

Corrosion ControlTM

Second Edition

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CORROSION CONTROL

Second Edition

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DEDICATION

To my parents,

Phariss Cleino Bradford (1905-1986) and

Arthur Lenox Bradford (1904-1987).

ACKNOWLEDGMENTS

My wife Evelin has helped me in a thousand ways by taking over duties I should have attended to, by making our home a pleasant place to work, and by providing continual encouragement for over forty years.

The publisher's appreciation is sent to all the suppliers of photographs, graphics and data that were used with permission in this book. Photographic enhancements, graphic creation and graphic editing were performed by Charles Bradford; Kevin Chu, EIT; and Michael Ling, EIT.

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PREFACE

Human beings undoubtedly became aware of corrosion just after they made their first metals. These people probably began to control corrosion very soon after that by trying to keep metal away from corrosive environments. “Bring your tools in out of the rain” and “Clean the blood off your sword right after battle” would have been early maxims. Now that the mechanisms of corrosion are better understood, more techniques have been developed to control it.

My corrosion experience extends over 10 years in industry and research and 25 years teaching corrosion courses to university engineering students and industrial consulting. During that time I have developed an approach to corrosion that has successfully trained over 1700 engineers.

This book treats corrosion and high-temperature oxidation separately. Corrosion is divided into three groups: (1) chemical dissolution including uniform attack, (2) electrochemical corrosion from either metallurgical or environmental cells, and (3) stress-assisted corrosion. It seems more logical to group corrosion according to mechanisms than to arbitrarily separate them into 8 or 20 different types of corrosion as if they were unrelated.

University students and industry personnel alike generally are afraid of chemistry and consequently approach corrosion theory very hesitantly. In this text the electrochemical reactions responsible for corrosion are summed up in only five simple half-cell reactions. When these are combined on a polarization diagram, which is explained in detail, the electrochemical processes become obvious.

The purpose of this text is to train engineers and technologists not just to understand corrosion but to control it. Materials selection, coatings, chemical inhibitors, cathodic and anodic protection, and

equipment design are covered in separate chapters. High-temperature oxidation is discussed in the final two chapters—one on oxidation theory and one on controlling oxidation by alloying and with coatings. Accompanying most of the chapters are questions and problems (~300 in total); some are simple calculations but others are real problems with more than one possible answer. This text uses the metric SI units (Système Internationale d'Unités), usually with English units in parentheses, except in the discussion of some real problems that were originally reported in English units where it seems silly to refer to a 6-in. pipe as 15.24-cm pipe. Units are not converted in the Memo questions because each industry works completely in one set of units.

For those who want a text stripped bare of any electrochemical theory at all, the starred (★) sections and starred chapter listed in the Table of Contents can be omitted without loss of continuity. However, the author strongly urges the reader to work through them. They are not beyond the abilities of any high school graduate who is interested in technology.

Samuel A. Bradford

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Chapter 1

INTRODUCTION

Any time corrosion comes up in casual conversation, people talk about their old cars. Everyone who owns a car over five years old has first-hand experience with rusting, along with the bitter knowledge of what it costs in reliability and resale value (see Figure 1.1). In recent years, automobile manufacturers have faced the problem and have begun to control corrosion by improving design, by sacrificial and inhibiting coatings, and by greater use of plastics.



Figure 1.1 Photograph of the author's latest mobile corrosion laboratory.

Chemical plants, with their tremendous variety of aqueous, organic, and gaseous corrodants, come up with nearly every type of corrosion imaginable. It becomes quite a challenge to control corrosion of the equipment without interfering with chemical processes. Petroleum refineries have the best reputation for corrosion control, partly because the value of their product gives them the money to do it correctly and partly because the danger of fire is always present if anything goes wrong. The cost of corrosion-resistant materials and expensive chemical inhibitors is considered to be necessary insurance.

Ships, especially the huge supertankers, illustrate another type of corrosion problem. Seawater is very corrosive to steel and many other metals. Some metals that corrode only slightly, such as stainless steels, are likely to crack in seawater by the combination of corrosion and high stresses. Corrosion can cause the loss of a ship and its crew as well as damage to a fragile environment. Corrosion control commonly involves several coats of paint plus cathodic protection, as well as designing to minimize stress concentration.

What is Corrosion?

Corrosion is the damage to metal caused by reaction with its environment. “Damage” is specified purposely to exclude processes such as chemical milling, anodizing of aluminum, and bluing of steel, which modify the metal intentionally. All sorts of chemical and electrochemical processes are used industrially to react with metals, but they are designed to improve the metal, not damage it. Thus these processes are not considered to be corrosion.

“Metal” is mentioned in the definition of corrosion, but any material can be damaged by its environment: plastics swell in solvents, concrete dissolves in sewage, wood rots, and so on. These situations are all very serious problems that occur by various mechanisms, but they are not included in this definition. Metals, whether they are attacked uniformly or pit or crack in corrosion, are all corroded by the same basic mechanisms, which are quite different from those of other materials. This text concentrates on metals.

Rusting is a type of corrosion but it is the corrosion of ferrous metals (irons and steels) *only*, producing that familiar brownish-red corrosion product, rust.

The environment that corrodes a metal can be anything; air, water, and soil are common but everything from tomato juice to blood contacts metals, and most environments are corrosive.

Corrosion is a natural process for metals that causes them to react with their environment to form more stable compounds. In a perfect world the right material would always be selected, equipment designs would have no flaws, no mistakes would be made in operation, and corrosion would *still* occur—but at an acceptable rate.

The Cost of Corrosion

Everybody is certain that *their* problems are bigger than anyone else's. This assumption applies to corrosion engineers also, who for years complained that corrosion is an immense problem. To see just how serious corrosion really is, the governments of several nations commissioned studies in the 1970s and 1980s, which basically arrived at numbers showing that corrosion is indeed a major problem. The study in the United States estimated the direct costs of corrosion to be approximately 4.9% of the gross national product for an industrialized nation. Of that 4.9%, roughly 1 to 2% is avoidable by properly applying technology already available—approximately \$300 per person per year *wasted*.

This cost is greater than the financial cost of all the fires, floods, hurricanes, and earthquakes in the nation, even though these *other* natural disasters make headlines.

How often have you seen a headline, “Corrosion ate up \$800 million yesterday”?

Direct costs include parts and labor to replace automobile mufflers, metal roofing, condenser tubes, and all other corroded metal. Also, an entire machine may have to be scrapped because of the corrosion of one small part. Automobile corrosion alone costs \$16 billion annually. Direct costs cover repainting of metals, although this expense is difficult to put precise numbers on, since much metal is painted for appearance as well as for corrosion protection. Also included is the cost of corrosion protection such as the capital costs of cathodic protection, its power and maintenance, the costs of chemical inhibitors, and the extra costs of corrosion-resistant materials.

Corrosion and corrosion control cost the U.S. Air Force over \$1 billion a year.

Indirect costs are much more difficult to determine, although they are probably at least as great as the direct costs that were surveyed. Indirect costs include plant shutdowns, loss or contamination of products, loss of efficiency, and the overdesign necessary to allow for corrosion. Approximately 20% of electronic failures are caused by corrosion.

An 8-in., oil pipeline 225 miles long with a 5/8-in.-wall thickness was installed several years ago with no corrosion protection. With protection it would have had a 1/4-in.-wall, which would save 3700 tons of steel (~\$1 million) and actually would increase internal capacity by 5%.

Corrosion leads to a depletion of our resources—a very real expense, but one that is not counted as a direct cost. It is estimated that 40% of our steel production goes to replace the steel lost to corrosion. Many metals, especially those essential in alloying, such as chromium and nickel, cannot be recycled by today's technology. Energy resources are also lost to corrosion because energy must be used to produce replacement metals.

Human resources are wasted. The time and ingenuity of a great many engineers and technicians are required in the daily battle against corrosion. Too often corrosion work is assigned to the new

engineer or technologist because it is a quick way for him/her to get to know the people, the plant operation, and its problems. Then, if they are any good they get promoted, and the learning cycle has to begin again with another inexperienced trainee.

Safety and Environmental Factors

Not all corrosion is gradual and silent. Many serious accidents and explosions are initiated because of corrosion of critical components, causing personal injury and death. Environmental damage is another danger; oil pipeline leaks, for example, take years to heal.

A few years ago the corrosion failure of an expansion joint in a chemical plant in England released poisonous vapors that killed 29 people.

Too often engineers take their cue from management whose motto is “Profit is the name of this game.” For engineers, getting the job done well and safely must take precedence over cost. Certainly, cost is a consideration; any engineer who uses tantalum in a situation that could be handled by steel deserves to be fired. But where tantalum is needed, an engineer who takes a major risk by gambling with steel should be kicked out of the profession.

The stated goals of NACE International (National Association of Corrosion Engineers) are:

- Promote public safety.
- Preserve the environment.
- Reduce the cost of corrosion.

The order in which these goals are given is significant. All decisions in engineering involve some risks, but the secret of successful engineering is to minimize the consequences of those risks. In simple terms, do not gamble with human life or irreparable environmental damage.

Chapter 2

BASIC CORROSION THEORY

Thermodynamics

Engineering metals are unstable on this planet. While humans thrive in the earth's environment of oxygen, water, and warm temperatures, their metal tools and equipment all corrode if given the opportunity. The metals try to lower their energy by spontaneously reacting to form solutions or compounds that have a greater thermodynamic stability.

The driving force for metallic corrosion is the Gibbs energy change, ΔG , which is the change in free energy of the metal and environment combination brought about by the corrosion. If a reaction is to be spontaneous, as corrosion reactions certainly are, ΔG for the process must be negative. That is, the energy change must be downhill, to a lower energy.

The term ΔG is only the difference between the Gibbs energies of the final and initial states of the reaction and, therefore, is independent of the various intermediate stages. Consequently, a corrosion reaction can be arbitrarily divided into either real or hypothetical steps, and the ΔG values are summed up for all the steps to find the true Gibbs energy change for the reaction. The units of ΔG are now commonly given in joules per mole (J/mol) of metal, or in the older units of calories per mole (cal/mol).

In corrosion measurements, the driving force is more often expressed in *volts* (V), which can be found from the equation:

$$E = \frac{-\Delta G}{nF} \quad (2.1)$$

where E is the driving force (in volts, V) for the corrosion process, n is the number of moles of electrons per mole of metal involved in the process, and F is a constant called the “faraday,” which is the electrical charge carried by a mole of electrons (or 96,490 C). Remember that joules = volts $\times$ coulombs. With ΔG being negative and with the minus sign in Equation 2.1, spontaneous processes always have a positive voltage, E .

Electrode Reactions

Aqueous corrosion is electrochemical. The principles of electrochemistry, established by Michael Faraday in the early nineteenth century, are basic to an understanding of corrosion and corrosion prevention.

The Corrosion Cell

Every electrochemical corrosion cell must have four components.

1. The anode, which is the metal that is corroding.
2. The cathode, which is a metal or other electronic conductor whose surface provides sites for the environment to react.
3. The electrolyte (the aqueous environment), in contact with both the anode and the cathode to provide a path for ionic conduction.
4. The electrical connection between the anode and the cathode to allow electrons to flow between them.

The components of an electrochemical cell are illustrated schematically in Figure 2.1. Anodes and cathodes are usually located quite close to one another and may even be on the same piece of metal. If any component were to be missing in the cell, electrochemical corrosion could not occur. Thus, analyzing the corrosion cell may provide the clue to stopping the corrosion.

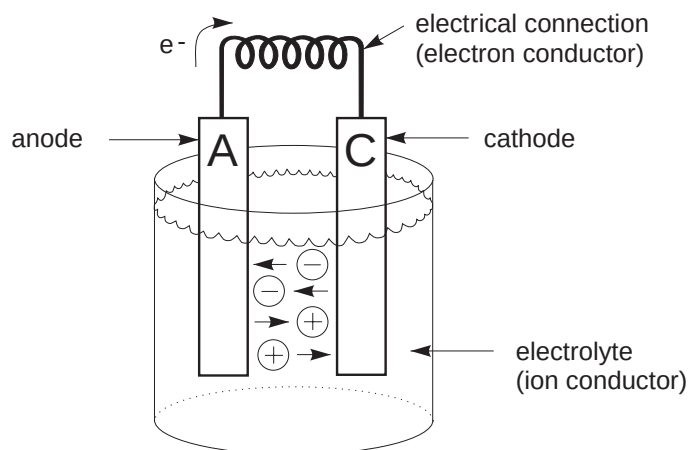


Figure 2.1 The components of an electrochemical corrosion cell.

Anode Reactions

Corrosion reactions can be separated into anode and cathode half-cell reactions to better understand the process. The anode reaction is quite simple—the anode metal M corrodes and goes into solution in the electrolyte as metal ions.



where n is the number of electrons (e^{-}) released by the metal. Chemists call this an “oxidation,” which means a loss of electrons by the metal atoms. The electrons produced do not flow into the solution¹ but remain behind on the corroding metal, where they migrate through the electronic conductor to the cathode, as indicated in Figure 2.1.

¹ Bradford's Law: Electrons can't swim.

For example, if steel is corroding, the anode reaction is



or if aluminum is corroding the reaction is

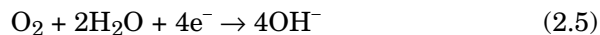


Cathode Reactions

The cathode reaction consumes the electrons produced at the anode. If it did not, the anode would become so loaded with electrons that all reaction would cease immediately. At the cathode, some reducible species in the electrolyte adsorbs and picks up electrons, although the cathode itself does not react. Chemists call this a “reduction” because the valence of the reactant is reduced.

Since it is the corrosive environment that reacts on the cathode, and many different corrosives can attack metals, several cathode reactions are possible.

1. The most common reaction is the one seen in nature and in neutral or basic solutions containing dissolved oxygen:



For example, oxygen in the air dissolves in a surface film of water on a metal surface, picks up electrons and forms hydroxide ions which then migrate toward the anode.

Workmen have collapsed and suffocated after entering rusting storage tanks. The O_2 content of the air inside can be depleted to only 5% or less.

2. The next most important reaction is the one in acids.



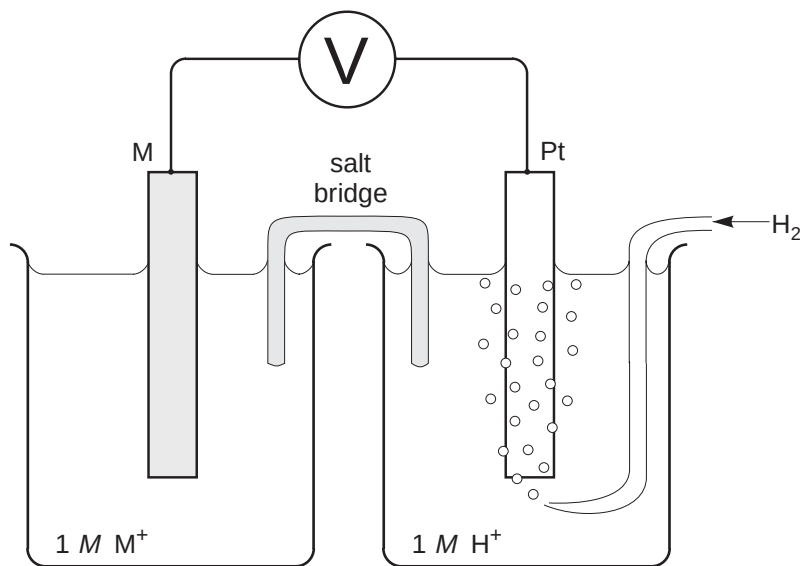


Figure 2.3 Arrangement for measuring standard emf of a metal against the standard hydrogen electrode.

While real corrosion processes are very unlikely to take place in 1 *M* solutions and almost never reach equilibrium, the standard series is useful in identifying anode and cathode reactions along with a rough estimate of how serious a driving force (voltage) the corrosion cell has.

Chemistry teachers often point out that copper will not corrode in hydrochloric acid (HCl) because the copper reduction potential is above hydrogen on the standard series. But a skeptical student who puts a penny in an open beaker of HCl finds that the copper *does* slowly corrode. Oxygen from the air dissolves in the acid, making the $\text{O}_2 + \text{H}^+$ cathode reaction (2.7) possible with $E^0 = 1.229 \text{ V}$, well above the value of 0.342 V for copper.

Fluid Velocity

The relative velocity between metal and environment can profoundly affect the corrosion rate. Either metal or environment can be moving: the metal in the case of a boat propeller, or the environment in the case of a solution flowing through a pipe.

Going from stagnant conditions to moderate velocities may lower corrosion by distributing a more uniform environment through the system. If inhibitors have been added, they also can be distributed more evenly and, therefore, may be more effective. In addition, moderate velocities can prevent suspended solids from settling out and creating crevice corrosion situations under the sediment. A more uniform environment also reduces the possibility of pitting.

On the other hand, increasing velocity may increase the supply of reactant (usually O_2) to the cathodes. Because the diffusion of the reactant is often the rate-controlling (i.e., slowest) step in the whole corrosion process, the corrosion rate of an *active* metal commonly increases with increasing velocity, until the velocity gets so high that diffusion is no longer rate controlling. This situation is illustrated in Figure 2.6a.

For metals that can *passivate*, increasing velocity could increase corrosion until conditions become oxidizing enough to form a passive film. From that point on, velocity has virtually no effect unless it becomes so great that it sweeps off the passive film (see Figure 2.6b). But take note that while passive films are so thin that they are invisible, they are also tough enough to withstand any reasonable velocity.

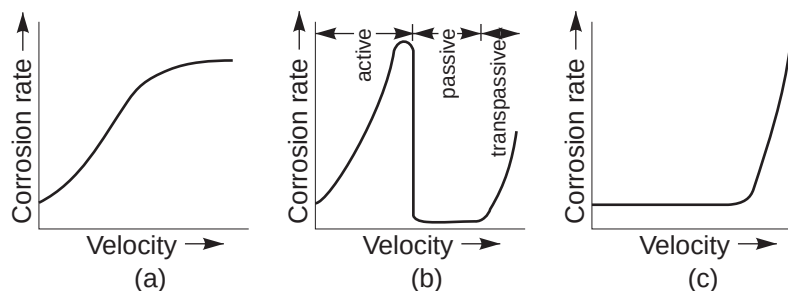


Figure 2.6 Effect of velocity on corrosion rate.

(a) Diffusion-controlled corrosion of an active metal with soluble corrosion products. (b) Active-passive metal. (c) Metal protected by a thick scale of corrosion product.

For metals that are protected by a thick layer of corrosion product, the corrosion rate may be satisfactory at low velocities but above a critical velocity the protective layer will be eroded away (see Figure 2.6c).

The critical velocity for copper in seawater is only 0.6-0.9 m/s (2-3 ft./sec.), but admiralty brass, a copper alloy developed particularly for seawater, is good up to 1.5-1.8 m/s (5-6 ft./sec.).

For the rather uncommon corrosion processes under *anodic control*, where corrosion occurs as fast as the metal atoms can detach themselves from the surface, the velocity of the solution has practically no effect on corrosion.

Temperature

An old rule of thumb is that increasing the temperature 10°C ($\sim 20^{\circ}\text{F}$) doubles the corrosion rate. This approximation gives some idea of the exponential effect that temperature can have on corrosion, although this rule can be misleading in some situations. Increasing temperature increases reaction rates, diffusion rates, and the rate of dissolution of gases in water. It also increases the ionization of water, which improves the ionic conduction and lowers its pH.

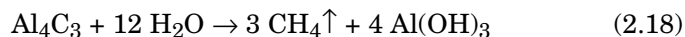
A new hydrofluoric acid plant designed to use concentrated H_2SO_4 at 120°C (250°F) showed high corrosion rates of the carbon steel equipment right from start-up. A renowned corrosion engineer was called in and spent several hours observing the production by looking over the operators' shoulders. He then informed the astounded engineers that the operators were actually running at 165°C (325°F). As Yogi Berra has said, "You can observe a lot just by watching."

Classifications of Corrosion

Corrosion takes on different appearances depending on the metal, the corrosive environment, the nature of the corrosion products, and all the other variables, such as temperature, stresses on the metal, and the relative velocity of the metal and the environment. It is easiest to differentiate the types of corrosion by the environment that is doing the attacking: aqueous liquids, nonaqueous liquids, or gases.

With aqueous liquids, corrosion is nearly always electrochemical. In electrochemical corrosion, the attack is most often approximately uniform over the entire surface of the metal that contacts the liquid. However, much more rapid corrosion occurs if differences in metallurgical composition set up an electrochemical cell, as discussed in detail in Chapter 4, or if environmental differences set up a cell, described in Chapter 5. The most serious types of corrosion, the disasters, develop when stress assists the corrosion (Chapter 6).

In rare instances, aqueous corrosion is not electrochemical. An example would be corrosion of a graphite/aluminum metal matrix composite (MMC) that was made by pouring molten aluminum around graphite fibers. In bonding with the fibers, the aluminum forms a film of aluminum carbide that may later react with an aqueous solution, thus:



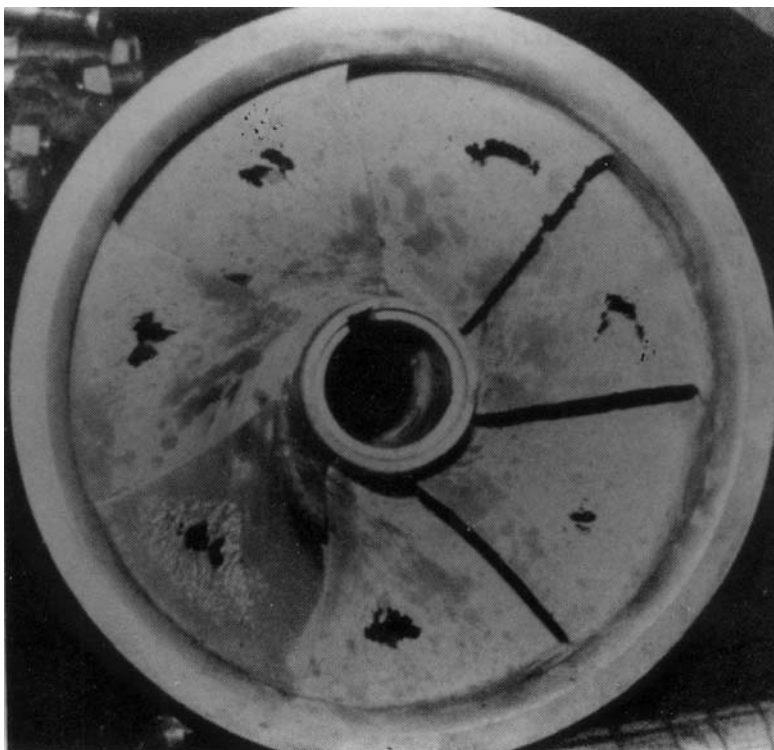


Figure 2.9 Example of corrosion of metal
(bronze pump impeller) in organic liquid.
(From C.P. Dillon, Ed., *Forms of Corrosion: Recognition and Prevention*, NACE Handbook 1, p. 86, 1982. Reprinted by permission, National Association of Corrosion Engineers.)

Electrochemical Corrosion

Uniform Attack

Uniform attack is by far the most common type of corrosion, but at the same time the least serious! As the metal corrodes it leaves a fairly smooth surface that may or may not be covered with corrosion products. A typical example would be the atmospheric corrosion of an old galvanized steel barn roof. Once the zinc galvanizing has corroded off, large areas of the steel quickly become heavily rusted

and while holes appear in only a few spots at first, all of the remaining steel is paper thin. An example of uniform corrosion is shown in Figure 2.10.



Figure 2.10 This ship ran aground near the mouth of the Columbia River 60 years earlier.

The corroding metal in uniform attack is serving as both the anode and the cathode. While the anode area is obvious in aqueous environments, since the entire surface of the metal is corroding, no separate cathode is identifiable. However, oxidation cannot occur without a corresponding reduction; thus the same metal surface must also be providing sites for the cathode reaction. The cathode sites are regions on the surface that are temporarily coated with a thicker layer of corrosion products or regions that are in contact with solution that is momentarily more concentrated in the reducible reactant. These cathode areas obviously move around constantly, because no region remains protected for long if the attack is uniform.

