A soil resistivity measurement is depicted in Fig. 10. This measurement technique, which is referred to as the four-pin method, is used to measure soil resistance when underground corrosion is a concern. The technique involves the insertion of four metal pins over the area of interest. The spacing between the pins is fixed (indicated by *a* in the diagram). A constant current is then applied between the outermost pins, and the potential between the inner two pins is then measured. This potential can be related

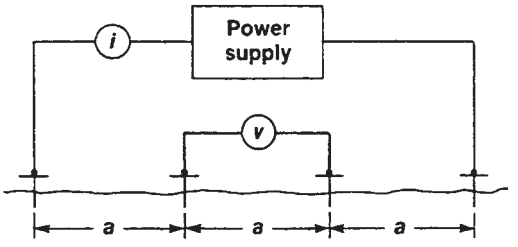


Fig. 10 Schematic of a soil resistance measurement

to the soil resistivity by the equation shown in Fig. 10. The method is a variation of Ohm's law, where the current is fixed, the potential is measured, and the resistance is calculated.

Current measurements are made in order to determine the current that flows between two components of a corrosion cell. A schematic diagram of a current measurement is shown in Fig. 11. An ammeter is attached between the working electrode (the specimen in the environment) and a counter, or auxiliary, electrode. An ammeter must have low internal resistivity in order to be appropriate for electrochemical test measurements. Because of the low resistance in the ammeter, the magnitude of the current that flows between the working electrode and the counter electrode is not significantly affected by the measuring device. Solid-state electronic devices can be used to build a zero-resistance ammeter, that is, a measuring device that has essentially zero resistance and, therefore, no effect on the operating electrochemical cell during the measurement.

Polarization experiments involve measuring the relationship between the electrochemical potential and the corrosion current. The potential-current response of the electrochemical cell is determined over a desired potential range. The experiments can be determined in two ways: potentiostatically, where the potential is controlled and the resulting current is measured, or galvanostatically, where the current is controlled and the resulting potential is measured.

The instrumentation setup for electrochemical polarization experiments is shown in Fig. 12. The potential of the working electrode, which is the metal specimen of interest, is measured with respect to a reference electrode coupled to the polarization cell by a salt-bridge probe. The salt-bridge probe is necessary in order to measure the potential near the working electrode surface. A counter (or auxiliary) electrode is placed

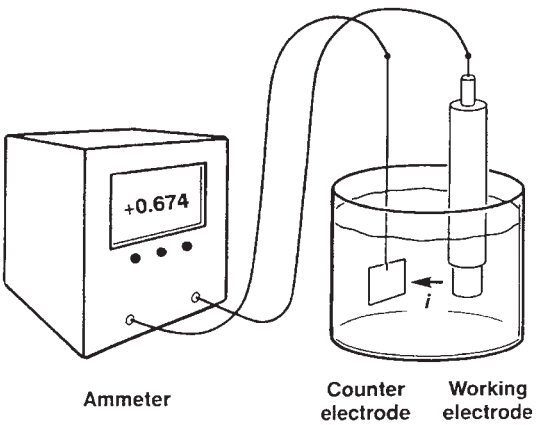


Fig. 11 Schematic of a current measurement. Source: NACE International

in the polarization cell to transmit impressed current through the solution, either to or from the working electrode surface.

The potentiostat is the electronic instrument that carries out the electrochemical polarization experiment. It comprises a power supply for impressed current on the electrochemical cell and circuits that measure and control the potential to set values. A high-impedance voltmeter measures the potential between the working electrode and the reference electrode without affecting the potential of the working electrode. A low-resistance ammeter measures the current flow between the counter and working electrodes, without affecting current flow.

An electrochemical cell is depicted in Fig. 13. The metal specimen, or working electrode, is contained in the center compartment of a three-electrode test cell. The counter electrode is contained in the compartment to the right, and a reference electrode is contained in the compartment to the left. A salt-bridge probe extends from the reference electrode compartment up to, but not touching, the working electrode.

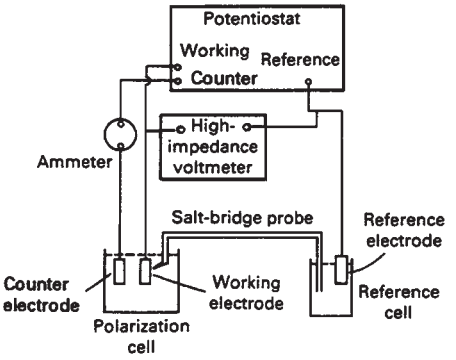


Fig. 12 Instrumentation setup for electrochemical polarization experiments

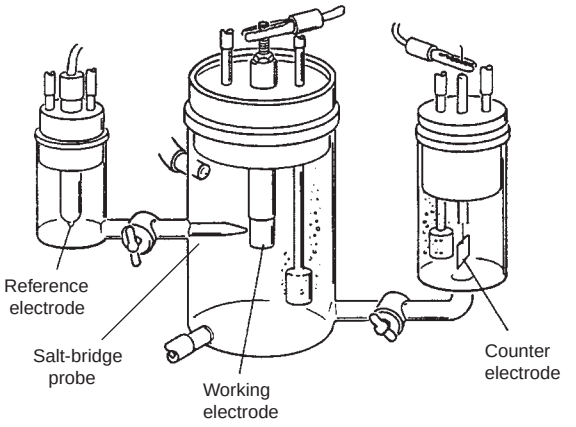


Fig. 13 An electrochemical cell for polarization experiments. Source: NACE International

Both the working electrode and counter electrode compartments are equipped with gas sparging tubes to allow the control of the solubility of gases in the environment. The working electrode and counter electrode are coupled by a solution path through a wetted stopcock joint. This permits the flow of current between the counter and working electrodes but reduces the likelihood of cross contamination of oxidation and reduction products between the two cell compartments.

Electrochemical test cells are available in many designs and are fabricated from many different materials, depending on the particular application. A schematic of a rather novel electrochemical test cell is shown in Fig. 14. This technique is used to determine the localized corrosion behavior (via polarization measurements) of orthopedic implant alloys in vivo, using a hamster as the test environment. The hamster was anesthetized and laid on a stainless steel plate. A specimen of the orthopaedic alloy was inserted underneath its skin. The reference electrode made contact through a saturated gauze pad. The results were compared with results from an in vitro test in saline and simulated biological fluids.

An electrochemical polarization test setup is shown in Fig. 15. The three-compartment electrochemical test cell is connected to a potentiostat, which is set to the desired voltage (for example, 0.674 V), with respect to a saturated calomel electrode (SCE). The potential of the working electrode surface is then measured, with respect to the SCE, by a high-impedance voltmeter. The potentiostat then provides the necessary current between the counter and working electrodes to control the potential of the working electrode surface to the desired value, that is, 0.674 V-SCE. If a potentiostatic polarization curve is being determined, then the current required to maintain the working electrode at 0.674 V would be determined, and the control voltage would be adjusted to the next desired value. This would be continued until the potential versus current behavior was measured over the desired potential range.

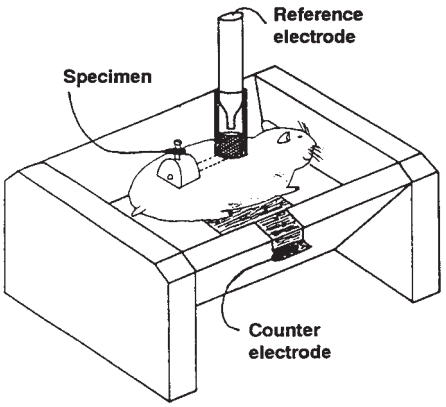


Fig. 14 Schematic of an in vivo electrochemical polarization test with a hamster

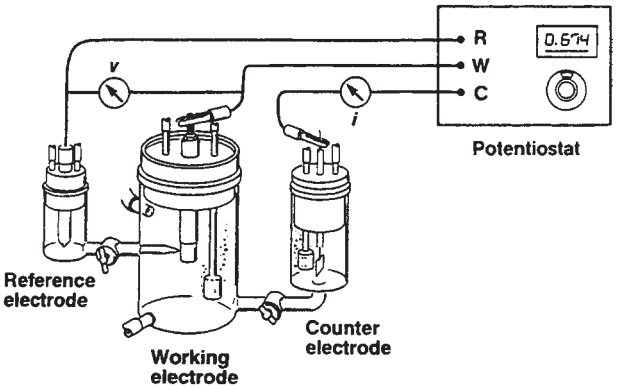


Fig. 15 Schematic of an electrochemical polarization test setup. Source: NACE International

Applications of Electrochemical Tests

Galvanic Series. Potential measurements can be used to determine a galvanic series for metals in the environment of interest. The relative position and distance between metals in the galvanic series depend on the particular environment. The galvanic series is further described in Chapters 2, 3, and 4.

The procedure to determine the galvanic series is to make a series of potential measurements for the metals of interest with respect to a reference electrode in the environment. The experimental setup is shown in Fig. 16. The metals are listed from the most noble, that is, the greatest positive value with respect to the reference cell, to the most active, that is, those with the greatest negative value of potential.

This galvanic series enables an estimation of the likelihood and magnitude of galvanic effects between dissimilar metals in the environment. The greater the separation between the metal in the series, the

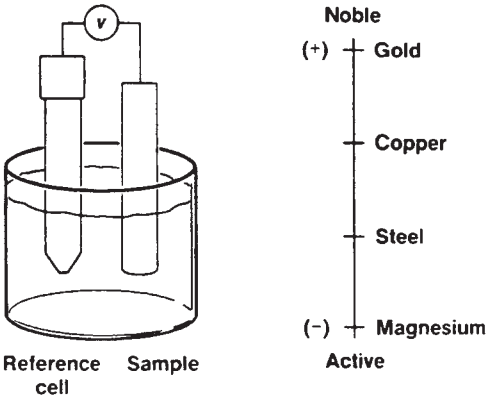


Fig. 16 Experimental setup to determine a galvanic series. Source: NACE International

more severe the galvanic effects can be. A metal that is more positive will act as a cathode, while a metal that is more negative will act as an anode, if the two metals are in electrical contact in the environment. The corrosion of the anodic metal in the galvanic couple will be increased by the detrimental galvanic action.

Galvanic Corrosion Rate. Although the galvanic series can both provide an estimate of the likelihood for galvanic action between dissimilar metals and identify which metal will be adversely affected by the galvanic couple, it cannot indicate the magnitude of the galvanic action. The measurement of the current that passes between two dissimilar metals gives a direct measure of the galvanic corrosion rate.

Figure 17 shows the current measurements for the galvanic corrosion rate between dissimilar metals. The current that flows from the anode to the cathode is measured by a low-resistance ammeter. This galvanic corrosion current can be expressed as a weight loss, or penetration rate, of the anodic material using Faraday's law and conversions that are based on the density of the metal and the exposed area of the anode. These measurements are useful supplements to galvanic series measurements, because they indicate the actual galvanic effect on the metal. The detrimental galvanic action is determined not only by the potential difference between the anodic metal and the cathodic metal, but also by their relative polarization behavior. The measurement provides a direct indication of the galvanic effect.

Cathodic Protection. Electrochemical measurements are used extensively in both the operation and evaluation of the effectiveness of a cathodic protection system. A combined potential and current measurement system is shown in Fig. 18. The level of cathodic protection for the underground steel structure can be determined by measuring the steel-to-soil potential. The potential of the steel structure is measured with respect to a reference electrode at ground level. One criterion for the cathodic protection of steels in soils is to maintain the steel-to-soil potential at a value more negative than –0.85 V, versus a copper/copper sulfate reference electrode.

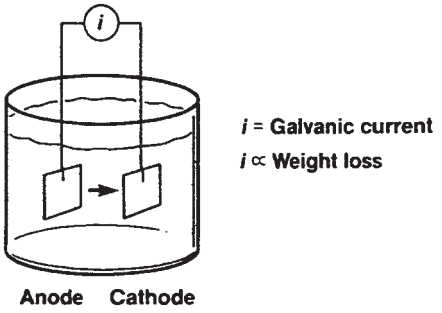


Fig. 17 Current measurement to determine the galvanic corrosion rate between dissimilar metals. Source: NACE International

The current measurement shown in Fig. 18 can be used to monitor the amount of current to the steel structure that is required to maintain the desired cathodic protection potential. The effectiveness and performance of the power supply and impressed-current anode system can also be followed during service. With time, the steel structure polarizes more readily, and the cathodic protection current demand decreases. The buildup of calcareous deposits on exposed areas of steel also decreases the cathodic protection current demand. If the protective coating on the steel begins to deteriorate with time, then the cathodic protection current demand will increase.

Corrosion Rate Based on the Extrapolation of Polarization Curves. The anodic and cathodic polarization curves for an active metal in a deaerated acid are shown in Fig. 19. This figure is adapted from ASTM Standard G 3, "Standard Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing." The electrode potential versus the log of the current density is determined using electrochemical polarization procedures. The solid lines in the diagram are the observed polarization plots. As the electrode potential is made more positive than the open-circuit potential, an anodic current measurement is taken from the metal specimen. At potentials greater than approximately 100 mV more positive than the open-circuit potential, the electrode potential versus log current density is linear. The slope of the oxidation reaction that represents metal becoming soluble metal ions is linear. The slope is equal to an anodic Tafel slope, β_a. The curve shows that for an active metal, as the electrode potential is made more positive or as the solution becomes more oxidizing, the metal dissolution increases.

The cathodic branch of the polarization curve is the solid line at more negative potentials than the open-circuit, or corrosion, potential. As the potential is made more negative than the open-circuit potential, a cathodic current to the metal specimen is measured. At potentials that are

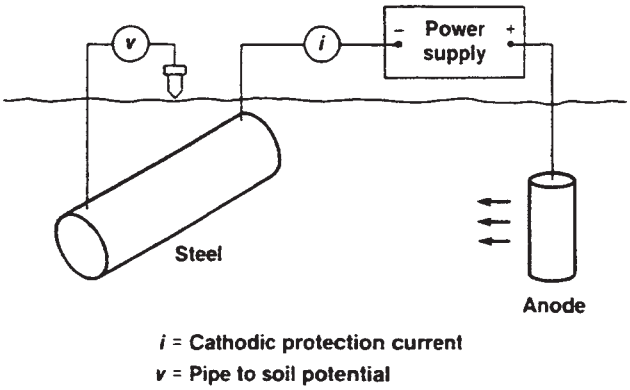


Fig. 18 Combined potential and current measurement for the cathodic protection of steel

more negative than approximately 100 mV to the open-circuit potential, the potential versus log current density becomes linear. The slope of the linear portion of the polarization curve is the cathodic Tafel slope, β_c. In a deaerated acid, the reduction reaction that accounts for the cathodic current is hydrogen ion reduction and the evolution of hydrogen gas. As the potential is made more negative, the rate of the reduction reaction of hydrogen increases.

The linear portion of the cathodic branch or the anodic branch of the polarization curve can be extrapolated back to the intersection with the open-circuit potential. The value of the current at this intersection yields the corrosion current density, which is equal to the rate of the anodic or corrosion reaction under freely corroding conditions. This extrapolation method can be used to determine the corrosion rate of metals when either the cathodic or anodic branch exhibit a well-defined linear region.

Corrosion Rate Based on Linear Polarization. A linear polarization technique is another method that utilizes polarization behavior to determine the corrosion rate of metals. The polarization behavior of a metal in an environment is shown in Fig. 20. The applied potential is plotted versus the current as opposed to the log current in the previously described technique. Within ±20 mV of the corrosion potential, the plot of applied potential versus measured current is often linear. Applied potentials that are more positive than the corrosion potential result in anodic current, whereas potentials that are more negative than the corro-

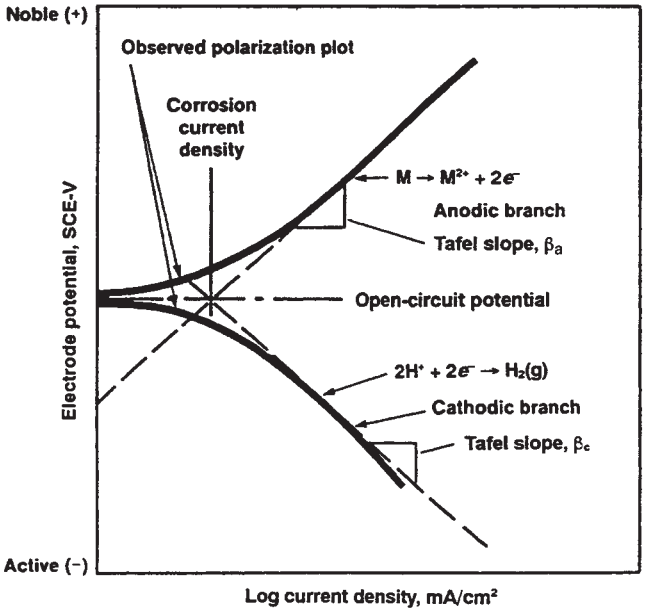


Fig. 19 Anodic and cathodic polarization curves for an active metal in deaerated acid. Source: ASTM Standard G 3

sion potential result in cathodic current to the specimen. At potentials that are further away from the corrosion potential, the linear relationship between potential and current is no longer obeyed. The usefulness of this measurement is that the slope of potential versus current plot, that is, $\Delta E/\Delta i_{app}$, is proportional to the corrosion rate of the metal in the environment.

