

about the book . . .

This invaluable reference describes a systematic procedure for using process and mechanical design information to select materials of construction suitable for a wide range of chemical and hydrocarbon processing plants.

Analyzing threshold values for degradation phenomena involving corrosion or thermal damage, *Materials Selection for Hydrocarbon and Chemical Plants* explores corrosion mitigation methods such as cathodic protection...covers the use of templates in the materials selection procedure...details how to develop and use a materials selection diagram...discusses corrosion testing and its relevance to materials selection...presents information on how to calculate corrosion rates for a variety of conditions...examines strain ageing and other forms of embrittlement...and much more.

Generously illustrated throughout and containing key literature citations, *Materials Selection for Hydrocarbon and Chemical Plants* is a vital reference for chemical, materials, mechanical, metallurgical, maintenance, plant, process, inspection, operating, heat transfer, rotating equipment, control systems, and welding engineers; piping and vessel engineers and designers; inspectors and stress analysts; and upper-level undergraduate and graduate students in these disciplines.

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Materials Selection for Hydrocarbon and Chemical Plants

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Materials Selection for Hydrocarbon and Chemical Plants

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PREFACE

This book is intended for engineers involved in the design, construction, operation and maintenance of plant facilities. Its purpose is to assist these engineers in the selection of materials of construction suitable for piping and equipment. Reflecting the authors' experience, the focus is on hydrocarbon and chemical process plants.

Many engineers regard materials selection as an activity associated with the design and construction of new facilities, plant additions, or revamps. However, materials selection is also part of a plant's routine maintenance activities. It is often the subject of discussion between operations, planning and maintenance personnel. Such discussions frequently illustrate that materials selected for short-term solutions differ from those adopted for long-term solutions. In either case, the materials selected, along with the specified fabrication procedures, must satisfy regulatory requirements. Thus, the process of materials selection must accommodate variable materials selection criteria, including those of the governing engineering and inspection codes.

For simple jobs such as replacements in kind or for jobs with which the responsible engineer has prior experience, materials selection is usually a straightforward task. However, some jobs involve complex combinations of requirements, which may include:

- Demanding mechanical requirements.
- Special fabrication requirements such as postweld heat treatment (PWHT).
- Aggressive corrodents or crack-inducing agents.¹

¹Crack-inducing agents are corrodents that cause a material to undergo stress corrosion cracking. Such agents cause little if any visible corrosion. Refer to Chapter 3 for a discussion of common crack-inducing agents.

- Upset conditions (i.e., non-standard operating conditions).
- Limited capital budgets.
- Tight schedules.

Since the lowest-cost material may have to accommodate a variety of criteria, the process of materials selection can become a complicated task. The process described in this book provides a structured method for selecting materials. It is designed to accommodate variable selection criteria and complex situations. This process utilizes a materials selection template. The template, usually prepared by a plant or project process engineer, is ordinarily customized for the plant.

The template should:

- Be comprehensive enough to accommodate all of the processes and services to be analyzed. It should include all of the process chemistries.
- Contain all necessary mechanical design information such as design temperatures and pressures. In addition, any anticipated operating conditions that could affect mechanical design should be indicated. Examples include fatigue and thermal cycling. This information is used to prepare the piping line classes and equipment data sheets and to alert designers to special design conditions such as cyclic operation.
- Define the upset (non-standard) and transient design conditions which the selected material of construction will be required to accommodate.
- Contain a "Notes" addendum that defines temperature, pressure and concentration *threshold values*. These are values above which the harmful effects of a process variable are considered. For example, a widely used threshold definition for "sour" water is a dissolved H_2S concentration of at least 50 ppmw.

The "Notes" addendum should also define any special requirements that would affect materials selection. Examples include using operating conditions rather than design conditions as the basis for materials selection, requirements for unusually high reliability or unusually long life, and product contamination concerns.

Using data and information from this book, as well as from process licensors, plant testing and the literature, the user must establish failure mechanism threshold values for the template. This information is used to evaluate the risks of early failure.

The utility of a template is that it provides, on a simple compact form, the technical information needed for materials selection. The template also serves to document the basis for the selection of the material of construction. The necessary components of a materials selection template are discussed in detail in Chapter 1.

Obviously, some knowledge of corrosion, corrosion mitigation measures, high-temperature degradation processes and metallurgy is needed to determine the

various kinds of information necessary to design and use a template. Chapters 2–4 provide the reader with the necessary background knowledge. Chapter 5 then shows how to apply this knowledge to the task of designing a template and using it to select an appropriate material of construction.

The book contains a Supplement to illustrate the use of templates and the materials selection procedure. The Supplement focuses on the logic of selecting materials, and on using the operating and design information provided by templates.

The process of materials selection starts with the minimum design temperature. Appendix 1 shows recommended minimum design temperatures for the most common metallic materials of construction. These values have been taken from the most common domestic vessel and piping codes used in the hydrocarbon and chemical process industries. Using Appendix 1, one can select a preliminary material of construction. The lowest-cost material suitable for the temperature should be chosen. In some cases, plant experience or process licensor recommendations indicate the need for an upgraded material. The preliminary material is then reviewed for risks of early failure due to thermal degradation or corrosion effects. This review uses threshold value information as the basis for considering materials degradation and possible materials upgrades.