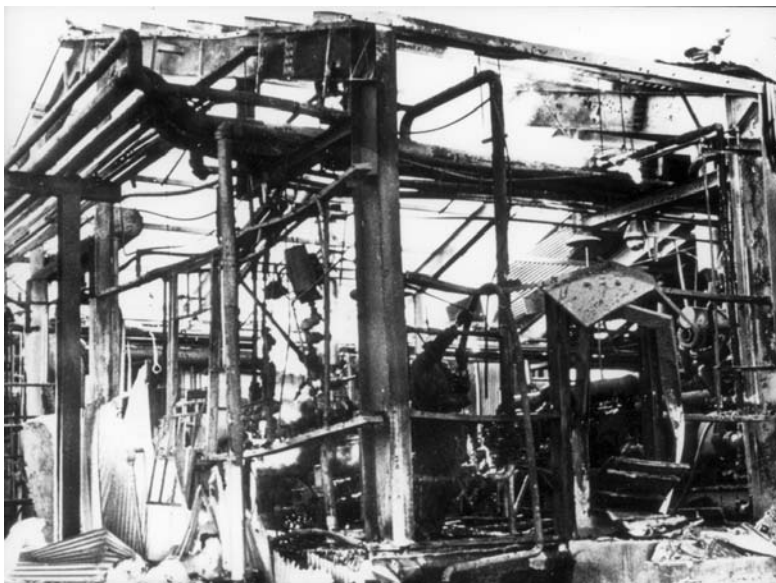


Figure 2.12 A small steam separator fractured in this gas plant.
One man died and one was burned severely.

★Pourbaix Diagrams

In 1938 Dr. Marcel Pourbaix presented his potential-pH diagrams to illustrate the thermodynamic state of a metal in dilute aqueous solutions. The advantages of depicting all the thermodynamic equilibria in a single, unified diagram was immediately evident to scientists and engineers, especially in corrosion, hydrometallurgy, and electrochemistry.

The axes of the diagram are the key variables that the corrosion engineer can control. The vertical axis shows the metal-solution potential, which can be changed by varying the oxidizer concentration in the solution or by applying an electrical potential to the metal. The horizontal axis shows the pH of the solution. The diagrams are divided into regions of stability, each labeled with the predominant species present.

For regions where metal ions are stable, the boundaries are usually drawn for equilibrium concentrations of $10^{-6} M$, chosen to show the limits of corrosion where soluble corrosion products would be barely detectable. However, in a specific corrosion situation, where solution concentrations are known to be greater than $10^{-6} M$ or the temperature is not 25°C (77°F), the diagram can be redrawn to fit the real conditions.

The potential-pH diagram for the iron-water system is shown in Figure 2.13. The *dotted lines* on the diagram show the theoretical limits of the stability of water. The upper line shows where O_2 should be generated on an anode and the lower line shows where H_2 should be given off at a cathode. Between the two dotted lines water is stable, so this is the important region in aqueous reactions. However, the actual stability range for water is usually much greater than the diagram indicates; water does not decompose as readily on most metals as it theoretically does on an ideal platinum surface. The $\text{H}_2/\text{H}_2\text{O}$ overpotential is usually less than 0.1 V but the $\text{O}_2/\text{H}_2\text{O}$ overpotential is usually around 0.3 – 0.4 V because the reaction is always irreversible.

Aside from the stability limits for water, Pourbaix diagrams have three different types of lines.

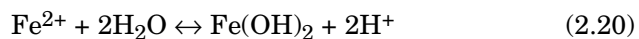
1. *Horizontal lines*, independent of pH. The equilibrium does not involve hydrogen ions. For example, the boundary between the Fe^{3+} and Fe^{2+} regions is for the equilibrium



with the Nernst equation giving

$$E = E^{\circ} - \frac{RT}{F} \ln \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \quad (2.19)$$

2. *Vertical lines*, not involving oxidation or reduction. The boundary between the Fe^{2+} and $\text{Fe}(\text{OH})_2$ regions shows the equilibrium



Iron remains in the +2 valence state with no electrons exchanged, so the reaction can take place at any potential, positive or negative.

3. *Sloping lines*, involving both hydrogen ions and electrons. The boundary between Fe^{2+} and $\text{FeO}(\text{OH})$ regions represents the equilibrium

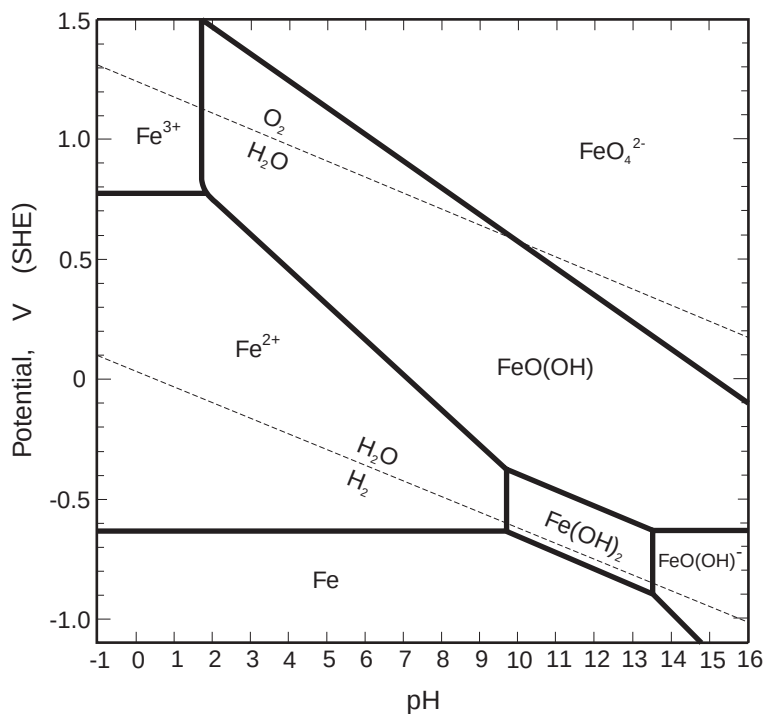
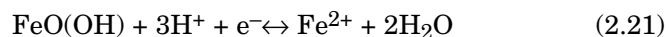


Figure 2.13 Pourbaix diagram for the Fe- H_2O system at 25°C (77°F) for $10^{-6} M$ activities of all metal ions.

Other information can be superimposed on a Pourbaix diagram, as shown in Figure 2.16, to reveal more than simply regions of corrosion, passivation, and immunity.

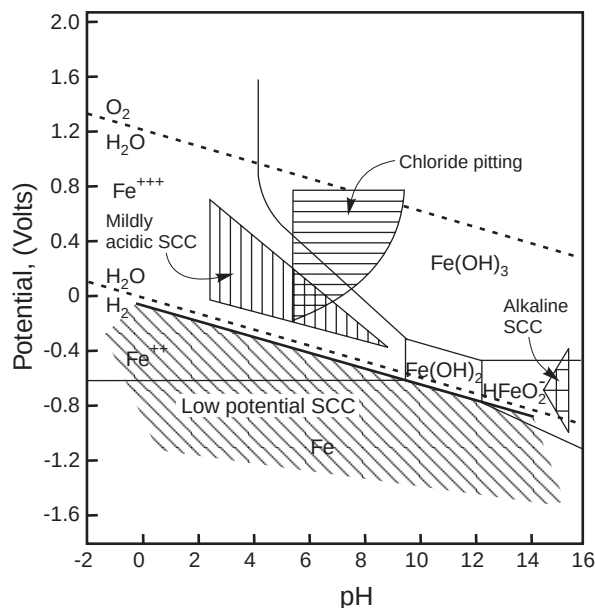


Figure 2.16 Iron-water Pourbaix diagram showing regions where stress corrosion cracking and chloride pitting could occur.

(From R.W. Staehle, Parkins Symposium on Fundamental Aspects of Stress Corrosion Cracking, 1992.

Reprinted by permission, The Metallurgical Society.)

Corrosion Rates

The extent of corrosion is commonly measured either of two ways. In uniform attack, the mass of metal corroded on a unit area of surface will satisfactorily describe the damage. However, if attack is localized, the amount of metal removed *on average* over the entire surface is meaningless. The depth of penetration, whether by uniform attack, pitting, or whatever, gives a much better description of almost any type of corrosion except cracking. (A crack of any length is a warning of imminent disaster.)

Chapter

3

★ELECTROCHEMICAL CORROSION THEORY

The driving force for corrosion is the potential difference developed by the corrosion cell

$$E_{\text{cell}} = E_{\text{red}}^{\text{cat}} - E_{\text{red}}^{\text{anode}} \quad (2.17)$$

However, the cell potential does not correctly predict the corrosion rate, and it is the corrosion rate that is the essential determiner of a metal's suitability in a corrosive environment. Logically, if the cell potential is small, the corrosion rate will be low. On the other hand, a large cell potential does not necessarily mean that the metal must corrode badly. It may passivate, for example, and corrode at an extremely low rate.

Corrosion kinetics, the *rate* of the electrode reaction, is related to the thermodynamic driving force that is measured by the cell potential. This relationship depends on several factors, all connected with the “polarization” of the electrodes in the cell.

The term “polarization” refers to a shift in potential caused by a flow of current. An anode increases its potential as more current flows from it into the electrolyte, while the cathode's potential decreases as current flows onto it. Both electrodes in the cell polarize until they reach essentially the same potential; the corrosion potential. Polarization is also often called “overvoltage,” a term commonly used in commercial electrochemical processes, such as electroplating, to

describe the additional voltage that must be applied to overcome the polarization of the electrodes. An understanding of the causes of polarization is essential to an understanding of corrosion.

Exchange Current Density

An electrode *at equilibrium* with its environment has no net current flow to or from the surface of the metal. Actually, a “dynamic equilibrium” is established in which the forward and reverse reactions are both occurring, but at equal rates. If the forward reaction is



with positive current (M^{n+} ions) flowing from the electrode, an exactly equal current flows back onto the surface as the metal plates back on:



Thus the net current flow is zero. The oxidation process is exactly reversed by its corresponding reduction process.

In terms of the current,

$$I_{\text{ox}} = I_{\text{red}} \quad (3.2)$$

In this equation I is the current in amperes (A) and the subscripts ox and red refer to oxidation and reduction. This equilibrium current, either I_{ox} or I_{red} , is called the *exchange current* I_0 . The exchange current cannot be measured directly but can be found by extrapolation, as is shown in Figure 3.1. The exchange current may be extremely small but it is not zero.

Often it is more convenient to use the *exchange current density* i_0 expressed as amperes per square metre (A/m^2), rather than the current in order to eliminate the variable of electrode size. The

exchange current density is a direct measure of the electrode's oxidation rate or reduction rate at equilibrium.

$$\text{rate}_{\text{ox}} = \text{rate}_{\text{red}} = \frac{i_0}{nF} \quad (\text{mol/m}^2 \cdot \text{s}) \quad (3.3)$$

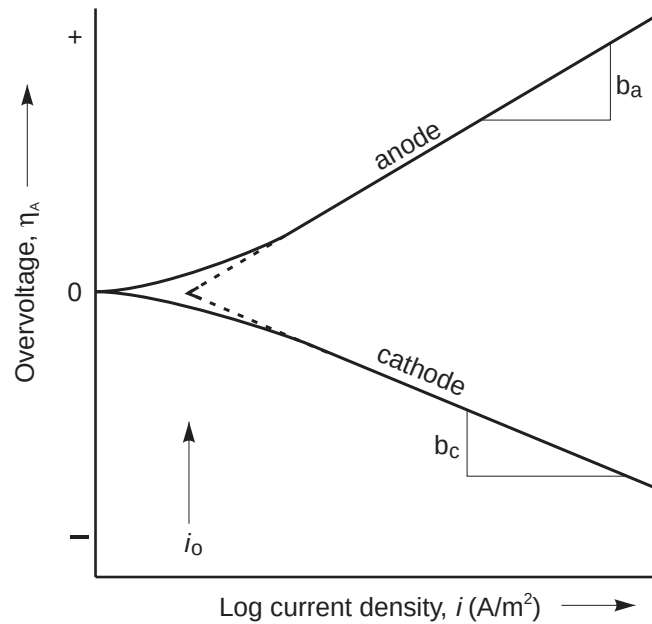


Figure 3.1. Experimentally measurable anodic and cathodic polarization curves showing activation polarization. Tafel slopes are b_a and b_c . Exchange current density is i_0 .

The term i_0 is a function of the reaction, the concentration of reactants, the electrode material, the temperature, and the surface roughness. Typical examples of exchange current densities for a variety of reactions and electrodes are given in Table 3.1.

Table 3.1 Approximate Exchange Current Densities at 25°C (77°F)

Reaction	Electrode	Solution	$i_o(\text{A/m}^2)$	Reference
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	Al	1 M H_2SO_4	10^{-6}	Parsons 1959
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	Cu	0.1 M HCl	2×10^{-3}	Bockris 1953
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	Fe	1 M H_2SO_4	10^{-2}	Bockris 1953
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	Ni	1 M H_2SO_4	6×10^{-2}	Bockris and Reddy 1970
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	Pb	1 M HCl	2×10^{-9}	Bockris 1953
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	Pt	1 M H_2SO_4	8	Bockris and Reddy 1970
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	Ti	1 M H_2SO_4	6×10^{-5}	Bockris and Reddy 1970
$2\text{H}^+ + 2\text{e}^- \leftrightarrow \text{H}_2$	Zn	1 M H_2SO_4	10^{-7}	West 1970
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^-$	Pt	0.1 M NaOH	4×10^{-9}	Bockris and Reddy 1970
$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^-$	Au	0.1 M NaOH	5×10^{-9}	Parsons 1959
$\text{Cu}^{2+} + 2\text{e}^- \leftrightarrow \text{Cu}$	Cu	Sulfate	4×10^{-1}	West 1970
$\text{Fe}^{2+} + 2\text{e}^- \leftrightarrow \text{Fe}$	Fe	Sulfate	2×10^{-5}	West 1970
$\text{Ni}^{2+} + 2\text{e}^- \leftrightarrow \text{Ni}$	Ni	Sulfate	2×10^{-5}	West 1970
$\text{Pb}^{2+} + 2\text{e}^- \leftrightarrow \text{Pb}$	Pb	Perchlorate	8	West 1970
$\text{Zn}^{2+} + 2\text{e}^- \leftrightarrow \text{Zn}$	Zn	Sulfate	3×10^{-1}	Bockris and Reddy 1970

Note that a platinum surface makes the H_2 reaction extremely easy, but not the O_2 reaction. The i_o values for corroding and plating metals are obviously *not* in the same order as their standard electrode potentials, E° .

Activation Polarization

All electrodes, both anodes and cathodes, undergo activation polarization when current flows. A slow step in the electrode reaction is responsible for the shift in electrode potential. If activation

Resistance Polarization

An additional overpotential, the resistance polarization η_R , is required to overcome the ohmic resistance of the electrolyte and any insoluble product film on the surface of the metal. This overpotential is defined by Ohm's Law as

$$\eta_R = IR \quad (3.10)$$

where I is the current and R is the resistance, in ohms (Ω), of the electrolyte path between anode and cathode and is directly proportional to the path length. In typical corrosion processes, the anodes and cathodes are immediately adjacent to each other so that resistance polarization makes only a minor contribution to the overall polarization, as indicated in Figure 3.5.

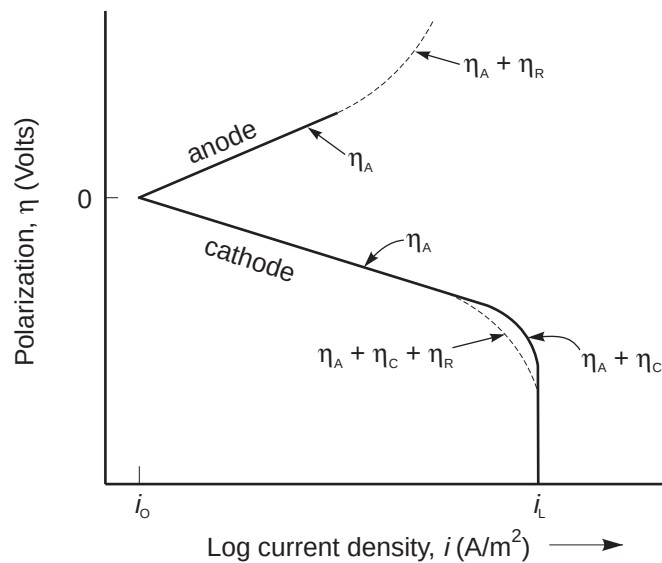


Figure 3.5 Polarization curves for anode and cathode reactions showing contributions for activation, η_A , concentration polarization η_C , and resistance polarization η_R .

Chapter

4

METALLURGICAL CELLS

Corrosion can change from uniform corrosion to a localized attack because of differences in the metal or because of variations in the environment. This chapter deals with the metallurgical differences and the types of corrosion resulting from them.

The important principle to remember is that corrosion attacks inhomogeneities in the metal. Real metals contain many inhomogeneities, most of them deliberately put in to achieve high strength. A perfectly pure metal crystallized in a perfect crystal structure would be both incredibly strong and highly corrosion resistant, but no such metal exists.

Metal Purity

Commercially pure metals typically contain a few tenths of 1% of impurities. These small amounts of extraneous atoms do not appear to have much effect on corrosion in natural environments such as soil and water, but they do affect the protective nature of the oxide scale in atmospheric corrosion.

In steels, the normal impurities do not change the corrodibility of the metal if the aqueous environment is between pH 4 and 13.5, but in acids, sulfur and phosphorus in the steel increase attack by making H₂ gas generation easier. Copper in steel also increases corrosion in acids, but improves atmospheric corrosion resistance. The so-called “weathering steels” achieve exceptional atmospheric resistance by

alloying with a few tenths of a percent of Cu, Ni, and Cr. Figure 4.1 illustrates a typical application of weathering steel.



Figure 4.1 Bridge girder of high-strength, low-alloy weathering steel.
(Courtesy of Charles N. Bradford.)

In recent years it has been found that extremely high-purity metals are extraordinarily resistant to corrosion. For example, 99.998% Al corrodes at only $1/30,000^{\text{th}}$ the rate of commercial 99.2% Al.

High-purity ferritic stainless steels now available are refined to extremely low carbon and nitrogen contents to give them a corrosion resistance that rivals the very best.

Crystal Defects

Although metals are crystalline, the crystal structures are not perfect. In addition to impurity atoms, they all contain many atom vacancies, that is, sites where atoms should be present but are not. The vacancies permit some diffusion of atoms within the crystal. In addition, all real crystals contain linear flaws called “dislocations,” where atoms are crowded too closely on one side of the line and are packed too loosely on the other side. These dislocation lines give the metal ductility but they also increase diffusion and corrode more rapidly than the surrounding crystal, as shown in Figure 4.2.

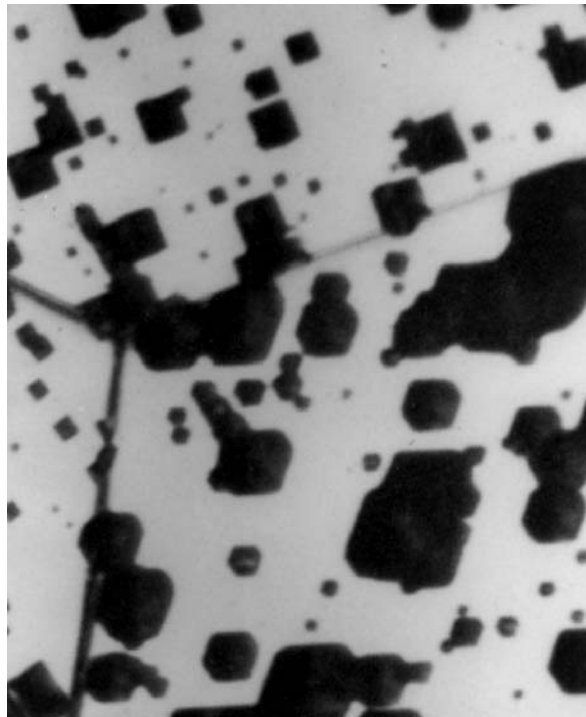


Figure 4.2 Etch pits in 3% silicon steel. Ferric sulfate solution has eaten out the distorted structure around dislocation lines where they intersect the metal surface. Magnification 1820X.

(From Metals Handbook, 8th ed., Vol.8, page 113, 1973.

Reprinted by permission, ASM International.)

Cold Work

Cold work (rolling, hammering, drawing, etc.) is usually done at room temperature, although it can be at any temperature below the metal's recrystallization temperature. While cold work strengthens the metal at very little cost, it greatly increases vacancy and dislocation densities. Impurities can then concentrate at the dislocations to create very localized corrosion cells that contribute to pitting. In acidic corrosion, cold working can increase H^+ adsorption sites at dislocations on the metal surface. Cold work also introduces internal stresses that make the metal more susceptible to stress corrosion cracking. Figure 4.3 shows the surface of cold-worked brass after it has been polished and etched with acid, revealing some of the dislocation lines and grain boundaries.



Figure 4.3 Corrosion of brass cold-worked 60%. Magnification 150X.

Grain Structure

Grain Size

The metal “grains,” the individual crystals, should be extremely small to give the best toughness, but that means that the grain boundaries, which are narrow regions of mismatch between the grains (see Figure 4.4), will be numerous and take up an appreciable fraction of the metal surface.

Atoms at the grain boundaries are easily corroded because they are not bonded as strongly as atoms within the grains. More importantly, the grain boundaries serve as collecting sites for impurity atoms that do not fit well inside the crystals. At moderate temperatures, diffusion is much more rapid along the boundaries than within the grains, so atoms collect more rapidly and form precipitates at the boundaries. All these inhomogeneities localize the corrosion attack.

Grain Shape

Cold work severely distorts the shape of the metal grains; rolling, for example, flattens the grains and elongates them in the rolling direction as in Figure 4.4*b*. A transverse cut of the same metal shows that the grains have been particularly flattened in the vertical, or “short transverse” direction, but the grain boundaries are not lined up the way they are in the long transverse or the longitudinal (rolling) directions.

A transverse cut through cold-worked metal exposes much more grain boundary area than a longitudinal cut does. Consequently, corrosion attack on the grain boundaries in a transverse cut can be much greater. Also, cold work tends to align certain crystal directions with the direction of working and forces more of the closely packed planes of atoms to lie parallel to the metal surface. The close-packed planes have the strongest bonding between atoms and, consequently, are more corrosion resistant than planes perpendicular to them that would predominate in a transverse cut.

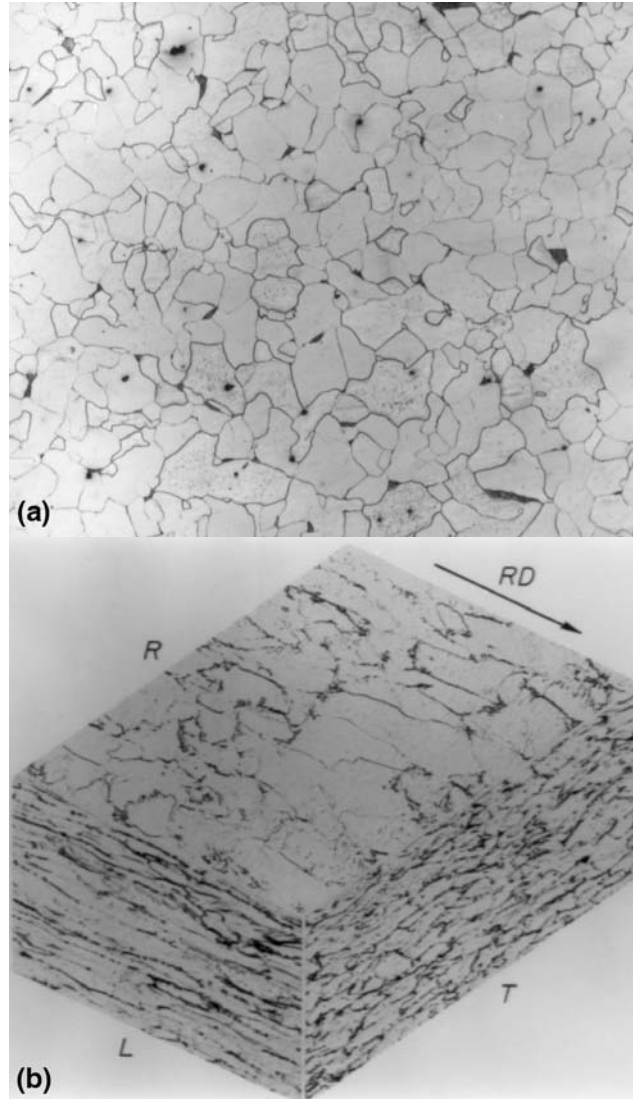


Figure 4.4 Photomicrographs of metal grain structures. (a) Grain boundaries in an annealed iron (130X). (b) Rolled surface (*R*), longitudinal (*L*), and transverse (*T*) sections of low-carbon steel cold-rolled 65% (330X). RD is the rolling direction. (From J.T. Michalak, *Metals Handbook*, 8th ed., Vol. 8, p. 220, 1973. Reprinted by permission, ASM International.)