The relationship of the slope of the linear polarization curve, $\Delta E/\Delta i_{app}$, to the corrosion current, i_{corr}, and the anodic and cathodic Tafel slopes, β_a and β_c, is:

$$\frac{\Delta E}{\Delta i_{app}} = \frac{\beta_a \beta_c}{2.3(i_{corr})(\beta_a + \beta_c)}$$

The slope of the linear polarization curve is determined experimentally, and the values of the anodic and cathodic Tafel slopes are either determined experimentally or estimated. After these values are obtained, the corrosion rate can be calculated from the calculated value of the corrosion current, i_{corr}.

For example, for a system where the anodic and cathodic Tafel slopes are equal to 0.12 V per decade (i.e., the change in potential is equal to 0.12 V for each tenfold change in current), the relationship between the slope of the linear polarization curve and the corrosion rate is:

$$\frac{\Delta E}{\Delta i_{app}} = \frac{0.026}{i_{corr}}$$

Combining linear polarization methods with weight-loss coupons to determine the corrosion behavior of metals is a powerful procedure. The benefit of determining the corrosion rate from the weight-loss coupons is that an exact measurement is made directly. The limitation of weight-loss coupons is that only the total corrosion over the entire length

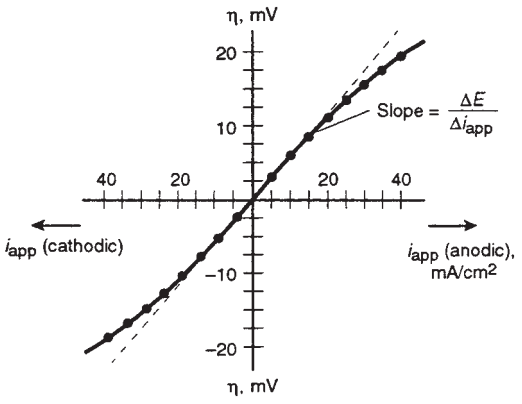


Fig. 20 Linear polarization behavior for a metal at potentials near the corrosion potential. η represents the overpotential.

of exposure of the coupon is measured. No information is gathered as to the corrosion rate as a function of time. By combining the weight-loss experiments and linear polarization measurements, the linear polarization measurements will measure the change in corrosion rate.

Three instances of corrosion rate change with time are shown in Fig. 21. For the data curve on which the x symbols are plotted, the corrosion rate remained constant throughout the time of exposure. For the data set of squares, the corrosion rate began at a relatively high value and decreased over the exposure period. This is representative of a case where protective corrosion products built up on the metal surface during the exposure. For the data set of circles, the corrosion rate was low during the initial period and then rose sharply as the exposure time increased. This is representative of a case where an incubation time for pitting or another localized form of corrosion was observed.

The shape of the corrosion rate versus time curve can be readily measured using the linear polarization technique. The weight-loss coupons can be used to determine the proper area underneath the curve. The combination allows the linear polarization measurements to be calibrated with respect to the weight-loss coupons. The combination of test techniques provides more information than either test technique by itself.

Metal Dissolution. The metal-dissolution behavior over a wide range of oxidizing conditions is readily determined using anodic polarization test techniques. An active metal, that is, a metal that does not develop corrosion-protective scales or films, is represented by the anodic polarization curve shown in Fig. 19. As the oxidizing potential of the environment increases, or as the electrode potential becomes more positive, the corrosion (or metal-dissolution) rate increases. Many metals exhibit active corrosion behavior in certain environments. An example is steel in hydrochloric acid.

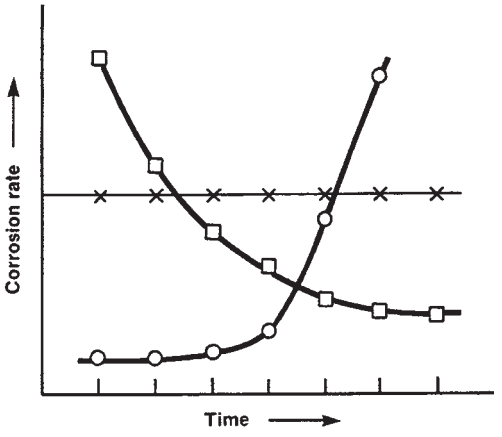


Fig. 21 Determination of the change in corrosion rate with time by the linear polarization technique

Another form of metal-dissolution behavior, known as *active-passive behavior,* is shown in Fig. 22. As the electrode potential increases to more positive values from the corrosion potential, the metal-dissolution rate increases, as it did in the active corrosion condition. At a potential value defined as the primary passivation potential, the corrosion current decreases rapidly over several orders of magnitude to the passive current density. Once in the passive region, the current remains stable over the entire passive region. At still more positive electrode potentials, the passive film on the metal breaks down, and the current increases rapidly once again. This latter region is the transpassive region. Many of the engineering alloys commonly used, such as stainless steels and aluminum and titanium alloys, depend on passivity for their corrosion resistance. The anodic polarization behavior represents a valuable tool for determining the effect of metal composition and structure, as well as environmental factors, on the ease of alloy passivation and the relative stability and durability of the passive films.

The use of anodic polarization curves for active-passive-transpassive metals is demonstrated by some of the data from a study on the localized attack of nickel-containing alloys in SO_2 scrubber environments (Ref 1). The corrosion behavior of a series of alloys was determined in simulated scrubber solutions. The anodic polarization behavior of type 317L stainless steel is shown in Fig. 23(a). The nominal composition of type 317L is 19% chromium (Cr), 13% nickel (Ni), 3.5% molybdenum (Mo),

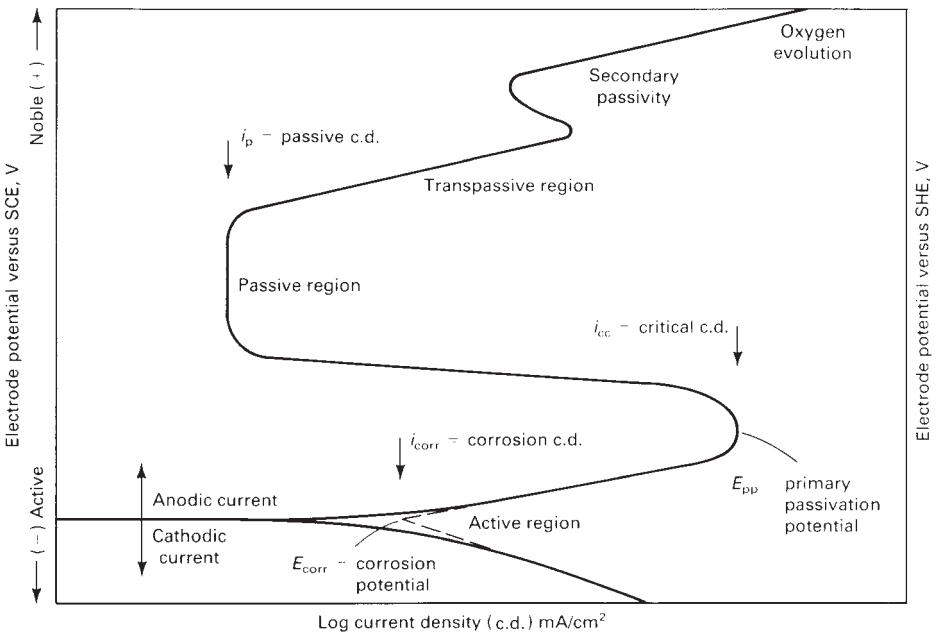
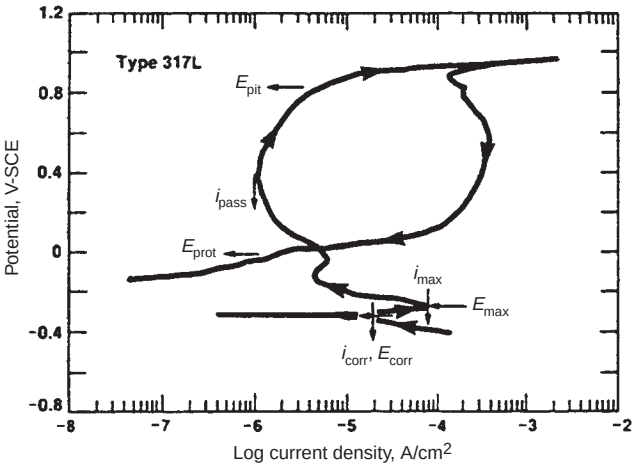
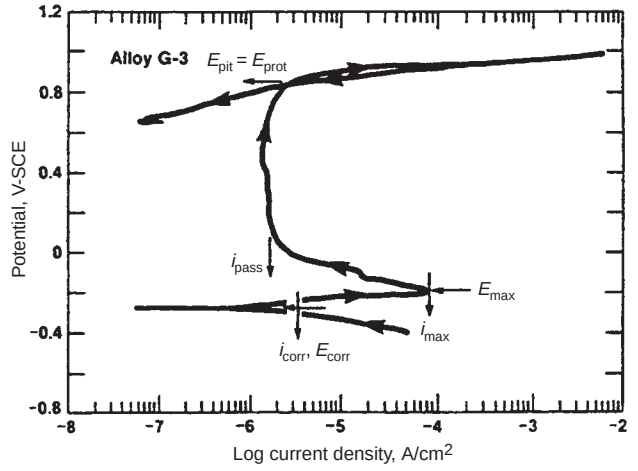


Fig. 22 Polarization behavior for a metal exhibiting active-passive anodic behavior. Source: ASTM Standard G 3

1.8% manganese (Mn), and 0.03% carbon (C). The potential versus log current density shows that this alloy exhibits active-passive-transpassive behavior in this environment. As the potential is made more positive from the corrosion potential, the anodic dissolution rate increases until the value identified as E_{max} is reached. Beyond this potential, the onset of passivity is observed, and the alloy remains passive to the potential identified as E_{pit}, at which point the passive film breaks down and the corrosion current increases rapidly. At this point, the potential scan in the polarization curve was reversed and the potential was made more negative at a uniform scan rate. A large hysteresis loop is observed when comparing the forward scan to more positive values



(a)



(b)

Fig. 23 Comparison of anodic polarization behavior of (a) type 317L stainless and (b) alloy G-3 in an acid-chloride solution. Source: Ref 1

with the reverse scan to more negative values. The potential at which the current density crosses the passive range at the reverse scan is defined as E_{prot}.

Some important data points from the anodic polarization behavior are i_{corr}, the corrosion current under freely corroding conditions; i_{max}, the maximum corrosion current observed prior to the onset of passivity; i_{pass}, the corrosion current that exists when the metal is exhibiting passive behavior; E_{pit}, the potential at which passivity breaks down; and E_{prot}, the potential at which the passivity, once broken down, will be reestablished. The corrosive environment for this experiment was a pH 1 sulfuric acid solution with 10,000 ppm chlorine, 1000 ppm fluorine, and 5000 ppm manganese at 50 °C (120 °F).

The anodic polarization curve for alloy G-3, in a sulfuric solution of the same composition as the corrosive environment previously described, is shown in Fig. 23(b). The nominal composition of alloy G-3 is 22% Cr, 44% Ni, 7% Mo, 1.9% copper (Cu), 5% cobalt (Co), 1.3% tungsten (W), 0.3% niobium (Nb) plus tantalum (Ta), and 19.6% iron (Fe). This alloy also shows active-passive-transpassive behavior in the corrosive environment. The most striking difference between the behavior of type 317L and alloy G-3 is the hysteresis observed on the reverse scan. Although a large hysteresis loop was observed for type 317L, little or no hysteresis loop was observed for alloy G-3. The value of the pitting potential, E_{pit}, and the protection potential, E_{prot}, are nearly identical. A more positive E_{prot} value and a small difference between E_{pit} and E_{prot} indicate greater resistance to localized corrosion.

A comparison of some of the important parameters from the anodic polarization curves of type 317L and alloy G-3 in the acid chloride solutions is presented in Table 10. The values for i_{max}, i_{pass}, and E_{pit} were nearly identical for the two materials. The corrosion current under freely corroding conditions, i_{corr}, for alloy G-3 was nearly an order of magnitude less than the corrosion current for type 317L. The greatest difference in comparing the two alloys was for the value of the protection potential, E_{prot}, after the breakdown of passivity.

The protection potential is a measure of the ease with which the passive film will reform after having been broken down. The passive film readily reforms for alloy G-3, but not for type 317L. Because of this difficulty in repassivation, there is a greater concern with the use of type 317L. If the passive film were to break down in service, because of ei-

Table 10 Comparison of alloys in acid chloride solution

Parameter	Type 317L	Alloy G-3
i_{corr}, A/cm^2	2×10^{-5}	3×10^{-6}
i_{max}, A/cm^2	0.9×10^{-4}	1×10^{-4}
i_{pass}, A/cm^2	1×10^{-6}	2×10^{-6}
E_{pit}, V-SCE	+0.9	+0.9
E_{prot}, V-SCE	0.0	+0.9

ther crevices from the fabrication of equipment or concentration cells caused by deposits on the alloy surface, then corrosion could continue. In any case, the usefulness of anodic polarizations for comparing the general corrosion behavior of alloys in a given environment is demonstrated by these data.

Susceptibility of Alloys to Pitting. The anodic polarization behavior of alloys in various environments can be used to determine their relative susceptibility to pitting. For metals that exhibit passive behavior, the potential at which passivity breaks down with increasing applied potential is defined as the pitting potential, E_{pit}. The more positive the value of the pitting potential, the more oxidizing conditions that the alloy can withstand prior to the onset of pitting. The application of this technique for comparing materials and determining environmental effects on pitting resistance is demonstrated by data for type 316 austenitic stainless steel and a duplex stainless steel in deaerated synthetic seawater (Fig. 24). Values of the pitting potential for each alloy are shown as a function of solution temperature in Fig. 24. For both alloys, the increase in susceptibility to pitting with increasing temperature is demonstrated by the decrease in pitting potential with increasing temperature. As the temperature increases, the oxidizing power of the solution that can be tolerated prior to the onset of pitting becomes lower. At any given temperature, the duplex stainless steel exhibited greater resistance to pitting than did type 316.

The determination of relative corrosion resistance based on anodic polarization behavior, in general, and pitting potentials, in particular, are best done within a given data set under identical conditions. The

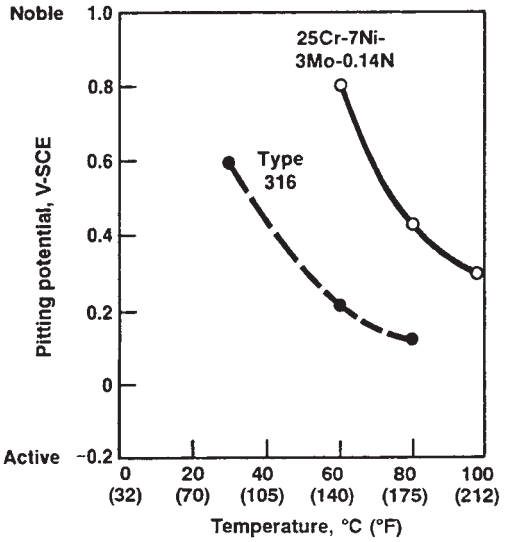


Fig. 24 Pitting potentials for type 316 stainless steel and a duplex stainless steel in deaerated synthetic seawater. Source: Ref 2

value of pitting potential is not a materials property. Rather, it depends on the environment to which the metal is exposed and, just as importantly, on the test procedures used. The value of pitting potential, for example, is quite sensitive to the rate at which the potential is made more positive during the anodic polarization test. If the oxidizing power of the solution in service will never approach the values of breakdown potentials measured in these experiments, then the data for pitting potentials are not particularly relevant in the material selection process. With these caveats in mind, the application of anodic polarization behavior to determine both pitting and protection potentials, as well as several other parameters, is quite useful when ranking alloys in terms of their corrosion behavior and when determining the effect of environmental changes on the corrosion response of alloys.