Chapters 2–4 provide threshold values for a variety of degradation phenomena. Chapter 5 provides guidelines on the use of testing to establish threshold values for new or modified processes. Appendices 2–11 contain charts and nomographs that are useful in evaluating many common corrosive or crack-inducing media.

As the review progresses, changes in material may be indicated. If a material upgrade is required, the process of materials selection becomes iterative. Thus, the upgraded material is subjected to the review process again to ensure compliance with all template requirements.

Once the material of construction has been specified for each stream and/or equipment item template, the selected materials are indicated on a simplified process flow diagram, which is used to create a materials selection diagram (MSD). The MSD ties together the materials selection process and generates several benefits:

- Inconsistencies in materials selection are highlighted. For example, if the materials of construction for the inlet and outlet piping of a vessel are different from the materials selected for the vessel, the MSD shows that either a change in criteria has occurred or an error has been made.
- Locations requiring cathodic protection, injection points for water washing or chemical treatment, as well as corrosion monitoring and sampling points, are indicated. This identification helps document the design basis for the selection of materials of construction.
- Large pressure drops, such as can occur at control valves, indicate if flash spools or splash plates are needed.

- Convenient specification breaks become evident. (Specification breaks are locations where the materials of construction change from one type to another.)
- The possibility of damage to upstream piping and equipment by corrosive reverse flows can be more easily identified.
- The potential effects of corrosion products on downstream equipment and piping can be anticipated. Examples include plugging and heat transfer degradation.

Refer to Examples 16–20 in the Supplement for an illustration of how an MSD is generated and used.

The book's focus is on conveying practical knowledge regarding materials and corrosion engineering to help the reader develop an understanding of corrosion and other degradation phenomena such as embrittlement. The information presented will help the reader to recognize the threshold conditions that increase risks of materials degradation. In addition, testing procedures that can help assess degradation risks are discussed, as are appropriate mitigation measures. This knowledge is essential for making good materials selection decisions.

By using templates and MSDs, materials selection can be made a relatively straightforward process. Although the process requires a broad knowledge of how materials behave, it should be part of the knowledge base of all engineers who have materials selection responsibilities in hydrocarbon and chemical plants.

Without the help of the following people, writing this book would have been much more difficult.

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David A. Hansen
Robert B. Puyear



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1

MATERIALS SELECTION TEMPLATE

A. INTRODUCTION

Many engineers regard materials selection as simply the selection of a material of construction. In reality, materials selection is more complex than that. It includes specifications of:

- The proposed material of construction. This requires the selection of corrosion allowance and valve trim for metallic materials if the job involves piping.
- Special materials testing requirements such as testing for resistance to hydrogen induced cracking.
- Required fabrication procedures such as postweld heat treatment.
- Inspection procedures and acceptance criteria such as those for hardness control.
- Required corrosion control programs. Examples include chemical inhibitor programs, wash water injection, chemical cleaning, protection by paint coating, and cathodic protection.

If one has some flexibility in specifying corrosion control measures, cost savings are usually possible via the selection of less costly materials. In addition, early consideration of the tradeoffs between materials selection and process changes may produce significant savings if a process revision allows substitution of a less expensive material of construction. For example, the operating temperature can be increased above the dew point in a wet CO₂ system, thereby permitting the

use of carbon steel instead of requiring a stainless steel. Also, early consideration of chemical treatment and/or process alternatives may permit the avoidance of fabrication requirements such as postweld heat treatment. These fabrication requirements are usually not excessively expensive in a shop but may be very costly if they involve field applications.

B. MATERIALS SELECTION CRITERIA

1. Mandatory Requirements

Although there are exceptions, most localities have legal requirements that mandate compliance with national engineering codes such as the ASME Boiler and Pressure Vessel Code [1]. These codes address mechanical design and include requirements on fabrication procedures such as postweld heat treatment. Such codes do not normally include guidelines on materials selection. However, they often contain advisory information about various degradation mechanisms. In order to minimize liability, most designers use this information as if it were mandatory. For the same reason, nonmandatory recommended practices such as NACE MR0175 [2] and API Publication No. 941 [3] are customarily used as mandatory documents. Thus, the user should become familiar with local mandatory and customary practices.

Because of safety concerns and potential liabilities related to process guarantees such as yield, materials selection guides provided by process licensors are usually regarded as mandatory. Normally, the materials recommendations by process licensors are more conservative than those made in accordance with a template. Nevertheless, process licensor recommendations should be reviewed for compliance with design life and safety requirements.

2. Design Conditions

Should materials selection should be based on operating or design conditions? In fact, both approaches are valid if used properly.

Materials Selection Based on Design Conditions

This materials selection strategy is used when the materials of construction must be capable of operating at the design conditions. This strategy is often required if the technology is new and/or the user wants to ensure a greater margin of safety. In the event that the basis of materials selection has not been defined, it is prudent to select materials on the basis of design conditions. It should be noted that the material of construction must always satisfy the mechanical requirements of the applicable engineering code for the design conditions. For the purposes of this book, *materials selection will be based on design conditions.*

It is worthwhile to question the design conditions whenever they differ significantly from the operating conditions. Such differences may be due to the design conditions representing unrealistic sustained operation or to a governing transient design condition.¹ However, sometimes the difference is due to design error. In such cases, correcting the error may result in cost savings or the avoidance of a potential materials problem.