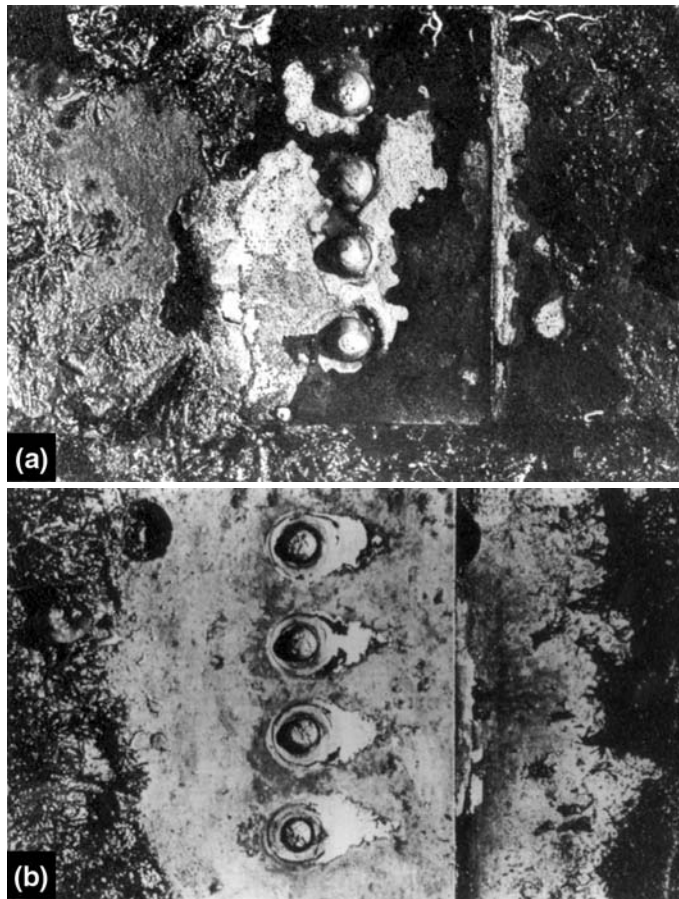


Figure 4.6 The area effect in galvanic corrosion. (a) Steel plates with copper rivets in seawater 15 months. (b) Copper plates with steel rivets, same environmental conditions. (*From Corrosion in Action, p. 18, 1955. Reprinted by permission, Inco Alloys International.*)

Could a layer of gray mill scale produced by hot-rolling steel be used as a protective coating for a buried steel pipeline? The scale is very brittle so you must expect some damage by handling and burying. Check the galvanic series and consider the cathode/anode area ratio.

The Distance Effect

In environments with low electrical conductivity, such as fresh water, galvanic corrosion occurs only near the connection point where the two metals make contact. The high resistivity of the solution confines the cell current to the region around the junction, causing a deep ditch to form in the anode metal where it touches the cathode. Attack in a narrow band on only one side of a metal junction confirms a diagnosis of galvanic corrosion. This “distance effect” offers another way to combat galvanic corrosion: space anode and cathode far enough apart and galvanic corrosion will virtually cease even though the metals are still electrically connected by an external conductor. In effect, that is what painting both the anode and the cathode does, by increasing the electrical resistance through the fine, winding paint pores.

Many old houses with steel water pipes have been modernized with additional plumbing made of copper. To prevent galvanic corrosion, the plumbers often put insulated connectors between the two kinds of piping (Figure 4.7). Building codes, however, require the plumbing to be electrically continuous for grounding purposes so electricians fasten external metal straps across the insulated couplings. Surprisingly, this procedure does not cause severe galvanic corrosion. The insulated spacer between the two pipes separates them enough so that the water’s resistance prevents the exchange of much current. (Also, old rusty steel is only about 0.2 V more reactive than copper so the driving force is not great.)

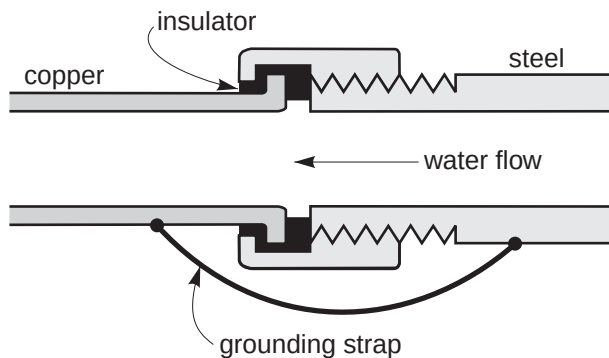


Figure 4.7 Insulated connector between steel and copper pipes, shorted by a grounding strap.

New Metal/Old Metal Galvanic Corrosion

Connecting new pipe, fresh from the mill, to old pipe of the same composition sets up a galvanic cell, corroding the new pipe severely. This often happens where a short section of a buried pipeline is replaced. The new pipe corrodes at a faster rate than the old pipe, as illustrated in Figure 2.4b where Rate 1 is much greater than Rate 2. The large cathode/anode area ratio makes the situation even worse.

For above-ground storage tanks, after an old tank bottom has corroded too much to be repaired, common practice is to pour in a layer of clean sand and weld in a new bottom. This sets up a bad galvanic cell that can only be stopped by installing cathodic protection anodes between the two bottoms. Another example: scoring from a pipe wrench removes protective corrosion products, and with the high cathode/anode area ratio, concentrates attack at the gouges on the metal surface.

Any mechanical damage such as scratches on anodized aluminum (having a thick passive film) creates an active/passive galvanic cell in a corrosive that doesn't passivate aluminum and quickly eats through the metal. Passive aluminum isn't listed in the Galvanic Series of Table 4.1 because aluminum doesn't passivate well in seawater, but compare active and passive stainless steels, and try to imagine how



Figure 4.13 Graphitic corrosion of cast iron elbow. (From *Corrosion in Action*, p. 6, 1955. Reprinted by permission, Inco Alloys International.)

“Graphitized” pipe looks like rusty pipe. Its shape is unchanged; even the manufacturer’s trademark cast into the pipe can still be read. If it has not been broken, the pipe can still carry water at internal pressures of up to around 3.5 MPa (500 psi), and packed in soil it may give good service. But being weak and brittle, it will break from frost heave, from water hammer, or any other mechanical stress.

Many a building has burned to the ground because the sudden change in water pressure for fire fighting has broken the water mains.

At the present time most of the major cities in North America have come to the realization that they must rapidly replace their cast iron water and sewer systems at a cost that will run into the billions of dollars.

One test for graphitic corrosion is the famous Clang and Clunk Test: Hit the pipe with a hammer. If the metal goes “clang,” it is good. If it goes “clunk,” or breaks, it is not.

Ductile, malleable, and white cast irons don’t undergo graphitic corrosion because they don’t have a graphite network (Figure 4.12) that would hold the corrosion products in place. Graphitic corrosion is sometimes called “graphitization,” (sic) but real graphitization occurs at high temperatures where carbon deposited on the surface diffuses into steel and embrittles it.

Intergranular Corrosion

Galvanic corrosion at the grain boundaries, although on a microscopic scale, is caused by compositional differences between the grain boundaries and the metal adjacent to the boundaries. The boundaries are collection sites for a great number of ill-fitting atoms that would distort the crystals if left inside, as indicated in Figure 4.14. Diffusion is rapid along the boundaries so that new phases can form rapidly, and the new phases do not require additional energy to produce new surfaces as they would within the crystals. An example of intergranular corrosion leading to a stress corrosion cracking failure is shown in Figure 6.14.

Sensitization of Stainless Steels

Stainless steels held in the temperature range of about 500-800°C (900-1500°F) often “sensitize” so that they become very susceptible to intergranular attack in certain corrosive environments. The surface then will just crumble (sometimes called “sugaring”) as the individual grains fall out. The metal also becomes very susceptible to stress corrosion cracking and corrosion fatigue. A typical example is shown in Figure 4.15.

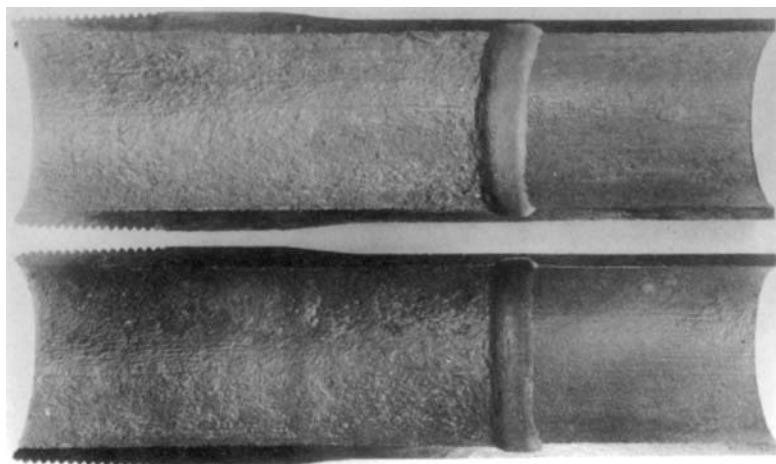


Figure 4.19 Ringworm corrosion of oil well tubing. (From Corrosion Control in Petroleum Production, TPC Publication No. 5, p. 15, 1979. Reprinted by permission, NACE International.)

Thermogalvanic Corrosion

Hot atoms in a metal vibrate more vigorously and thus are more weakly bonded than cold atoms. Consequently, the hot end of a pipe is likely to be anodic to the colder, more cathodic end. But this is an oversimplification. Other factors must be considered: the amount of temperature difference, the distance between hot and cold ends, possible plating out of metal atoms, possibility of passivation, and heat transfer conditions.

Differential Temperature Cells

Differential temperature cells may localize corrosion in such equipment as heat exchangers, boilers, immersion heaters, and reactor cooling systems, because these cannot have isothermal surfaces if they are to work. A hot spot in a boiler tube often corrodes severely because it is anodic to the large surrounding cooler area—the cathode/anode area ratio effect again.

In theory, the hot metal should be more reactive than the cool metal if both are active or both are passive, but in many cases the temperature difference is no more than 75°C (135°F), which creates a potential difference of only a few millivolts. However, copper alloys will corrode if the temperature difference is 65°C (117°F) or more, with the hot end being the anode. The closer the hot and cold ends are to each other and the better the electrical conductivity of the electrolyte, the more severe the differential temperature cell becomes, due to the distance effect.

Active-Passive Galvanic Cells

If the difference in temperature changes the character of passive surface films, even small temperature differences can create severe galvanic cells. A metal that passivates at low temperatures but becomes transpassive at high temperatures will corrode seriously at the hot location, with the colder, passivated metal serving as cathode. On the other hand, if corrosion conditions are not severe enough to passivate the metal at low temperatures but will passivate at high temperatures, the cold end corrodes.

Most household hot water tanks were galvanized steel at one time. The zinc was anodic to steel in the 60°C (140°F) water. With the advent of automatic washing machines, water temperatures had to be raised to 80°C (175°F), which passivated the zinc and destroyed the steel by galvanic action. Glass-lined or Monel (Cu-Ni alloy) tanks are now used, or cathodic protection is applied.

Differential temperature cells persist for the life of the equipment and may lie dormant causing no trouble for years until some minor change in the environment affects the protective nature of the film on either the hot or cold metal. A higher conductivity, a slight increase in aggressive ion concentration, or whatever, can suddenly trigger a disastrous localized attack.

Cathodic Plating

A few metals, notably copper, silver, and lead, may even contribute another cathode reaction to the corrosion: they may plate out at the cathode. Copper in water, for example, adds the reaction



at the cold metal in addition to the usual cathode reaction of oxygen reduction. Diffusion of the copper ions is slow, though, so the process usually requires a solution flowing from hot end to cold end to transport the ions.

Aluminum cannot be plated from aqueous solution. Iron, nickel, and usually zinc, cadmium, and tin, have high overvoltages and do not plate out, either.

Surface Temperatures

Bear in mind that the surface temperature of the metal is often hotter than the process fluid. The actual skin temperature is much more important than either the total amount of heat transfer or the temperature of the environment.

Heat transfer situations can be tricky. For example, one engineer was chagrined to find that a steel heater that held boiling tar acid corroded four times as fast as the test he had made with a steel sample just immersed in the stuff.

Stress Cells

An electrochemical cell develops locally where a metal is stressed. Elastically strained metal is anodic to annealed metal and, in addition, the stress may damage a protective film. An example is the spring in Figure 4.20 where the center of the spring, being strained the most, also corroded the most.

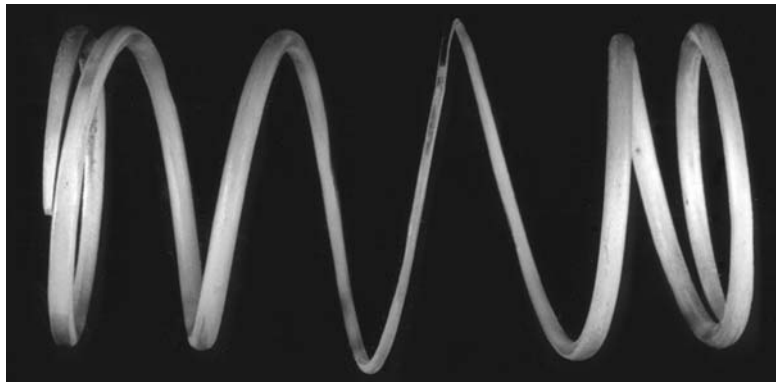


Figure 4.20 Variation in corrosion of a stainless steel spring from a sulfuric acid pump, caused by differences in stress along the spring.

Plastic deformation produced by cold work increases dislocation density greatly as well as leaving residual internal stresses in the metal. Corrosion attacks the deformed surfaces, although the corrosion potential may not shift greatly (~ 40 mV is typical), because both anodic and cathodic process are stimulated. Figure 4.21 shows localized corrosion of the cold-formed head and point of a nail.

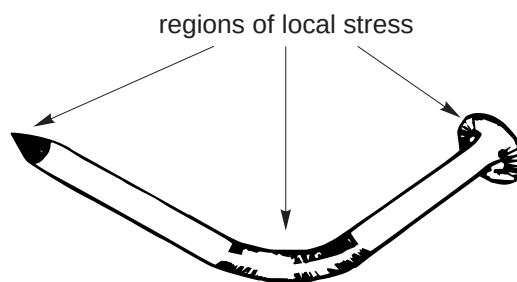


Figure 4.21 Anodic regions revealed in the corrosion of a nail.
The shank acts as a cathode.

Stolen automobiles often have their engine numbers ground off the block and different numbers stamped on. Police labs treat the numbers with an acid that brings back the original numbers by corroding the cold-worked metal under the original stamping.

Chapter

5

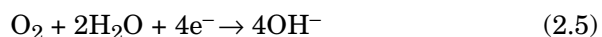
ENVIRONMENTAL CELLS

One drop of water sitting on a metal surface creates an electrochemical cell. The metal may be approximately uniform in composition but the water drop is not, and that is all that is required to start localized attack. The environment needs only to vary in concentration, velocity, or temperature to set up local anode and cathode areas on the metal. The cathodes, of course, will be where the environment reacts best. More corrosion in industry is caused by concentration cells than from any other cause.

Corrosive Concentration

Oxygen Concentration Cells

The most common cathode reaction of all is the reduction of oxygen from the air.



The drop of water mentioned above sets up an electrochemical cell because the water surface dissolves oxygen from the air, while in the center of the drop the oxygen concentration is lowest. In this way an oxygen concentration cell develops, with the metal at the circumference of the drop being the cathode and the metal in the center the anode. This situation is depicted in Figure 5.1.

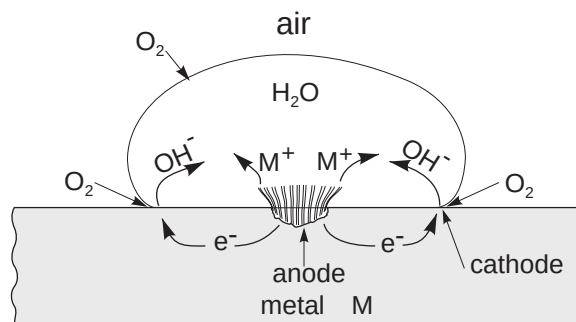


Figure 5.1. Diagram of corrosion of metal under a water droplet.

Any place that the metal contacts solution having an exceptionally high oxygen concentration will be a cathode, and any place where the oxygen is especially low will tend to be anodic, if it is not located too far from the cathode. The distance effect is always important in electrochemical cells, as is the cathode/anode area ratio.

An inspection of old highway culverts by the Wyoming Highway Department found that most corrosion occurred in the center of the culvert pipes under the paving centerline, where the oxygen concentration in the soil was at its lowest.

Other Concentration Cells

While oxygen concentration cells are the most common, any cathode reactant that varies in concentration on the metal surface can create a corrosion cell. A variation in pH, for example, can establish a cathode region where pH is low, provided it is low enough (perhaps below pH 4) to make hydrogen reduction (Reaction 2.6) an important cathode process.

If corrosion is caused by a strong oxidizer, the cathodes will tend to be located at regions of high oxidizer concentration. Oxidizers commonly used in the chemical industries include O_2 , ozone (O_3), nitric acid (HNO_3), hot concentrated H_2SO_4 , hydrogen peroxide (H_2O_2), and

solutions containing ferric ion (Fe^{3+}), chromate (CrO_4^{2-}), dichromate ($\text{Cr}_2\text{O}_7^{2-}$), permanganate MnO_4^- , or perchlorate (ClO_4^-).

Offshore drilling platforms have two oxygen concentration cells on each leg. The first is in the splash zone and just below the water surface. Corrosion is moderate at lower depths. The second concentration cell is at the mud line where the O_2 concentration is much higher in the water than in the mud (see Figure 5.2).

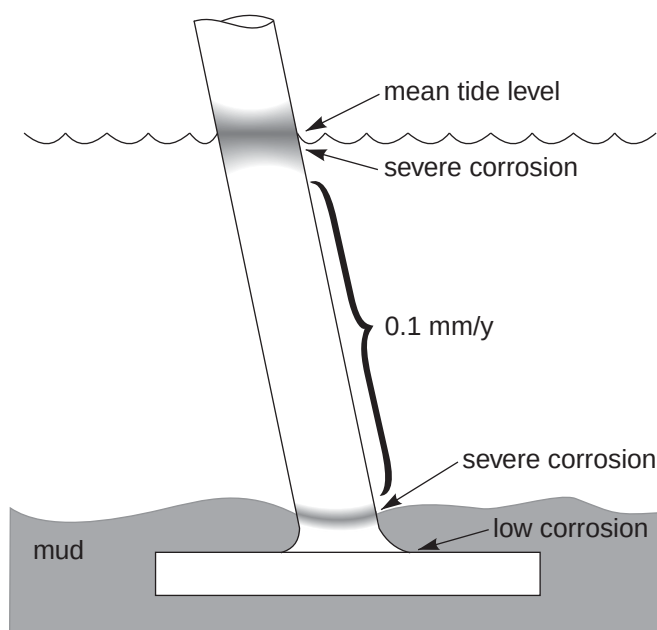


Figure 5.2 Oxygen concentration cells on legs of offshore steel structure.

Critical Humidity

Any significant corrosion in gases at temperatures below 100°C (212°F) actually is almost always electrochemical because an extremely thin film of moisture condenses on the metal surface to serve as the electrolyte. Other pollutants in the gas (SO_2 , CO_2 , salts, etc.) dissolve in the moisture to increase its conductivity and in some cases offer alternative cathode reactions. Temperature fluctuations

Automobiles used to have bolted-on fenders to make replacement easier. Canvas gaskets between fenders and body prevented squeaking, but once moisture got through the paint to the canvas, the fenders tended to fall off.

When liquid is flowing outside, crevices must be quite tight (in the order of a micron) (<0.1 mil) to keep the solution inside stagnant. Chloride ions speed the development of corrosion in the crevice, but even so, a long incubation period precedes any localized attack. Within the crevice the metal commonly looks like it has pitted, as Figure 5.8 shows on a stainless steel flange. Stainless steels are particularly susceptible because they become active within the crevice and passive outside, developing a large potential difference between anode and cathode areas. Crevice corrosion often initiates stress corrosion cracking or corrosion fatigue.



Figure 5.8 Crevice corrosion of stainless steel pipe flange under a composition gasket. (From E.V. Kunkel, *Corrosion*, Vol 10, p. 260, 1954. Reprinted by permission, NACE International.)

When corrosion begins, the crevice corrodes uniformly just as the metal outside the crevice does, but in time the O₂ within the crevice has all reacted and no more O₂ enters because the crevice is so narrow. The cathode reaction continues outside the crevice, however, with electrons being supplied from the anode within the crevice. Corrosion outside actually decreases because of the electron current coming from the crevice.

The production of positive metal ions attracts anions, particularly Cl⁻, into the crevice to form metal chloride. These soluble chlorides hydrolyze, reacting with water according to the reaction



where M is the metal that has corroded.

Hydrochloric acid lowers the pH in the crevice and, in ionizing, also releases the Cl⁻ ions to react with more metal ions. The high acidity breaks down passive films, increasing the dissolution of the metal, as the increasing salt concentration reduces O₂ solubility.

You want to see a really serious example of crevice corrosion? Examine a piece of old, “rotten” wire rope. It may look good on the outside but will break under even light loads.

One petroleum refinery, notorious for its corrosion troubles, had a problem in the coolers that handled the light ends because H₂O and HCl vapors were condensing in the tubes. The engineer added ammonia (NH₃) to neutralize the condensate but great amounts of ammonium chloride (NH₄Cl) crystals precipitated in the tubes causing crevice corrosion throughout. New tubes cost \$800,000.

Chloride ions are not the only anions that migrate into the crevice, of course; other aggressive ions, such as thiosulfate (S₂O₃²⁻) can produce the intense attack. However, if hydroxide ions, which migrate even faster than chloride ions, are present, they help to shut down the attack by tying up the metal ions as insoluble metal hydroxides.

Crevice corrosion can be prevented in several ways.

1. Eliminate crevices: weld butt and lap joints with a continuous weld, not a skip weld; use nonabsorbent gaskets, such as Teflon; caulk seams.
2. Keep the metal clean: remove deposits; filter out solids; avoid intermittent flow that might allow debris to settle out.
3. Add alkalies to neutral chloride solutions.

A 30-in. cast iron pipe buried near a coal storage yard quickly developed a leak. The work crew that dug it up found that the soil contained 17 g/L of H_2SO_4 that had leached from the coal. They patched the leak by welding a ½-in.-thick steel sleeve completely around the pipe. A year later the pipe was leaking again (new steel is anodic to rusted cast iron). They dug up the pipe, patched it, and coated the area with coal tar enamel reinforced with fiberglass cloth. They installed a drain tile to remove the acid and they added an impressed current cathodic protection system with a graphite anode. Within another year they had to install a Duriron anode to replace the graphite, which had dissolved in the acid. The next year the pipe started leaking again. When they dug it up they found a new problem: crevice corrosion caused by a wooden board left lying on the pipe in a previous excavation. They repaired the pipe once more and finally had no more trouble.

Filiform Corrosion

Filiform corrosion appears as fine filaments of corrosion products growing across the metal surface, usually under a thin, protective organic coating. A common example is the pattern of fine, red-brown lines of rust that form on the surface of painted or lacquered tin cans stored at high humidity for long times.

The filament is a crevice that is continuing to grow. Usually initiating at defects or scratches in the coating, the filament's head is the anode, with a low O_2 concentration and low pH. Its tail,

3. Add inhibitor, but in sufficient amounts to protect the entire surface.
4. Use cathodic or anodic protection.
5. Shot peen the surface. Shot peening increases the potential of steel about 100 mV, reducing pitting tendency.
6. Select a more resistant material. When chloride is present, type 304 stainless steel is often replaced by 316 or 317, containing Mo. Even more resistant are the nickel alloys Alloys G-3, 625, and C-276.
7. Use protective coatings: organic coatings, zinc-rich paints, and metallic zinc are commonly used.
8. Increase thickness of the metal. For example, the time for a pit to penetrate aluminum varies as the cube of thickness; doubling the thickness increases the life by a factor of eight.
9. Passivate the metal. After cleaning, stainless steel is usually washed with 20% HNO_3 to give it a strong passive film.

Microbial Corrosion

Localized corrosion by microbial growths has only recently been recognized as a serious industrial problem, but it is now appearing in such diverse places as the soil, inside pipelines, oil wells, in heat exchangers and condensers, and aircraft fuel tanks. Nearly all common engineering alloys are susceptible, except titanium with its incredibly resistant passive film. The problems are commonly referred to as MIC, microbially influenced corrosion.