Polarization Behavior to Study Inhibition. Anodic and cathodic polarization behaviors can be quite useful in the determination of mechanisms by which inhibitors are effective. Inhibitors can reduce the corrosion rate of metals by individually reducing the anodic or cathodic reaction rates or by reducing both the anodic and cathodic reaction rates. Inhibitors are then referred to as being anodic, cathodic, or mixed-mechanism inhibitors, respectively. The use of polarization behavior to determine the mechanism of inhibition is demonstrated by the data for two different inhibitors (Fig. 25). The data on the left indicate that the inhibitor is anodic; that is, the reduction in corrosion rate is the result of decreasing the metal dissolution kinetics. The data on the right indicate that the mechanism of inhibition is mixed; that is, both the anodic dissolution kinetics and the cathodic reduction kinetics are re-

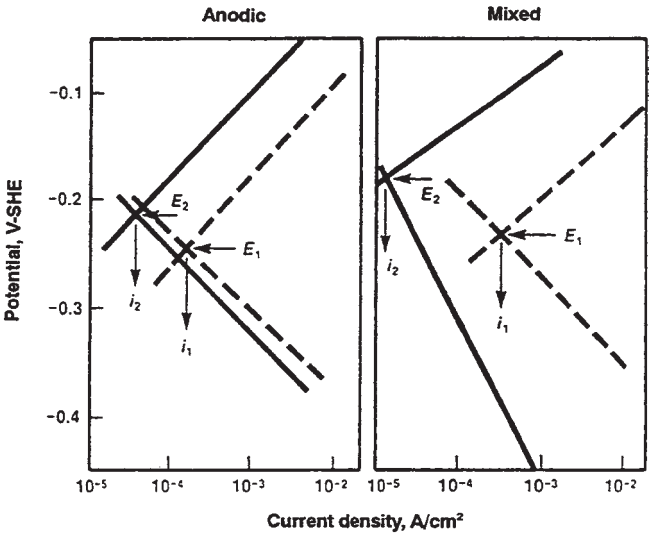


Fig. 25 Effect of an anodic inhibitor and a mixed inhibitor on the polarization behavior of steel in sulfuric acid. Source: Ref 3

duced upon adding the inhibitor to the solution. The anodic inhibitor was a 0.6 m*M* nonylamine in a 5% sulfuric acid solution at 25 °C (75 °F). The corrosion rate of iron in the uninhibited solution is shown by the intersection of the dashed lines at E_1 and i_1. With the addition of the primary amine inhibitor, the corrosion rate is decreased, as indicated by the movement of the intersection to E_2 and i_2. The corrosion current decreases by nearly an order of magnitude. The mechanism of inhibition is an adsorption of the primary amine on the anodic sites.

The mixed inhibitor was a 5 m*M* dibutyl-thioether in a 10% sulfuric acid solution at 30 °C (85 °F). In this environment, mild steel had a corrosion rate indicated by the intersection of the dashed curves at E_1 and i_1. The addition of the sulfur-substituted ether compound decreased the corrosion rate to the intersection indicated by E_2 and i_2. The corrosion rate of mild steel was decreased by greater than an order of magnitude on the addition of the inhibitor. The behavior indicated by the polarization curves showed that this inhibitor was effective by its general absorption and blocking at both anodic and cathodic sites. The polarization techniques are not only useful in determining the level of effectiveness of the inhibitor but also provide valuable information as to the mechanism of inhibition.

Corrosion Monitoring

Corrosion monitoring, which can also be thought of as in-service corrosion testing, has become an important aspect of the design and operation of modern industrial plants because it enables plant engineers and management personnel to be aware of the damage caused by corrosion and the rate of deterioration. The main objectives of corrosion monitoring are the following:

- Diagnose a corrosion problem
- Monitor a corrosion-control method
- Warn of damaging conditions
- Invoke process control
- Determine a maintenance schedule
- Determine a useful life

The objective is to install a monitoring system that senses, analyzes, and either signals the action to be taken or initiates the action directly. A sensor alone is not as useful.

Numerous corrosion-monitoring methods and devices are available. Many are suitable for on-line or in-service use, whereas others require access during downtime, outages, or shutdowns. Some of the devices

measure corrosion directly, but many monitor the corrosion indirectly, for example, by potential change, electrochemical methods, or hydrogen probes. The instrumentation for a variety of corrosion-monitoring

Table 11 Instrumentation for corrosion monitoring

Method	Measures or detects	Notes	Use
Linear polarization (polarization resistance)	Corrosion rate is measured by the electrochemical polarization resistance method with two or three electrode probes	Suitable for most engineering alloys, if process fluid is of suitable conductivity. Portable instruments at modest cost to more expensive automatic units are available.	Frequent
Electrical resistance	Integrated metal loss is measured by the resistance change of a corroding metal element. Corrosion rates can be calculated.	Suitable for measurements in liquid or vapor phase on most engineering metals and alloys. Probes, as well as portable and more expensive multichannel units, are available.	Frequent
Potential monitoring	Potential change of monitored metal or alloy with respect to a reference electrode	Measures directly state of corrosion of facility (active, passive, pitting, stress-corrosion cracking) via use of a voltmeter and reference electrode	Moderate
Corrosion coupon testing	Average corrosion rate over a known exposure period by weight loss or weight gain	Most suitable when corrosion is a steady rate. Indicates corrosion type. Moderately cheap method, with corrosion coupons and spools readily made	Frequent
Analytical	Concentration of the corroded metal ions or concentration of inhibitor	Can identify specific corroding equipment. Wide range of analytical tools available. Specific ion electrodes readily used.	Moderate
Analytical	pH of process stream	Commonly used in effluents. Standard equipment available through robust pH responsive electrodes, such as antimony, platinum, or tungsten, can be preferable to glass electrodes. Solid Ag/AgCl is useful reference electrode.	Frequent
Analytical	Oxygen concentration in process stream	Useful where oxygen control against corrosion using oxygen scavengers such as bisulfite or dithionite is necessary. Electrochemical measurement	Moderate
Radiography	Flaws and cracks by penetration of radius and detection on film	Very useful for detecting flaws in welds. Requires specialized knowledge and careful handling	Frequent
Ultrasonics	Thickness of metal and presence of cracks, pits, etc. by changes in response to ultrasonic waves	Widely used for metal thickness and crack detection. Instrumentation is moderately expensive, but simple jobs can be contracted out at fairly low cost.	Frequent
Eddy-current testing	Uses a magnetic probe to scan surface	Detects surface defects, such as pits and cracks, with basic instrumentation of only moderate cost	Frequent
Infrared imaging (thermography)	Spot surface temperatures or surface temperature pattern as indicator of physical state of object	Used most effectively on refractory and insulation furnace tube inspection. Requires specialized skill. Instrumentation is costly.	Infrequent
Acoustic emission	Leaks, collapse of cavitation, bubbles, by vibration level in equipment. Cracks, by detection of the sound emitted during their propagation	A technique capable of detecting leaks, cavitation, corrosion fatigue, pitting, and stress-corrosion cracking in vessels and lines	Infrequent
Zero-resistance ammeter	Galvanic current between dissimilar metal electrodes in suitable electrolyte	Indicates polarity and direction of bimetallic corrosion. Useful as dewpoint detector of atmospheric corrosion or leak detection behind linings	Infrequent
Hydrogen sensing	Hydrogen probe used to measure hydrogen gas liberated by corrosion	Used in mild steel corrosion involving sulfide, cyanide, and other poisons likely to cause hydrogen embrittlement	Frequent in petrochemical industry
Sentinel holes(a)	Indicates when corrosion allowance has been consumed	Useful in preventing catastrophic failure due to erosion at pipe bends, etc. Leaking hole indicates corrosion allowance has been consumed.	Infrequent

(a) A sentinel hole is a hole that is drilled from the outside of a vessel and that partially penetrates the vessel wall. As the corrosion attack of the vessel proceeds, the vessel wall thins. When the corrosion allowance has been consumed, a sentinel hole that is drilled to that depth will indicate that condition by the leakage of fluid from it. Source: NACE International

Table 12 Characteristics of corrosion monitoring techniques

Techniques	Time for individual measurement	Type of information	Speed of responses to change	Possible environments	Type of corrosion	Ease of interpretation	Technological culture needed
Electrical resistance	Instantaneous	Integrated corrosion	Moderate	Any	General	Normally easy	Relatively simple
Polarization resistance	Instantaneous	Rate	Fast	Electrolyte	General	Normally easy	Relatively simple
Potential measurement	Instantaneous	Corrosion state and indirect indication of rate	Fast	Electrolyte	General or localized	Normally relatively easy, but requires knowledge of corrosion. Can need expert	Relatively simple
Galvanic measurements (zero-resistance ammeter)	Instantaneous	Corrosion state and indication of galvanic	Fast	Electrolyte	General or unfavorable conditions localized	Normally relatively easy, but requires knowledge of corrosion	Relatively simple
Analytical methods	Normally fairly fast	Corrosion state, total corrosion in system, item corroding	Normally very fast	Any	General	Relatively easy, but requires knowledge of facility	Moderate to demanding
Acoustic emission	Instantaneous	Crack propagation and leak detection	Fast	Any	Cracking cavitation, and leak detection pitting	Normally relatively easy	Specialized for crack propagation; otherwise relatively simple
Thermography	Relatively fast	Distribution of attack	Poor	Any (must be warm or subambient)	Localized	Easy	Specialized and difficult
Optical aids (closed-circuit TV, light tubes, etc.)	Fast when access available, otherwise slow	Distribution of attack	Poor	Any	Localized	Easy	Relatively simple
Visual, with aid of gages	Slow (requires entry on shutdown)	Distribution of attack, indication of rate	Poor	Any	General or localized	Easy	Relatively simple, but experience needed
Corrosion coupons	Long duration of exposure	Average corrosion rate and form	Poor	Any	General or localized	Easy	Simple
Ultrasonics	Fairly fast	Remaining thickness or presence of cracks and pits	Fairly poor	Any	General or localized	Easy	Simple
Hydrogen probe	Fast or instantaneous	Total corrosion	Fairly poor	Nonoxidizing electrolyte or hot gases	General	Easy	Simple
Sentinel holes	Slow	Go/no-go remaining thickness	Poor	Any (gas or vapor preferred)	General	Easy	Relatively simple
Radiography	Relatively slow	Distribution of corrosion	Poor	Any	Pitting, possibly cracking	Easy	Simple, but specialized. Radiation hazard

Source: NACE International

Table 13 Types of corrosion monitors

Direct measurement	**Analytical methods**
Corrosion coupons	Metal ion
Sentinel holes	Inhibitor concentration
Electrical methods	pH
Electrical resistance	Oxygen
Potential	Hydrogen
Current	**Nondestructive test methods**
Conductivity	Ultrasonic
Electrochemical methods	Acoustic emission
Anodic and cathodic polarization	Liquid penetrant and particle
Linear polarization	Eddy current
Polarographic	Magnetic field
	Remote visual
	Thermography
	Radiography

techniques is listed in Table 11, and the characteristics of these techniques are identified in Table 12.

The types of corrosion monitors can be categorized as shown in Table 13. Direct measurements of corrosion include corrosion coupons and sentinel holes. A sentinel hole is a hole that is drilled from the outside of a vessel and that partially penetrates the vessel wall. As the corrosion attack of the vessel proceeds, the vessel wall thins. When the corrosion allowance has been consumed, a sentinel hole that is drilled to that depth will indicate that condition by the leakage of fluid from it.

Electrical and electrochemical methods are used extensively to monitor corrosion because they measure the fundamental properties of corrosion reactions; that is, the potential, current, and resistance elements of the corrosion cell. Analytical methods are widely used to follow the corrosion.

The measurement of metal ion concentration in solution is a direct measure of the amount of corrosion. Indirect means of monitoring corrosion by analytical methods include measuring the concentration of inhibitor, pH, oxygen, or hydrogen in a reaction fluid.

Nondestructive test techniques are used extensively to monitor corrosion. Their advantage is that equipment usually need not be taken out of service. There are many techniques in this category, including visual inspection (e.g., borescopes or other optical enhancement devices), eddy current inspection, radiography, ultrasonic thickness measurements, infrared thermography, magnetic particle inspection, and liquid-penetrant inspection. Both ultrasonic and radiographic inspection methods can measure metal loss.

Selecting a Corrosion-Monitoring Method

Although a variety of techniques exist, the most widely used and simplest method of corrosion-monitoring in-plant tests involves the exposure and corrosion evaluation of actual test coupons (specimens). The

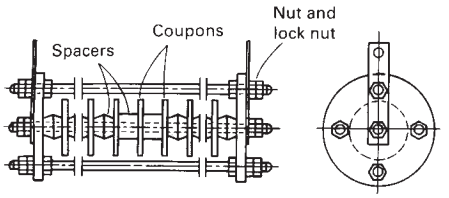


Fig. 26 Typical spool-type coupon rack

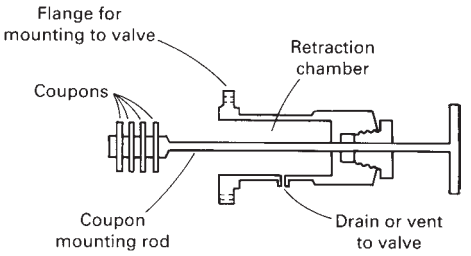


Fig. 27 Retractable coupon holder

ASTM standard G 4, "Standard Method for Conducting Corrosion Coupon Tests in Plant Equipment," was designed to provide guidance for this type of testing.

One important consideration is whether there is access to the process steams and equipment in question. If access is available, then methods that involve probes or coupons become more feasible. Otherwise, nondestructive methods may be required. An important factor in the selection of monitoring methods is the response time required to obtain the desired information from the method. Coupon-based methods and techniques that require plant shutdown tend to be relatively slow in generating information. On the other hand, equipment that measures instantaneous corrosion rates can provide fast results.

Another consideration is safety. In an operating plant, equipment failure can lead to a leak, which can result in loss of product, a hazard potential, and the possible shutdown of the plant.

Test rack design is also an important consideration. Although it may be possible to expose corrosion coupons under stagnant or slowly flowing conditions by simply hanging them on an insulated wire or plastic cord, this procedure is generally inadequate. Instead, specimen holders and test racks are usually used to support and insulate the coupons. These racks must hold coupons firmly in place to prevent mechanical damage and metal loss from causes other than corrosion. They must also electrically isolate the coupons from contact with one another and from the vessel itself to prevent unintentional electrochemical interactions. A typical coupon rack is shown in Fig. 26, and a retractable coupon holder is shown in Fig. 27.

Strategies in Corrosion Monitoring

The monitoring location often influences the quality of information gained from a corrosion-monitoring program. Therefore, deciding where to locate the corrosion-monitoring devices is a critical part of any corrosion-monitoring program. Because corrosion will probably not occur uniformly throughout the plant, it is desirable to find sites at which the highest corrosion rates will be experienced.

The problems involved in developing corrosion-monitoring programs for a plant are exemplified by the distillation column shown in Fig. 28. The most logical points for corrosion monitoring in a distillation column are the feed point, the overhead product receiver, and the reboiled, or bottoms, product line. These points are the locations at which the highest and lowest temperatures are encountered, as well as the points at which the most and least volatile products are concentrated. However, these points are usually not the locations of the most severe corrosion.

The species causing the corrosion will often concentrate at an intermediate point in the column because of chemical changes within the column. Therefore, when the concentration of a corrosion species within the distillation column is possible, several monitoring points are required throughout the column to ensure that the corrosion-monitoring program is comprehensive.

High-velocity gas streams in pipes can cause problems with monitoring systems. In this case, the presence of an aqueous phase is usually restricted to a thin layer on the surface of the pipe. A probe that protrudes

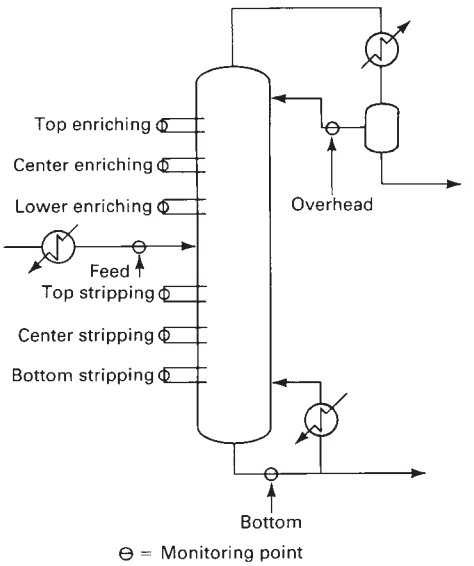


Fig. 28 Preferred locations for corrosion-monitoring probes in a distillation column.

into the pipe may miss the liquid layer that is only present close to the pipe wall. A flush-mounted surface probe can be used in such cases.

Probe location is also critical in storage tanks containing nonaqueous liquids. The most corrosive location in these tanks may be at the liquid level if the liquid in the tank has a density exceeding that of water. In this case, the corrosion-monitoring probe should always be mounted on a floating platform, in order to detect the presence of a corrosive aqueous phase. However, when the liquid stored in the tank is less dense than the water, the corrosion-monitoring device should probably be positioned at the bottom of the tank.

Redundancy is also an important element in the design of corrosion-monitoring programs. The use of at least two different types of corrosion-monitoring devices at any location is often desirable. For example, the use of an electrical resistance probe with a polarization resistance probe allows the measurement of both instantaneous corrosion rates and an average corrosion rate. The data thus obtained can be correlated, which is very helpful in identifying spurious or inaccurate readings.