Materials Selection Based on Operating Conditions

This option is usually chosen for mature technologies having well-documented histories of successful applications. Mechanical design is based on the design conditions, while materials selection is usually based on the maximum sustained normal operating conditions. The design conditions are taken to be the maximum sustained normal operating conditions plus a design margin (discussed below).

The maximum sustained normal operating conditions should be determined by the most severe of the normal operating conditions. This principle is particularly important for those processes in which the operating variables change from start-of-run to end-of-run. In some cases, the maximum sustained operating condition may be displaced by a governing upset or transient design condition, as discussed below.

Two different categories of design conditions must be evaluated to ensure a satisfactory materials selection.

Sustained Conditions

Ordinarily, materials of construction are required to withstand service under sustained design conditions without accumulating significant degradation. However, there are at least two exceptions to this policy.

1. In high-temperature services, some materials of construction can become embrittled by sustained exposure to operating temperatures, for example, temper embrittlement of some Cr-Mo low alloy steels. (Refer to Part 1 of Chapter 3 for a discussion of embrittlement.) However, in many cases, such embrittlement is a risk only at lower temperatures, primarily during shutdowns. Generally, this type of embrittlement does not affect high-temperature ductility.

The risk of fracture at low temperatures is avoided by making sure that, during startup, the material is heated to a temperature above the embrittlement threshold before being pressurized. Thus, the material remains suitable for sustained operation at design conditions. For example, temper embrittled 2½Cr-1Mo steel is regarded as ductile at temperatures of 250°F and warmer.

¹Transient conditions should be regarded as governing if they can cause significant damage to the proposed material of construction or if they cause the conditions of mechanical design to change.

Accordingly, pressure vessels made of this alloy are usually heated to 250°F (120°C) during startup before pressurizing.

2. In some low-pressure services where "leak-before-break" will occur, such as low-pressure piping, agreement to a plan of early replacement may permit using materials with less than normal design lives.

Transient Conditions

Transient conditions are temporary departures from normal sustained operating conditions. Transient conditions include:

- Planned operating conditions such as startup and shutdown, and catalyst regeneration.
- Anticipated upset conditions such as loss of flow.

In some cases, a transient condition such as carryover of a crack-inducing agent may cause significant damage to the proposed material of construction. In other cases, a transient condition may require a change in the design conditions. For example, if autorefrigeration effects are not permitted by the engineering code, the minimum design temperature must be changed accordingly. Transient conditions such as nitrogen purging may be benign, that is, they may not damage the proposed material of construction and would therefore not affect the conditions of mechanical design.

Transient conditions should be regarded as governing if they can cause significant damage to the proposed material of construction or if they cause the conditions of mechanical design to change.

- A governing condition can affect the selection of a material of construction without affecting the conditions of mechanical design. For example, the maximum design stress and temperature will determine the section thickness of a carbon steel process line containing dry H₂S (if wet, H₂S is a potential crack-inducing agent). However, even on a transient basis, liquid water in the presence of H₂S can initiate sulfide stress corrosion cracking in carbon steel. This may require additional postweld heat treatment and/or a materials upgrade, but does not change the conditions of mechanical design.
- A governing condition can affect mechanical design without affecting the choice of the material of construction. For example, carbon steel is conventionally used for steam piping for temperatures of 800°F (425°C) and less. However, the maximum allowable stress for carbon steel changes for temperatures above 650°F (345°C). Thus, for steam piping, maximum design temperatures up to and including 800°F (425°C) will determine the section thickness, but will not affect the selection of the material of construction.

Significant transient conditions, that is, conditions that may be governing, should be discussed in the "Upset Conditions" section of the template.

3. Design Temperatures

Design temperatures are required for mechanical design. They can also affect materials selection.

The first consideration in materials selection is the minimum design temperature that must be used to select materials capable of resisting brittle fracture at the minimum design temperature. This is purely a mechanical design requirement. One of three different criteria may be used to establish the minimum design temperature:

1. The minimum design temperature may be established by the user, based on consideration of the lowest expected operating temperature, the lowest ambient temperature or an operational upset such as autorefrigeration or Joule-Thomson cooling, or other source of low temperature. A transient condition such as autorefrigeration may be governing, particularly if the restart procedure does not permit warmup before repressurizing.
2. The minimum design temperature may be established as the minimum exemption temperature allowed by the applicable engineering code. For example, the ASME B31.3 piping Code [4] permits most carbon steel piping with wall thicknesses of 0.5" (12.7 mm) or less to be exempt from impact testing if used at temperatures no colder than -20°F (-29°C).
3. If the material of construction is impact tested, the minimum design temperature is usually taken to be the impact test temperature.

Determining the maximum design temperature may involve concerns other than mechanical design requirements:

- For processes that are not corrosive or otherwise degrading, the maximum design temperature is usually determined solely by mechanical design requirements. In such cases, the maximum design temperature is often defined not by the process or ambient conditions, but by the highest temperature permitted by the code's maximum allowable stress.
For example, for ASME Section VIII, Div. 1 [1], 650°F (345°C) is the maximum temperature listed for the maximum allowable stress of carbon and low-alloy steels. (Low-alloy steels contain less than 12 wt. percent alloying). Although the maximum process, upset and ambient temperatures may be much lower than 650°F (345°C), it is the ambient temperature that would probably be adopted as the maximum design temperature for a benign process.
- For processes that are corrosive or otherwise degrading, the maximum design temperature should be determined by the corrosion/degradation

mechanism. For example, if the process involves high-temperature, high-pressure hydrogen, the maximum design temperature must be less than the threshold temperature at which hydrogen will attack the material of construction.