A wide variety of bacteria, algae, and fungi have been identified as causing problems. They all require some water and most types require organic matter for food. In addition, most bacteria need oxygen for metabolic processes, although some types are anaerobic,

growing only in the absence of oxygen. Faculative bacteria prefer oxygen if it is available but can also use sulfite (SO_3^{2-}), nitrate (NO_3^-), or ferric (Fe^{3+}) ions as oxidizers. Typically, bacteria grow best in temperate climates and at fairly neutral pH values, but exceptional types thrive at acidities as great as pH 0 and temperatures from at least -10 to $+99^\circ\text{C}$ (15 - 210°F). The corrosion usually takes the form of pits under the microbial colony, particularly at welds and their HAZ's.

Corrosion by sulfate-reducing bacteria was first discovered in Holland in 1934. Waterlogged soil with a neutral pH (the sea just pumped from it) corroded steel severely. But since the soil had no oxygen, no acid, and no oxidizing ions, it had no known cathode reaction!

All microbial colonies set up an *oxygen concentration cell*. Under their protective biofilm or slime the oxygen concentration is very low, creating an anodic region for crevice corrosion. This situation develops for both aerobic types, where the microbes consume the O_2 , and anaerobic types, where bacteria shield themselves from air by growing a protective biofilm. In addition, under the colonies the microbial activity often concentrates ions such as chloride that can damage passive films.

Sulfate-Reducing Bacteria. For steel in soils the most common bacterial corrosion is caused by various anaerobic sulfate-reducing bacteria (SRB). In their metabolic process these bacteria reduce sulfate in the soil to sulfide, consuming hydrogen in the process



with the reaction being catalyzed by an enzyme (hydrogenase) produced by the bacteria. These bacteria remove adsorbed hydrogen from the steel surface, “depolarizing” the cathode areas; that is, these bacteria speed up the cathode process, which is usually rate controlling. The sulfide produced in this reaction reacts with Fe^{2+} produced at the anode and forms FeS , a jet black precipitate on the metal. The FeS provides a cathode much more efficient than steel for H_2 evolution and, thus, further increases the corrosion. The attack

may reach 2.5 mm/y (100 mpy). Recent research strongly indicates that the SRB also generate an extremely corrosive, phosphorus-containing, metabolic product other than hydrogenase. Although these bacteria are anaerobic and should not be able to grow in aerated conditions, they are often found in the O₂-depleted regions under colonies of aerobic bacteria. In fact, attack is most aggressive in alternating aerobic/anaerobic environments.

Acid-Producing Bacteria (APB). Acid producers, such as the sulfur-oxidizing types are aerobic. These bacteria oxidize elemental sulfur or sulfide to H₂SO₄ as a waste product of their metabolism. They are often found in soils around sulfur storage facilities, in oil fields, and sewage disposal sites. Nitrifying bacteria in cooling waters can oxidize ammonia to nitric acid. Other types of APB make highly corrosive organic acids, with acetic acid being the most common. These acids attack metals, concrete, and polymer coatings.

We do not refer to sulfur-oxidizing bacteria by initials. In an oil field that term is usually reserved for the tool push (the boss).

Iron-Oxidizing Bacteria. Iron-oxidizing bacteria (IOB), also aerobic, feed on Fe²⁺ and exude Fe³⁺ through their biofilm, forming a crust of rust around themselves. The growing bacterial colony often bursts this crust, grows beyond it, forms another crust, and so on. The result will be “tubercles,” or knoblike mounds of Fe₂O₃ rust (examples are shown in Figures 5.11 and 5.12). Tubercles sometimes grow to the size of softballs in six months. The IOB cause crevice corrosion, accelerate the anode process, and some are now known to concentrate Cl⁻, which makes them especially bad for stainless steels. The oxygen-starved regions inside the tubercles permit the growth of SRB also.

Biocides can be completely effective but must be selected to match the type of bacteria present without endangering the natural environment or animal life. The types of biocides available are discussed in Section 11.7. However, slimes produced by bacteria are extremely difficult to penetrate with biocides. Cleaning the system is the best defense; microbial corrosion is never detected on a clean metal surface.

Stainless steels such as types 304 and 316 are often no more resistant to MIC than plain carbon steel, and sometimes less resistant. However, superaustenitic stainless steels containing at least 6% Mo are quite resistant although not immune. No problems have been reported with the Ni-Cr alloys (e.g. Alloy 600) or the Ni-Cr-Mo alloys such as C-276, but these are most often used for environments and temperatures that bacteria can't take.

Condensate Corrosion

Localized corrosion occurs where moisture-laden hot gases contact a cooler metal surface and condense. This attack on cold metal, sometimes called "dewpoint corrosion," causes almost as much corrosion as on hot metal in many industries. Figure 5.14 shows the deep pits that can result.

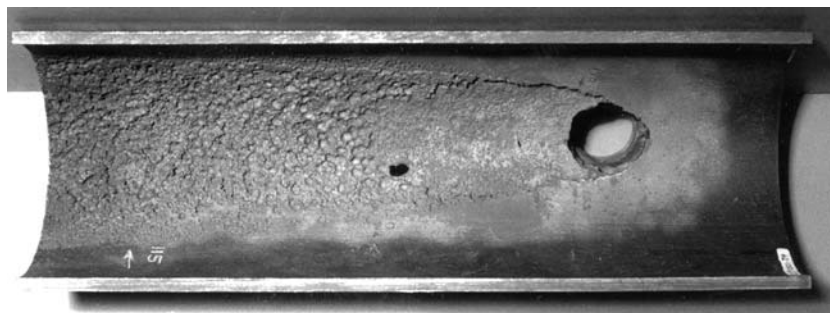


Figure 5.14 Condensate corrosion at an injection point on a gas line.



Figure 5.19 Cast iron pipe from domestic water distribution system, graphitized and attacked locally by stray current. (From *Materials Protection and Performance*, Vol. 11, No. 10, front cover, 1972. Reprinted by permission, NACE International.)

One method that does *not* work, although it has been tried many times, is coating the metal where it is corroding. This technique reduces the anode area, causing all current to discharge through minute flaws in the coating and thus immediately drills holes through the pipe or tank. Stray current pick-up could be prevented if

the *entire* structure were coated but that is usually impractical if the structure is already in place.

Study Problems

- 5.1 Briefly explain the *most probable* cause of corrosion where
- (a) rust blisters have formed inside a steel pipe carrying fresh water, and
 - (b) a stainless steel pipe carrying seawater at moderate velocity looks perfect except for one hole in it.
- 5.2 Name the general type, or types, of bacteria for which each of the following descriptions applies:
- (a) anaerobic,
 - (b) black iron sulfide forms,
 - (c) tubercles of rust form,
 - (d) pH is reduced,
 - (e) inhibitors are ineffective, and
 - (f) concrete is damaged.
- 5.3 Lake water for cooling is pumped to a nearby plant through a 6-in. steel pipe. It was inspected after 1 year of service and found to be in excellent shape. After 3 years it had numerous deep, internal pits arranged in a line along the bottom of the pipe. How would you solve the problem? Explain.
- 5.4 A pipe carrying river water is corroding badly only at low spots in the line.
- (a) What type of corrosion is probably occurring. Explain.
 - (b) The obvious answer to the problem is, “Don’t have any low spots.” What would be the next-best answer?

Memos

(These real corrosion problems may have several solutions or they may have no completely satisfactory solution. The more helpful advice you can offer to Chet the better, but you will need to explain why he should take your advice.)

5.19 Memo To: Corrosion Engineer

From: Chet Bailey, Production Supervisor

In the old plant we've got a 6-in. 304 stainless pipe 100 ft. long carrying light fuel oil with some water, ethylene dichloride, and hydrochloric acid at 150°F that has been in service 3 years. It's holding up pretty well except for two sections, both about 5 ft. long that are badly pitted and leaking. I plan to have the bad section cut out and new pipe welded in, but am supposed to check with you first, since you're supposed to be some sort of hot-shot expert in this corrosion thing. The entire system will be phased out in another year.

5.20 Memo To: Corrosion Engineer

From: Chet Bailey, Production Supervisor

One of our engineers in the Processing Section suggests substituting 50% H_2SO_4 in their operation instead of the 95% H_2SO_4 we've always used. Briefly, his reasons are (1) yield will not be substantially changed; (2) production will decrease 20%, but at the present time we have 50% more capacity than we need; (3) lower cost of the dilute acid will achieve a saving of \$10,000/year; and (4) corrosion of the steel reaction tank and piping will be reduced. The idea looks good to us but the manager thought we should check with you on item 4, since you're supposed to know something about corrosion.

5.21 Memo To: Corrosion Engineer

From: Chet Bailey, Production Supervisor

We have a problem with pitting of a 304 stainless steel pressure vessel containing a 50% $\text{Al}_2(\text{SO}_4)_3$ solution, pH 2, at 225°F with rapid agitation. After we spot-weld the pits we will try cutting down on the stirring, since I suspect it isn't needed anyway.

Chapter 6

STRESS-ASSISTED CORROSION

A synergistic interaction exists between corrosion and stress. The stresses may be applied directly through the metal as tension, torsion, or compression, or they may be applied to the metal surface through the environment, such as occurs with high-velocity liquids and impingement by suspended solids.

Stresses on the metal increase its corrosion: these stresses create stress cells of course, but more importantly they disrupt the surface film that has protected the metal to some extent. The resulting cell of filmed versus unfilmed metal increases and localizes the corrosion attack, particularly for passivated metals.

Combined wear-corrosion interactions increase the corrosion rate of dental amalgams by at least 1000 times. Don't grind your teeth over this.

Petroleum refineries have found pipe wall thickness decreasing as much as 3 mm/y ($\frac{1}{8}$ ipy) due to erosion-corrosion.

Localized corrosion concentrates the stress: intergranular corrosion, for example, creates a notch that acts as a stress raiser. Corrosion can even produce additional stresses by charging the metal with hydrogen that creates internal pressures, or by forming voluminous solid corrosion products that create a pressure on the metal in crevices. In these circumstances the corrosion is often rapid, or if fracture is initiated, failure will be sudden. The possibility of a disaster is always present.

them less resistant to erosion-corrosion than alloys with solid solution hardening.

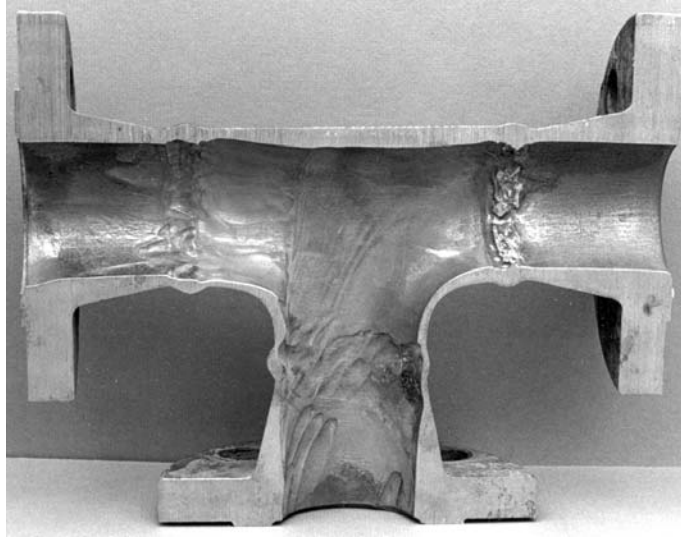


Figure 6.4 Wavy surface, showing erosion-corrosion.

As you would expect, the problem is usually worse at high velocities, high temperatures, and high concentrations of the corrosive. However, if the corrosive environment strengthens the protective film, it sometimes happens that increasing velocity will reduce erosion-corrosion; this situation may occur with austenitic stainless steels in some environments.

Generally, erosion-corrosion is related to velocity by the equation

$$\text{Failure rate} \propto (\text{velocity})^n \quad (6.1)$$

with the exponent n generally in the range of 0.3 – 2. Heat exchangers operate more efficiently at high velocities where n may be as high as 2.5. This equation, however, does *not* hold if the protective film is not damaged. Below a critical velocity the failure rate is zero.

Environments that cause erosion-corrosion include gases, liquid metals, and organic liquids, as well as aqueous solutions. Liquid metals are particularly troublesome because of the high temperatures involved and their high density, which causes great mechanical wear when they are in motion.

Turbulence

Most erosion-corrosion problems occur in turbulent flow. The tubes in a heat exchanger, for example, often suffer erosion-corrosion only in the first few inches at the inlet end. Where the fluid has settled down to laminar flow the tubes look good.

This “inlet-tube corrosion” can be combatted by extending the tubes a few inches beyond the tube sheet, or by inserting short replaceable liners (ferrules) at the tube inlets, or even by reversing flow when the tubes are nearing the end of their life.

Turbulence is created by a change in pipe diameter, an abrupt change in flow direction, or an obstruction in a pipe, such as a weld bead protruding into the stream by $\frac{1}{8}$ in. or more. Erosion-corrosion then occurs just downstream from the weld, as illustrated in Figure 6.5.

One of the great corrosion engineers, now deceased, hated welders, especially welders who tried to do a perfect job. If they didn't sensitize the metal they left big weld beads inside the pipes to create turbulence. He would clamp patches on a pipe until there was no room for another patch before he would call in a welder.

Corrosion Fatigue

The cracking of a metal in a corrosive environment may be caused by corrosion fatigue, hydrogen embrittlement, stress corrosion cracking, or liquid-metal embrittlement. Alternatively, metallurgical factors unrelated to corrosion, such as hot shortness, could be responsible. Corrosion fatigue failures occur in conditions of fluctuating or cyclic stresses that are tensile at least part of the time. Common examples are failures of ship propeller shafts, wire cables used in water or humid air, and pipes cracking from thermal cycling.

The fatigue strengths of metals in air are only about one-half their tensile strengths. Their corrosion fatigue strengths may possibly be no more than 10% of their fatigue strengths. The number of stress cycles that any metal can resist before cracking is always less for corrosion fatigue than for fatigue (shown in Figure 6.9).

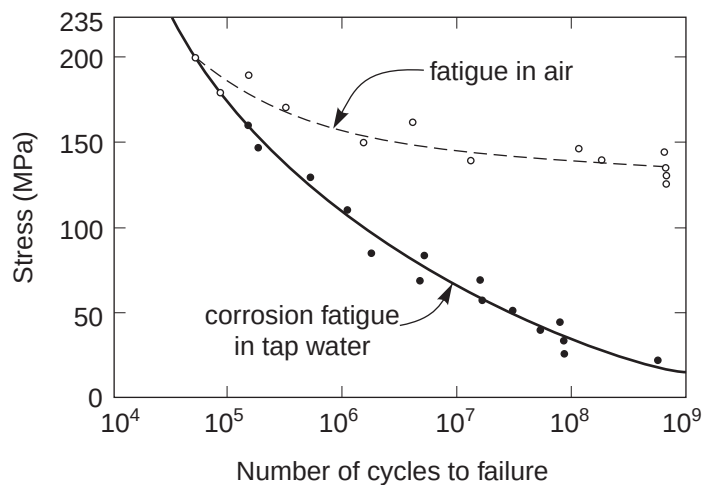


Figure 6.9 Comparison of fatigue and corrosion fatigue curves for an aluminum alloy. (From *Corrosion Basics; An Introduction*, p. 104, 1984. Reprinted by permission, NACE International.)

Fatigue of steels in air is unlike that of nonferrous metals such as the aluminum in Figure 6.9. The curves for steels level off so that they have endurance limits—a maximum cyclic stress that the steel can

Table 6.1 Common Metal-Environment Combinations Susceptible to Stress Corrosion Cracking

Alloys	Environments
Carbon steels, moderate strength	Caustic; nitrates; carbonates and bicarbonates; anhydrous liquid NH_3 ; moist H_2S
Carbon steels, high strength	Natural waters; distilled water; aerated solutions of Cl^- , NO_3^- , SO_4^{2-} , PO_4^{3-} , OH^- ; liquid NH_3 ; many organic compounds
Stainless steels	Chlorides; caustic; polythionic acids; water + O_2
Nickel alloys	Hot caustic; molten chlorides; polythionic acids; high-temperature water and steam contaminated with O_2 , Pb , Cl^- , F^- , or H_2S
Copper alloys	Ammonia; fumes from HNO_3 ; SO_2 in air + water vapor; mercury
Aluminum alloys ^a	Aqueous solutions especially with halogen ions; water; water vapor; N_2O_4 ; HNO_3 ; oils; alcohols; CCl_4 ; mercury
Titanium alloys	Red fuming HNO_3 ; dilute HCl or H_2SO_4 ; methanol and ethanol; chlorinated or brominated hydrocarbons; molten salt; Cl_2 ; H_2 ; HCl gas
Zirconium alloys	Organic liquids with halides; aqueous halide solutions; hot and fused salts; halogen vapors; conc. HNO_3
Magnesium alloys	H_2O + O_2 ; very dilute salt solutions

a. Resistances of Al alloys to SCC are detailed in Table 9.4.

Cracking

Stress corrosion cracks initiate in various ways: from notches created by intergranular corrosion, from pitting damage of a passive film, from pits formed by crevice corrosion or erosion-corrosion, or from localized attack of slip traces on film-protected surfaces. Figure 6.16 shows SCC that has initiated from a pit.

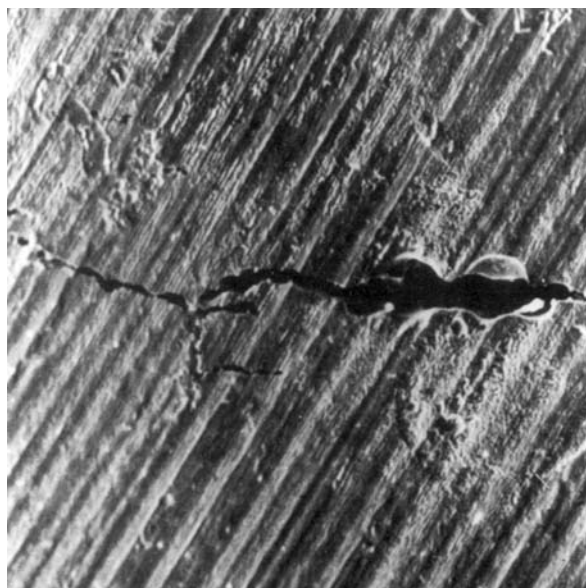


Figure 6.16 Stress corrosion crack initiating from a corrosion pit in a high-strength turbine steel exposed to oxygenated, demineralized water. (From R.H. Jones and R.E. Ricker, *Metals Handbook*, 9th ed, Vol. 13, p. 149, 1987. Reprinted by permission, ASM International.)

In chemical plants, the most common source of SCC is initiation by crevice corrosion under thermal insulation that has gotten wet. An infrared scan can spot the danger by detecting cold spots caused by wet insulation.

The average crack velocity varies with approximately the fourth power of the stress or the square of the stress intensity, suggesting a diffusion-controlled process. The cracks are usually fine, branching

cracks, often filled with corrosion products, and running only approximately perpendicular to the applied stress (see Figure 6.17). The pH inside the cracks is much lower than the bulk solution, since the cracks are crevices with the same reactions as any crevice. Conditions there are favorable for hydrogen evolution even if the bulk solution is basic.

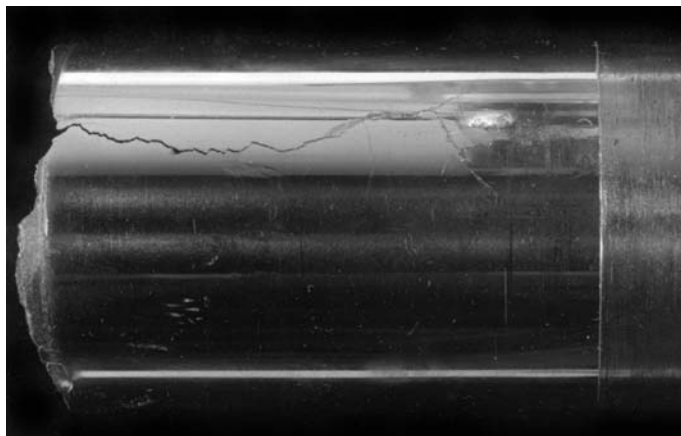


Figure 6.17 Stress corrosion cracking of a vertical pump shaft sleeve operating in a salt slurry.

For most metal-environment combinations the cracks are intergranular, unlike corrosion fatigue, but for some combinations, most notably unsensitized stainless steels in chlorides, the cracks are transgranular. A crack may propagate entirely through the metal section or it may stop if the stress concentration has been relaxed or if the crack tip hits an obstacle, such as an unfavorably oriented grain boundary, inclusion, or the like.

Whether the crack moves along grain boundaries or splits crystal planes depends not only on the metal and the environment but sometimes also on the temperature and stress.

Mechanisms

Stress corrosion cracking is a general term for several processes, so one or more of the following mechanisms may be operative. Other mechanisms have also been proposed and may be important in some cases.

1. Hydrogen embrittlement is a major mechanism of SCC for steels and some other metals. Hydrogen is produced on the crack surfaces that are the cathodes, while the crack tip is the anode. Atomic hydrogen diffuses through the metal ahead of the crack tip and embrittles the metal in that region.
2. A film-rupture mechanism is important for passive metals (stainless steel, aluminum, and titanium), for metals that tarnish (brass is an example), and perhaps even for metals with adsorbed ions or adsorption inhibitors. Stress ruptures the surface film locally, setting up an active-passive cell that causes rapid corrosion at the rupture until the metal repassivates. The corrosion site becomes a stress raiser that ruptures the film again, repeating the cycle.
3. Preexisting weak or corrodible paths, a mechanism proposed 50 years ago, is valid for special cases, such as sensitized stainless steel with its Cr-depleted regions that are both very corrodible and weak. The cracks follow the grain boundaries (see Figure 6.18). Similarly, aluminum alloys precipitation hardened to near maximum hardness are sensitized and fail by intergranular SCC.
4. An adsorption mechanism in which the damaging species adsorbs on the crack surfaces, lowering the fracture stress, could explain cracking in liquid metals and organic liquids.

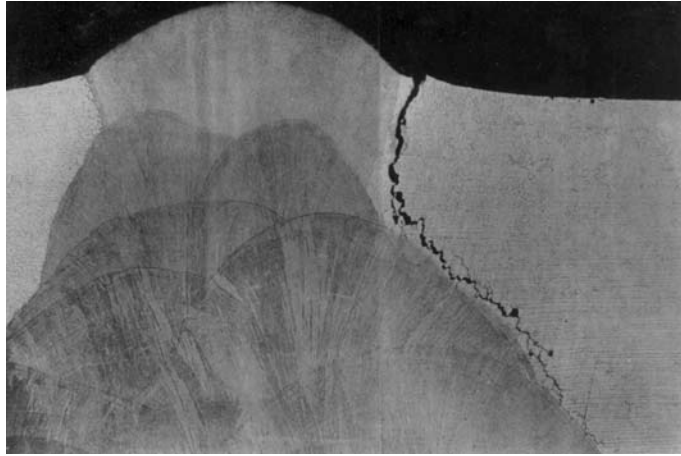


Figure 6.18 Intergranular SCC in the HAZ of a 304 stainless steel weld. Magnification 15X. (From Barry M. Gordon and Gerald M. Gordon, *Metals Handbook*, 9th ed., Vol. 13, Joseph R. Davis, Senior Editor, p. 930, 1987. Reprinted by permission, ASM International.)

Prevention

Prevention or reducing the likelihood of SCC can be accomplished in the following ways.

1. Select a material not known to crack in the specific environment involved; ensure that the microstructure is not susceptible to intergranular corrosion.
2. Lower internal stresses on the metal and use at the minimum required hardness. A stress relief anneal can double or triple the life of chemical equipment.
3. Design to minimize tensile stresses and stress raisers. Avoid tensile fabricating stresses. Use materials with similar coefficients of expansion.
4. Put in compressive stresses: shot peen, swage, roll in threads.

Chapter 7

CORROSION IN MAJOR ENVIRONMENTS

No metal is suitable under all conditions for any one environment, but the corrosion engineer will immediately think of certain particularly compatible environment-metal combinations that will work in most circumstances. Anyone involved in materials selection for corrosive environments should remember the 11 environment-metal combinations in Table 7.1.

Environments will differ at different places on the metal: a boiler tube may contact hot gases, cold and hot water, steam, mineral deposits, and more. And the environments change with time as crevices develop, deposits form, and temperatures increase.

Natural Environments

The Atmosphere

Atmospheres are classified as rural, industrial, or marine in an effort to describe the different types of corrosion a little more accurately, but this classification is sadly inadequate. The wide variations in rainfall, humidity, temperature fluctuations, wind, and pollutants prevent classification schemes from giving more than a mere indication of corrosion rates.

Two variables deserve particular mention.