A primary difficulty with corrosion-monitoring equipment is the need to install wires from the probes to the control room or to the instruments and data storage systems. Hard-wire systems are usually more expensive than the probes and electronic instruments. In addition, wiring systems are often sources of problems that are caused by breakage, moisture entry, and connection difficulties. One option is to use devices that transform the data to coded CB radio signals to provide the desired information to a base station on command.

Leaks represent another important consideration in corrosion-monitoring systems, because they can cause hazards and plant shutdowns. The corrosion-monitoring system must be installed such that leaks from the probe can be handled with minimal interruption. Because a device that penetrates the wall of the vessel may leak, it is essential to have contingency plans for dealing with leaks before the devices are installed.

A related problem concerns packaging glands on pressure vessels that have removable devices. The pressure within a system exerts a force on any removable device. Therefore, it is important to prevent the device from being blown out, which could either injure personnel attempting to remove the device or expose them to the fluid within the vessel. For this reason, restraining rods, chains, and so on, must be used.

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CHAPTER **12**

Techniques for Diagnosis of Corrosion Failures

TECHNIQUES applicable to the diagnosis of corrosion failures include the following:

- Visual and microscopic examination of corroded surfaces and microstructure
- Chemical analysis of the metal, corrosion products, and bulk environment
- Nondestructive evaluation methods
- Corrosion testing techniques
- Mechanical testing techniques

Each of these techniques is described in this chapter. A guide to investigative techniques used in corrosion failure analysis is provided in Table 1.

Factors That Influence Corrosion Failures

Several factors, as well as the possibility of their interactions, must be considered by the failure analyst in determining whether corrosion was the cause of, or contributed in some way to, a failure and in devising effective and practical corrective measures. The type of corrosion, its rate, and the extent to which it progresses are influenced by the nature,

Table 1 Investigative techniques for diagnosing corrosion failures

Technique	Type of information provided	Advantages	Limitations
		Metallography and fractography	
A.1 Macroexamination			
Examination of bulk failure or sample by eye or low-power optical device	General incidence/extent of failure/damage. Juxtaposition of failure/damage. Orientation and direction of failure/damage (e.g., beach markings on fatigue fracture surfaces, chevron markings on brittle fracture surfaces)	May be carried out on site. Whole sample/plant may be examined. Photographic recording possible. Requires no specialized equipment	Low resolution of damage initiation/mechanism(s), etc.
A.2 Optical (light) microscopy			
Examination of small region or area of either unprepared or polished and normally etched surface at magnification of 25 to 1000×. Normally examination is of a sample cut from the bulk, but on-site examination and replication techniques are possible.	Surface condition/damage. Subsurface damage (on cross sections) including damage initiation, secondary damage/ cracking, crack branching and propagation, etc. Microstructural features (metallography). Relationship between structure and damage/properties	Relatively simple sampling and preparation techniques. May be carried out on site. Photographic recording and quantitative analysis possible	Resolution limit about 0.5 μm. Small depth of focus.
A.3 Electron microscopy			
A.3.1 Transmission (TEM) examination of very thin section (foil) or surface replica through which electrons are transmitted. Magnification 2,000 to 40,000×	Microstructural features, including crystallography and defect structure. Surface (including fracture) phenomena (replicas only)	Provides highest microstructural detail. Resolution about 2 nm. Phases may be identified by electron diffraction or x-ray spectrometry (C.6, C.8).	Sampling and preparation may be difficult and time consuming. Interpretation is moderate to difficult requiring experience. Specialized equipment required. Maximum area for examination between 30 μm and 3 mm diam
A.3.2 Scanning (SEM) examination of unprepared (e.g., fracture) or prepared (e.g., polished and etched) surface or surface replica. Surfaces must be electrically conductive, which may be achieved by coating with, for example, Au-Pd by evaporation. Magnification 100 to 20,000×	Surface phenomena, particularly on fracture faces. Microstructural features (metallography) and relationship between structure and damage. Incidence and distribution of porosity, voids and cracks, etc.	Little specimen preparation required. Large depth of focus. Resolution about 20 nm. Suitable for large sample size range (e.g., from dust up to 50 mm^2. Elemental chemical analysis in situ is possible (C.6).	Electron diffraction analysis not possible. Interpretation is moderate to difficult and may require experience. Specialized equipment required
		Nondestructive evaluation	
B.1 Magnetic susceptibility			
Application (contact or close proximity) of a permanent magnet to a material/sample/ structure	Degree of ferromagnetism or ferrimagnetism, either qualitatively (by simple hand application) or semiquantitatively (by use of a magnetic balance). Differentiation between magnetic and nonmagnetic particles in fluids (e.g., in lubricants) (technique known as ferrography)	Rapid and simple sorting technique for metals (e.g., ferritic iron alloys and nickel and cobalt alloys vs. austenitic iron alloys) and oxides (e.g., Fe_3O_4 vs. Fe_2O_3). May be carried out on-site. Often no specialized equipment required. Nondestructive	Semiquantitative techniques must be applied with caution (e.g., the use of a magnetic balance to determine the ferrite content of austenitic steel weldments provides information of limited value compared with a metallographic examination). (Ferrography requires specialized equipment.)
B.2 Electrical resistance			
Application of known DC or high-frequency AC current and measurement of resulting potential(s) or of relative change of potential(s)	Surface-breaking crack or defect depth (potential drop technique). Corrosion or wastage rate (continuous or intermittent monitoring technique). Integrity of surface coatings (nondestructive)	Simple techniques for on-site or in situ testing and monitoring. Interpretaion relatively easy. May be nondestructive	Crack depth techniques only accurate if crack is normal to the surface, and if the crack length is 3 times or more its depth. Calibration is required for reasonable accuracy. Temperature compensation may be necessary.

(continued)

Table 1 (continued)

Technique	Type of information provided	Advantages	Limitations
B.3 Dye-penetrant inspection			
Enhancement of detail of cracks or defects by application and subsequent "development" of a penetrating dye	General incidence/extent of cracks or defects, which break the surface	Rapid and simple technique, requiring no specialized equipment. Resolution down to 0.5 mm length. Useful in conjunction with photographic recording. Suitable for on-site/remote use. Nondestructive (but see limitations). National and international standards for inspection exist.	Only surface-breaking cracks or defects detected. May not detect either closed or very open cracks. Dye may contaminate surface corrosion products/films, etc., making subsequent chemical identification impossible. Resolution/sensitivity depends critically on surface cleanliness and is operator dependent.
B.4 Magnetic particle inspection			
Similar to B.3 above but with use of magnetic particles in a carrier fluid attracted to cracks or defects causing perturbations in an applied magnetic field	General incidence/extent of cracks or defects, which break or are very close to the surface.	Rapid and simple technique. Better resolution/sensitivity than dye penetrant inspection. Can detect closed cracks (i.e., resolution is infinitely small across the crack). Suitable for on-site/remote use. Nondestructive (but see limitations). National and international standards for inspection exist.	Only surface-breaking or very-close-to-surface cracks or defects detected. Inspected sample/structure must be ferromagnetic. Carrier fluid may contaminate surface corrosion products/films, etc., making subsequent chemical identification impossible.
B.5 Eddy-current inspection			
Detection of cracks or defects and thickness of coatings, which cause variation in eddy currents induced by an applied alternating magnetic field	General incidence/extent of cracks or defects, which break or are very close to the surface. (Note with low frequencies deeper detection is possible at the expense of resolution/sensitivity.) Thickness of nonconductive coatings	Rapid and simple technique that will work over surface paint or corrosion products. Resolution/sensitivity better than dye penetrant inspection. Suitable for on-site/remote use. Nondestructive. Suitable for all electrically conducting materials. National and international standards for inspection exist.	Only surface-breaking or very-close-to-surface cracks or defects detected. May not detect closed cracks. Specialized equipment matched to specific application required. Interpretation moderately difficult, requiring experience or more sophisticated equipment. Resolution is operator sensitive.
B.6 Ultrasonic inspection			
B.6.1 Longitudinal waves. Application and detection of reflection of pulsed (typically 1000 s^{-1}) high-frequency wave (typically 5 to 10 MHz), normal to surface	Thickness (i.e., corrosion loss or wastage) of material up to 250 mm	Very high sensitivity (e.g., down to 0.01 mm resolution). Interpretation relatively easy. Highly portable equipment available, suitable for on-site applications and wide range of materials. Nondestructive	Use requires some discretion because cracks/bonds, etc. normal to wave may give false reading. Specialized equipment required
B.6.2 Shear waves. As B.6.1, but with wave angled to surface	Volumetric incidence/extent/location/orientation of cracks and defects in materials up to 250 mm thick (and particularly in welds)	High resolution (practically, about 0.1 to 0.2 mm in steel) at high frequency. Suitable for on-site use and for wide range of materials at temperatures up to 500 °C (930 °F). Nondestructive National and international standards for inspection exist.	Time consuming for large area/volume inspection. Sensitivity and penetration lower at high frequencies. Interpretation difficult, requiring experience. Difficult for complex shapes. Difficult for coarse-grained (e.g., cast) or anisotropic (e.g., highly directionally structured) materials. Specialized equipment required
B.7 Radiography			
Penetration of sample/structure (and subsequent photographic recording) by x-rays or γ-rays. Extent of penetration depends on thickness and on material and its contained cracks and defects.	Volumetric incidence/extent/location/orientation of cracks and defects	Thickness of material penetrated limited only by power of x- or γ-ray source. Easily interpreted images. Good for complex shapes. Large areas/volumes may be inspected at one time. γ-ray sources very portable. Both x-ray and γ-ray techniques suitable for on-site use. Nondestructive National and international standards for inspection exist.	Mostly penetration is normal to surface, thus cracks parallel to the surface not easy to detect. Radiation safety precautions must be observed. Specialized equipment and storage facilities (for γ-ray sources) required. Upper temperature limit for use is about 50 °C (120 °F)

(continued)

da/*dn*, fatigue crack growth rate. Source: Ref 1

Table 1 (continued)

Technique	Type of information provided	Advantages	Limitations
B.8 Acoustic emission			
Detection by multiple transducers of acoustic signals emitted by growing cracks	Incidence and location of growing cracks (particularly in pressure vessels undergoing proof testing)	May be applied to large structures/ plant, intermittently or continuously. Limited equipment required. Suitable for on-site use.	Interpretation moderate to difficult, requiring experience. Largely passive technique. Not strictly nondestructive
B.9 Temperature measurement			
B.9.1 Temperature indicators (crayons/paints/lacquers), which undergo color change or soften over specific temperature range, applied to surface	Surface temperature within specific ranges	Rapid, reliable, and simple technique. Requires no specialized equipment. Easy interpretation. Suitable for on-site use. Nondestructive	Technique indicates surface temperature only. Poor resolution of temperature (typically ± 50 °C, or 90 °F). Upper temperature limit is less than 1000 °C (1830 °F)
B.9.2 Radiation pyrometry. Matching by color a heated electrical filament and the target using emitted visible radiation (optical pyrometry). Detection of both infrared and visible radiation emitted by the target (total radiation pyrometry). Detection by scanning of infrared radiation emitted by the target (Thermography).	Surface and/or volumetric temperature over a large temperature range (–20 to 2000 °C, or –5 to 3630 °F, or higher).	Rapid and relatively simple techniques. Infrared radiation techniques can detect temperature beneath cladding etc. Good temperature resolution down to 0.1 °C, (0.2 °F). For Thermography, recording on video tape is possible. Easy interpretation. Suitable for on-site use. Nondestructive.	Infrared techniques subject to error in presence of water vapor and CO_2, which absorb radiation. Specialized equipment required
B.10 Pressure measurement			
Pressure transducer "plumbed" in or temporarily attached to a pressure line or vessel	Continuous and/or transient fluid pressure	Relatively simple measurement and interpretation for on-site use. Equipment required is simple with good resolution in range 0 to 45 MPa (0 to 6500 psig)	Equipment may require special attachment to be provided.
Chemical Analysis			
C.1 Spot test(s)			
Application of selected reagent(s) to surface and detection, by eye or with aid of a microscope, of subsequent reaction	Qualitative (sometimes semiquantitative) presence or absence of specific elements. (Principally for alloy elements in metallic materials)	Simple sorting technique. Suitable for on-site use. No specialized equipment required.	Detection limits vary depending on element. Only one specific element detected per test.
C.2 Classical wet analytical chemistry			
Gravimetric/volumetric/ colorimetric/electrochemical/ atomic absorption techniques	Quantitative chemical composition	Relatively simple techniques and equipment requirements. Suitable for solid or liquid samples. Detection limits from 0.001 to 100%. Accuracy ±1% of detected level. (Most accurate of all analytical techniques and thus, used for "referee" analysis.)	Time consuming. Requires dissolution of solid samples for most elemental analysis. Only one specific element detected per procedure/test
C.3 Emission spectrography			
Recording on a photographic plate of the visual and ultraviolet spectrum produced by sparking a solid sample or by introduction of a solution into a plasma. Spectral line densities compared, subsequently, with a standard	Qualitative/quantitative bulk or local chemical composition. Major and minor constituents	Detection limits from 1 ppm to 30%. Rapid technique for qualitative elemental scan. (Quantitative analysis requires more time.) Portable versions exist for semiquantitative on-site use, with detection limit not less than 0.1%	Requires specialized equipment. Accuracy ±5% of detected level. Light elements (H, C, N, O, S, P, Cl) not detected
C.4 Mass spectrography			
Recording on a photographic plate of the spectrum produced after ionizing a solid sample and accelerating the ions through a magnetic field. Spectral line densities compared, subsequently, with a standard	Quantitative bulk or local chemical composition. Minor and trace constituents	Detection limits from 10 ppb to 1%. Detects all elements from lithium (atomic weight, 7) to uranium (atomic weight, 238) and, with specialized equipment, H, N, O, etc. in metals	Requires expensive and specialized equipment. Accuracy ±5% of detected level

(continued)

Table 1 (continued)

Technique	Type of information provided	Advantages	Limitations
C.5 Emission/mass spectrometry			
As C.3 and C.4, but the output is converted using photomultipliers to direct reading of elemental concentrations	As C.3 and C.4	As C.3 and C.4. Rapid techniques for quantitative information in which up to 20 elements may be determined during each analysis	As C.3 and C.4. (Note C, S, and P in metals may be detected by vacuum emission equipment.) Full range of photomultipliers may not be available.
C.6 Electron probe microanalysis			
Analysis by crystal spectrometry or energy dispersion of x-rays emitted as a result of applying a focused (1 μm diam) electron beam to a surface	Qualitative and quantitative elemental composition of excited volume (a few cubic μm)	Carried out in conjunction with scanning electron microscopy (A.3.2) Enables accurate locational analysis of structural phases or corrosion products. Elements from boron up (in atomic number) may be detected. Accuracy often better than ±1% of detected level. Rapid technique. X-ray mapping of 0.25 mm^2 area or line scanning is possible.	Requires specialized equipment in conjunction with an electron microscope. Electron penetration depth about 10 μm so limited use in analysis of surface films
C.7 Electron spectroscopy			
Analysis of either photoelectrons or Auger electrons emitted from a surface excited by an x-ray beam or an electron beam. (Techniques known as x-ray photoelectron spectroscopy, XPS, or Auger electron spectroscopy, AES	Quantitative chemical analysis of outermost atomic layers of surfaces	Only true "surface analysis" techniques, sampling surface to a depth of about 2 nm. Suitable for analysis of all chemical compounds. Detects all elements except hydrogen and helium	Requires specialized equipment. Requires relatively large surface area (cm^2 for XPS)
C.8 Electron diffraction			
Scattering of electrons, transmitted through a thin film or reflected from a solid surface (from depths up to 50Å) by crystal lattice in a 1 μm diam sampled area	Identification of crystal structure or crystalline phases	Diffraction techniques are only methods of identifying crystal structure.	Requires specialized equipment (i.e., electron microscope). Limited to crystalline solids
C.9 X-ray diffraction			
Scattering of x-rays transmitted through or reflected from a solid sample	Quantitative crystalline phase analysis	As C.8. Detection limit 1–5%. Accuracy between ±1 and ±10% of detected level. Sample may be in powder form so ideal for analysis of corrosion products.	Requires specialized equipment. Limited to crystalline solids
Mechanical testing			
D.1 Tensile test			
Load specimen in tension at known loading or deflection rate. Normally test carried out at low strain rate and ambient pressure and temperature	Elastic limit and modulus (the latter to moderate accuracy only), proof stress, yield strength, ultimate tensile strength, and fracture stress and strain. Percentage elongation on predetermined gage length and reduction in area of fracture	Well-established and simple technique but requires appropriate equipment. National and international standards for testing available	Standard specimens may not be available, making interpretation of results more difficult. Standard specimens sometimes polished on gage length, not normally representative of "engineering" surfaces
D.2 Impact test			
Specimen (usually prenotched) loaded at high strain rate. Tests may be carried out at range of temperatures (low). Energy absorbed in impact failure recorded	Upper and lower-shelf impact energies. Impact energy transition (ductile-to-brittle) temperature	Well-established and simple techniques but require appropriate equipment. National and international standards for testing available	Standard specimens may not be available, making interpretaion of results more difficult. Results may be very sensitive to orientation of specimen with respect to wrought direction, etc.