Appendix 1 provides additional information on the recommended temperature ranges for various common materials of construction. The temperature ranges for which the maximum allowable stresses are provided either for ASME Section VIII [1] or ASME B31.3 [4] materials are indicated. In addition, ASTM specifications [5] are indicated for various product forms including bolting, plate, pipe, tubing, fittings, forgings, bars and castings.

4. Process Requirements

There is no part of the materials selection process more important than properly defining the requirements for each piping run and equipment item. If these requirements are improperly defined, selection of the material of construction will be based on incorrect or inadequate information. The importance of defining the operating environments and the range of temperatures, pressures and flow conditions cannot be overemphasized. Process requirements must be defined for abnormal operations as well as normal operating conditions.

Process Flow Diagrams

A process description is the normal starting point for defining materials selection information requirements. This document describes the composition of the process fluids entering and leaving each piece of equipment and the reactions occurring within the equipment. This information may be in the form of a narrative description of the process or in the form of a process flow diagram. The latter is usually preferred, as it visually portrays the sequence of processes and includes the major equipment items, connecting piping, valves, pumps, packaged equipment, etc. The description, in either form, should include a materials balance.

The information contained in a process flow diagram should be regarded as only the initial information necessary. In order to develop all the information needed for materials selection, the process should be analyzed for relevant upset conditions and for anticipated variations in operations and process chemistries. The materials selection template provides an orderly and thorough means to define all the information required.

While it is necessary to describe the chemical processes as completely as possible, this is frequently difficult to accomplish. In some cases, the variables important to the materials selection process are relatively unimportant to the engineers designing the process or the various equipment units. For example, dew

point water formation in an overhead system containing a crack-inducing agent can be immediately damaging to the material of construction. In this situation a team approach to materials selection can be successful. The person responsible for materials selection works with process and equipment designers to seek out and define process and operating variables that could affect materials selection. Consideration is given to possible process contaminants, carry-overs, mechanical problems, formation of dew point water, etc. Pertinent information is then documented via the materials selection template.

In other cases, the process may be a prototype that cannot be completely defined without some sort of pilot plant or in-plant testing. Remarkably short equipment life can result from basing materials selection on a materials balance containing several hundred parts per million of an "unknown" constituent. In such cases, it is often necessary to conduct corrosion tests in actual process fluids where these "unknown" constituents are present so that their effects can be evaluated. The materials selection template may not be very useful until the effects of "unknown" constituents are determined.

Changes in process fluid compositions may occur because of changes in feed stocks. For these situations, the person responsible for materials selection must work with process and equipment designers to anticipate a range of conditions within which the materials of construction must perform. Again, the required information is then requested via the materials selection template.

Process Objectives

If the process has any special objectives, they must be described in the "Notes" section of the template addendum. One of the most common of the special objectives is avoiding product contamination. If product purity is a concern, such as in the production of fine chemicals, the limits of acceptability should be defined. A closely related objective is avoidance of contaminating downstream catalyst beds.

In some cases, materials which may be suitable for mild to moderately corrosive services are unacceptable because of the potential for downstream fouling or because of product purity concerns. Such considerations are particularly important in equipment having large surface areas, such as heat exchangers and packed beds. If such concerns will affect materials selections, they too should be included in the "Notes" section of the template addendum.

Equipment Concerns

It is easy to overlook the fact that many equipment items have special materials requirements. Heat exchangers must be made of materials with high thermal conductivity to transfer heat. Reactors may require special surface treatments such as electropolishing; they may also incorporate requirements for internal agitators or

heat transfer surfaces. Pumps that handle slurries have different materials of construction requirements than those handling clear liquids. The person making materials selection decisions must be familiar with the function of the equipment and its special requirements.

Integration of Corrosion Control into Design

Incorporation of control measures into process design often permits the selection of lower cost materials of construction. Measures such as corrosion inhibitor or wash water injection are often used for this purpose.

Anodic protection is used in a few specific applications such as with stainless steel acid coolers in sulfuric acid plants. Cathodic protection is widely used to protect metallic structures exposed to a variety of environments, including internal and external exposure. If either cathodic or anodic protection is specified, their use must be integrated into the design of the equipment to be protected. Electrode (or sacrificial anode) placement is very important, as is designing to avoid shielding effects. Also, electrical isolation of the protected surfaces must be included in designs. Specific requirements and techniques for anodic and cathodic protection are outside the scope of this book.

5. Special Requirements

The required design life will affect materials selection and/or the determination of the recommended corrosion allowance for almost all jobs. Normally, the user or process licensor will define design life requirements. (See Part 3 of Chapter 3 for a discussion of recommended design lives for various system components.) It is helpful to define the design life requirements in the "Notes" section of the template addendum.

Materials selection for some jobs or projects is affected by special or unusual job or project objectives such as minimal capital cost, minimal maintenance, short schedule, extended design life or the need to address the consequences of a leak or rupture. Occasionally, objectives may be in conflict. For example, minimal capital cost vs. short schedule. When this occurs, compromises are made in order to meet the higher priority objective. Or an otherwise superior material might not be selected if its delivery schedule would seriously delay startup. Such compromises should always be made with consideration to safety and environmental protection.