1. The type and amount of pollutants carried in the air. Most important of these is SO_2 gas, commonly produced by industries burning high-sulfur coal. With moisture and oxygen, SO_2 produces dilute sulfurous and sulfuric acids, which are extremely corrosive to almost all metals, except the compatible combination with lead. The other most serious pollutant is the chloride carried by the air, with marine atmospheres being considerably more corrosive than rural. NO_x gases form nitric and nitrous acids with the moisture and also catalyze the conversion of SO_2 to H_2SO_4 . Water-soluble contaminants such as sulfates and chlorides increase conductivity of the moisture film and reduce the critical level of relative humidity where the film will begin to form. Solid pollutants, even dust, tend to be hygroscopic and hold moisture against the metal surface.

Table 7.1 Compatible Combinations

Environment	Metal	Comments
The atmosphere:		
Low stresses	Aluminum	May be anodized
High stresses	Galvanized steel	Zinc hot-dipped
Water	Copper, Cu alloys	Fresh water or seawater
Soil	Steel	Plus cathodic protection
Sulfuric acid:		
Dilute	Lead	Below 70% acid
Concentrated	Steel	Above 70% acid
Hydrochloric acid	Alloy B	Developed for HCl
Nitric acid	Stainless steels	
Alkalies	Nickel, Ni alloys	
Food	Tin	Coating on steel
Strong oxidizers	Titanium	Even at high temperatures

Table 7.3 Typical Corrosion Rates
of Common Metals in Fresh Water^a

Metal	Water	Corrosion Rate (mm/y)
Carbon steel	Clean river water	0.06-0.09
Carbon steel	Polluted river water	0.06-0.15
Carbon steel	Natural hard water	0.15
410 Stainless steel	Tap water	Unattacked
304 stainless steel	Tap water, 20°C (68°F)	<0.0025
304 Stainless steel	Tap water, 70°C (158°F)	<0.0025, small pits
Nickel	Distilled water, 25°C (77°F)	<0.0025
Nickel	Domestic hot water	<0.005
Aluminum	Tap water	Satisfactory
Copper	Potable water	0.005-0.025
Copper	Very soft water	0.0025-0.125
Chemical lead	Tap water, 25°C (77°F)	0.009
Chemical lead	Aerated lake water	0.114
Magnesium	Pure water, 100°C (212°F)	Up to 25
Mg-Zn alloys	Pure water, 100°C (212°F)	0.0025-0.005
Tin	Distilled water, 20°C (68°F)	0
Zinc	Hard water	0.0025-0.005
Zinc	Soft river water	0.020
Zinc	Soft tap water	0.005-.010

a. Data taken from various sources.

Copper and copper alloys make a compatible combination with fresh water but steel is also often used where corrosion is less important than cost. Tin-coated metals are commonly used to handle distilled water. Table 7.3 shows typical corrosion values for many common metals in various waters.

Acid Rain

Acid rain is caused by volcanic activity, by lightning, and by manmade air pollution from combustion of fossil fuels such as from automobile exhaust and industrial operations. Most damage is done

Table 7.6 Corrosion of Common Metals in Soils

Soil/Metal	Corrosion Rate (mm/y)	Maximum Pit Depth (mm)
Clay loam, good aeration		
Steel	0.012	1.72
Gray cast iron	<0.014	3.93
Aluminum ^a	0.001	0.53
Copper, tough pitch	0.001	0.15
Yellow brass	0.001	<0.15
Chemical lead	0.002	0.45
Zinc	0.007	0.43
Galvanized steel	0.002	<0.15
Peat, high S²⁻, poor aeration		
Steel	0.064	2.98
Gray cast iron	0.063	4.33
Aluminum ^b	Destroyed	1.6+
Copper, tough pitch	0.035	1.16
Yellow brass	0.065	2.63
Chemical lead	0.002	0.83
Zinc	0.110	2.53
Galvanized steel	0.067	2.22

a. Fine sandy loam; fair aeration

b. Muck; very poor aeration

Source: Romanoff, 1957

Organic Environments

Organic Acids

Formic Acid. Formic acid, HCOOH, usually considered the most corrosive monocarboxylic acid, is used for dyeing and finishing textiles and paper, for insecticides, and production of other chemicals. Carbon steels are attacked rapidly. Type 304 stainless is usually used for storing the acid but Alloy 20 stainless is necessary for high temperatures. The Alloy C nickel alloys are excellent, as is titanium,

adjacent metals. In that case the electric current that flows through the gums causes intense pain. Also, bacterial corrosion can occur from SRB or acid-producing bacteria.



Figure 7.2 Examples of medical implants removed because of infection, pain from corrosion, or corrosion fatigue.

Sewage and Waste

Few metals can withstand the chlorides, sulfates, hydrogen sulfide, and bacteria present in municipal sewage or the extreme fluctuations in composition of industrial waste water. Cations of NH_4^+ , Cr^{3+} , and Fe^{3+} are especially damaging because their salts hydrolyze to create acids. Combine these chemicals with high-temperature processes for oxidation and incineration, which are becoming frequently necessary, and the list of satisfactory materials becomes quite limited.

However, 28 million Americans do not yet have modern sewage treatment facilities.

Austenitic stainless steels (304, 316, 316L, etc.) can withstand chloride concentrations up to 400 mg/L (or ppm) in municipal sewage sludge for oxidation processes at temperatures of 175-315°C (350-600°F) without pitting or cracking. At higher chloride contents, even over 5000 mg/L,

titanium performs with no problem. Alloys C-276 and C-22 also resist these high-chloride, high-temperature environments well.

With less severe environments, lower chlorides and lower temperatures, other nickel alloys such as Alloy 625 and Alloys B and G have served well. For sewage handling and treatment at ambient temperatures, good resistance is reported for aluminum alloys, copper, and copper alloys except high-zinc brasses, which dezincify.

One failure analysis of Type 409 stainless steel in rotating biological-contactor units handling raw waste water with up to 3000 mg/L of chloride showed that cracks always initiated at pits under bacterial colonies growing at welds and HAZ's. In another study of chloride-containing mist with H_2S at waste-water treatment facilities, galvanized steel rusted and pitted badly but aluminum performed well.

Nonmetallics such as cement, fiberglass-reinforced plastics, and high-density polyethylene generally withstand wastewater better than metals do.

Mineral Acids

Sulfuric Acid

Sulfuric acid, generally considered the most important industrial chemical, is used in making fertilizers, chemicals, paints, in petroleum refining, and others. The concentrated acid has a concentration of 95-98%.

Steel is the most common material for storage and transport of H_2SO_4 concentrations of 70% or higher near room temperature because a film of $FeSO_4$ forms to protect the metal. As temperature increases the film begins to dissolve or as velocity increases, the film erodes. At 50°C (122°F) the corrosion rate of steel reaches 0.5 mm/y for the concentrated acid and more than 1 mm/y for concentrations less than 90%. Figure 7.3 with its table shows pure metals and alloys suitable for H_2SO_4 solutions.

Chemical lead (containing 0.01% Ag) corrodes at less than 0.1 mm/y at 100°C (212°F) for all H₂SO₄ concentrations up to 70%, which explains why lead and dilute sulfuric acid are listed as a compatible combination (Table 7.1).

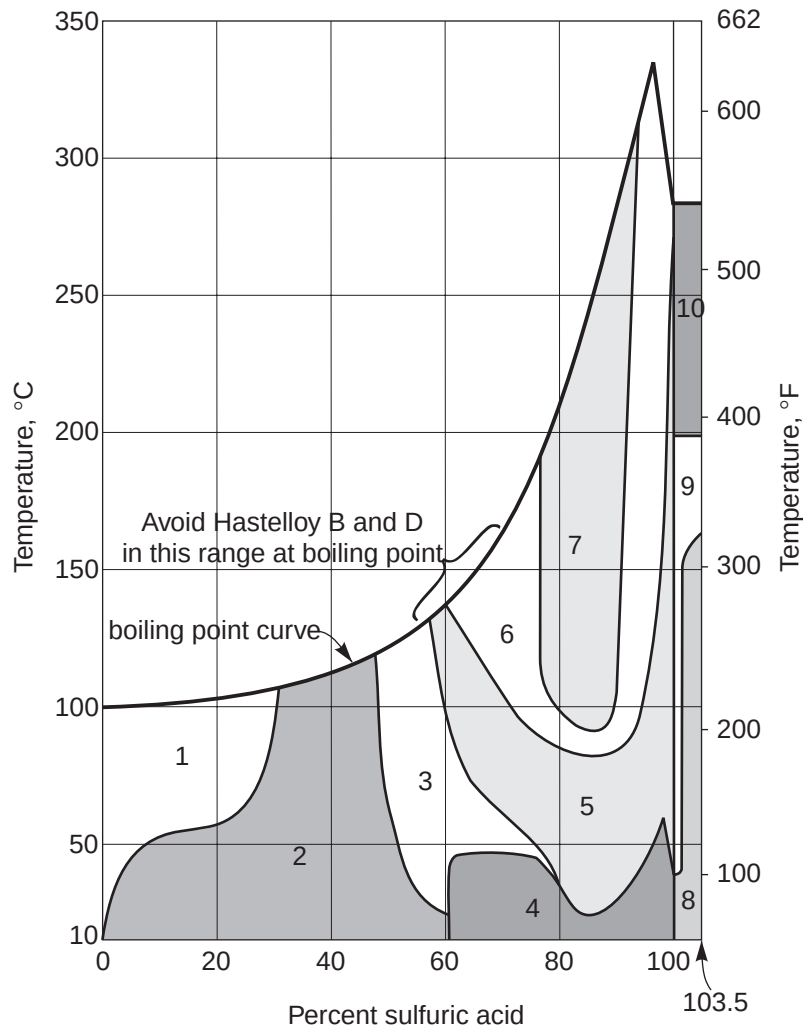


Figure 7.3 Materials with less than 0.5 mm/y corrosion in sulfuric acid. (Materials resistant in each numbered zone are listed in the following Table.) [Reprinted with permission from Shell Development Co.]

Common Inorganics

Alkalies

The term “alkali” refers to the hydroxides and carbonates of the alkali metals (Li, Na, K, etc.) and the ammonium NH_4^+ ion. In more general terms, an alkali is any strong base that produces OH^- ions in water. Those alkalies that are important in industry and will present particular corrosion problems for metals are KOH, NaOH, and NH_4OH .

Nickel alloys make compatible combinations with solutions of caustics (strong, corrosive bases) and are used extensively in caustic production. Figure 7.7 shows the corrosion rates of pure nickel in sodium hydroxide concentrations at temperatures up to the boiling point of the solutions. However, nickel is unsuitable for NH_4OH even in concentrations as low as 1%, while stainless steels handle NH_4OH solutions readily.

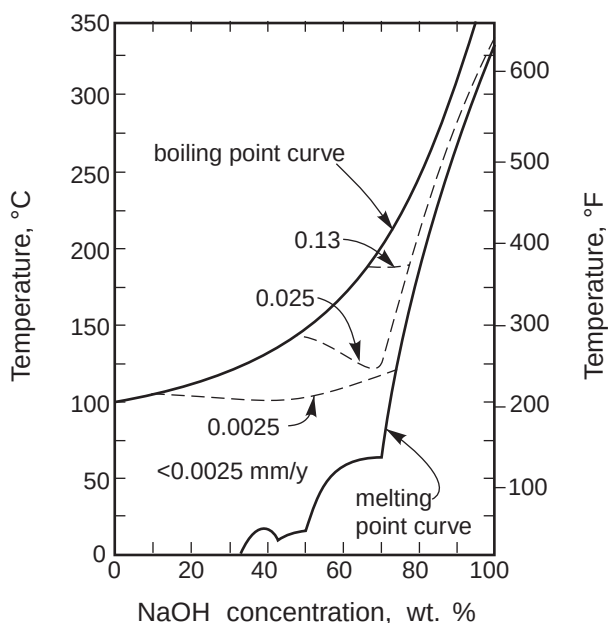


Figure 7.7 Corrosion of Nickel 200 and 201 in NaOH solutions.
[Reprinted with permission of Inco Alloys International.]

Figure 7.8 is a diagram suitable for both Types 304 and 316 stainless steels in NaOH. Note that stainless steels may suffer SCC at high temperatures, unlike the nickel alloys. Iron and carbon steels can handle caustic up to about 70% and 80°C (175°F), but also with the danger of SCC. Table 7.16 lists many pure metals and alloys that are resistant to a wide variety of alkali solutions.

In alkali solutions of up to 40% concentration at temperatures up to about 50°C (120°F), lead corrodes at a satisfactory rate. Magnesium is suitable for any concentration of alkali at room temperature. However, tantalum, the most corrosion resistant of all metals, cannot withstand strong alkalies even at room temperature. The resistance of plastics to alkalies is shown in Table 9.6.

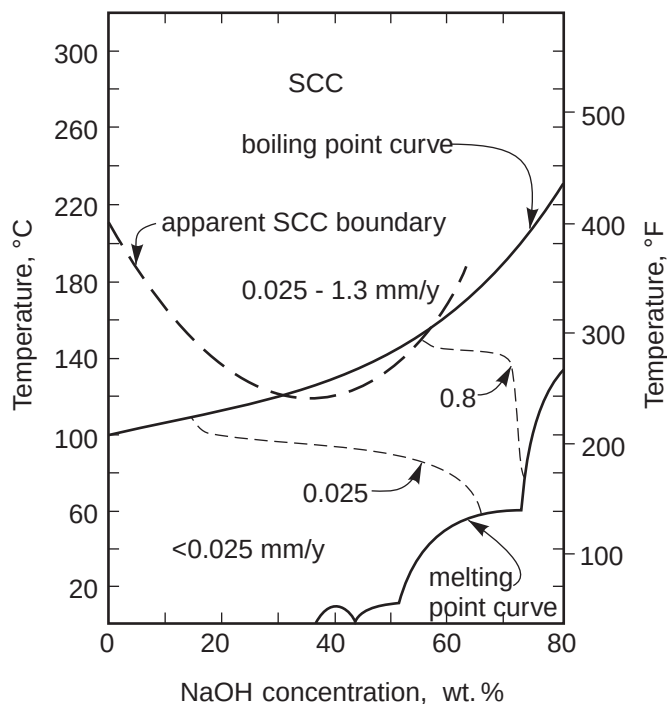


Figure 7.8 Corrosion of 304 and 316 stainless steels in NaOH solutions. [Reprinted with permission from NACE International.]

Road Salt

Reinforcing steel in concrete would seem to be in a near-ideal environment: alkaline conditions with a heavy coating to shield the metal from moisture. But sometimes the steel corrodes and the volume of rust exerts pressure on the concrete, cracking or spalling it, which allows more air and water to reach the steel.

The problem is most acute on highway bridges (see Figure 7.9) but is also seen in parking garages, on marine structures at or near the waterline, and industrial plants. The main culprit is chloride. For bridges and garages the source is deicing salt (both NaCl and CaCl_2) used in the northern half of the United States and in southern Canada. As moisture penetrates pores in the concrete, chloride ions and O_2 are also carried along to develop acid conditions next to the steel reinforcing bars (“rebar”) by the usual crevice corrosion mechanism. Chloride penetration is not uniform, so local anodes and cathodes are created. Since rust has approximately six times the volume of the steel corroded, the swelling breaks up the concrete. Because of rebar corrosion, somewhere in the U.S. every two days a bridge collapses.



Figure 7.9 Rebar exposed by corrosion in support pillar of bridge.
(Reprinted by permission, Harco Technologies Corporation.)

Chapter

8

CORROSION MEASUREMENT AND FAILURE ANALYSIS

Corrosion testing involves evaluation of materials, coatings, or inhibitors that allegedly will be satisfactory for a certain corrosive environment. Tests may be made on new products or just to see if the products being delivered meet their specifications.

Monitoring of equipment in service measures how the corrosion protection (inhibitor additions, cathodic protection, etc.) is doing and also measures the corrosion rate. The monitoring shows how changes in conditions affect the corrosion and allows a prediction of equipment life.

Failure analysis prevents a repeat of our mistakes. It can indicate how a change in materials, equipment design, operating conditions, or whatever will be necessary.

Testing

A corrosion test must yield results that satisfy one criterion: Are they valid? Does the test truly indicate how this product will perform in service? To be valid the test has to be reasonably reproducible, but reproducibility does not necessarily make it valid. In some cases the test does not have to give the same corrosion rate that will show up in service, but only has to rank products in the proper order. Cost or quick results are often wrongly emphasized as most important,

although certainly these must both be considered in designing the test.

Tests use either the real corrosive environment or a simulated environment. Hopefully, a simulated environment will perform the same way as the real corrosive but will be more reproducible, cheaper, or faster.

A synthetic seawater is available commercially for corrosion testing. It is considerably more reproducible than the natural environment but also considerably more expensive.

Tests may use the real service conditions for the material, they may simulate service, or in many cases they omit service conditions. Service conditions are the fluid velocities, the turbulence, the applied stresses, the thermal gradients and heat transfer conditions, the crevices—all the factors other than the material and environment themselves that in some circumstances might significantly influence corrosion.

Types of Tests

Laboratory Tests. In the lab, tests can be run in the real environment but more often are conducted in a simulated environment for better reproducibility. Small test specimens, commonly called “coupons,” are placed in the environment with service conditions simulated only if they appear to be important.

Pilot Plant Tests. Testing in a pilot plant is an excellent way of selecting materials of construction for the full-scale plant. The environment is real (approximately) with all the variations that can occur during shutdowns and when things just go wrong. Coupons can be exposed with simulated service or no service, but parts of the pilot plant itself can be build of candidate materials that will be in service conditions very closely simulating real service. Unfortunately, the trend these days is to omit the pilot plant stage in order to save about a year of time, but often this omission has later proved to be an extremely costly error in judgment.

One plant costing in the hundreds of millions of dollars was built after brief pilot plant tests in an old garage without any tests on materials. The plant opened with great fanfare and ran almost one week. It then ran sporadically for the next two years while it was rebuilt.

Field and Plant Tests. Field tests typically involve large numbers of coupons placed in the real environment (exposed to sea air, buried, put in a process tank, etc.) but usually without service conditions, such as stresses or heat transfer. Coupons are often fastened to a rack, but electrically insulated from the rack and from each other to avoid galvanic effects. Paints and other coatings are most often tested in this way as shown in Figure 8.1.

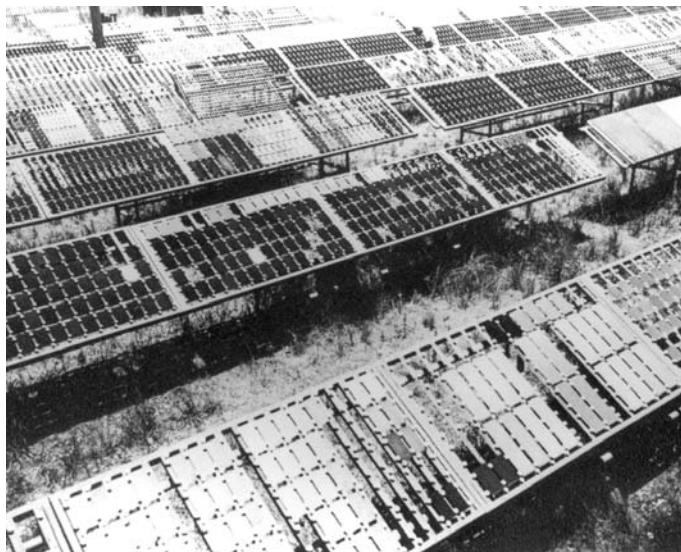


Figure 8.1 INCO test facility for atmospheric corrosion at Kure Beach, NC. (From *Corrosion in Action*, p. 28, 1955. Reprinted by permission, Inco Alloys International.)

Figure 8.2 shows a specimen rack mounted under an automobile. Several automobiles were used to average out differences in driving patterns, roads, garaging, and cleaning.

A new sample (D) is put in on Day 14. Its corrosion of 5 g/m^2 in the 2-week-old solution compared with the 1-day test (A) in the original fresh solution (4 g/m^2) shows that the solution has become more corrosive with time. To find how metal corrodibility is changing with time, compare the new test specimen (D) with the old ones (B and C) in the same 2-week-old solution. A 5 g/m^2 loss is greater than the weight change for the old specimens: $(60-56 \text{ g/m}) = 4 \text{ g/m}^2$, so the metal corrodibility has decreased in 2 weeks.

Measuring solution corrosivity shows when it is time to change the solution, but even if the solution has altered, the metal corrodibility can be determined.

Electrochemical Tests

Electrochemical tests produce results more quickly than any other laboratory test. An entire polarization curve showing both anodic and cathodic behavior of a metal in an environment with a wide range of oxidation and reduction potentials requires only minutes to a few hours.

Some old-time corrosion engineers are leery of these newfangled electrochemical tests, arguing that tests run in a few minutes cannot tell what will happen when a thick layer of corrosion products gradually builds up on a metal. That is true, but electrochemical tests are still invaluable.

The most-used method is the *potentiostatic or potentiodynamic polarization scan* (ASTM G5), which uses a test cell like the one shown in Figure 8.3, a reference electrode connected to the cell via the salt bridge probe, and an electronic device called a potentiostat. The specimen to be tested is the working electrode while the auxiliary electrode is usually platinum or graphite.

The potentiostat monitors the potential of the specimen by comparing it with the reference electrode. If the potential is not the desired value set on the instrument, then the potentiostat alters the cell current (DC) flowing between working and auxiliary electrodes to

bring the potential to the desired value. The potential and resulting current are recorded, the potential is increased slightly, and the process is repeated. The potential can be increased either stepwise (potentiostatic) or continuously (potentiodynamic), and the result is an anodic polarization curve, such as the sketch in Figure 8.4*a* or *b*.

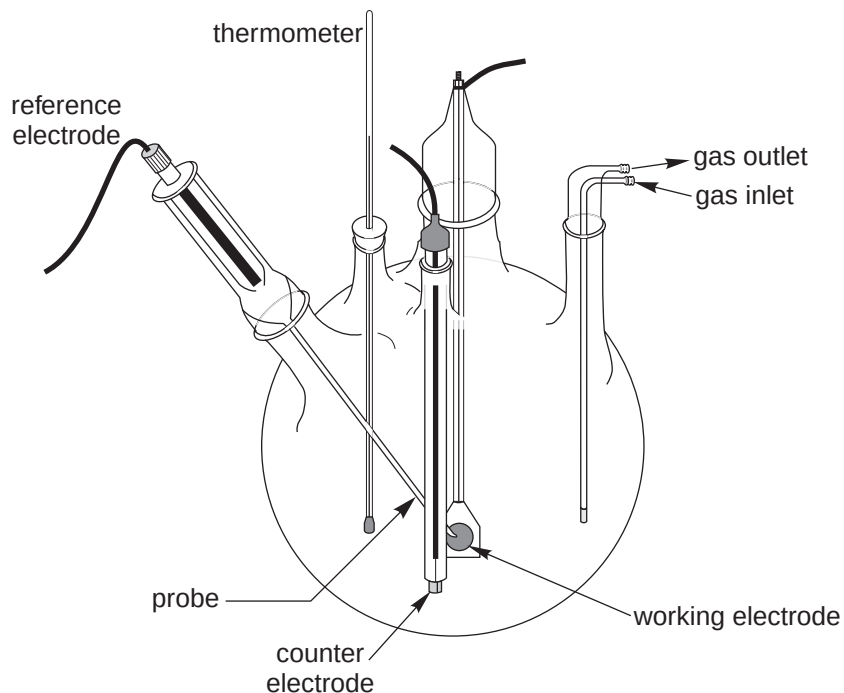


Figure 8.3 Polarization cell used with a potentiostat for rapid determination of corrosion behavior of metal samples.

The polarization curves show how the solution potential affects the corrosion rate, as calculated from the current density by Faraday's Law (Equation 2.22). They show how well the metal passivates and even if aeration of the solution will passivate: If the critical current density for passivation (the peak current density) is no more than about 1 A/m^2 , the metal will passivate in an air-saturated solution.

Accelerated Corrosion Tests

Accelerating corrosion to get quick results often just produces quick misinformation. It never determines true corrosion rates and may not even rank materials in the correct order. But it may be necessary. If a new plant is to be built without going through a pilot plant stage, materials must be selected quickly without the luxury of thorough testing. If production people propose a major change in operation, such as altering flow rates, temperatures, concentrations, or the like, they will not be willing to wait for long-term testing before improving their production.

Asphalt fouling closed down an entire refinery after 6 months operation. Asphalt had been converted to asphaltines (polymers with molecular weights over a million) due to pitting that created hot spots. Corrosion tests had to be finished in a matter of hours.