(continued)

da/*dn*, fatigue crack growth rate. Source: Ref 1

Table 1 (continued)

Technique	Type of information provided	Advantages	Limitations
D.3 Hardness test			
D.3.1 Bulk (macro) indentation of specimen surface by standard indenter (pyramid, ball, or cone) under known load, normally in range 1 to 3000 kgf	Resistance to indentation (hardness) expressed as either load divided by actual or projected area of indentation or on an arbitrary scale according to the depth of indentation. (Estimates of tensile mechanical properties for ductile materials and of fracture toughness (K_{Ic}) of brittle materials may be made.)	Very rapid and simple techniques suitable for small and large specimens (samples) and may be performed on site. Only minimum surface preparation required. National and international standards for testing available	Volume of material "sampled" is relatively small, thus number of replicates required for reasonable accuracy. Difficult to relate "hardness" to other mechanical properties, such as yield strength
D.3.2 Micro. Similar to D.3.1 but with pyramid diamond indenters only under load in range 0.001 to 3.5 kgf	As D.3.1 but primarily used on metallographically prepared surfaces to determine hardness of individual microstructural features	Rapid technique that may aid in differentiating microstructural features and in determining extent of local hardening (e.g., by plastic deformation)	Laboratory technique only, requiring hardness attachment to metallurgical microscope. Results subject to errors associated with loading and indentation measurement. Good surface preparation required
D.4 Static load			
D.4.1 Creep. Maintain load on specimen subjected to high temperature (relative) for periods of up to 100,000 h	Creep strength (stress rupture) at given temperature and time. Creep strain at given load, temperature, and time, or apparent creep modulus (applied stress divided by creep strain)	Only reliable method for determining high temperature, time-dependent properties	Time consuming and expensive. Normally specimens have circular cross section, and surface finish may not be representative of "engineering" surfaces
D.4.2 Stress corrosion. Maintain load on specimen, often notched or precracked, subjected to specific environment. Load applied normally up to 0.9 yield strength and exposure often limited to 1000 h. (Note for some techniques load is allowed to fall during the test.)	Susceptibility (e.g., threshold stress) to stress-corrosion cracking (SCC), critical stress intensity factor for stress-corrosion cracking. K_{Iscc}, and crack growth rate vs. stress intensity factor, da/dN vs. K_{Iscc}	Only reliable method for determining K_{Iscc}, and, in absence of published information, of determining susceptibility to SCC of specific material/environment combination. National and international standards for testing available	Time consuming and relatively expensive. Results may be very sensitive to orientation of specimen with respect to wrought direction, etc. Data from tests on smooth specimens have limited use, often only for relative ranking or quality assurance purposes.
D.5 Cyclic load			
Application of cyclic load to smooth or prenotched or precracked specimens sometimes subjected to specific environment. Normally a range of loads is applied.	Fatigue stress, S, versus number of cycles to failure, N, data (from replicate tests at a range of loads). Fatigue crack growth rate data (normally vs. stress-intensity range, ΔK) and threshold stress intensity for fatigue crack growth	Only reliable method for establishing fatigue crack initiation and growth data National and international standards for testing available	Time consuming and expensive. S-N data susceptible to considerable scatter. Data from tests on smooth specimens has limited use.
D.6 Fracture toughness			
Application of tensile load to prenotched and/or cracked specimen of known crack dimensions. Maximum load and/or crack opening displacement (COD) recorded	Linear elastic fracture mechanics properties or elastic-plastic fracture properties (i.e., K_c, K_{Ic}, etc.)	Major method for quantifying the resistance to crack propagation. National and international standards for testing available	Relatively expensive but fast. Standard specimen sizes may not be available, making interpretation more difficult. Data must be used with caution and requires experience.

da/*dn*, fatigue crack growth rate. Source: Ref 1

composition, and uniformity (or nonuniformity) of the environment and the metal or nonmetal surface in contact with that environment. These factors usually do not remain constant as corrosion progresses but are affected by externally imposed changes and by changes that occur as a direct consequence of the corrosion process itself.

Other factors that have major effects on corrosion processes include temperature gradients at the metal/environment interface, the presence of crevices in the metal part or assembly, relative motion between the environment and the metal part, and the presence of dissimilar metals in an electrically conductive environment. Processing and fabrication operations, such as surface grinding, heat treating, welding, cold working, forming, drilling, and shearing, produce local or general changes on metal parts that, to varying degrees, affect their susceptibility to corrosion.

The specific application determines the amount of metal that can be lost before a part is considered to have failed by corrosion. In some applications, especially where uniform corrosion occurs, a substantial reduction in thickness of a part can be tolerated. In applications where appearance is important or where discoloration or contamination of a food or other product in processing or storage is unacceptable, the dissolution of even a minute amount of metal constitutes failure.

Localized attack, for example, by pitting, can penetrate the walls of vessels, piping, valves, and related equipment to cause leakage that constitutes failure. Even relatively shallow localized attack can provide stress concentrations or can generate hydrogen on the metal surface, and the result may be failure by mechanisms other than corrosion.

Analysis of Corrosion Failures

The rate, extent, and type of corrosive attack that can be tolerated in a part vary widely, depending on the specific application. When investigating a corrosion failure, an analyst must do the following:

- Determine the failure mode
- Determine the failure cause
- Estimate the extent of damage and the likelihood of additional failures
- Design and implement an appropriate corrective action
- Follow up to ensure that the corrective action is first implemented and then is sufficient to prevent another failure

It is important to bear in mind the difference between the failure mode and the failure cause. The mode will usually be one of the various forms of corrosion described and illustrated in Chapter 4 (e.g., general corrosion, pitting, crevice corrosion, and so on). The failure cause is the root reason for the actual occurrence of the failure. For example, the failure mode might be stress-corrosion cracking (SCC). Failure cause, however, might be chloride ions that were introduced

into the system or residual stress in the component, which in turn made it susceptible to SCC.

The principal stages of the investigation and analysis of corrosion failures are the following:

- Collection background information and sampling
- Preliminary laboratory examination
- Detailed metallographic and fractographic examinations
- Chemical analysis of corrosion products and bulk materials
- Corrosion testing for quality control
- Mechanical testing for quality control
- Analysis of results and report writing

Each of these is discussed in more detail in this chapter. Additional information on the analysis of corrosion failures can be found in *Failure Analysis and Prevention,* Volume 11, *ASM Handbook.* In fact, much of the material presented in this chapter has been adapted from this publication (particularly, Ref 2 and 3).

Collection of Background Data

Initially, the failure investigation should be directed toward becoming familiar with all pertinent details relating to the failure, such as collecting the available information regarding the manufacturing, processing, and service histories of the failed component or structure and reconstructing, insofar as possible, the sequence of events leading to the failure. The collection of background data on the manufacturing and fabrication history of a component should begin with obtaining specifications and drawings and should encompass all the design aspects of the component. Data relating to manufacturing and fabrication may be grouped into the following categories:

- *Mechanical processing:* May include cold forming, stretching, bending, machining, grinding, and polishing
- *Thermal processing:* May include details of hot forming, heat treating, welding, brazing, or soldering
- *Chemical processing:* May provide details of cleaning, electroplating, and application of coatings by chemical alloying or diffusion

Service History. Before taking samples or conducting tests that might destroy evidence relating to the failure, it is best to obtain and evaluate all the available information that time permits about the circumstances of the failure, the history of the failed part, and the seriousness or potential seriousness of the failure. Information about the type of environment to which the failed part was exposed is of primary

concern. The corrosion behavior of the part is affected by both local and upstream chemical composition in the system, by whether exposure to the environment is continuous or intermittent, by temperature, and by whether these and other factors varied during the service life of the part.

If available, engineering drawings and material and manufacturing specifications for the part should be examined, with particular attention being paid to any part changes that may have been made. Missing information should be obtained from operating and inspection personnel, at the same time verifying the accuracy of any relevant documentary information, such as daily log sheets or inspection reports. The investigator should try to learn what, if any, tests or changes that could affect physical evidence relating to the failure may have already been made after the failure occurred. Often, only a small part of the desired information will be available to the failure analyst, information obtained may be of questionable accuracy, or it may be impossible to verify some of the information that is obtained.

On-Site Examination

On-site examination is generally the same for corrosion failures as it is for other types of failures. The region of failure itself should be visually examined using hand magnifiers and any other suitable viewing equipment that is available.

The areas immediately adjacent to and near the failure, as well as related components of the system, should be examined for possible causative effects on the failure. Remotely located but related equipment should also be examined, particularly in complex systems and where liquids or gases flow. Also, the possibility of the introduction of chemicals or other contaminants from upwind or upstream areas should be checked.

Photography. The failed component and related features of the system should be photographed before samples are removed. Color photographs are particularly useful when colored corrosion products are present; accurate color rendition is enhanced by the use of a gray background, which is used as a guide in developing and printing.

On-Site Sampling

In conducting on-site sampling, the investigator should be guided by the information already obtained about the history of the failure. The bulk environment to which the failed part was exposed should be sampled, and suitable techniques should be used to obtain samples and make observations, for example, pH, on the local environment at the point of failure.

In addition to taking samples from the failed area, samples from adjacent areas or from apparently noncorroded regions should be obtained

for comparison purposes. New or unused parts can provide evidence of the initial or unexposed condition of the part.

Precautions. Removal of specimens and of samples of corrosion product from the failed part requires careful consideration in the selection of locations and method of removal. Suitable precautions must be taken to avoid the destruction of evidence that could be of value in investigating the failure and to avoid further damage to the part or to other related components and structures.

Torch cutting is frequently used for the removal of specimens because of its speed and convenience. Cuts should be made at a sufficient distance from the failure site to prevent alteration of the microstructure, thermal degradation of residues that may be present, and the introduction of contaminants. If an abrasive cut-off wheel or saw is used, the same precautions to avoid overheating apply. Also, coolants or lubricants that can contaminate or alter the part or any deposits present should not be used.

Protection of Samples. Small parts, as well as samples taken from large parts can be protected during transportation to the laboratory by individual packaging. Glass vials and polyethylene film and bags are useful.

Preliminary Laboratory Examination

The procedures followed in the preliminary laboratory examination will vary, depending on whether an on-site examination has already been performed by the failure analyst and on the completeness of any such examination. An on-site examination by a well-equipped investigator will have included much of the work that would otherwise have to be done in the preliminary laboratory examination. When there has been no on-site examination, records on the part and environment, the remainder of the failed part (or at least a good photographic record of it), along with undamaged or unused parts and related components, plus samples of the environment, will assist greatly in the performance of a complete and accurate failure analysis.

Preservation of Evidence. Whether or not an on-site investigation has taken place, the course of action should be based on the handling of all samples in such a way that maximum information can be gained before any sample is damaged, destroyed, or contaminated to the extent that other potentially useful tests cannot be performed on it. Also, a complete written and photographic record should be maintained throughout all stages of the investigation.

Visual Examination and Cleaning. Samples are first examined visually, preferably with the aid of a hand magnifier or other suitable viewing aid. At this stage, such features as the extent of damage, general appearance of the damage zone, and color, texture, and quantity of surface

residues are of primary interest. If substantial amounts of foreign matter are visible, cleaning is necessary before further examination. The residues can be removed in some areas, leaving portions of the failure region in the as-received condition to preserve evidence. When only small amounts of foreign matter are present, it is sometimes preferable to defer cleaning so that the surface can be examined microscopically before and after cleaning or to defer cleaning until necessary for surface examination at higher magnifications.

Washing with water or solvent, with or without the aid of an ultrasonic bath, is usually adequate to remove soft residues that obscure the view. Inhibited pickling solution will remove adherent rust or scale on steel. It is generally advisable to save the cleaning solutions for later analysis and identification of the substance removed. Alternatively, plastic replicas can be used in cleaning; the replicas also retain and preserve surface contaminants, thus making them available for analysis.

Nondestructive Examination. For a part in which internal damage may have resulted from corrosion or the combined effects of corrosion, stress, and imperfections in the metal, the application of a nondestructive detection method before cutting may be desirable. Such methods include radiography, ultrasonic flaw detection and measuring, liquid-penetrant inspection, magnetic-particle inspection, eddy-current testing, and holographic examination. However, some of these techniques may introduce contaminants into the test specimen, and this possibility must be weighed carefully.

Microscopic Examination

Both light microscopy and scanning electron microscopy (SEM) can be used to observe minute features on corroded surfaces, to evaluate microstructure of the metallic parts, and to observe the manner in which, and the extent to which, the metal was attacked by the corrodent. Table 1 reviews the information provided by microscopy.

Corroded Surfaces. Examination should start at relatively low magnifications, such as those provided by a stereomicroscope. Viewing the cleaned surface stereomicroscopically clearly shows gross topographic features (e.g., pitting, cracking, or surface patterns) that can provide information about the failure mechanism, the type of corrosion, and whether other mechanisms, such as wear and fracture, were also operative.

If the features cannot be observed clearly using an optical microscope or stereomicroscope, SEMs, which produce images with a greater depth of field, can often resolve the features, especially on very rough surfaces. Transmission electron microscopy (TEM), using replica specimens, may be needed to resolve extremely fine features.

Microstructure. Microscopic examination of polished or polished-and-etched sections can reveal not only microstructural features and additional damage, such as cracking, but also the manner in which the corrodent attacked the metal, such as grain-boundary attack or selective leaching.

The corrosion products should be retained if they possess sufficient coherence and hardness to be polished. One method of keeping the surface material in place is to impregnate the sample with a castable resin, which is allowed to harden before samples are cut. Polishing on napless cloths with diamond abrasives is recommended for maximum edge retention.

Careful microscopic analysis also provides insight into the metallurgical condition of the material, which can be important in assigning a cause of failure. Intergranular cracking of austenitic stainless steels can indicate that the material was sensitized as a result of improper heat treatment, welding, or some other cause. The sensitized condition can be confirmed by optical metallography.

Chemical Analysis

In a failure investigation, chemical analysis is recommended to ensure that the metal matches that specified for the application. In general, slight deviations from specified compositions are not likely to be of major importance in failure analysis. In fact, because only a minority of service failures result from unsuitable or defective material, the results of chemical analysis rarely disclose the reason for failure. In specific investigations, particularly where corrosion and stress corrosion are involved, chemical analysis of any deposit, scale, or corrosion product, or of the medium with which the affected material has been in contact, is required to assist in establishing the primary cause of failure.

If analysis shows that the content of a particular element is slightly greater than that specified, it should not be concluded that this situation is responsible for the failure. It is often doubtful whether such a deviation has played even a contributory role in failure. For example, sulfur and phosphorus contents in structural steels are limited to 0.04% in many specifications, but rarely can a failure in service be attributed to a sulfur content slightly in excess of 0.04%. Within limits, the distribution of the microstructural constituents in a material is of more importance than their exact proportions. A chemical analysis (with the exception of a spectrographic analysis restricted to a limited region of the surface) is usually made on drillings that represent a considerable volume of material and, therefore, provide no indication of possible local deviations due to segregation and similar effects.

Also, certain gaseous elements, or interstitials, that are normally not reported in a chemical analysis can have profound effects on the me-

chanical properties of some metals. In steel, for example, the effects of oxygen, nitrogen, and hydrogen are of major importance. Oxygen and nitrogen may give rise to strain aging and quench aging. Hydrogen may induce brittleness, particularly when absorbed during welding, cathodic cleaning, electroplating, or pickling. Hydrogen is also responsible for the characteristic halos or fisheyes on the fracture surfaces of welds in steels and in such cases, is often introduced through the use of damp electrodes.

Surface Chemical Analysis. A variety of analytical techniques and tools have been developed to provide investigators with information regarding the chemical composition of surface constituents (Table 1). Energy-dispersive and wavelength-dispersive x-ray spectrometers are employed as accessories for SEMs and permit simultaneous viewing and chemical analysis of a surface. To detect the elements in extremely thin surface layers, Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), Mössbauer spectroscopy, secondary ion mass spectroscopy (SIMS), low-energy ion-scattering spectroscopy (LEISS), and a host of other techniques also are useful. Figure 1 shows the depths to which several of these techniques are capable of analysis.

AES can provide qualitative and semiquantitative determinations of elements with atomic numbers of 3 or higher. The size of the area examined varies greatly with test conditions and may be from 1 to 50 μm in diameter.