6. Template Information

A template should be designed to request only the information necessary for mechanical design and to ensure that the material selected will be cost effective and suitable for the full range of design and upset conditions. Table 1-1 shows an example of a material selection template. The following categories of information should be considered when developing a template.

Table 1-1 Materials Selection Template

STREAM OR EQUIPMENT NUMBER: _____

Design Temperature (Minimum/Maximum): _____

Operating Temperature (Minimum/Maximum): _____

Design Pressure (Minimum/Maximum): _____

Operating Pressure (Minimum/Maximum): _____

Commodity¹: _____ Phases: _____ Liquid Water (Y/N): _____

Corrodents: _____

Crack-Inducing Agents: _____

Upset Conditions: _____

Material of Construction: _____

PWHT² (Y/N): _____ Valve Trim²: _____ Corrosion Allowance²: _____

Notes^{3,4}: _____

¹Commodity helps to define the composition of the process. This is usually done by indicating the major constituent(s) of the process, for example, hydrocarbon, rich amine, hydrochloric acid, steam plus hydrocarbons.

²Applicable only for metallic materials of construction.

³General notes indicate special requirements that may affect materials selection. Examples include:

- Selection based on maximum sustained operating conditions rather than on design conditions
- Product purity or process fouling
- Special design life requirements
- Special reliability requirements

⁴Threshold notes define threshold values above which materials selection may be affected. Examples might include:

- Chloride stress corrosion cracking may occur in austenitic stainless steels in neutral saline services with temperatures exceeding 140°F (60°C).
- High-temperature sulfidic corrosion must be considered for temperatures above 500°F (260°C).
- Indicate amines as crack-inducing agents for all concentrations exceeding 2 wt. percent.
- Vapor processes such as wet hydrogen sulfide are subject to the requirements of wet sour service if all of the following apply:
 - a. The vapor contains liquid water.
 - b. H₂S is present at a vapor pressure of at least 0.05 psia (0.34 kPa).
 - c. The total system pressure is at least 65 psia (0.45 MPa).

Stream Number or Equipment Number

This number identifies the subject piping run or equipment on the process flow diagram and the materials selection diagram.

Design Temperature, Minimum

The minimum design temperature is the lowest temperature at which the component can be expected to operate. Most engineering codes require that all anticipated operating temperatures, including those involving upset conditions, be considered. For ferrous materials the minimum design temperature is used in determining the necessity for Charpy impact testing. Some users require that the minimum design temperature be colder than the lowest operating temperature, usually by a margin of 10–25°F (5–14°C). This requirement may generate unjustified costs if it mandates impact testing or forces an upgrade in materials.

Currently, there is not much agreement among the common design standards and engineering codes on how to establish minimum design temperatures. In addition, the codes differ considerably in establishing toughness testing exemptions and/or toughness acceptance criteria. Consequently, the minimum design temperatures, testing exemptions and/or toughness acceptance criteria may (and probably will) differ from piping, to vessels, to tanks, to pumps, etc. Accordingly, the materials of construction may be different for various components of a system due to the lack of agreement among the relevant codes.

Refer to the following in establishing minimum design temperatures:

Application	Standard
Vessels and heat exchangers	ASME Section VIII, Division 1, para. UG-20 [1] ASME Section VIII, Division 2, para. AD-121.2 [1]
Piping	ASME B31.3, para. 301.3.1 [4]
Pumps	API 610 "Centrifugal Pumps for General Refinery Service" para. 2.11.5 [6]
Tanks	API Standard 620 "Recommended Rules for Design and Construction of Large, Low Pressure Storage Tanks" para. 2.2.1 [7] API Standard 650 "Welded Steel Tanks for Oil Storage" para. 2.2.9 [8]

The inherent toughness of metals and alloys is a function of section thickness. This relationship has been incorporated into many of the common domestic engineering codes. Examples are ASME Section VIII [1] and ASME B31.3 [4].

Sometimes it is not obvious whether the material of choice, in the thickness necessary, can be qualified at the desired minimum design temperature. Occasionally a material is selected that cannot be qualified at the desired minimum design temperature. Such occurrences result in significant extra costs and schedule delays. For guidance, start by reviewing ASTM A20, which contains a table that indicates the practical limits of impact test temperatures versus thickness for a variety of carbon and low-alloy steel plate materials. For more detailed guidance, consult mill technical staff or experienced fabricators.

Design Temperature, Maximum

Typically, the maximum design temperature is the maximum operating temperature plus a margin [usually 25–50°F (14–28°C)]. The maximum design temperature is used to obtain the high-temperature allowable stress. In conjunction with the maximum design pressure, the maximum code-allowable stress permitted by the maximum design temperature determines the section thickness. In high-temperature applications, the maximum design temperature may also be used by a designer for creep evaluations.

The maximum design temperature is used to evaluate the risk of temperature-dependent failure mechanisms such as oxidation, hydrogen attack, stress corrosion cracking, thermal embrittlement, spheroidization, etc. The maximum design temperature can also influence the choice between fine and coarse grain practice in carbon steels.