One obvious way of speeding corrosion is to make the environment more corrosive than the real one. Concentration of the solution or aeration might be increased. This is often done where the corrosion mechanism is well understood: quick pitting and crevice corrosion can often be produced by ferric chloride additions (a powerful oxidizer, Fe^{3+} , combined with Cl^- that damages passive films). Stainless steels are often tested for SCC susceptibility in boiling MgCl_2 , combining high temperature and high chloride.

Increasing the temperature to increase corrosion is tried, and high-temperature data are sometimes extrapolated to low temperatures to find corrosion rates, based on the Arrhenius equation:

$$\text{Rate} = A \exp \left(\frac{-Q}{RT} \right) \quad (8.2)$$

where A is a constant, “exp” refers to the exponent of e , the base of natural logarithms, Q is the activation energy required to begin the corrosion process, R is the gas constant (8.314 J/K·mol or 1.987 cal/K·mol) and T is the absolute temperature in kelvins ($^{\circ}\text{C} +$

273° or $(\frac{5}{9})^{\circ}\text{F} + 255^{\circ}$). This means that data obtained quickly at high temperatures will fall on a straight line if graphed as log Rate versus $1/T$. The line can then be extrapolated to low temperatures *if* all factors, such as amount of dissolved oxygen, remain constant, and *if* the corrosion mechanism does not change with temperature. Those are big *ifs*.

Other methods of accelerating corrosion damage such as simulating crevices, simulating high velocities with a rotating disk sample, and simulating SCC with the SSRT test have already been described.

Electrochemical stimulation of corrosion can be achieved by making a sample more positive in an electrochemical cell, thus making it more corrodible. This is a very common test that takes only a few minutes. It does not build up a thick layer of corrosion products that can only form slowly and therefore may not provide accurate information about long-term corrosion rates. It does show whether a metal will passivate well and does indicate susceptibility to pitting and crevice corrosion.

Inspection and Monitoring

Risk-based inspection, becoming increasingly popular, focuses inspection on the most critical, high-risk equipment while providing the minimum required inspection of low-risk equipment. In this process, risk is defined as:

$$\text{Risk} = \text{Likelihood of failure} \times \text{Consequences of failure} \quad (8.3)$$

A quantitative approach requires a team of experts and is usually applied to only a few critical pieces of equipment. Possible modes of failure must be identified, their likelihood assessed, and their consequences converted to economic and safety impacts. Consequences are not just costs of downtime and replacement but also include fires, explosions, toxic releases, and the like. The American Petroleum Institute (API) has developed a complete risk-based process.

Potential Measurements

The potential of a metal in its environment indicates how likely it is that the metal is corroding. A high corrosion potential means that the metal would tend to be noble, uncorroding. (Remember the standard emf series, Table 2.1.) Measured against a standard reference electrode such as calomel, Ag/AgCl, or Cu/CuSO₄ which do not change potential (polarize) if a little current flows through them, the corrosion potential of a structure shows the probability of corrosion occurring.

Highway departments check steel reinforcing bars (rebar) in concrete bridges by wetting down the concrete well, for good ionic conduction, pressing a reference electrode against the concrete, and measuring the potential difference with a voltmeter. Of course, all the rebar in the bridge was wired together during construction.

For large structures such as long, buried pipelines where structure potentials change because of changes in soil conditions, coating quality, or stray currents, frequent or continuous measurements must be made along the length of the line.

With cathodically protected structures, potential measurements show whether the protection is sufficient, as explained in Chapter 12. Government regulations now require almost continuous corrosion monitoring of pipelines carrying hazardous fluids such as gasoline and natural gas. These structures are all cathodically protected but they cannot be easily disconnected from all other systems they are tied in with, in order to measure their potentials. Therefore, coupons of the same steel, coated the same way, with some coating defects as probably occur on the pipeline are buried a few inches from the pipe and connected to it. These coupons *can* be momentarily disconnected from the pipe and all other structures so that the polarized potential of the coupons can be measured and the cathodic protection on the pipeline evaluated.

Coupons are also used to monitor corrosion rates inside pipe and vessels that cannot be easily inspected. A coupon of the same metal

as a pipeline is inserted in the line and removed from time to time for inspection and measurement. It is assumed that a coupon of the same metal and in the same environment will corrode at the same rate as the pipe.

Electrochemical Noise

As a metal corrodes, its corrosion potential fluctuates slightly as conditions on the surface are continually varying; likewise, the corrosion current flowing from its surface fluctuates as more or less corrosion momentarily occurs. These fleeting variations in potential and current are termed electrochemical noise (EN). However, unlike audible noise that is a senseless disturbance of information transfer, this electrochemical noise conveys meaning that we are still learning to interpret.

Either potential or current noise can be studied, or the two can be combined by computer techniques to calculate noise resistance,

$$R_n = \frac{\sigma E(t)}{\sigma I(t)} \quad (8.4)$$

where σ is the standard deviation of potential or current that are functions of time, t . Certain noise patterns can be identified as uniform attack, initiation of crevice corrosion, pitting, SCC, and the like.

With the intense research now being carried out internationally, these techniques seem likely to develop quickly into better monitoring methods as well as revealing more about mechanisms involved in corrosion processes. The equipment is expensive because a huge volume of information must be processed, and the methods have not yet been standardized, but EN probes are now commercially available.

Flaw Detection

Electromagnetic waves: acoustic, ultrasonic, infrared, and X-rays. The traditional method of checking rebar to see if its corrosion has cracked concrete is to hit the concrete with a claw hammer. If the claws ring like a tuning fork, that concrete is solid. Similarly for bridge decks, dragging chains over them gives out a ringing sound if the rebar has not corroded. These methods, however, only detect corrosion after it has reached a serious stage.

One young engineer was dragging chains over the floor of a city parking garage at 7 a.m. on a quiet Sunday morning when he was suddenly grabbed by two burly policemen who took him to headquarters for an interview with a psychiatrist: “When you hear chains being dragged across concrete, how do you feel deep down *inside*?” Moral: Always carry your work order with you.

Ultrasonic inspection involves sending out a high-frequency sound vibration through a pipe wall, a tank floor, or whatever, where it is reflected from the back side and back to a sensor that transforms it into an electric current. If the pulse echo returns early, external corrosion has thinned the metal; if the echo is late, the metal has corroded internally at that location.

A laser passed through the length of a boiler tube should reflect its light at a constant angle back to a sensor. If a pit is reached, the beam is deflected at an angle related to the pit depth. Scale buildup does not affect the laser beam so the tubing does not have to be cleaned first.

Infrared photography or an infrared sensor can detect heat losses caused by leaks of hot fluid under thermal insulation or leaks of hot crude oil in underground pipelines. A vehicle-mounted infrared detection system detects cracks and corrosion in bridge decks by using two wavelengths instead of one to get a closer measurement of temperature differences.

Galvanic Probes

These probes are used in situations where corrosion is not supposed to be happening. They consist of two electrodes, usually steel and brass, which will set up a galvanic corrosion cell if an electrolyte is present, thus allowing current to flow to sound an alarm or turn on equipment to correct the problem (Figure 8.12.) For example, current flow may indicate the presence of oxygen that has leaked into a closed system, or the failure of a corrosion inhibitor. While the galvanic probe does not measure the corrosion rate of the equipment, it does indicate that a corrosion situation exists, and can even be used to turn on a sump pump or take some other corrective action.



Figure 8.12 Galvanic probe. (From Corrosion Control in Petroleum Production, TPC Publication No. 5, NACE Handbook 1, p. 35, 1982. From Fincher Engineering. Reprinted by permission, NACE International.)

Chapter 9

MATERIALS SELECTION

Corrosion problems can be solved in the following ways:

1. Select a material that is resistant to the corrosive environment.
2. Give metal a protective coating.
3. Change the service conditions, such as temperature, pressure, or velocity.
4. Change environment chemistry, such as pH, concentration, aeration, or impurities.
5. Add a corrosion inhibitor.
6. Shift the electrical potential of the metal by cathodic or anodic protection.
7. Modify the design of the equipment or system.
8. Let it corrode and replace it (often a viable alternative!).

The methods listed above are the accepted ways of dealing with a corrosion problem, but not all of them apply in a given situation. In particular, the corrosion engineer often cannot change the service conditions or environment chemistry. These may be as unalterable as the ocean, or nearly as unalterable: an industrial process that is running fairly smoothly where any change will be fanatically opposed by the production people.

Most corrosion problems originate with either improper design or improper materials selection. However, a good choice of material can overcome severe environmental conditions and even some deficiencies in design.

Once the engineer has determined that there is no danger of a catastrophe, deciding which way to combat corrosion usually comes down to the economics of the situation. To give some idea of the relative costs of materials, at the present time the approximate price per foot of a 0.61-m (24-in.) diameter pipe is \$35 for carbon steel, \$70 for filament-wound polyester, \$300 for 316 stainless steel, \$680 for Alloy 400, and \$730 for Alloy C-276. However, relative costs vary considerably for different shapes and sizes.

Stainless Steels

Stainless steels are usually the first choice for a “probably corrosive” environment with unknown properties, because these alloys are resistant to a wide range of oxidizers, but they cannot withstand strong reducing solutions, such as hydrochloric acid. Stainless steels *can* be corroded, despite their name.

A stainless steel is defined as a ferrous alloy containing enough chromium to passivate in some environment, such as air and water. At least 10% Cr (but usually ~12%), is required to form a passive film (mainly Cr_2O_3). The carbon content is typically quite low in stainless steels, so the terms “carbon steels” and “steels” refer to *nonstainless* steels, since stainless steels have nothing in common with ordinary steels in terms of corrodibility.

The stainless steels are classified into five general groups according to their metallurgical structures, with the choice of which one to use depending not only on corrosion resistance but also on required strength and cost. Table 9.1 lists common wrought stainless steels, their compositions, and their UNS (Unified Numbering System) numbers that will be used more in the future than they are at present. Wrought alloys are formed by rolling, drawing, forging, and the like, as distinguished from cast metals. A new application for stainless steels is shown in Figure 9.1.

Table 9.1 Compositions of Wrought Stainless Steels

Type	UNS	Cr, %	Ni, %	C, %	Other Elements, %	Typical Uses
Martensitic Types						
403	S40300	11.5-13.0		0.15 max		Turbine valves
410	S41000	11.5-13.5		0.15 max		Furnace parts
414	S41400	11.5-13.5	1.25-2.5	0.15 max		Petroleum towers
416	S41600	12.0-14.0		0.15 max	0.6Mo max	Screws, bolts
420	S42000	12.0-14.0		0.15 min		Cutlery
422	S42200	11.5-13.5	0.5-1.0	0.20-0.25	1Mo, 1W, 0.2V	Generator blades
431	S43100	15.0-17.0	1.25-2.5	0.20 max		Aircraft parts
440A	S44002	16.0-18.0		0.60-0.75	0.75Mo	Cutters
440B	S44003	16.0-18.0		0.75-0.95	0.75Mo	Valve seats
440C	S44004	16.0-18.0		0.95-1.20	0.75Mo	Springs
XM30	S41040	11.5-13.5		0.15 max	0.5 Nb	Furnace parts
Ferritic Types						
405	S40500	11.5-14.5		0.08 max	0.2Al	Boiler tubing
409	S40900	10.5-11.75	0.5 max	0.08 max	0.7Ti	Mufflers
429	S42900	14.0-16.0		0.12 max		Solenoid valves
430	S43000	16.0-18.0		0.12 max		Architecture
434	S43400	16.0-18.0		0.12 max	1Mo	Auto trim
436	S43600	16.0-18.0		0.12 max	1Mo, 0.6Nb	
439	S43035	17.0-19.0	0.5 max	0.07 max	0.1Al, 1Ti	Welded equipment
442	S44200	18.0-23.0		0.20 max		Furnace parts
444	S44400	17.7-19.5	1.0 max	0.025 max	2Mo, 0.025N, 0.7(Ti+Nb)	
446	S44600	23.0-27.0		0.20 max	0.25N	Burner nozzles
Duplex (Ferritic-Austenitic Types)						
329	S32900	23.0-28.0	2.5-5.0	0.20 max	1-2Mo	
2205	S31803	21.0-23.0	4.5-6.5	0.03 max	3Mo, 0.15N	Sulfuric acid
2304	S32304	21.5-24.5	3.0-5.5	0.030 max	0.3Mo, 0.3Cu, 0.1N	Dry product chutes
255	S32550	24.0-27.0	4.5-6.5	0.04 max	3Mo, 2Cu, 0.2N	Weak H ₂ SO ₄



Figure 9.1 50 million tonnes of carbon steel is used annually to reinforce concrete. Stainless steel, either austenitic or duplex, is no more expensive, over a 100-year life of a bridge. (From Nickel, Vol. 14, No. 1, p. 15, 1999. Reprinted by permission, The Nickel Development Institute.)

Martensitic Stainless Steels

Martensitic stainless steels can be hardened by air cooling and tempering, like many alloy carbon steels. The corrosion resistance of martensitic stainless steels is good in the atmosphere but only fair in chemical solutions, although it is better in the hardened state than annealed. The tensile strengths are typically 500-1000 MPa (70,000-140,000 psi) with a few reaching 2700 MPa (390,000 psi). While hardening makes these alloys somewhat brittle, they are used for

applications where high strength must be combined with moderate corrosion resistance. Resistance to SCC is very good but they are difficult to weld.

The basic martensitic alloy is Type 410 with modifications made to it for special purposes: more Cr and Ni added for better corrosion resistance, C increased for higher strength or decreased for better toughness, P and Si increased to improve machinability, Se added to give better machined surfaces, or high-temperature strength and toughness improved with Mo, V, and W.

Ferritic Stainless Steels

The body-centered cubic structure of ferritic stainless steels cannot be hardened by heat treatment and will harden only moderately with cold work. They are generally straight chromium types with 11-27% Cr and low C content. Their corrosion resistance is good with almost total immunity to stress corrosion cracking (SCC). Although they are not strong, having tensile strengths in the 400-650 MPa (60,000-90,000 psi) range, they do have good ductility and formability, excellent weldability, low cost, and are excellent at high temperatures if high strength is not required.

Type 430 ferritic stainless steel is the basic alloy that is modified with alloy additions for specific applications: Cr increased to improve scaling resistance or decreased to improve weldability; Al added to prevent martensite formation; P, S, and Si added for machinability; Mo added to resist pitting; or Ti and Nb added to prevent sensitization.

“Superferritic” stainless alloys, recently developed, are Cr-Mo stainless steels with extremely low C and N interstitial impurity levels. Their corrosion resistance is excellent, even equivalent to the austenitic stainless alloys in many environments and they are superior in resistance to SCC. They have 50% higher thermal conductivities than the austenitics, but still only one-half that of steel. The commercial alloys are often described by the Cr-Mo contents, such as 18-2, 26-1, and 29-4-2, which is 29%Cr-4%Mo-2%Ni.

Welding Problems

Stainless steels can suffer intergranular corrosion when sensitized in the heat-affected zones adjacent to welds, as described in the Intergranular Corrosion section of Chapter 4. In addition, arc welding produces a heat tint composed of iron and chromium oxides that leave Cr-depleted regions underneath which are susceptible to localized corrosion. The heat tint can be ground off or removed by etching in a pickling solution as described in ASTM standard A380. The same standard also gives recipes for passivating solutions to be used after removing the tint.

Duplex stainless steels should be 40 to 60% ferrite to obtain the advantages of both the ferrite and austenite structures. However, in weld metal and HAZ the ferrite can vary anywhere from 20 to 80%. High ferrite plus hydrogen charging make welds susceptible to hydrogen cracking for some time after welding, so filler metals are high in nickel content.

In welding any stainless steel, extreme care must be taken not to contaminate the weld with zinc from galvanized steel or even traces of zinc-rich paint. Molten zinc will penetrate grain boundaries, leading to intergranular corrosion and SCC. Likewise brazing with copper or silver alloys will do the same—the only difference being that here the contaminated grain boundaries will be cathodes instead of anodes.

The new superaustenitics can't be welded with the same metal because segregation of alloying elements during welding is likely to cause pitting. Instead, nickel-based welding rods are used.

Nickel-Copper Alloys

Alloys 400 and 500 are modifications of the basic 70Ni-30Cu alloy. Alloy 400 has corrosion resistance similar to nickel but is stronger and cheaper. These alloys resist seawater well and can handle caustics without SCC. They are the metals usually selected for hydrogen fluoride (HF) service, although corrosion rates are rather high if the acid is aerated, and SCC has been reported for cold-worked Ni-Cu alloys in HF so stress relief is advisable.

Nickel-Molybdenum Alloys

Alloy B-2 is nearly unique in resisting hydrochloric acid at all concentrations and all temperatures up to boiling, as well as other nonoxidizing acids. This alloy is not resistant to oxidizing environments, not even aerated hydrochloric acid. The composition has evolved from the basic 70Ni-30Mo alloy.

Nickel-Chromium-Iron Alloys

Several of these alloys are technically stainless steels but are grouped with the nickel alloys because of their high nickel contents and high corrosion resistance (and high price). These alloys have better corrosion resistance than the 300-series austenitic stainless steels; the high nickel content resists reducing environments and the chromium resists oxidizing ones.

Alloy 20, sold under the trade names of Carpenter 20, Durimet 20, and so on, with a long history of satisfactory service in a variety of environments, has been improved by even higher nickel and stabilization with niobium (also called columbium). Alloy 800 shows excellent resistance to high-temperature air because of its high iron content. Alloy 825, stabilized with titanium and containing more nickel than Alloy 20 shows similar or slightly better resistance in some environments.

Alloy 600 is particularly resistant to exhaust gases containing a mixture of air, CO₂, and steam, as well as environments of caustic

Aluminum and Magnesium Alloys

Aluminum. Aluminum is a very reactive metal in the standard emf series (Table 2.1); it immediately reacts with air to form a passive film consisting of two layers: an inner, compact, amorphous oxide and an outer, thicker, more permeable hydrated oxide. Aluminum is naturally compatible with the atmosphere and withstands many solutions well if the pH lies between about 4 and 9, as the Pourbaix diagram (Figure 2.14) shows. Either strong acids or moderately strong bases destroy aluminum's passive film. Chloride ions are particularly damaging because they attack the film only at weak spots and pit the aluminum alloys, disastrously, sometimes explosively.

One renowned corrosion engineer continually griped that his tax money had been spend on 12 million dollar, corrosion-resistant "moon buggies" when a carbon steel vehicle would be just as good on the moon. But the lunar modules were made of Al and Ti alloys because of their excellent strength-to-weight ratios, not for corrosion resistance.

The 1000 series of wrought aluminum alloys is essentially pure aluminum with different amounts of impurities. The corrosion resistance of all these alloys is good, although second-phase impurity precipitates can weaken the passive film locally and allow the corrosive to attack the underlying metal. The 2000 series consists of Al-Cu alloys that are strengthened by precipitation of an aluminum-copper intermetallic compound. These two-phase alloys are strong but not corrosion resistant, as Table 9.4 shows. The 4000, 6000, and 7000 series are also two-phase alloys when strengthened and all are readily corroded, but not as badly as the 2000 series where the second phase contains relatively noble copper.

Wrought alloys of the 3000 series, containing manganese, have excellent corrosion resistance. Some manganese-containing precipitates are present but they have almost the same potential as the aluminum solid solution. These alloys are widely used in food processing equipment and chemical plants.



Figure 9.4 Kuwait desalination plants destroyed in the Gulf War are being rebuilt. Of several stainless steel and nickel alloys tested, only C71500 resisted bio-fouling. From Nickel, vol. 16, no. 1, p. 4 (2000).

Reprinted by permission of the Nickel Development Institute.

Titanium and Zirconium Alloys

Titanium Alloys. Titanium alloys were developed in the 1950s for aircraft and aerospace applications because of their high strength/weight ratio. Since then, their corrosion resistance to chloride environments and to strong, hot oxidizers has given them an important place in many chemical process operations.

The TiO_2 passive film that forms on the metal in aqueous solutions is the most stable and most protective of all such films. It remains intact down to pH 2 and in fluid velocities up to 30 m/s (100 ft./sec.) In addition, TiO_2 is an electronic semiconductor so that the passivated metal can be used as an electrode in electrochemical processes, such as the production of Cl_2 gas from molten NaCl and for cathodic protection with impressed current.

Titanium alloys seldom pit but can undergo crevice corrosion at temperatures above 75°C (167°F) that breaks down the passive film. For example, steel gouged into a titanium surface corrodes a very

round pit-like hole that is actually crevice corrosion caused by acid formation under the steel. Titanium should never be coupled with active metals. It serves as a cathode when in contact with a corroding metal such as steel, and becomes charged with hydrogen in aqueous solutions at temperatures above 80°C (175°F). Hydrogen diffusing into the metal embrittles titanium by forming needle-shaped brittle titanium hydrides. A graph of the limits for hydrogen pickup and for crevice corrosion of titanium and some of its alloys is given in Figure 9.5.

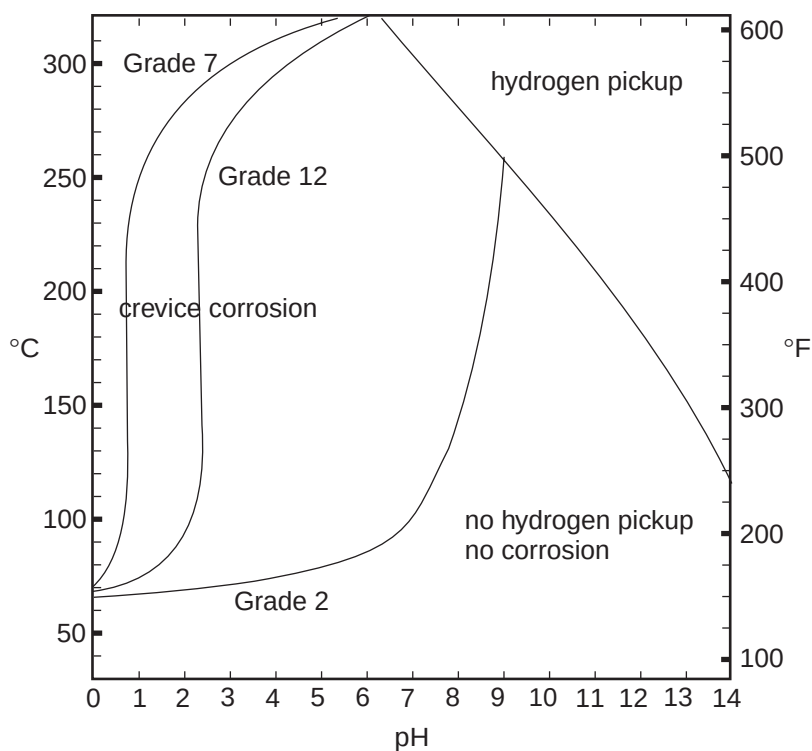


Figure 9.5 Temperature-pH limits for titanium alloys in NaCl brines.

Grade 2 = unalloyed Ti; Grade 7 = Ti+0.15% Pd; Grade 12 = Ti + 0.3%Mo+0.8%Ni. (After R.W. Schultz, MP 31, no. 11, p. 55, 1992.)

Plastics

The three general classes of plastics are

1. *Thermoplastics.* The thermoplastics consist of long hydrocarbon chains with molecular weights in the thousands. These plastics are relatively weak and soften further as temperature increases. Cross-linking, adding bulky side groups to the chains, or partial crystallization strengthens the polymers.
2. *Elastomers.* Elastomers are thermoplastics with coiled or kinked chains. High-temperature strength is greatly improved by occasional cross-links (e.g., by vulcanization with sulfur). These thermoplastics can be deformed elastically several hundred percent. In corrosion service, elastomers are mainly used as gaskets and as coatings.
3. *Thermosets.* Thermosets have been polymerized into three-dimensional, noncrystalline structures that make them strong and rigid. These plastics do not soften when heated and are relatively expensive. Thermosets are all reinforced for industrial applications.

Table 9.6 rates 30 types of commercial plastics for corrosion resistance and also gives tensile strength and percent elongation. The ratio of tensile strength to elongation is a measure of stiffness. Polar solvents include reactive organic liquids, such as formic acid, methanol, water-ethanol mixtures, and acetic acid. Important nonpolar solvents are the ethers, alkanes (e.g. hexane), carbon tetrachloride, benzene, and acetone. Also listed is the temperature of heat distortion as measured by the ASTM D-668 standard test, but keep in mind that the safe temperature for continuous heating is usually a few degrees less.

Concrete

Concrete is used for large tanks, for large-diameter pipe, and as a lining for vessels and steel pipes. It is commonly reinforced with steel in all types of construction work where tensile stresses might occur.