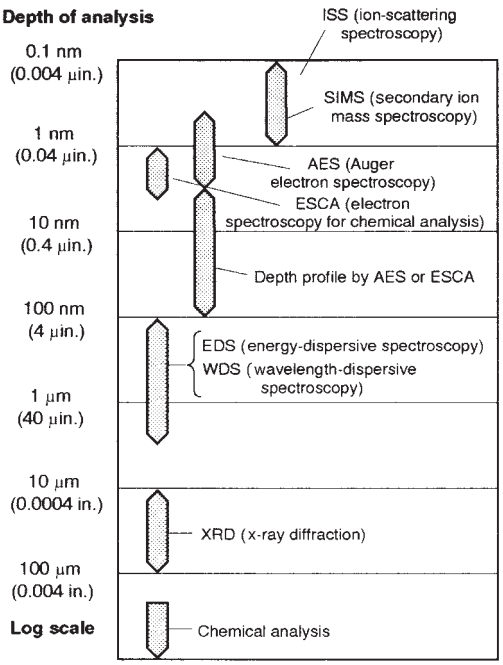


Fig. 1 Relative depth of penetration of various surface analysis techniques

XPS, also known as electron spectroscopy for chemical analysis (ESCA), is a surface-sensitive chemical analysis method. It measures elemental concentrations and can provide information on chemical state, for example, whether sulfur is present as sulfide or sulfate.

Mössbauer spectroscopy is primarily used to identify corrosion products on steel. It examines a depth of 300 mm or less by measuring emitted gamma rays.

The electron probe microanalyzer is widely used for chemical analysis of surface areas as small as 1 μm in diameter. This instrument can determine the concentration of all but the low atomic number elements ($Z < 11$) and has a threshold sensitivity for elemental detection of approximately 0.02%.

In-depth composition profiles of oxide surface layers and corrosion films are possible using SIMS. Hydrogen concentrations in embrittled metals and alloys can also be determined. The compositions of oxidation, corrosion, and other contaminating films (oils, greases, and so on) can be determined using LEISS, a technique capable of detecting elements with atomic numbers of 2 or higher.

Spot tests are relatively simple qualitative chemical tests that can be used to identify the metal in the failed part, as well as the alloying elements, deposits, and corrosion products. These tests require little equipment, none of which is complicated or expensive, and can be performed quickly. Spot tests can be performed both in the laboratory and in the field; they do not require extensive training in analytical chemistry. The only requirement is that the substance to be tested be dissolvable; hydrochloric acid or even aqua regia may be used to dissolve the substance.

Spot tests for metallic elements, such as chromium, nickel, cobalt, iron, and molybdenum, are usually carried out by dissolving a small amount of the alloy in acid and mixing a drop of the resulting solution with a drop of a specific reagent on absorbent paper or a porcelain plate. Spot colorings produced in this way indicate the presence or absence of the metal or radical under test. Samples may be removed from large surfaces by spotting the specimen with a suitable acid, allowing time for dissolution, and collecting the acid spot with an eyedropper.

Bulk Material Analysis

Various analytical techniques can be used to determine elemental concentrations and to identify compounds in alloys, bulky deposits, and samples of environmental fluids, lubricants, and suspensions. Techniques such as emission spectroscopy, atomic absorption spectroscopy, inductively coupled plasma atomic emission spectroscopy, and classical wet analytical chemistry can be used to determine dissolved metals. Combustion methods, such as high-temperature combustion and inert-

gas fusion, are used to determine the concentrations of carbon, sulfur, nitrogen, hydrogen, and oxygen. X-ray diffraction (XRD) methods identify crystalline compounds either on the metal surface or as a mass of particles and can be used to analyze corrosion products and other surface deposits. X-ray fluorescence (XRF) analysis can be used to analyze both crystalline and amorphous solids, as well as liquids and gases. Infrared and ultraviolet spectroscopy are used to analyze organic materials. When organic materials, such as solvents, oils, greases, rubber, and plastic, are present in a complex mixture, the mixture is first separated into its individual components by gas chromatography.

Nondestructive Evaluation

Many conventional nondestructive evaluation (NDE) methods are quite useful for the detection of corrosion, even in its early stages (Table 1). In advanced stages, corrosion is often visible to the unaided eye, and suspect areas such as pits and rust discoloration on austenitic stainless steels are readily visible. The applications and effectiveness of various NDE techniques on specific alloys are shown in Table 2.

Visual, dye-penetrant, magnetic-particle, and eddy-current inspection are widely used for corrosion detection. However, their use is limited to periods of plant shutdown, or to times when systems can be made available for inspection. Obviously, these techniques can also be used to locate cracks on samples removed from service. Liquid-penetrant examination is useful in locating corrosion, but it may not reveal fine cracks. Because the substances found in liquid penetrants can be chemically similar to those that may cause SCC, the use of penetrants

Table 2 Nondestructive evaluation (NDE) techniques for evaluating suspected damage due to stress-corrosion cracking

Material	Ultrasonic, shear wave	Ultrasonic, longitudinal wave	Ultrasonic, surface wave	Magnetic particle, dry	Magnetic particle, wet fluorescent	Penetrant, visible	Penetrant, fluorescent	Radiographic, gamma ray	Radiographic, x-ray	Eddy current, standard	Eddy current, remote field	Acoustic emission	Visual	In situ metallography
Austenitic stainless steel	P	P	F	NA	NA	G	E	F	G	E	F	F	F	G
Martensitic stainless steel	P	P	F	P	E	G	E	F	G	NA	F	G	P	G
Ferritic stainless steel	P	P	F	P	E	G	E	F	G	NA	F	G	P	G
Nickel and nickel-base alloys	P	P	F	E(a)	E(a)	G	E	F	G	E(b)	F	F	P	G
Copper and copper-base alloys	P	P	F	NA	NA	G	E	F	G	E	F	F	P	F
Aluminum and aluminum alloys	P	P	F	NA	NA	G	E	P	G	E	F	F	P	F
Titanium and titanium alloys	P	P	F	NA	NA	G	E	P	G	E	F	F	P	F
Carbon and low-alloy steels	F	P	F	P	E	G	E	F	G	NA	F	G	F	E

Note: Detectability: NA, not applicable to this material; E, excellent; G, good; F, fair; P, poor. (a) For magnetic alloys only. (b) For nonmagnetic alloys only. Source: Ref 4

may interfere with identification of fracture-surface deposits. Consequently, their undesirable side effects on the overall analysis must be considered.

Ultrasonic inspection can be used for on-line monitoring, provided that surface contact is maintained. Unfortunately, this technique is time intensive and requires highly skilled personnel. Therefore, it is often impractical for thoroughly inspecting large vessels and extensive piping systems.

Acoustic emission allows detection of corrosion cracks online in particularly large vessels or systems that are generally too complex to inspect using other NDE techniques. However, operational or extraneous noise is often difficult to distinguish from crack growth. To compensate for the low amplitude of emission stemming from SCC, a considerably greater number of transducers than normal often must be used. Once the general location of the crack is located using acoustic emission, the crack orientation and dimensions can be determined using dye-penetrant or ultrasonic methods.

Corrosion Testing

Various corrosion-testing techniques are used to investigate corrosion failures. Laboratory corrosion testing can be particularly useful in helping investigators to decide which of two or more possible causes of failure was the most likely.

The laboratory corrosion-test techniques used in failure analysis may include accelerated tests, simulated-use tests, and electrochemical tests. A discussion of these tests follows, and they are described in more detail in Chapter 11.

Accelerated Tests. Some accelerated test methods have been accepted as industry standards. These methods usually accelerate corrosion and shorten test times by increasing temperature or using a more aggressive environment than that found in service. Because these factors and others vary widely in their influence on corrosion processes and time dependence, results of accelerated tests must be carefully interpreted.

Simulated-use tests can be more helpful than accelerated tests in failure investigations because, as the name implies, they more closely approximate the conditions encountered in service. In these tests, either actual components or test specimens are exposed to a synthetic or natural environment. The test conditions should simulate as closely as possible the environmental and mechanical conditions to which the failed part was subjected in service.

In designing and running simulated-use tests, the following guidelines should be considered carefully:

- Temperature, which may be steady or fluctuating and may also affect stress
- Single-phase or two-phase environment, which may involve alternate wetting and drying
- Environmental composition, including major and minor constituents, concentration, and changes in constituents, dissolved gases, and pH
- Electrochemical conditions, including such factors as galvanic coupling and applied cathodic protection
- Mechanical loading, which may be either static or cyclic. Under cyclic loading, the magnitude and direction (compressive or tensile) of mean stress, as well as stress wave shape and period, should be defined.
- Specimen surface damage, whether from fretting, abrasion, cavitation, erosion, or other mechanisms

Electrochemical tests can establish criteria for passivity or anodic protection against corrosion and can determine critical breakdown or pitting potentials. For the most part, however, electrochemical tests are more valuable for evaluating the corrosion resistance of materials and the effect of changes in the corrosive environment than as a failure analysis tool.

Mechanical Testing

Hardness testing is the simplest of the mechanical tests and is often the most versatile tool available to the failure analyst. Among its many applications, hardness testing can be used to assist in evaluating heat treatment (comparing the hardness of the failed component with that prescribed by specification), to provide an approximation of the tensile strength of steel, and to detect work hardening or to detect softening or hardening caused by overheating, decarburization, or carbon or nitrogen pickup. Hardness testing is also essentially nondestructive, except when preparation of a special hardness-test specimen is required, as in microhardness testing.

Other mechanical tests are useful in confirming that the failed component conforms to specification or in evaluating the effects of surface conditions on mechanical properties. Where appropriate, tensile, fatigue, or impact tests should be carried out provided sufficient material for the fabrication of test specimens is available. The determination of plane-strain fracture-toughness values may also be justifiable. It may be necessary to make some tests either at slightly elevated or at low temperatures to simulate service conditions. In addition, it may be helpful to test specimens after they have been subjected to particular heat treatments that simulate the thermal treatment of the failed component in

service in order to determine how this treatment has modified mechanical properties.

The failure analyst should exercise care in interpreting mechanical-test results. For example, the fact that a material has a tensile strength 5 to 10% below the minimum specified value does not mean that this is the prime cause of its failure in service. Also, it should be understood that laboratory tests on small specimens may not adequately represent the behavior of a much larger structure or component in service. For example, it is possible for brittle fracture of a large structure to occur at or near ordinary temperature, while subsequent laboratory tests of Charpy or Izod specimens show a transition temperature well below –18 °C (0 °F). The effects of size in fatigue, stress-corrosion, and hydrogen-embrittlement testing are not well understood. However, on the basis of the limited evidence available, it appears that resistance to these failure processes decreases as specimen size increases. Detailed information on various mechanical test procedures is provided in *Mechanical Testing*, Volume 8 of the *ASM Handbook*. The type of information provided by mechanical tests is also reviewed in Table 1.

Analyzing the Evidence, Formulating Conclusions, and Writing the Report

At a certain stage in every investigation, the evidence revealed by examinations and tests that are outlined in this chapter is analyzed and collated, and preliminary conclusions are formulated. Obviously, many investigations will not involve a series of clear-cut stages. If the probable cause of failure is apparent early in the examination, the pattern and extent of subsequent investigations will be directed toward confirmation of the probable cause and the elimination of other possibilities. Other investigations will follow a logical series of stages, as outlined in this chapter, and the findings at each stage will determine the manner in which the investigation proceeds. As new facts modify first impressions, different hypotheses of failure will develop and will be retained or abandoned as dictated by the findings. Where extensive laboratory facilities are available to the investigator, maximum effort will be devoted to amassing the results of mechanical tests, chemical analysis, fractography, and microscopy before the formulation of preliminary conclusions is attempted. Finally, in those investigations in which the cause of failure is particularly elusive, a search through published reports of similar instances may be required to suggest possible clues.

Some of the work performed during the course of an investigation may be thought to be unnecessary. It is important, however, to distinguish between work that is unnecessary and that which does not produce useful results. During an examination, it is to be expected that some of the work done will not assist directly in determining the cause

of failure; nevertheless, some negative evidence may be helpful in dismissing some causes of failure from consideration.

On the other hand, any tendency to curtail work essential to an investigation should be guarded against. In some cases, it is possible to form an opinion regarding the cause of failure from a single aspect of the investigation, such as visual examination of a fracture surface or examination on a single metallographic specimen. However, before final conclusions are reached, supplementary data confirming the original opinion, if available, should be sought. Total dependence on the conclusions that can be drawn from a single specimen, such as a metallographic section, may be readily challenged unless a history of similar failures can be drawn upon.

The following checklist, which is in the form of a series of questions, has been proposed as an aid in analyzing the evidence derived from examinations and tests and in formulating conclusions (Ref 5). The questions are also helpful in calling attention to details of the overall investigation that may have been overlooked. The questions are as follows:

- Has failure sequence been established?
- If failure involved cracking or fracture, have the initiation sites been determined?
- Did cracks initiate at the surface or below the surface?
- Was cracking associated with a stress concentrator?
- How long was the crack present?
- What was the intensity of the load?
- What was the type of loading—static, cyclic, or intermittent?
- How were the stresses oriented?
- What was the failure mechanism?
- What was the approximate service temperature at the time of failure?
- Did temperature contribute to failure?
- Did wear contribute to failure?
- Did corrosion contribute to failure? What type of corrosion?
- Did the crack surface corrode during the failure or subsequent to the failure?
- Was the proper material used? Is a better material required?
- Was the cross section adequate for the class of service?
- Was the quality of the material acceptable in accordance with specification?
- Were the mechanical properties of the material acceptable in accordance with specification?
- Was the component that failed properly heat treated?
- Was the component that failed properly fabricated?
- Was the component properly assembled or installed?

- Was the component properly protected (paint thickness, kind of surface protection and so on)?
- Was the component repaired during service? If so, was the repair performed correctly?
- Was the component properly run in?
- Was the component properly maintained?
- Was the component properly lubricated?
- Was failure related to abuse in service?
- Can the design of the component be improved to prevent similar failures?
- Are failures likely to occur in similar components now in service? What can be done to prevent their failure?

In general, the answers to these questions will be derived from a combination of records and the examinations and tests previously outlined in this article. However, the cause or causes of failure cannot always be determined with certainty. In this case, the investigation should determine the most probable cause or causes of failure, distinguishing findings based on demonstrated fact from conclusions based on conjecture.

Writing the Report. The failure analysis report should be written clearly, concisely, and logically. One experienced investigator has proposed that the report be divided into the following principal sections (Ref 5):

- Description of the failed component
- Service conditions at the time of failure
- Prior service history
- Manufacturing and processing history of the component
- Mechanical and metallurgical study of failure
- Metallurgical evaluation of quality
- Summary of the mechanisms that caused failure
- Recommendations for prevention of similar failure or for correction of similar components in service

Obviously, not every report will require coverage under every one of these sections. Lengthy reports should begin with an abstract. Because readers of failure analysis reports are often purchasing, operating, and accounting personnel, the avoidance of technical jargon wherever possible is highly desirable. A glossary of terms may also be helpful. The use of appendixes containing detailed calculations, equations, and tables of chemical and metallurgical data can serve to keep the body of the report clear and uncluttered.

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APPENDIX 1

Glossary of Corrosion-Related Terms

A

accelerated corrosion test. Method designed to approximate, in a short time, the deteriorating effect under normal long-term service conditions.

acid rain. Atmospheric precipitation with a pH below 5.6 to 5.7. Burning of fossil fuels for heat and power is the major factor in the generation of oxides of nitrogen and sulfur, which are converted into nitric and sulfuric acids washed down in the rain. See also *atmospheric corrosion.*

active. The negative direction of *electrode potential.* Also used to describe corrosion and its associated potential range when an electrode potential is more negative than an adjacent depressed corrosion rate (passive) range.

active metal. A metal ready to corrode, or being corroded.

active potential. The potential of a corroding material.

aeration cell (oxygen cell). See *differential aeration cell.*

aerobic. Exposed to oxygen.

alclad. Composite wrought product comprised of an aluminum alloy core having on one or both surfaces a metallurgically bonded aluminum or aluminum alloy coating that is anodic to the core and thus electrochemically protects the core against corrosion.

alligatoring. (1) Surface cracking of an organic film leaving an appearance similar to that of an alligator hide. (2) A special form of *checking* in which the surface hardens and shrinks at a much faster rate than the body of the coating.

alternate-immersion test. A corrosion test in which the specimens are intermittently exposed to a liquid medium at definite time intervals.

amphoteric metal. A metal that is susceptible to corrosion in both acid and alkaline environments.

anaerobic. Free of air or uncombined oxygen.

anion. A negatively charged ion that migrates through the electrolyte toward the *anode* under the influence of a potential gradient. See also *cation* and *ion.*

anode. The *electrode* of an electrolyte cell at which oxidation occurs. Electrons flow away from the anode in the external circuit. It is usually at the electrode that corrosion occurs and metal ions enter solution. Contrast with *cathode.*

anode bed. An array of electrodes intentionally placed in an *electrolyte* (soil or water) to complete an *electrolytic cell* being used to mitigate *corrosion* through *cathodic protection.*

anode corrosion. The dissolution of a metal acting as an *anode.*

anode corrosion efficiency. The ratio of the actual corrosion (weight loss) of an *anode* to the theoretical corrosion (weight loss) calculated by *Faraday's law* from the quantity of electricity that has passed.

anodic inhibitor. A chemical substance or mixture that prevents or reduces the rate of the anodic or *oxidation* reaction. See also *inhibitor.*

anodic polarization. The change of the *electrode potential* in the noble (positive) direction due to current flow. See also *polarization.*

anodic protection. (1) A technique to reduce the corrosion rate of a metal by polarizing it into its passive region, where dissolution rates are low. (2) Imposing an external electrical potential to protect a metal from corrosive attack. (Applicable only to metals that show active-passive behavior.) Contrast with *cathodic protection.*

anodic reaction. Electrode reaction equivalent to a transfer of positive charge from the electronic to the ionic conductor. An anodic reaction is an *oxidation* process. An example common in corrosion is the following: $M \rightarrow M^{n+} + ne^{-}$.

anodizing. Oxide coating formed on a metal surface (generally aluminum) by an electrolytic process.

anolyte. The *electrolyte* adjacent to the *anode* in an *electrolytic cell.*

antifouling. The prevention of marine organism attachment or growth on a submerged metal surface, generally through chemical toxicity caused by the composition of the metal or coating layer.

aqueous. Pertaining to water; an aqueous solution is made by using water as a solvent.

atmospheric corrosion. The gradual degradation or alteration of a material by contact with substances present in the atmosphere, such as oxygen, carbon dioxide, water vapor, and sulfur, nitrogen, and chlorine compounds.

auxiliary electrode. An *electrode* commonly used in *polarization* studies to pass current to or from a test electrode. It is usually made from a noncorroding material.