Many equipment engineers want to designate the maximum design temperature as equal to the highest temperature permitted by the maximum code-allowable stress. However, for processes that are degrading or corrosive to the material of choice, using the highest temperature permitted by the maximum code-allowable stress could dictate an unnecessary change in the material of construction. As an example, for ASME Section VIII, Div. 1 [1], 650°F (345°C) is the maximum temperature listed for the maximum allowable stresses of carbon and low-alloy steels. Assuming a high-pressure hydrogen service with a maximum operating temperature of only 300°F (150°C), using 650°F (345°C) as the maximum design temperature will dictate an unnecessary, costly materials upgrade.

Design Pressure, Minimum

The minimum design pressure is usually the coincident pressure at the minimum design temperature. However, in some applications, the minimum design pressure is the lowest pressure expected in operation. For example, in equipment such as vessels that may be designed to operate under an internal vacuum. For such equipment, the minimum design pressure may determine the section thickness and,

consequently, the engineering code requirements for postweld heat treatment and welding preheat.

In conjunction with the minimum design temperature, the minimum design pressure may influence the requirement for impact testing of ASME Section VIII, Div. 1 [1] vessels.

Design Pressure, Maximum

The maximum design pressure, in addition to other loads and in conjunction with the maximum code-allowable stress, determines section thickness and, consequently, the engineering code requirements for postweld heat treatment and welding preheat. It also influences choices among grades of carbon steel.

In addition, analysis of maximum design pressure may:

- Dictate upgrading to Cr-Mo or stainless steels. For hydrogen or mixtures of H_2 and H_2S , such analysis is done via partial pressure calculations.
- Permit a reduction in corrosion allowance because, in low-pressure systems, component thickness may be established by the minimum standard available thickness or by a thickness adequate for welding. In such cases, virtually all of the thickness is corrosion allowance.
- Permit elimination of process-required postweld heat treatment. As discussed later, low-pressure applications may have such low stresses that brittle crack propagation may not be possible in service.
- Influence concerns, via partial pressure calculations, about wet acid gas corrosion and the various problems associated with wet sour service.

The corrosion potential of a gaseous corrodent is often indicated in terms of its partial pressure. Two examples illustrate this:

1. For hydrogen services, the hydrogen partial pressure will be required. This is calculated as follows, using the maximum anticipated hydrogen mole fraction:

$$P(H_2) = [\text{mole fraction } H_2] \times [\text{Maximum Design Pressure, in psia (or MPa)}]$$

2. Similarly for acid gases, the partial pressure is usually required. For example, using hydrogen sulfide:

$$P(H_2S) = [\text{mole fraction } H_2S] \times [\text{Maximum Design Pressure, in psia (or MPa)}]$$

Note that the mole fraction required for partial pressure calculations is the mole fraction in the *vapor phase*. Often, the process flow diagram lists the mole fraction in the total stream flow, not the mole fraction in the vapor phase.

The maximum design pressure should be determined with the same care used in establishing the maximum design temperature. If an unrealistically high maximum design pressure is specified, unnecessary costs can emerge for two reasons:

1. Excessive section thickness specifications. This generates extra materials costs as well as the potential for extra fabrication costs such as for extra welding and postweld heat treatment.
2. Unnecessary material upgrades or mitigation measures such as postweld heat treatment, especially if the process contains hydrogen gas, both hydrogen and H_2S , organic sulfur compounds or wet acid gas.

Operating Temperatures and Pressures

In the event that materials selection is based on operating conditions rather than design conditions, indicate the minimum and maximum operating temperatures and pressures. Of these, the maximum operating temperature usually determines the selection of materials. However, for low-temperature applications, the minimum design temperature is used for materials selection, since this is typically a requirement of the engineering codes.

Operating pressures usually do not affect the selection of materials unless corrodents or crack-inducing agents are involved.

Commodity (Process Stream Constituents)

This information helps to define the nature of the process. The most frequently used means is to list the major constituent(s) of the process stream such as H_2S , rich amine, steam, hydrocarbons, or hydrocarbons plus steam. Such information helps to alert the user that an evaluation may be necessary for corrosion or other degradation problems.

Phases

List the phases present in the process stream. Include any significant solids such as catalyst or condensed salts. This information will influence the evaluation of process corrosivity and alert the user to the possibility of erosion or erosion corrosion.

Liquid Water

Specify "Yes" or "No" for normal service. This information is critical in determining whether corrodents or crack-inducing agents will be electrolytically active. If some other electrolyte such as an organic acid is present, indicate its presence with a suitable note.

Corrodents

Two types of corrodents are of concern.

1. High-temperature oxidation may occur in some processes. Both oxidants such as oxygen, sulfur and chlorine, and corrosive compounds such as H_2S can corrode metals and alloys at high temperatures in the absence of liquid electrolytes. List the corrodent and its concentration. In cases where the corrodent is present as a vapor, its concentration may be represented by either its partial pressure or its mole fraction.
2. In most cases the primary corrosion concern is electrochemical corrosion. Listing the corrodents and their concentrations is necessary if an electrolyte is present during either normal or upset operating conditions. Note that, while water is the most common electrolyte, most organic acids and some organic chemicals such as phenol, can act as electrolytes.

Crack-Inducing Agents

Crack-inducing agents are ions or compounds that can cause various types of cracking in materials of construction and/or their weldments. For example, one of the most common crack-inducing agents in the hydrocarbon industry is wet H_2S , which can initiate several types of cracking in carbon steel and in carbon steel weldments. Crack-inducing agents are discussed extensively in Chapter 3.