Being alkaline, concrete is readily attacked by all acids. Calcium ions in the concrete will leach out in corrosives containing sulfates or they exchange with magnesium ion solutions, turning the concrete into a soft, porous mass. Carbon dioxide, ammonium ions, strong alkalies, and some organic compounds also degrade concrete. Special cement formulations are available that resist sulfates but the aggregate (gravel and sand that make up roughly $\frac{3}{4}$ of the volume) must also resist the environment. Concrete tanks and pipes must be lined if strong corrosives are involved.

Concrete containing 30% fly ash has only $\frac{1}{10}$ the permeability of ordinary concrete and so can protect reinforcing steel much better. Fluoride surface treatment or sodium silicate washes densify and harden the concrete surface to make it more corrosion resistant.

Polymer concretes, using resins of epoxies, polyesters, vinyl esters, or urethanes, are now being widely used. Their strengths are comparable with portland cement concretes but they have higher bond strength and much lower permeability. Applications include bridge overlays, floor drains, and acid-resistant sewer pipe.

Carbon and Graphite

Carbon is a hard, brittle, porous (up to 30%) material with reasonable strength at room temperature (tensile strength about 7.5 MPa (1100 psi), and compressive strength of 43.5 MPa (6300 psi), which increases with temperature until at 1650°C (3000°F) it is one of the strongest materials known. While amorphous carbon is a thermal and electrical insulator, graphite is a good conductor. Both carbon and graphite are extremely resistant to thermal shock.

Chapter 10

PROTECTIVE COATINGS

The major purpose of coating a metal is to protect it from a corrosive environment when the metal is otherwise suitable for the service conditions in terms of mechanical and physical properties. Coating metal with good mechanical properties (usually steel) is often more practical in terms of cost and required life than selecting a more corrosion resistant but expensive material.

Protection can be achieved in five ways, with many coatings functioning in more than one way.

1. A barrier coating that prevents the corrosive environment from contacting the base metal.
2. A sacrificial metal coating that corrodes while giving cathodic protection to the underlying metal.
3. A noble metal coating that ensures that the base metal passivates.
4. An inhibitor coating that slows electrode reactions.
5. An electrically resistive coating that stifles electrochemical corrosion cells. Paints fall into this last category.

No coating can be serviceable for long if the metal surface underneath is rusted or is contaminated with oil, salts, or the like. The key to

good protection is good surface preparation, a step even more important than the properties of the coating itself.

Most coatings consist of more than one layer. For example, a phosphate conversion coating might be covered with a paint undercoat and several more paint layers. An electroplated coating may consist of two or three different metals plated on top of each other. Each layer contributes its own properties in providing protection to the base metal.

Metal Coatings

The coating metal is either cathodic or anodic to the substrate metal. If cathodic, the coating must be a perfect barrier layer or galvanic corrosion will attack the underlying metal at any pore or scratch in the coating, unless the base metal passivates very readily. An anodic coating can provide both barrier and sacrificial protection so that even corrosion of cut edges is prevented. The thicker a sacrificial coating is, the longer the cathodic protection continues.

Before coating, typical surface preparation involves degreasing in solvent vapor or a solvent emulsion, intermediate cleaning in hot alkali, and an acid pickle to remove oxide films left by the previous steps and to lightly etch the surface. Each step is followed by water rinses.

Electroplated Coatings

Metals that are applied as electroplatings for corrosion protection include nickel, chromium, zinc, cadmium, and tin. Copper is electroplated as an undercoat for multiplate systems. The part to be plated is made the cathode in an electrochemical bath containing ions of the plating metal with an anode usually composed of the plating metal that dissolves during the plating. Direct current is applied to the cell so that the cathode becomes negative enough to reduce the metal ions on the cathode surface. Current interruptions or periodic current reversals may be used to smooth the plated layer.

Cadmium. Like zinc, cadmium is anodic to steel and is plated thinly (5-15 μm or 0.2-0.6 mil) onto steel springs, fasteners, television chassis, and electronic parts because of its good ductility and electrical conductivity. Its atmospheric corrosion resistance is similar to zinc's, it is poisonous, and it is not resistant to common chemicals. Unlike zinc, cadmium plating is not usually painted.

Cadmium can cause liquid metal (and solid metal) embrittlement of high-strength steels above 230°C (450°F). High-strength steels can also be embrittled by hydrogen charged into the metal during electroplating, especially cadmium plating, and must be baked at about 200°C (400°F) immediately after plating. Baking as little as 3 h may be needed for steels with tensile strengths below 1500 MPa (220 ksi) but up to 24 h is required for higher strengths and sections over 25 mm (1 in.) thick.

Tin. Tin coatings on steel are almost always electroplated, in coats as thin as 0.4 μm (0.02 mil), followed by a flash melting to reduce porosity. Tin is noble to steel in water but is sacrificial to steel inside sealed tin cans of food with no air present. Being nonpoisonous and seemingly tasteless, it is frequently used for food handling equipment. Tinplate is also widely used in the electronics industry because it solders well and resists tarnishing.

Tin is not toxic in any practical sense. It is reported that several thousand ppm tin will sicken cats.

A large commercial sausage stuffer made of cast iron was used for several years. It was then set outside for 5 years, where it rusted. Cleaned of rust by power brushing and then oiled, it was put back into service but it discolored the meat! The answer: re-tin, in this case by hot dipping to put on a thick layer.

Hot Dip Coatings

Galvanized Steel. Galvanizing is used wherever steel must remain serviceable in the atmosphere, soil, or water for 10-25 years. Structural steel for electrical transmission towers, culverts, reinforcing

Anodizing

While magnesium and zinc are sometimes anodized, the process is very common for aluminum. The aluminum is made the anode in an electrochemical cell and deliberately corroded to build up a thicker layer of protective oxide than forms by passivation in natural environments.

Different types of cell baths are used depending on properties desired for the anodizing. A bath of boric acid and borates produces a very thin and impervious aluminum oxide layer that has the high dielectric constant and oxidation resistance needed for electrolytic condensers and rectifier plates. To make a thicker oxide, the cell electrolyte must slowly dissolve the oxide to leave pores for current to flow. Dilute sulfuric, chromic, or oxalic acid baths produce thick, porous oxide that is then sealed in boiling, deionized water to plug the pores (up to 10^{11} pores/cm² or 10^{12} pores/in.²), by converting Al_2O_3 to $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. If color is desired in the coating, dyeing is done before sealing.

Oils and waxes may be used to seal the anodizing to give better resistance to industrial atmospheres, or dichromate sealants used to give added protection in saline environments. Bright automotive trim requires an anodized thickness of only about 6 μm (0.25 mil), while architectural aluminum will have anodizing up to 30 μm (1 mil) thick.

Phosphate Coatings

Iron, steel, galvanized steel, or aluminum can be sprayed or immersed in a dilute solution of phosphoric acid plus zinc, iron, or manganese phosphates that react with the metal to form a gray to black surface layer of insoluble metal phosphate. The phosphate layer provides a bit of corrosion protection, aids cold forming, and increases wear resistance, but primarily it is used as a base for paints on such products as automobile bodies and refrigerator cabinets. The phosphate improves paint adhesion and retards the spread of any corrosion under the paint film. As a dielectric it insulates the local

Rust Converters

A variety of chemical formulations, most containing tannin and phosphoric acid, are sold for application on rusted steel to penetrate and react with the rust, converting it to nonporous, stable compounds that serve as a barrier layer to protect the steel. They do penetrate and do convert the rust to a partial barrier layer of Fe_3O_4 , which in some cases protects the steel. However, they do not remove moisture from the rust and do not counteract the effects of aggressive salts, especially chlorides, in the rust, so corrosion can continue unabated under the converted rust. Rust converters are effective only on clean, uncontaminated rust less than $2.5\text{ }\mu\text{m}$ (0.1 mil) thick, in mild service conditions, for a short term.

Organic Coatings and Linings

The difference between a polymer coating and a lining is the difference in thickness and, therefore, in service conditions and a difference in mechanism of protection. A coating is thin (by definition less than 0.5 mm or 20 mils), typically $50\text{--}100\text{ }\mu\text{m}$ (2-4 mils) while a lining will usually be around 3 mm (0.1 in.). A lining is thick enough to be a complete barrier between the metal and the environment but a coating is not. Linings are applied to the interior of tanks and vessels, where they are subjected to immersion conditions while coatings are applied to the exterior, where they may be subjected to weathering, condensation, fumes, splashes, and the like but not immersion, which is particularly severe.

A detached plastic lining plugged an 11 ft Houston sewer 4 years after it was installed. Clean-up cost 1 million, along with major environmental contamination.

Coatings and linings can be applied either in the mill or in the field. They will perform much better if they can be mill applied, mainly because surface preparation is much better in the mill. Also, field application will usually be at least twice as expensive. On the other hand, mill-applied coatings must be more resistant to weathering and



Figure 10.7 California offshore drilling platform coated with inorganic zinc and vinyl topcoats after 15 years of service. (*From C.G. Munger, MP, Materials Performance, Vol. 32, No. 9, p. 41, 1993. Reprinted by permission, NACE International.*)

Glass and Cement Coatings

This section describes the ceramic glasses and cement coatings used to protect metals from corrosive liquids. Refractory ceramics resistant to high-temperature gases, discussed in the Oxide Coatings section of Chapter 15, are entirely different in composition and characteristics.

Chapter 11

CORROSION INHIBITORS

An inhibitor is a chemical added to the corrosive environment in small amounts to reduce the corrosion rate. Some inhibitors interfere with the anode reaction, some with the cathode reaction, and some with both. They are usually used to prevent general corrosion but most are not effective in preventing localized attack, such as crevice corrosion, pitting, or SCC.

Inhibitors generally interact with the metal surface in some way: to form a passive film, to form a barrier film of adsorbed inhibitor that may be only a monolayer or less, or to form a thick barrier layer of reaction products or inhibitor.

In considering the use of inhibitors, the corrosion engineer must understand what problems can be solved with inhibitors, which inhibitors can be used in the particular environment without interfering with other metals or with the process, and whether or not inhibitor additions will be economically practical.

How would you go about selecting an organic corrosion inhibitor for cast iron municipal water mains? Answer: Forget it. (1) Cast iron corrodes very slowly in water; (2) citizens only tolerate additives in their drinking water for health reasons, and reluctantly even then; (3) the expense of inhibiting all that water would be prohibitive.

Inhibitors have a critical concentration that must be reached or exceeded for them to be effective, and in some cases to prevent them from making corrosion worse. Consequently, the inhibitor additions

Barrier Inhibitors

Inhibitors can act as a barrier layer between the metal and environment by adsorbing as a film over the metal surface or by precipitating a compound scale on the surface. These barrier inhibitors usually cover the entire surface, both anode and cathode areas, although some affect only cathode areas or only anode areas. It is possible to identify the types of sites affected because anodic inhibitors shift the metal's corrosion potential in the positive direction, cathodic inhibitors shift it negatively, and general inhibitors have little effect on it.

Adsorption inhibitors that block the entire surface must have at least a monolayer of coverage, but if they block only a certain type of site the coverage will be much less—as little as 4% of a complete monolayer in one case. Typically they are added at concentrations of 50-100 ppm (mg/L).

Organic Adsorption Inhibitors

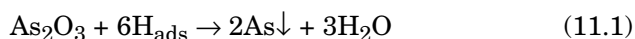
Organics that coat metal with an oily surface layer will protect it. These inhibitors are commonly used in acids, although a few function in neutral or alkaline solutions. In adsorbing on the metal, they replace adsorbed water molecules and their hydrophobic action prevents water from solvating metal ions or prevents H^+ ions from adsorbing at cathode sites where reduction to $H_2(g)$ could occur. The organic adsorption inhibitors are commonly used in acid storage, pickling, acidized oil wells, wet abrasive blasting, and the like.

Organic adsorption inhibitors will adsorb on any surface—metal, porous rust, dirt—whatever is offered. A dirty system can soak up a fortune in inhibitor without slowing corrosion appreciably.

Physical Adsorption. The electrostatic attractive forces between organic ions or dipoles and the electrically charged regions on the surface of the metal cause physical adsorption, although a bit of covalent bonding may also take place.

Poisons

Poisons inhibit the cathode reaction—hydrogen or oxygen reduction. In acids, the combining of hydrogen atoms on cathode sites to form molecular hydrogen (H_2) is poisoned by elements of Group VA: P, As, Sb, and Bi. Addition of arsenic trioxide to acid, for example, gives the following reaction:



plating out arsenic on cathode sites. Sulfide and selenide ions also poison the cathodes by adsorbing on them, but their solubilities are too low to make them generally useful as inhibitors, and H_2S and H_2Se gases are dangerous.

All of these cathode poisons are toxic to humans but they also can damage metals by causing hydrogen blistering or hydrogen embrittlement in steels and other susceptible metals. Embrittlement can be removed after pickling in acid by baking out the hydrogen as is done after electroplating (described in the Metal Coatings section of Chapter 10).

Oxygen reduction can also be poisoned. Brass in seawater or fresh water is prone to dezincification where the cathode reaction is formation of OH^- ions from dissolved O_2 . Inhibited admiralty brass contains 0.1% of As, Sb, or P to prevent dezincification. As the brass corrodes, the O_2 reduction raises the pH at the surface and forms $As(OH)_4^-$ ions that adsorb on the cathodes (surface sites with Cu atoms) and prevent O_2 adsorption.

Would adding a cathodic poison to an acid cleaning solution be effective? Answer: Only if you do not want it to clean.

★Polarization with Inhibitors

Passivating inhibitors are anodic inhibitors because they depend on the shape of the anode polarization curve (Figure 11.4) to achieve passivation and because they shift the corrosion potential in the noble (+) direction. As the figure shows, insufficient passivator increases corrosion instead of reducing it, and it is even possible for excessive amounts of passivator to increase corrosion by raising the corrosion potential into the transpassive region.

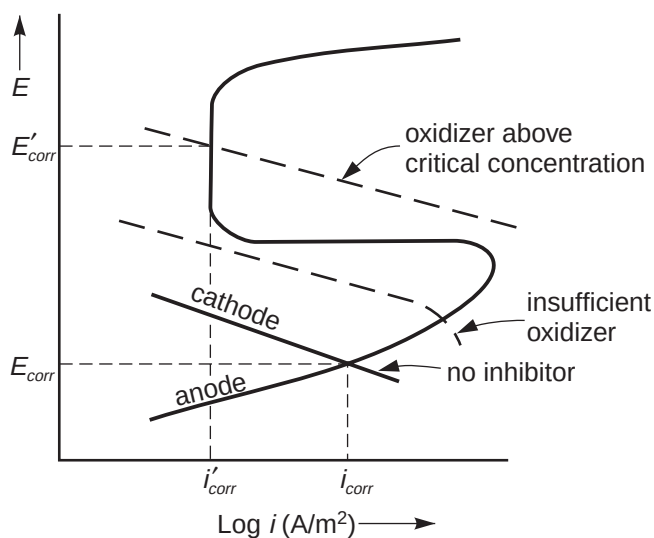
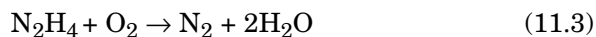


Figure 11.4 Effect of a passivator on corrosion kinetics.

Anodic barrier inhibitors, however, adsorb or precipitate at anodic sites on the metal surface, thus reducing the exchange current density of the anode reaction and shifting the anode curve to the left. They may also increase the activation polarization of the anode in making it more difficult for metal ions to collect their solvation sheath of water molecules that they must have to escape into the solution. The effect on the polarization diagram is shown in Figure 11.5a. The corrosion potential shifts in the positive direction as with an oxidizer.

Phosphites were patented in 1936 for O₂ scavenging of boiler waters but they were so powerful that they reduced the magnetite protective scale, exposing bare steel.

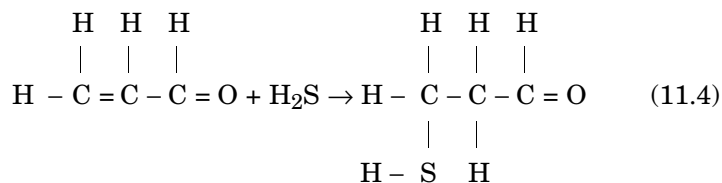
Hydrazine (N₂H₄) is another scavenger often used for boilers, especially for high-pressure, high-temperature systems. It is slow acting at low temperatures, although some proprietary preparations sold as concentrated aqueous solutions include catalysts. It has an advantage in leaving no solid residue.



Oxygen scavengers remove oxygen, not H⁺ ions, and so are ineffective in acids.

Scavengers are often added with other corrosion inhibitors, but not passivators. Why not? Answer: The two types would work at cross-purposes—one trying to prevent oxidation and the other trying to oxidize the metal.

Sulfide scavengers have also been found. Nitrite scavenges H₂S, inhibits sulfate-reducing bacteria, and reduces iron sulfides. Acrolein (propenal) also scavenges H₂S from solution:



It removes FeS_x deposits on the steel, too, and converts them to water-soluble products.

Scale Inhibitors

It is not always possible or necessary to remove every trace of oxygen from water to render it noncorrosive. In many cases, if a scale of corrosion products builds up gradually on steel, the rust layer can be

Chapter

12

CATHODIC AND ANODIC PROTECTION

Cathodic protection converts all anodic areas on a metal surface to cathodes so that corrosion ceases. The protected metal has positive current flowing onto it from the electrolyte everywhere on the surface so that no current flows off. This result can be achieved in two distinctly different ways.

1. By connecting a corrodible anode to the metal that is to be protected. This method is called sacrificial protection or galvanic protection.
2. By applying an electric current from a separate power source, a technique called impressed-current cathodic protection.

Anodic protection, on the contrary, makes the entire metal surface anodic—so anodic that the metal completely passivates. Obviously, then, this technique is limited to metals that can form protective passive films. Since passivated metals still corrode at a low rate, anodic protection almost, but not completely, stops corrosion.

Cathodic Protection

The metal to be protected is made the cathode in an electrochemical cell, where the anode is either a more corrodible, sacrificial metal, or an inert electrode with impressed DC current. Corrosion in soils and

most aqueous environments can be completely prevented at a cost far less than for inhibitors or coatings.

Cathodic protection protects against both general corrosion and localized attack, such as intergranular corrosion, pitting, and dealloying. It can stop SCC but not hydrogen-induced cracking. In fact, cathodic overprotection can cause hydrogen embrittlement. Cathodic protection can eliminate corrosion fatigue, but not straight mechanical fatigue failure.

Cathodic protection *cannot* be used in the following situations.

1. Above the water line, in vapor. Electric current will not flow through a gas, at least not at the moderate voltages used in cathodic protection.
2. In nonconducting liquids, such as oil. An electrolyte is one of the essential ingredients of an electrochemical cell.
3. In electrically screened areas. This is an important limitation that will be described in the next paragraph.
4. In extremely corrosive environments. While theoretically possible, cathodic protection would be impractical because of horrendous power costs. With strong acids, the danger of hydrogen embrittlement is coupled with the possible release of large volumes of potentially explosive H_2 gas.

Shielding. Shielding, or screening, prevents the flow of protective current through a low-conductivity electrolyte, where the current can find a much better conducting metallic path. For example, in Figure 12.1 the current flowing from the sacrificial anode protects all the tank wall area below the waterline, as well as the screen at the bottom. Very little current flows down the pipe beyond the screen because the current will divide proportionally with the conductance of the paths, most of it choosing the high-conductance path through the metal back to the anode. (To give some idea of the differences in conductivity, at 25°C (77°F) a saturated NaCl brine has a

conductivity of 0.25 S/cm while steel's is 60,000 S/cm.) [The siemens (S) is now the unit of conductance, equivalent to and replacing ohm^{-1} and mho.]

Other examples of shielding would be:

1. A bundle of pipes in an electrolyte. Although the outside surfaces of the bundle would receive protective current, no current would penetrate the narrow path of electrolyte to the center of the bundle.
2. A pipe buried in a landfill of cinders. Cinders, being fairly good electrical conductors but also very inhomogeneous, will catch all the current, which then flows to the pipe through a few high-conductance paths. Much of the pipe surface receives no protective current. Cathodic protection in this case just increases the cathode/anode area ratio.
3. Protective current flowing down a pipe. Cathodic protection will only protect down a pipe for a length equal to three or four diameters. Within that distance almost all current has found some metal to flow through.

Actually, the "distance effect" in galvanic corrosion is another example of shielding: The current wants to return to a metallic path as quickly as possible.

Impressed-Current Cathodic Protection

The sketch of an impressed-current cathodic protection system shown in Figure 12.2 illustrates one main difference from sacrificial protection: An external DC power source is required, with the negative wire connected to the protected structure. The other main difference is that sacrificial anodes are not used; the anodes are chosen to be as noncorroding as possible.

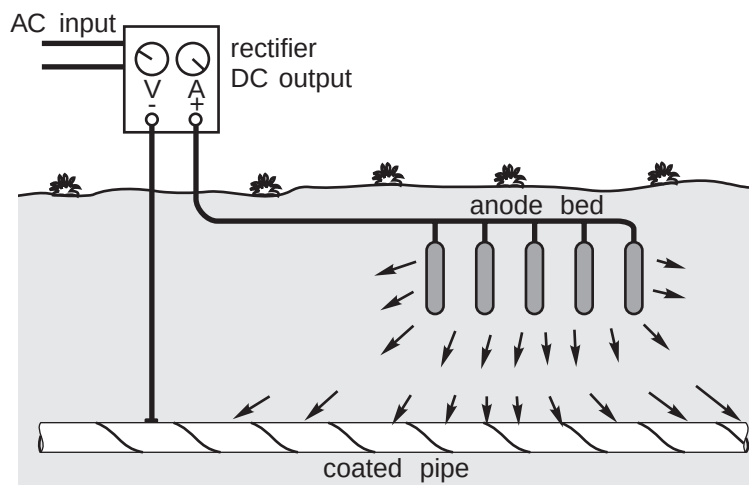


Figure 12.2 Diagram of impressed-current cathodic protection system for a buried pipeline.

A cathodic protection rectifier had to be moved to allow widening of a road. An ordinary electrician, unfamiliar with DC power, reconnected the unit backwards—positive wire to the pipe. *Result:* three leaks appeared almost immediately.

Chapter 13

DESIGNING FOR CORROSION

Mistakes in plant design are the most frequently cited (58%) cause of corrosion failure in chemical-process industries. Design mistakes are even blamed slightly more than incorrect materials selection. Although “get a better material” might seem to be the answer to any corrosion problem, it becomes obvious, as a failure is investigated, that in most cases the design could be improved.

Unfortunately for corrosion engineers, most plants are built at minimum cost with the idea that troubles will be met when they develop by upgrading the equipment as needed. Even so, careful design can overcome many of the shortcomings of materials.

Consumer goods, such as automobiles, outboard motors, or whatever, are offered in a highly competitive market where price is a major factor. In times past the manufacturers dodged corrosion problems by giving short-term guarantees. The manufacturers regarded corrosion as a process that operated in their favor, guaranteeing frequent replacement. Consumer groups changed all that with their unfavorable publicity, making consumers much more concerned about corrosion and other design problems. When manufacturers began trying to improve the corrosion resistance of their products, better designs solved many problems at no additional cost.

Design engineers must understand corrosion or they become part of the problem. “As long as design engineers are around, corrosion engineers will always have jobs,” one corrosion engineer remarked sarcastically.

All design engineers know that they are supposed to make allowances for corrosion by increasing wall thickness, and so on, but a generation ago that was all they needed to know, or so they thought. The following points identify the major corrosion principles necessary for a successful design.

Allow For Uniform Attack

The design engineer selects a material with a satisfactory corrosion rate in the environment involved. Handbook data, results of lab tests, pilot plant and field tests, or previous service are considered. Any metals showing localized corrosion are eliminated at the start. Then, knowing the required life of the equipment and assuming uniform corrosion, the engineer calculates the corrosion allowance to be added to the metal thickness, plus a safety factor, because real life is not as precise as mathematics.

Remember that modern engineering structures do not have to last as long as the pyramids. Corrosion at a reasonable rate can be tolerated unless the corrosion products themselves create a problem: contaminate the desired product, plug up flow lines, or the like.

Minimize Attack Time

Corrosion takes time. The design engineer tries to reduce the time that the environment will contact metal. If dirt and sediment can collect they hold moisture next to the metal long after the other metal surfaces are dry. Figure 13.1 shows how braces of channels and angle iron should be positioned to prevent liquids from sitting and corroding.

Corrosion is often particularly severe on sheltered surfaces where dirt and salts are not washed off and evaporation of moisture is slow. Avoid structural shapes (Figure 13.2) that collect dirt and moisture with no way to orient these shapes to prevent this accumulation.