B

backfill. Material placed in a drilled hole to fill space around *anodes,* vent pipe, and buried components of a *cathodic protection* system.

bimetallic corrosion. See *galvanic corrosion.*

biological corrosion. Deterioration of metals as a result of the metabolic activity of microorganisms.

blistering. Formation of dome-shaped projections in paints or varnish films resulting from local loss of adhesion and lifting of the film from an underlying paint film (intercoat blistering) or the base substrate.

blushing. Whitening and loss of gloss of a usually organic coating caused by moisture. Also called blooming.

brackish water. (1) Water having salinity values ranging from approximately 0.5 to 17 parts per thousand. (2) Water having less salt than seawater but undrinkable.

breakdown potential. The least *noble* potential where *pitting* or *crevice corrosion,* or both, will initiate and propagate.

brine. Seawater containing a higher concentration of dissolved salt than that of the ordinary ocean.

C

calcareous coating or deposit. A layer consisting of a mixture of calcium carbonate and magnesium hydroxide deposited on surfaces being cathodically protected because of the increased pH adjacent to the protected surface.

calomel electrode. An *electrode* widely used as a reference electrode of known potential in electrometric measurement of acidity and alkalinity, *corrosion* studies, voltammetry, and measurement of the potentials of other electrodes. See also *electrode potential, reference electrode,* and *saturated calomel electrode.*

CASS test. See *copper-accelerated salt-spray test.*

cathode. The *electrode* of an *electrolytic cell* at which *reduction* is the principal reaction. (Electrons flow toward the cathode in the external circuit.) Typical cathodic processes are *cations* taking up electrons and being discharged, oxygen being reduced, and the reduction of an

element or group of elements from a higher to a lower valence state. Contrast with *anode*.

cathodic corrosion. Corrosion resulting from a cathodic condition of a structure usually caused by the reaction of an *amphoteric metal* with the alkaline products of *electrolysis.*

cathodic disbondment. The destruction of adhesion between a coating and its substrate by products of a *cathodic reaction.*

cathodic inhibitor. A chemical substance or mixture that prevents or reduces the rate of the cathodic or reduction reaction.

cathodic polarization. The change of the *electrode potential* in the active (negative) direction due to current flow. See also *polarization.*

cathodic protection. (1) Reduction of corrosion rate by shifting the *corrosion potential* of the electrode toward a less oxidizing potential by applying an external *electromotive force.* (2) Partial or complete protection of a metal from corrosion by making it a *cathode,* using either a galvanic or an impressed current. Contrast with *anodic protection.*

cathodic reaction. Electrode reaction equivalent to a transfer of negative charge from the electronic to the ionic conductor. A cathodic reaction is a *reduction* process. An example common in corrosion is: $Ox + ne^- \rightarrow Red$.

catholyte. The *electrolyte* adjacent to the *cathode* of an *electrolytic cell.*

cation. A positively charged ion that migrates through the electrolyte toward the *cathode* under the influence of a potential gradient. See also *anion* and *ion.*

caustic. A strongly alkaline substance. Also, a hydroxide of a light metal, such as sodium hydroxide or potassium hydroxide.

caustic embrittlement. An obsolete historical term denoting a form of *stress-corrosion cracking* most frequently encountered in carbon steels or iron-chromium-nickel alloys that are exposed to concentrated hydroxide solutions at temperatures of 200 to 250 °C (400 to 480 °F).

cavitation. The formation and instantaneous collapse of innumerable tiny voids or cavities within a liquid subjected to rapid and intense pressure changes. Cavitation produced by ultrasonic radiation is sometimes used to effect violent localized agitation. Cavitation caused by severe turbulent flow often leads to *cavitation damage.*

cavitation corrosion. A process involving conjoint *corrosion* and *cavitation.*

cavitation damage. The degradation of a solid body resulting from its exposure to *cavitation.* This can include loss of material, surface deformation, or changes in properties or appearance.

cavitation-erosion. Progressive loss of original material from a solid surface due to continuing exposure to *cavitation.*

cell. See *electrochemical cell.*

chalking. The development of loose removable powder at the surface of an organic coating usually caused by weathering.

checking. The development of slight breaks in a coating that do not penetrate to the underlying surface.

concentration cell. An *electrochemical cell,* the *electromotive force* of which is caused by a difference in concentration of some component in the electrolyte. This difference leads to the formation of discrete *cathode* and *anode* regions.

concentration polarization. That portion of the *polarization* of a cell produced by concentration changes resulting from passage of current through the *electrolyte.*

conductivity. The ratio of the electric current density to the electric field in a material. Also called electrical conductivity or specific conductance.

contact corrosion. See *galvanic corrosion.*

continuity bond. A metallic connection that provides electrical continuity between metal structures.

copper-accelerated salt-spray (CASS) test. An *accelerated corrosion test* for some electrodeposits and for anodic coatings on aluminum.

corrodkote test. An *accelerated corrosion test* for electrodeposits.

corrosion. The chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties.

corrosion-erosion. See *erosion-corrosion.*

corrosion fatigue. The process in which a metal fractures prematurely under conditions of simultaneous *corrosion* and repeated cyclic loading at lower stress levels or fewer cycles than would be required in the absence of the corrosive environment.

corrosion fatigue strength. The maximum repeated stress that can be endured by a metal without failure under definite conditions of *corrosion* and *fatigue* and for a specific number of stress cycles and a specified period of time.

corrosion inhibitor. See *inhibitor.*

corrosion potential (E_{corr}). The *potential* of a corroding surface in an *electrolyte,* relative to a reference electrode. Also called rest potential, open-circuit potential, or freely corroding potential.

corrosion product. Substance formed as a result of *corrosion.*

corrosion rate. The amount of *corrosion* occurring in unit time. For example, mass change per unit area per unit time; penetration per unit time.

corrosion resistance. Ability of a metal to withstand *corrosion* in a given *corrosion system.*

corrosion system. System consisting of one or more metals and all parts of the environment that influence *corrosion.*

corrosivity. Tendency of an environment to cause *corrosion* in a given *corrosion system.*

counterelectrode. See *auxiliary electrode.*

cracking (of coating). Breaks in a coating that extend through to the underlying surface.

crazing. A network of checks or cracks appearing on a coated surface.

crevice corrosion. *Localized corrosion* of a metal surface at, or immediately adjacent to, an area that is shielded from full exposure to the environment because of close proximity between the metal and the surface of another material.

critical humidity. The *relative humidity* above which the *atmospheric corrosion* rate of some metals increases sharply.

critical pitting potential (E_{cp}, E_p, E_{pp}). The lowest value of oxidizing potential (voltage) at which pits nucleate and grow. It is dependent on the test method used.

current. The net transfer of electric charge per unit time. Also called electric current. See also *current density.*

current density. The *current* flowing to or from a unit area of an electrode surface.

current efficiency. The ratio of the *electrochemical equivalent current density* for a specific reaction to the total applied current density.

D

deactivation. The process of prior removal of the active corrosive constituents, usually oxygen, from a corrosive liquid by controlled corrosion of expendable metal or by other chemical means, thereby making the liquid less corrosive.

dealloying. The selective corrosion of one or more components of a solid solution alloy. Also called parting or selective leaching. See also *dezincification* and *graphitic corrosion.*

depolarization. The removal of factors resisting the current in an *electrochemical cell.*

deposit corrosion. Corrosion occurring under or around a discontinuous deposit on a metallic surface. Also called poultice corrosion.

descaling. Removing the thick layer of oxides formed on some metals at elevated temperatures.

dezincification. Corrosion in which zinc is selectively leached from copper-zinc alloys. See also *dealloying.*

dielectric shield. In a cathodic protection system, an electrically nonconductive material, such as a coating, plastic sheet, or pipe, that is placed between an anode and an adjacent cathode to avoid current wastage and to improve current distribution, usually on the cathode.

differential aeration cell. An *electrolytic cell,* the *electromotive force* of which is due to a difference in air (oxygen) concentration at one

electrode as compared with that at another electrode of the same material. See also *concentration cell.*

diffusion. (1) Spreading of a constituent in a gas, liquid, or solid, tending to make the composition of all parts uniform. (2) The spontaneous movement of atoms or molecules to new sites within a material.

diffusion-limited current density. The *current density,* often referred to as *limiting current density,* that corresponds to the maximum transfer rate that a particular species can sustain because of the limitation of *diffusion.*

disbondment. The loss of adhesion between a coating and the substrate.

dissmilar metal corrosion. See *galvanic corrosion.*

double layer. The interface between an *electrode* or a suspended particle and an *electrolyte* created by charge-charge interaction leading to an alignment of oppositely charged ions at the surface of the electrode or particle. The simplest model is represented by a parallel plate condensor.

drainage. Conduction of electric current from an underground metallic structure by means of a metallic conductor.

dry corrosion. See *gaseous corrosion.*

E

electrochemical cell. An electrochemical system consisting of an *anode* and a *cathode* in metallic contact and immersed in an *electrolyte.* The anode and cathode can be different metals or dissimilar areas on the same metal surface.

electrochemical equivalent. The weight of an element or group of elements oxidized or reduced at 100% efficiency by the passage of a unit quantity of electricity.

electrochemical impedance. The frequency dependent, complex valued proportionality factor, $\Delta E/\Delta I$, between the applied potential (or *current*) and the response *current* (or potential) in an *electrochemical cell.* This factor becomes the impedance when the perturbation and response are related linearly (the factor value is independent of the perturbation magnitude) and the response is caused only by the perturbation. The value can be related to the corrosion rate when the measurement is made at the *corrosion potential.*

electrochemical potential. The partial derivative of the total electrochemical free energy of a constituent with respect to the number of moles of this constituent where all factors are kept constant. It is analogous to the chemical potential of a constituent except that it includes the electric as well as chemical contributions to the free energy.

electrochemical series. Same as *electromotive force series.*

electrode. A conductor used to establish contact with an *electrolyte* and through which *current* is transferred to or from an electrolyte.

electrode polarization. Change of *electrode potential* with respect to a reference value. Often the *free corrosion potential* is used as the reference value. The change can be caused, for example, by the application of an external electrical current or by the addition of an oxidant or reductant.

electrode potential. The potential of an *electrode* in an *electrolyte* as measured against a reference electrode. The electrode potential does not include any resistance losses in potential in either the solution or external circuit. It represents the reversible work to move a unit charge from the electrode surface through the solution to the reference electrode.

electrode reaction. Interfacial reaction equivalent to a transfer of charge between electronic and ionic conductors. See also *anodic reaction* and *cathodic reaction.*

electrokinetic potential. This potential, sometimes called zeta potential, is a potential difference in the solution caused by residual, unbalanced charge distribution in the adjoining solution, producing a double layer. The electrokinetic potential is different from the *electrode potential* in that it occurs exclusively in the solution phase; that is, it represents the reversible work necessary to bring unit charge from infinity in the solution up to the interface in question but not through the interface. Also called zeta potential.

electrolysis. Production of chemical changes of the *electrolyte* by the passage of current through an *electrochemical cell.*

electrolyte. A chemical substance containing ions that migrate in an electric field.

electrolytic cell. An assembly, consisting of a vessel, electrodes, and an electrolyte, in which *electrolysis* can be carried out.

electrolytic cleaning. A process of removing soil, scale, or corrosion products from a metal surface by subjecting it as an *electrode* to an electric current in an electrolytic bath.

electrolytic protection. See *cathodic protection.*

electromotive force series (emf series). A list of elements arranged according to their standard *electrode potentials,* with *noble* metals such as gold being positive and *active* metals such as zinc being negative.

embrittlement. The severe loss of ductility, toughness, or both, of a material, usually a metal or alloy.

environment. The surroundings or conditions (physical, chemical, mechanical) in which a material exists.

environmental cracking. Brittle fracture of a normally ductile material in which the corrosive effect of the *environment* is a causative factor. Environmental cracking is a general term that includes *corrosion fatigue, high-temperature hydrogen attack, hydrogen blister-*

ing, hydrogen embrittlement, liquid metal embrittlement, stress-corrosion cracking, and *sulfide stress cracking.* The following terms have been used in the past in connection with environmental cracking, but are becoming obsolete: *caustic embrittlement,* delayed cracking (or fracture), *season cracking,* static fatigue, stepwise cracking, sulfide corrosion cracking, and sulfide stress-corrosion cracking.

equilibrium (reversible) potential. The potential of an electrode in an electrolytic solution when the forward rate of a given reaction is exactly equal to the reverse rate. The equilibrium potential can only be defined with respect to a specific electrochemical reaction.

erosion. The progressive loss of material from a solid surface due to mechanical interaction between that surface and a fluid, a multicomponent fluid, or solid particles carried with the fluid.

erosion-corrosion. A conjoint action involving *corrosion* and *erosion* in the presence of a moving corrosive fluid, leading to the accelerated loss of material.

exchange current. When an electrode reaches dynamic equilibrium in a solution, the rate of anodic dissolution balances the rate of cathodic plating. The rate at which either positive or negative charges are entering or leaving the surface at this point is known as the exchange current.

exchange current density. The rate of charge transfer per unit area when an electrode reaches dynamic equilibrium (at its reversible potential) in a solution; that is, the rate of anodic charge transfer (*oxidation*) balances the rate of cathodic charge transfer (*reduction*).

exfoliation. Corrosion that proceeds laterally from the sites of initiation along planes parallel to the surface, generally at grain boundaries, forming corrosion products that force metal away from the body of the material, giving rise to a layered appearance.

external circuit. The wires, connectors, measuring devices, current sources, etc., that are used to bring about or measure the desired electrical conditions within the test cell. It is this portion of the cell through which electrons travel.

F

Faraday's law. (1) The amount of any substance dissolved or deposited in *electrolysis* is proportional to the total electric charge passed. (2) The amounts of different substances dissolved or deposited by the passage of the same electric charge are proportional to their equivalent weights.

fatigue. The phenomenon leading to fracture under repeated or fluctuating stresses having a maximum value less than the tensile strength of the material. Fatigue fractures are progressive and grow under the action of the fluctuating stress.

filiform corrosion. Corrosion that occurs under some coatings in the form of randomly distributed threadlike filaments.

fouling. An accumulation of deposits. This term includes accumulation and growth of marine organisms on a submerged metal surface and also includes the accumulation of deposits (usually inorganic) on heat exchanger tubing.

free corrosion potential. *Corrosion potential* in the absence of net electrical current flowing to or from the metal surface.

fretting corrosion. The accelerated deterioration at the interface between contacting surfaces as the result of corrosion and slight oscillatory movement between the two surfaces.