List the known crack-inducing agents and their concentrations only if an electrolyte is present during either normal or upset operating conditions. Indicate the concentration for each crack-inducing agent only if it exceeds the threshold concentration (otherwise, indicate "None" or "Trace"). The threshold concentrations of the crack-inducing agents should be indicated in the "Notes" addendum of the materials selection template.

Upset Conditions

Evaluate upset and anticipated transient conditions that could damage materials. Consider startups, which could be a risk for embrittled materials. Shutdowns should also be considered, especially for the risk of dew point water formation. Other examples are steamouts, boilouts, chemical cleaning, loss of flow, presulfiding and catalyst regeneration. An upset or transient condition that worsens any of the template variables may become a governing condition. It is helpful to use the Notes section at the bottom of the template to describe upsets and transients that may be harmful.

Material Considerations

- *Corrodents:* evaluation of the risk of damage due to an upset condition involving corrodents is done as follows:

1. Determine if the upset condition will introduce or concentrate a corrodent or cause a resident corrodent to become active as a result of:
 - Causing liquid water to be present, for example, formation of dew point water during a low-temperature excursion in a vapor system.
 - Crossing a temperature, concentration or partial pressure threshold.
 - Promoting concentration effects at liquid-vapor interfaces and at crevices such as socket welds.
 2. Use the estimated duration of the upset to determine a prorated corrosion rate. The prorated rate is then used to evaluate whether there is a need for extra corrosion allowance, an upgrade in materials selection or the specification of an additional mitigation measure such as a paint coating. Generally, the duration of an intermittent corrosion episode due to an upset is so short that it has essentially no effect on materials selection.
- *Crack-inducing agents:* prorating is not normally permitted for crack-inducing agents. The presence of even a transient active crack-inducing agent should be considered as a governing condition for the purpose of materials selection. The conventional response to a transient active crack-inducing agent is a materials upgrade or the adoption of a preventive measure such as a paint coating.
 - *High-temperature excursions:* evaluate the effects, if any, of high-temperature transient conditions. If a high-temperature excursion will result in unacceptable corrosion, significantly degrade the material of construction, or accelerate the activity of a crack-inducing agent, the upset condition should be regarded as governing. In such cases, the maximum design temperature is determined by the high-temperature excursion.

Mechanical Design

Describe upset or transient conditions that may affect the design temperatures and/or pressures. If a transient condition will not damage the material of construction, it may not affect the design conditions. The decision whether to regard the upset condition as governing becomes a code question involving mechanical design. The design engineer is usually consulted on such questions.

- Some codes allow occasional temporary operating conditions outside the design envelope. If it can be established that an otherwise benign upset condition is permitted, the condition should not be regarded as governing. There is often an economic benefit in such decisions.
- In some cases, the component may be exempt from code requirements, for example, heat exchanger tubes. In such cases, common sense may indicate that the upset condition is not governing.

Discussion

In the early stages of a major project, the process flow diagram and process equipment and piping designs are changed often. Detailed materials selection at this stage is usually a waste of time, since such decisions have to be remade after the process design has been completed. However, some early materials selection work is often necessary for cost estimating. In addition, an early review of the proposed processes may be beneficial. This review should investigate process changes and mitigation measures such as chemical treatment that would reduce materials costs, the risks of corrosion or other degradation problems.

REFERENCES

1. *ASME Boiler and Pressure Vessel Code*, American Society of Mechanical Engineers, New York (latest edition).
2. *Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment*, NACE MR0175, NACE International, Houston (latest edition).
3. *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants*, API Publication No. 941, API, Washington, D.C. (latest edition).
4. *Chemical Plant and Petroleum Refinery Piping*, ASME B31.3, American Society of Mechanical Engineers, New York (latest edition).
5. *Annual Book of ASTM Standards*, American Society for Testing and Materials, Philadelphia (latest edition).
6. *Centrifugal Pumps for General Refinery Service*, API Standard 610, API, Washington, D.C. (latest edition).
7. *Recommended Rules for Design and Construction of Large, Low Pressure Storage Tanks*, API Standard 620, API, Washington, D.C. (latest edition).
8. *Welded Steel Tanks for Oil Storage*, API Standard 650, API, Washington, D.C. (latest edition).

2

BASIC MATERIALS ENGINEERING

Corrosion is the most common cause of failure in a plant. Accordingly, the basic principles of the most common type of corrosion, electrolytic corrosion, will be discussed in detail in the first part of this chapter. An understanding of these principles is necessary to choose effectively from the wide variety of mitigation measures available to control corrosion. Typical means of corrosion control such as barrier coatings, inhibitors, and cathodic protection are also discussed.

A basic understanding of materials engineering is helpful in differentiating among the various alloys, non-metallic materials and composite materials available for use in modern plants. The second part of this chapter begins with defining some of the terms commonly used in metallurgy and proceeds to discuss the various families of commonly used alloys. Such information proves to be useful in avoiding improper choices during the process of selecting material upgrades. The most commonly used non-metallic materials are also discussed.

Coatings and linings are primarily used to provide protection from corrosion and/or erosion. In most cases the driving force for their use is reduced cost. Improper use of these materials can cause unexpected problems. Knowledge of the most common pitfalls is useful when sorting through the various available coating and lining alternatives.