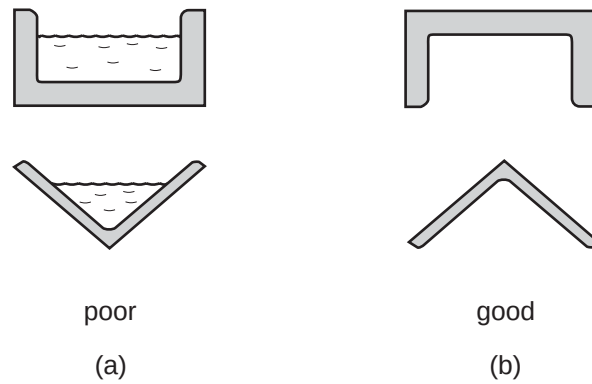


Figure 13.1 Arrangement of steel shapes (a) that hold moisture, and (b) those that do not.

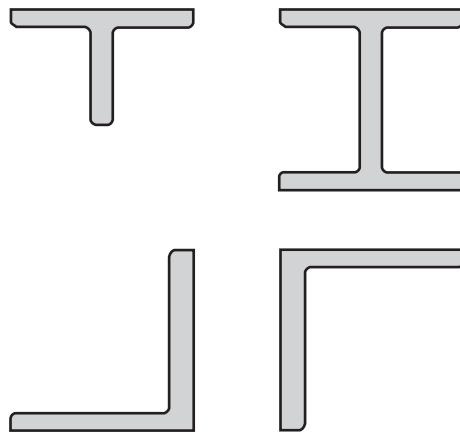


Figure 13.2 Structural shapes that collect dirt and moisture.

Drainage Problems

Find a way to allow water to drain off metal surfaces. Figure 13.3 illustrates how structural members and armored electrical cable should be oriented to allow moisture to drain from the metal.

Concentrating Liquids

Spills, splashing, spray, and intermittent flow leave a thin film of liquid that may become more corrosive with time. Condensed moisture and spills will run down the walls of a tank to the bottom, where droplets will sit, absorbing O_2 , and slowly evaporating while concentrating dissolved corrosives. A drip skirt should be welded on (Figure 13.10). The bottom of the drip skirt corrodes badly but that is only a cosmetic problem.

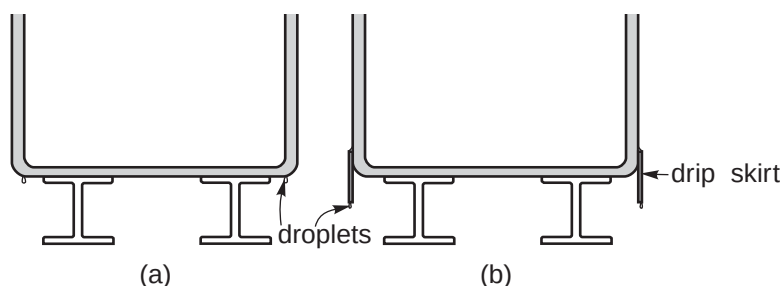


Figure 13.10 Tank (a) without and (b) with drip skirt that moves corrosive spills to a harmless location.

The design for liquid flow into a container should prevent liquid from running down the wall (Figure 13.11a), where it can wet the wall and absorb oxygen, or where the concentrated solution can contact the metal before mixing. Splashing of liquid up on the wall (Figure 13.11b and c) can be prevented by feeding into the center of the tank (Figure 13.11d).

Do not let solutions concentrate on a metal surface. In Figure 13.12a the splashing solution can dry and concentrate on the hot coil, in contrast to the coil in Figure 13.12b, which is completely submerged.

As with welds, fasteners (rivets, bolts, screws, etc.) should be at least as noble as the much larger area of metal they fasten. Figure 4.6 illustrates this principle.

All galvanic corrosion can be stopped if the two metals can be electrically insulated from each other. Figure 13.15 shows ways of insulating one metal from another. However, insulating washers, and the like, cannot be used at extremely high stresses or temperatures, or in corrosives that will attack the insulating material.

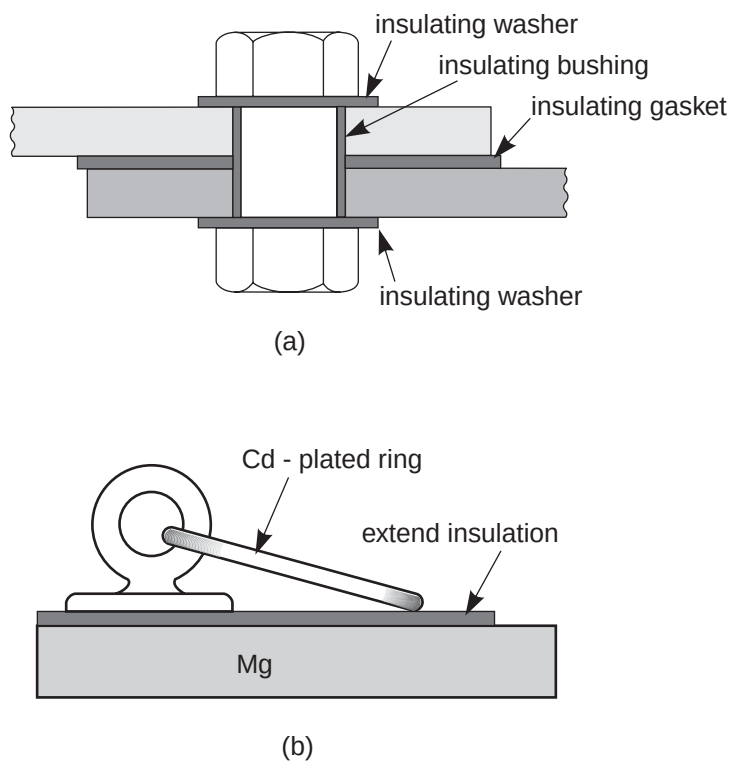


Figure 13.15 Methods of insulating metals. (a) Two plates insulated from each other and from the fastener. (b) Cadmium-plated ring prevented from touching magnesium plate.

Protect Against Environmental Cells

Crevices

Geometric crevices often occur when two pieces of metal are put together, especially if rough machining marks on the surface prevent intimate mating.

Avoid deposits on the metal by making sure that designs do not include ledges, pockets, flanges, or obstructions that will provide a location for entrained solids to settle out of the liquid. The design should ensure that flow rates are rapid enough to keep metal surfaces washed but not so rapid that erosion-corrosion could be initiated.

If crevices must be in the system, seal them. Weld, caulk, or solder rather than use fasteners, such as rivets or bolts. Welding must be continuous, not skip or spot welds (Figure 13.21), and butt welds are better than welded lap joints (Figure 13.3a).

Where crevices cannot be sealed by any practical method they must be protected. Galvanizing both bolt and nut protects their threads from crevice attack. Painting metals with a zinc-rich or zinc chromate primer before assembling them prevents crevice corrosion for years. Although painting the metal outside a crevice may not seal the crevice, it does reduce the cathode area of the corrosion cell. Inhibited greases provide temporary protection while also lubricating threaded fasteners.

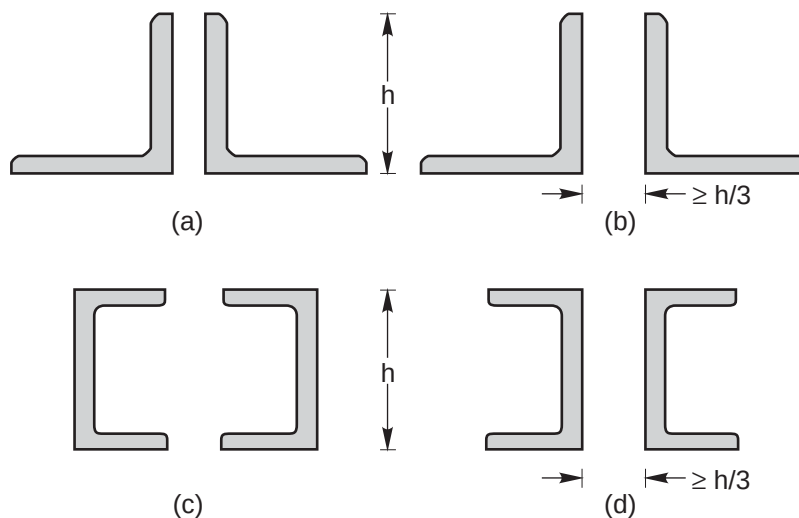


Figure 13.32 Profiles that cannot (a, c) or can (b, d) be painted.

Tubing is easier to paint than I or H shapes, while lattice construction is almost impossible to paint well. Sharp corners, weld spatter, and rough surfaces receive very little protection by paint because the film is particularly thin at these points (Figure 10.5). The design should call for rounded corners and edges since painted metal invariably rusts at sharp edges first.

Try to make the design foolproof. No human being is infallible and some seem *particularly* fallible. Design with these people in mind.

A plant designed for versatility had a CaCl_2 brine line connected through a valve to a steam line. One day someone opened the connecting valve, of course, just because it was there. An entire steam turbine was corroded beyond repair.

While “anything that can go wrong, will go wrong,” is an excellent premise for corrosion control design, Capt. Edward A. Murphy, Jr. (USAF) actually said, “If there are two or more ways of doing something, and one of them can lead to catastrophe, then someone will do it.”

Chapter

14

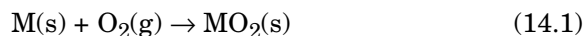
OXIDATION: METAL-GAS REACTIONS

Engineering metals react with air. If they react slowly they are usable, but at high temperatures many metals react disastrously because chemical reaction rates increase exponentially with temperature. The principal reactant in air is oxygen, so all gas-metal reactions have come to be called “oxidation,” using the term in its broadest sense. The reacting gas may be water vapor, hydrogen sulfide, chlorine, and so on, but the reaction mechanisms are essentially the same as for reaction with oxygen.

At temperatures below 100°C (212°F) metals usually have a thin film of moisture adsorbed on the surface, so that they react with oxygen by the common electrochemical processes of uniform or localized corrosion. At temperatures above 100°C (212°F) the gas either reacts directly with the metal or the reaction becomes controlled by solid-state diffusion through an oxide layer on the metal.

★Thermodynamics of Oxidation

A typical oxidation reaction can be expressed as



with the metal M forming a solid oxide MO_2 , MO , M_2O_3 , or whatever, and the notations (s) and (g) indicating solid and gas phases. As with

all chemical reactions, the driving force is ΔG , the Gibbs energy that must be *negative* if oxidation proceeds, and will become zero at equilibrium. For this reaction ΔG can be expressed in terms of the standard Gibbs energy change (ΔG°) as

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{a_{\text{prod}}}{a_{\text{react}}} \right) \quad (14.2)$$

in which a_{prod} and a_{react} are the activities of products and reactants. Activities of solids are usually invariant; that is, their activities equal 1, and for the high temperatures and moderate pressures of most gas-metal reactions the activity of oxygen can be approximated by its pressure, p_{O_2} . The driving force for the oxidation reaction (Equation 14.1), where a solid oxide product forms, is then

$$\Delta G = \Delta G^\circ + RT \ln \left(\frac{1}{p_{\text{O}_2}} \right) \quad (14.3)$$

At equilibrium, where $\Delta G = 0$

$$\Delta G^\circ = RT \ln p'_{\text{O}_2} \quad (14.4)$$

The driving force for oxidation then can be expressed as

$$\Delta G = RT \ln \left(\frac{p'_{\text{O}_2}}{p_{\text{O}_2}} \right) \quad (14.5)$$

where p'_{O_2} is the equilibrium oxygen pressure and p_{O_2} is the actual O_2 pressure of the gas. Thus gold, for example, would form Au_2O_3 with an equilibrium O_2 pressure of 10^{19} atm at 25°C (77°F), so that the environment would have to exceed an oxygen pressure of 10^{19} atm before ΔG becomes negative and reaction would occur. Consequently, gold does not oxidize. On the other hand, aluminum oxide has an equilibrium O_2 pressure of 10^{-184} atm at 25°C (77°F), so that aluminum will oxidize in just about any real gas—or vacuum.

Oxide Structure

The Pilling-Bedworth Ratio

The first basic understanding of oxidation mechanisms came in 1923 when N.B. Pilling and R.E. Bedworth divided oxidizable metals into two groups: those that form protective oxide scales and those that do not. They proposed that a scale will be unprotective if the oxide layer on the metal occupies a smaller volume than the volume of metal reacted. The Pilling-Bedworth ratio is the volume of oxide divided by the volume of metal that formed the oxide.

If the ratio is less than 1, as it is for alkali and alkaline earth metals, the scales are usually unprotective, being porous or cracked, because the volume of oxide on the metal surface is insufficient to cover the entire surface as it replaces the reacted metal. If the ratio is greater than 1, the scale shields the metal from the gas so that further reaction can occur only after solid-state diffusion, which is slow even at high temperatures.

If the ratio is much greater than 2, and the scale is growing at the metal-oxide interface, large compressive stresses build up in the scale so that *if* the scale grows thick it will likely buckle and spall off, leaving the metal unprotected.

For example, in the oxidation of iron:



the Pilling-Bedworth (PB) ratio is:

$$\begin{aligned} \text{PB ratio} &= \frac{\text{Volume of 1 mol Fe}_3\text{O}_4}{\text{Volume of 3 mol Fe}} \\ &= \frac{44.7 \text{ cm}^3}{3 \times 7.10 \text{ cm}^3} \\ &= 2.10 \end{aligned}$$

Example Problem:

Aluminum, atomic mass 26.98 g/mol and density 2.70 g/cm³, oxidizes to Al₂O₃, molar mass 101.96 g/mol and density 3.97 g/cm³. Calculate the Pilling-Bedworth ratio.

Solution:

The oxidation reaction is $2\text{Al} + \frac{3}{2}\text{O}_2 \rightarrow \text{Al}_2\text{O}_3$

$$\begin{aligned} \text{PB ratio} &= \frac{\text{volume of 1 mol Al}_2\text{O}_3}{\text{volume of 2 mol Al}} \\ &= \frac{\left(\frac{101.96 \text{ g/mol}}{3.97 \text{ g/cm}^3} \right)}{(2 \text{ mol}) \left(\frac{26.98 \text{ g/mol}}{2.70 \text{ g/cm}^3} \right)} = 1.28 \end{aligned}$$

Although the Pilling-Bedworth ratio is a gross oversimplification, which is not always correct, it provides information about the protective nature of metal oxides as a rough rule of thumb. Volume ratios for common oxide-metal systems are listed in Table 14.1.

Defect Structures of Ionic Oxides

Ions can move through crystalline oxides via either Schottky defects or Frenkel defects or both. Schottky defects (Figure 14.1a) are combinations of cation vacancies and anion (oxygen) vacancies in the correct ratio to maintain electrical charge balance in the oxide. A Frenkel defect is a combination of a cation vacancy and an interstitial cation, illustrated in Figure 14.1b. Ions can move around in an oxide when the appropriate type of ion diffuses into a neighboring vacancy or, with Frenkel defects, when cations diffuse interstitially.

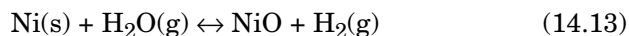
Generally, metals oxidize much faster than can be accounted for simply by diffusion through Schottky and Frenkel defects because metal oxides are seldom if ever stoichiometric.

Other Gas-Metal Reactions

Metals often oxidize at high temperatures with gases other than oxygen. Reactions with the gases commonly involved in fuel combustion and waste incineration are described in this section.

Water Vapor

Water vapor is an oxidizing atmosphere much like O₂, although water reacts with metal to form hydrogen gas as well as oxide.



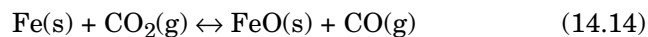
The reaction follows the parabolic rate law. The reaction above shows that oxide forms if the gas phase is primarily water vapor but the reaction will reverse and decompose the oxide if the gas contains a lot of H₂.

Because water vapor produces H₂ when it reacts, it is not quite as strong an oxidizer as oxygen. Steam oxidizes nickel at only about one-third to one-fifth the rate that oxygen does at 650-1050°C (1200-1925°F). However, steam oxidizes iron faster than O₂ at 700-900°C (1300-1650°F) because only a layer of FeO forms with steam, without a covering layer of the more protective Fe₃O₄, which would form in O₂.

Iron and steel parts are sometimes blued in steam at around 500°C (1000°F) to improve wear and corrosion resistance as well as for appearance. At 500°C only Fe₃O₄ forms.

Carbon Dioxide and Carbon Monoxide

Carbon dioxide is usually less aggressive than air or water vapor. A typical reaction is



Chapter 15

OXIDATION CONTROL

No pure refractory (high-melting) metal performs well in high-temperature air. In fact, not even metals melting as low as 1850°C (3360°F) oxidize satisfactorily, with the sole exception of chromium. Table 15.1 gives the melting points of high-melting pure metals and explains the problems they undergo at high temperatures.

Because all of the pure metals with any high-temperature strength oxidize so badly, they must be protected by alloying or with a coating if they are to be usable. In either case, the object is to form a barrier layer between the metal and the gaseous environment. Alloying does provide excellent protection for iron-, cobalt-, and nickel-based metals. However, while alloying may improve the oxidation resistance of metals with melting points above iron [1535°C (2795°F)], it always worsens their mechanical properties. Unlike alloying, protective coatings can be used on any metal.

Alloy Theory

Alloying to Improve the Oxide

Parabolic oxidation provides the best protection for a metal exposed to a reactive gas. The oxidation rate slows with time and may become negligible if diffusion rates are slow through the protective oxide and if stresses remain low. Slowing the diffusion rate by modifying the defect structure is an obvious approach that has been moderately successful.

Table 15.1 Oxidation of Pure Metals

Metal	Melting Point, °C (°F)	Oxidation Problems
Tungsten	3433 (6211)	Catastrophic ox. Paralinear >500°C (950°F)
Rhenium	3106 (5623)	Catastrophic oxidation
Osmium	3032 (5490)	Embrittled; oxide volatile
Tantalum	3020 (5468)	Breakaway oxidation >500°C (950°F)
Molybdenum	2623 (4753)	Catastrophic oxidation
Niobium	2469 (4476)	Embrittled; breakaway, linear oxidation
Iridium	2447 (4437)	Embrittled; oxide volatile
Ruthenium	2334 (4233)	Embrittled; oxide volatile
Hafnium	2231 (4048)	Embrittled. Linear ox. >800°C (1500°F)
Rhodium	1963 (3565)	Embrittled; oxide volatile
Vanadium	1910 (3470)	Catastrophic oxidation
Chromium	1863 (3385)	Embrittled by N ₂
Zirconium	1855 (3371)	Embrittled

The p-type semiconducting oxides, such as NiO, are cation deficient because a few higher valent cations are present in their structures. The more cation vacancies they have, the easier diffusion becomes, and the faster the metal oxidizes. To reduce the number of cation vacancies, lower valence cations, such as Li⁺, should replace some of the Ni²⁺ in the oxide structure. Two Li⁺ ions in the oxide eliminate one cation vacancy to maintain charge balance; the two Li⁺ ions counteract two Ni³⁺ that would otherwise cause a cation vacancy to form. This is depicted schematically in Figure 15.1.

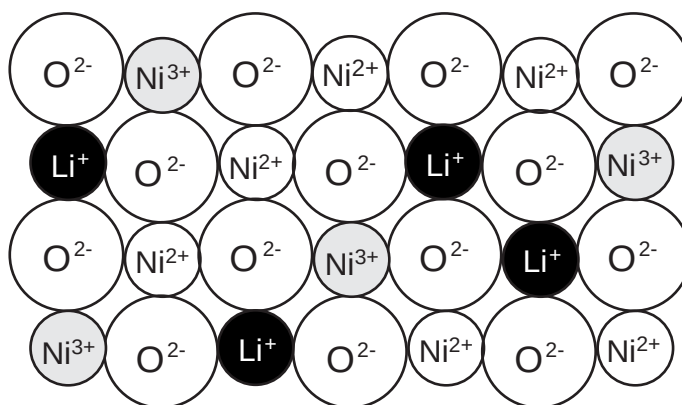


Figure 15.1 Ionic arrangement in p-type NiO scale doped with Li^+ , where Li^+ ions balance out the Ni^{3+} ions. Compare with Figure 14.2 for the undoped oxide.

Thus, alloying nickel with a small amount of lithium should slow the oxidation, although the amounts of Li used must be small enough that the solubility of Li in NiO is not exceeded. Otherwise Li will start forming its own oxide (and Li_2O with its Pilling-Bedworth ratio of 0.57 is not desired). The solubility limits in oxides are generally quite low so that the alloying, or “doping,” is severely limited.

“Doping” is a term borrowed from semiconductor production to describe the deliberate contamination of high-purity semiconductors with extremely small amounts of certain impurities that greatly enhance their performance. (The term probably originated with horse racing.)

Doping a p-type oxide like NiO with higher valent cations, such as Al^{3+} , would be equivalent to adding more Ni^{3+} , thus producing more cation vacancies and making oxidation worse. Alloying with cations having the same valence, such as Co^{2+} , has little effect.

The n-type oxides behave exactly opposite to the p-type. For the n-type oxides that grow by diffusion of anions inward through anion vacancies, typified by ZrO_2 , the anion vacancies exist because some cations have a lower valence (Zr^{2+}) than they should have for a

Table 15.2 Approximate Scaling Temperatures in Air

Alloy	Scaling Temperature ^a	
	°C	°F
1010 Steel	480	900
5Cr-0.5Mo Steel	620	1150
9Cr-1.0Mo Steel	620	1150
70Cu-30Zn Brass	700	1300
410 Stainless (12Cr)	730	1350
Alloy B	760	1400
Nickel	790	1450
430 Stainless (17Cr)	830	1530
18-8 Stainless (302, 304, 321, 347)	900	1650
316 Stainless	900	1650
Chromium	900	1650
442 Stainless (21Cr)	930	1700
446 Stainless (25Cr)	1040	1900
N-155 (Fe-base superalloy)	1040	1900
309 Stainless	1090	2000
HW (12Cr-60Ni-bal. Fe)	1120	2050
310 Stainless	1150	2100
HS-21 (Co-base superalloy)	1150	2100
Alloy C-276	1150	2100
HT (15Cr-35Ni-bal. Fe)	1150	2100
HX (17Cr-66Ni-bal. Fe)	1150	2100
HU (19Cr-66Ni-bal Fe)	1150	2100
Alloy X (Ni-base superalloy)	1200	2200
Ceramics	°C	°F
Si ₃ N ₄ and SiC ceramics	(1450) ^b	(2650) ^b
Alumina and chromia ceramics	(1750)	(3200)
Yttria and calcia ceramics	(2000)	(3600)
Thoria ceramics	(2500)	(4500)

Source: Adapted from Fontana, 1987; Elliott, 1989

a. Scaling temperature at which the material shows a weight gain of 3 g/m²·h, generally considered negligible.

b. Temperatures in parentheses are approximate maximum service temperatures.

Coating Requirements

In designing a coating to protect a metal from hot gases, the coating must satisfy a long list of requirements.

1. The coating must be stable in the environment.
2. It must adhere well to the metal.
3. Mobilities of reactants through the coating should be low.
4. The coating should not react with the substrate metal to worsen the mechanical properties of either the coating or the metal. Interdiffusion between the two should be slow, although a bit of interdiffusion does improve adherence.
5. The thermal expansion of the coating should be close to that of the metal.
6. The coating must withstand creep and plastic deformation.
7. The coating should be able to resist impact, erosion in a gas stream, and abrasion.
8. It is desirable, although not a necessity, that the coating should be self-repairing, or at least that defects can be easily repaired.

Coatings may be refractory oxides or they may be metals or compounds that will produce a refractory oxide layer when reacted with the gas.

Oxide Coatings

The metal oxides with high enough melting points and low enough vapor pressures to be generally considered suitable as high-temperature coatings on metals are SiO_2 , TiO_2 , Al_2O_3 , La_2O_3 , Y_2O_3 , Cr_2O_3 , BeO , CaO , ZrO_2 , MgO , ThO_2 , complex oxides, and spinels. Of

ABOUT THE AUTHOR



Samuel A. Bradford is Professor Emeritus of Metallurgical Engineering at the University of Alberta, where he concentrates on giving short courses in various aspects of corrosion, writing about corrosion, and working as a consultant in metal failures and corrosion.

He received his B.S. and M.S. degrees in chemistry from the University of Missouri at Rolla, and his Ph.D. in metallurgy from Iowa State University. Sam served as a radio officer in Korea during the conflict there. He has worked in industry as an analytical chemist and spent six years in research and development at Bethlehem Steel. He also worked in corrosion research at the Fontana Corrosion Center of the Ohio State University.

Most of his career has been devoted to teaching at the University of Alberta with courses in materials, thermodynamics and kinetics, and of course, corrosion at both undergraduate and graduate levels.

Sam and his wife, Evelin, are the parents of one daughter and three sons, and the grandparents of one extraordinary granddaughter.