G

galvanic anode. A metal which, because of its relative position in the galvanic series, provides *sacrificial protection* to metals that are more *noble* in the series, when coupled in an *electrolyte*.

galvanic cell. A cell in which chemical change is the source of electrical energy. It usually consists of two dissimilar conductors in contact with each other and with an *electrolyte*, or of two similar conductors in contact with each other and with dissimilar electrolytes.

galvanic corrosion. Accelerated corrosion of a metal because of an electrical contact with a more *noble* metal or nonmetallic conductor in a corrosive *electrolyte*. Also called bimetallic corrosion, contact corrosion, dissimilar metal corrosion, and two-metal corrosion.

galvanic couple. A pair of dissimilar conductors, commonly metals, in electrical contact. See also *galvanic corrosion.*

galvanic couple potential. See *mixed potential.*

galvanic current. The electric current that flows between metals or conductive nonmetals in a *galvanic couple.*

galvanic series. A list of metals and alloys arranged according to their relative *corrosion potentials* in a given environment. Compare with *electromotive force series.*

galvanostatic. An experimental technique whereby an *electrode* is maintained at a constant current in an *electrolyte.*

gaseous corrosion. Corrosion with gas as the only corrosive agent and without any aqueous phase on the surface of the metal. Also called *dry corrosion.*

general corrosion. *See uniform corrosion.*

Gibbs free energy. The thermodynamic function $\Delta G = \Delta H - T\Delta S$, where H is enthalpy, T is absolute temperature, and S is entropy. Also called free energy, free enthalpy, or Gibbs function.

grain-boundary corrosion. Same as *intergranular corrosion.*

graphitic corrosion. Deterioration of gray cast iron in which the metallic constituents are selectively leached or converted to corrosion

products leaving the graphite intact. The term *graphitization* is commonly used to identify this form of corrosion, but is not recommended because of its use in metallurgy for the decomposition of carbide to graphite. See also *dealloying*.

graphitization. A metallurgical term describing the formation of graphite in iron or steel, usually from decomposition of iron carbide at elevated temperatures. Not recommended as a term to describe *graphitic corrosion.*

groundbed. A buried item, such as junk steel or graphite rods, that serves as the *anode* for the *cathodic protection* of pipelines or other buried structures.

H

half cell. A (pure metal) *electrode* immersed in a suitable *electrolyte* of known concentration, designed for measurements of *electrode potential.*

halogen. Any of the elements of the halogen family, consisting of fluorine, chlorine, bromine, iodine, and astatine.

heat-affected zone (HAZ). Area adjacent to a weld where the thermal cycle has caused microstructural changes, which generally affect corrosion behavior.

high-temperature hydrogen attack. A loss of strength and ductility of steel by high-temperature reaction of absorbed hydrogen with carbides in the steel resulting in decarburization and internal fissuring.

holidays. Discontinuities in a coating (such as porosity, cracks, gaps, and similar flaws) that allow areas of base metal to be exposed to any corrosive environment that contacts the coated surface.

hot corrosion. An accelerated corrosion of metal surfaces that results from the combined effect of *oxidation* and reactions with sulfur compounds and other contaminants, such as chlorides, to form a molten salt on a metal surface that fluxes, destroys, or disrupts the normal protective oxide. See also *gaseous corrosion.*

humidity tests. A corrosion test involving exposure of specimens at controlled levels of humidity and temperature. Contrast with *salt fog test.*

hydrogen blistering. The formation of subsurface planar cavities, called hydrogen blisters, in a metal resulting from excessive internal hydrogen pressure. Growth of near-surface blisters in low-strength metals usually results in surface bulges.

hydrogen damage. A general term for the embrittlement, cracking, blistering, and hydride formation that can occur when hydrogen is present in some metals.

hydrogen embrittlement. A loss of ductility of a metal resulting from absorption of hydrogen.

hydrogen-induced cracking. Stepwise internal cracks that connect adjacent hydrogen blisters on different planes in the metal, or to the metal surface. Also called stepwise cracking.

hydrogen overvoltage. Overvoltage associated with the liberation of hydrogen gas.

hydrogen stress cracking. Cracking that results from the presence of hydrogen in a metal in combination with tensile stress. It occurs most frequently with high-strength alloys.

I

immunity. A state of resistance to *corrosion* or anodic dissolution of a metal caused by thermodynamic stability of the metal.

impingement corrosion. A form of *erosion-corrosion* generally associated with the local impingement of a high-velocity, flowing fluid against a solid surface.

impressed current. Direct current supplied by a device employing a power source external to the electrode system of a *cathodic protection* installation.

inclusions. Particles of foreign material in a metallic matrix. The particles are usually compounds (such as oxides, sulfides, or silicates) but can be of any substance that is foreign to (and essentially insoluble in) the matrix.

incubation period. A period prior to the detection of corrosion while the metal is in contact with a corrodent.

industrial atmosphere. An atmosphere in an area of heavy industry with soot, fly ash, and sulfur compounds as the principal constituents.

inhibitor. A chemical substance or combination of substances that, when present in the *environment,* prevents or reduces *corrosion* without significant reaction with the components of the environment.

intercrystalline corrosion. See *intergranular corrosion.*

interdendritic corrosion. Corrosive attack of cast metals that progresses preferentially along paths between dendrites.

intergranular corrosion. Corrosion occurring preferentially at grain boundaries, usually with slight or negligible attack on the adjacent grains. Also called intercrystalline corrosion.

intergranular stress-corrosion cracking (IGSCC). *Stress-corrosion cracking* in which the cracking occurs along grain boundaries.

internal oxidation. The formation of isolated particles of corrosion products beneath the metal surface. This occurs as the result of preferential oxidation of certain alloy constituents by inward diffusion of oxygen, nitrogen, sulfur, and so forth.

intumescence. The swelling or bubbling of a coating usually because of heating.

ion. An atom, or group of atoms, that has gained or lost one or more outer electrons and thus carries an electric charge. Positive ions, or *cations,* are deficient in outer electrons. Negative ions, or *anions,* have an excess of outer electrons.

iron rot. Deterioration of wood in contact with iron-base alloys.

isocorrosion diagram. A graph or chart that shows constant corrosion behavior with changing solution (environment) composition and temperature.

K

knife-line attack. *Intergranular corrosion* of an alloy, usually stabilized stainless steel, along a line adjoining or in contact with a weld after heating into the *sensitization* temperature range.

L

Langelier index. A calculated saturation index for calcium carbonate that is useful in predicting *scaling* behavior of natural water.

limiting current density. The maximum current density that can be used to obtain a desired electrode reaction without undue interference such as from *polarization.*

linear elastic fracture mechanics. A method of fracture analysis that can determine the stress (or load) required to induce fracture instability in a structure containing a cracklike flaw of known size and shape.

liquid metal embrittlement. Catastrophic brittle failure of a normally ductile metal when in contact with a liquid metal and subsequently stressed in tension.

local action corrosion. Corrosion due to the action of *local cells,* that is, galvanic cells resulting from inhomogeneities between adjacent areas on a metal surface exposed to an *electrolyte.*

local cell. A *galvanic cell* resulting from inhomogeneities between areas on a metal surface in an *electrolyte.* The inhomogeneities can be of physical or chemical nature in either the metal or its environment.

localized corrosion. Corrosion at discrete sites, for example, *crevice corrosion, pitting,* and *stress-corrosion cracking.*

long-line current. Current that flows through the earth from an anodic to a cathodic area of a continuous metallic structure. Usually used only where the areas are separated by considerable distance and where the current results from *concentration-cell* action.

luggin probe. A small tube or capillary filled with electrolyte, terminating close to the metal surface under study, and used to provide an ionically conducting path without diffusion between an electrode under study and a *reference electrode.*

M

metal dusting. Accelerated deterioration of metals in carbonaceous gases at elevated temperatures to form a dustlike corrosion product.

microbial corrosion. Corrosion that is affected by the action of microorganisms in the environment.

mill scale. The heavy oxide layer formed during hot fabrication or heat treatment of metals.

mixed potential. The potential of a specimen (or specimens in a galvanic couple) when two or more electrochemical reactions are occurring. Also called *galvanic couple* potential.

N

Nernst equation. An equation that expresses the exact *electromotive force* of a cell in terms of the activities of products and reactants of the cell.

Nernst layer. The diffusion layer at the surface of an electrode in which the concentration of a chemical species is assumed to vary linearly from the value in the bulk solution to the value at the electrode surface.

noble. The positive direction of *electrode potential,* thus resembling noble metals such as gold and platinum.

noble metal. (1) A metal whose potential is highly positive relative to the hydrogen electrode. (2) A metal that occurs commonly in nature in the free state. (3) A metal or alloy whose corrosion products are formed with a small negative or a positive free-energy change.

noble potential. A potential more cathodic (positive) than the standard hydrogen potential.

O

open-circuit potential. The potential of an electrode measured with respect to a reference electrode or another electrode when no current flows to or from it.

overvoltage. The change in potential of an electrode from its equilibrium or steady-state value when current is applied.

oxidation. (1) A reaction in which there is an increase in valence resulting from a loss of electrons. Contrast with *reduction.* (2) A corrosion reaction in which the corroded metal forms an oxide; usually applied to reaction with a gas containing elemental oxygen, such as air.

oxygen concentration cell. See *differential aeration cell.*

P

parting. See *dealloying.*

passivation. (1) A reduction of the *anodic reaction* rate of an electrode involved in corrosion. (2) The process in metal corrosion by which metals become *passive*. (3) The changing of a chemically active surface of a metal to a much less reactive state.

passivator. A type of *inhibitor* that appreciably changes the potential of a metal to a more *noble* (positive) value.

passive. (1) The positive direction of *electrode potential*. (2) The state of the metal surface characterized by low corrosion rates in a potential region that is strongly oxidizing for the metal.

passive-active cell. A corrosion cell in which the *anode* is a metal in the *active* state and the *cathode* is the same metal in the *passive* state.

passivity. A condition in which a piece of metal, because of an impervious covering of oxide or other compound, has a potential much more positive than that of the metal in the active state.

patina. A thin layer of corrosion product, usually green, that forms on the surface of metals such as copper and copper alloys exposed to the atmosphere. Also used to describe the appearance of a weathered surface of any metal.

pH. (1) The negative logarithm of the hydrogen ion activity written as the following:

$$pH = -\log_{10}(a_{H^+})$$

where a_{H^+} = hydrogen ion activity = the molar concentration of hydrogen ions multiplied by the mean ion-activity coefficient. (2) A measure of the acidity or alkalinity of a solution. At 25 °C (77 °F), 7.0 is the neutral value. Decreasing values below 7.0 indicate increasing acidity; increasing values above 7.0, increasing alkalinity.

pickling. Removing surface oxides from metals by chemical or electrochemical reaction.

pitting. *Localized corrosion* of a metal surface, confined to a point or small area, that takes the form of cavities called pits.

pitting factor. Ratio of the depth of the deepest pit resulting from corrosion divided by the average penetration as calculated from weight loss.

polarization. (1) The change from the open-circuit electrode potential as the result of the passage of current. (2) A change in the potential of an electrode during electrolysis, such that the potential of an *anode* becomes more *noble*, and that of *cathode* more active, than their respective reversible potentials. Often accomplished by formation of a film on the electrode surface.

polarization admittance. The reciprocal of *polarization resistance* (di/dE).

polarization curve. A plot of *current density* versus *electrode potential* for a specific electrode-electrolyte combination.

polarization decay. The decrease in *electrode potential* with time resulting from the interruption of applied current.

polarization resistance. The slope (dE/di) at the *corrosion potential* of a potential (E)/current density (i) curve. Also used to describe the method of measuring corrosion rates using this slope.

polarized potential. The potential across the structure/electrolyte interface that is the sum of the *corrosion potential* and the *cathodic polarization*.

potential-pH diagram. See *Pourbaix (potential-pH) diagram.*

potentiodynamic. A technique wherein the potential of an electrode with respect to a *reference electrode* is varied at a selected rate by application of a current through the electrolyte.

potentiostat. An instrument for automatically maintaining an *electrode* in an *electrolyte* at a constant potential or controlled potentials with respect to a suitable reference electrode.

potentiostatic. The technique for maintaining a constant *electrode potential.*

poultice corrosion. See *deposit corrosion.*

Pourbaix (potential-pH) diagram. A graphical method of representing the regions of thermodynamic stability of species for metal/*electrolyte* systems.

primary passive potential (passivation potential). The potential corresponding to the maximum active *current density* (critical anodic current density) of an electrode that exhibits *active-passive* corrosion behavior.

protection potential. The most *noble* potential where *pitting* and *crevice corrosion* will not propagate.

R

redox potential. The potential of a reversible *oxidation-reduction* electrode measured with respect to a reference electrode, corrected to the hydrogen electrode, in a given *electrolyte.*

reduction. A reaction in which there is a decrease in valence resulting from a gain in electrons. Contrast with *oxidation.*

reference electrode. An electrode whose *open-circuit potential* is constant under similar conditions of measurement), which is used for measuring the relative potentials of other electrodes.

relative humidity. The ratio, expressed as a percentage, of the amount of water vapor present in a given volume of air at a given temperature to the amount required to saturate the air at that temperature.

rest potential. See *corrosion potential.*

rust. A visible corrosion product consisting of various iron oxides and hydrated oxides of iron. Applied only to ferrous alloys. See also *white rust.*

S

sacrificial anode. An alloy electrode less *noble* than the structure to which it is connected, meant to induce *galvanic corrosion* on the *electrode* (*anode*) in preference to that of the structure.

sacrificial protection. Reduction of corrosion of a metal in an *electrolyte* by galvanically coupling it to a more anodic metal; a form of *cathodic protection.*

salt fog test. An *accelerated corrosion test* in which specimens are exposed to a fine mist of a solution usually containing sodium chloride, but sometimes modified with other chemicals.

salt spray test. See *salt fog test.*

saturated calomel electrode. A reference electrode composed of mercury, mercurous chloride (calomel), and a saturated aqueous chloride solution.

scaling. (1) The formation at high temperatures of thick corrosion product layers on a metal surface. (2) The deposition of water-insoluble constituents on a metal surface.

season cracking. An obsolete historical term usually applied to *stress-corrosion cracking* of brass.

selective leaching. See *dealloying.*

sensitization. In austenitic stainless steels, the precipitation of chromium carbides, usually at grain boundaries, on exposure to temperatures of about 550 to 850 °C (about 1000 to 1550 °F), leaving the grain boundaries depleted of chromium and therefore susceptible to preferential attack (*intergranular corrosion*) by a corroding (oxidizing) medium.

sheltered corrosion. Corrosion occurring in locations where moisture condenses or accumulates and does not dry out for long periods.

sour gas. A gaseous environment containing hydrogen sulfide and carbon dioxide in hydrocarbon reservoirs.

sour water. Waste waters containing fetid materials, usually sulfur compounds.

spalling. The spontaneous chipping, fragmentation, or separation of a surface or surface coating.

standard electrode potential. The reversible potential for an electrode process when all products and reactions are at unit activity on a scale in which the potential for the standard hydrogen half-cell is zero.

stray-current corrosion. Corrosion resulting from direct current flow through paths other than the intended circuit. For example, by an extraneous current in the earth.

stress-corrosion cracking (SCC). Cracking of a metal produced by the combined action of corrosion and tensile stress (residual or applied).

subsurface corrosion. Formation of isolated particles of corrosion products beneath a metal surface. This results from the preferential reactions of certain alloy constituents to inward diffusion of oxygen, nitrogen, or sulfur.

sulfidation. The reaction of a metal or alloy with a sulfur-containing species to produce a sulfur compound that forms on or beneath the surface on the metal or alloy.

sulfide stress cracking (SSC). Brittle failure by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide. See also *environmental cracking.*

T

Tafel line, Tafel slope, Tafel diagram. When an electrode is polarized, it frequently will yield a current/potential relationship over a region that can be approximated by: $\eta = \pm B \log (i/i_o)$, where η is the change in open-circuit potential, i is the current density, and B and i_o are constants. The constant B is also known as the Tafel slope. If this behavior is observed, a plot on semilogarithmic coordinates is known as the Tafel line and the overall diagram is termed a Tafel diagram.

tarnish. Surface discoloration of a metal caused by formation of a thin film of corrosion product.

thermogalvanic corrosion. Corrosion resulting from an *electrochemical cell* caused by a thermal gradient.

throwing power. The relationship between the current density at a point on a surface and its distance from the *counterelectrode*. The greater the ratio of the surface resistivity shown by the electrode reaction to the volume resistivity of the electrolyte, the better the throwing power of the process.

transpassive. The *noble* region of potential where an *electrode* exhibits a higher than passive current density.

tuberculation. The formation of *localized corrosion* products scattered over the surface in the form of knoblike mounds called tubercles.

two-metal corrosion. See *galvanic corrosion.*

U

underfilm corrosion. Corrosion that occurs under organic films in the form of randomly distributed threadlike filaments or spots. In many cases this is identical to *filiform corrosion.*

uniform corrosion. (1) A type of corrosion attack (deterioration) uniformly distributed over a metal surface. (2) Corrosion that proceeds at approximately the same rate over a metal surface. Also called general corrosion.

V

voids. A term generally applied to paints to describe *holidays*, holes, and skips in a film. Also used to describe shrinkage in castings and welds.

W

weld decay. *Intergranular corrosion,* usually of stainless steels or certain nickel-base alloys, that occurs as the result of *sensitization* in the heat-affected zone during the welding operation.

white rust. Zinc oxide; the powdery product of corrosion of zinc or zinc-coated surfaces.

working electrode. The test or specimen electrode in an *electrochemical cell.*

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