PART 1: CORROSION

A. INTRODUCTION

Concerns about corrosion often dominate materials selection. Accordingly, understanding corrosion and the common strategies used to deal with it are central to the selection of appropriate materials.

This section establishes a practical understanding of corrosion. In Chapter 3, "Failure Modes," the effects of various common corrodents and crack-inducing agents are discussed. Typical corrosion control measures are also discussed.

B. CORROSION BASICS

There are three *simultaneously* necessary conditions for electrolytic corrosion to occur:

1. An electrolyte must be present. Usually this is water containing dissolved salts.
2. A corrosion cell must exist. The cell consists of an *anode*, the area being corroded (i.e., oxidized), and a *cathode*, the area where electrons enter the electrolyte.
3. The anode and cathode must be connected by an electronically conductive path.

If *any* of the above conditions is not satisfied, electrolytic corrosion cannot occur.

Figure 2-1 illustrates corrosion of iron exposed to wet CO_2 (carbonic acid). Electrons are given up by the iron at the anode and flow through the metal to the cathode. Simultaneously, hydrogen ions generated at the anode diffuse through the electrolyte to the cathode. At the cathode, the hydrogen ions combine with electrons arriving from the anode to generate hydrogen gas.

Chemically, the relevant reactions are:

- Overall: $\text{Fe} + \text{H}_2\text{CO}_3 \rightarrow \text{FeCO}_3 + \text{H}_2$
- Ionically: $\text{Fe} + 2\text{H}(+) + \text{CO}_3(=) \rightarrow \text{Fe}(++) + \text{CO}_3(=) + \text{H}_2$
- Anode reaction (*oxidation*): $\text{Fe} \rightarrow \text{Fe}(++) + 2\text{e}(-)$
- Cathode reaction (*reduction*): $2\text{H}(+) + 2\text{e}(-) \rightarrow \text{H}_2$

Note that the anode is an *electron donor* while the cathode is an *electron acceptor*.

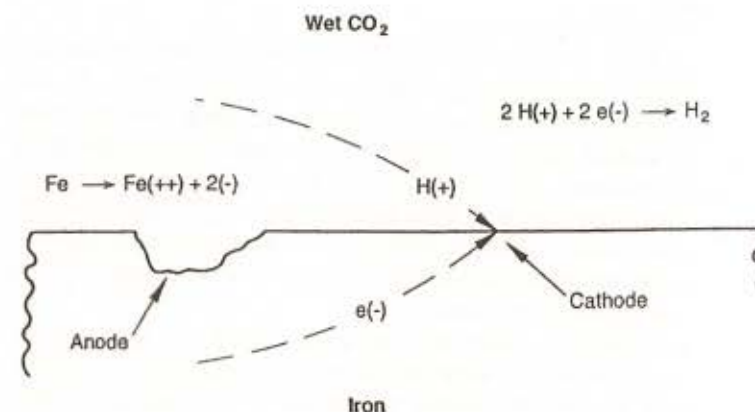


Figure 2-1 Illustrating the essential features of an electrolytic corrosion cell.

In this example, both the anode and cathode are iron. However, the two sites *must* differ in some important aspect. The differences can be transient, leading to situations in which the site changes back and forth from being an anode to being a cathode. Cyclic stresses can cause this type of behavior.

Thermodynamically, an anode differs from a cathode by having a greater Gibbs free energy. Anything that will cause a site to have greater or increased Gibbs free energy will tend to cause that site to be an anode. For examples, both cold work and residual tensile stresses increase the local Gibbs free energy in metals and alloys. In the case of two dissimilar metals, the different inherent corrosion resistance of the two metals translates into one having a greater Gibbs free energy than the other.

The difference in Gibbs free energy between the cathode and the anode results in the two sites having a difference in electrical potential. Thus, in accordance with Ohm's law,¹ corrosion rates become a function of current flow and electrical resistance. Later in this section (see Corrosion Control, p. 21), this feature of electrolytic corrosion will be used to explain some of the mitigation measures used to control corrosion.

Some examples of cathodes and anodes follow.

¹ $V = IR$, where V is the electrical potential (in volts), I is the current (in amperes) and R is the electrical resistance (in ohms).

1. Cathodes

- In hot-formed carbon steel products, the cathode is very often the area still covered by mill scale (Fe_3O_4), while the anode sites are cracks in the mill scale. This is a very common anode/cathode relationship in carbon steels. It is the normal situation in a form of CO_2 /carbon steel corrosion called "mesa" corrosion. Mill scale is conductive and is slightly cathodic with respect to clean carbon steel. Note that this is an example of a galvanic cell.
- The cathode area is sometimes the non-cold-worked areas in a component that has been partially cold worked, for example, the straight-run tubing in a U-bend heat exchanger bundle.
- In heat exchangers, pumps and vessels, the internals are often made of more corrosion resistant alloys than is the pressure retaining component. Thus, the internals are cathodic with respect to the pressure retaining component. This situation should always be reviewed for conformance with design life and safety requirements.

2. Anodes

The anode area may be the metal under a deposit on an otherwise clean surface. A similar situation involves crevices such as socket welds, in which the metal in the crevice is anodic with respect to the adjacent outside metal.

Crevice corrosion and under-deposit corrosion can be serious problems in oxide-stabilized materials such as aluminum and stainless steel. These materials depend on the formation and stability of a very thin oxide layer that is inert, easily "healed" if damaged and tenacious. At sites where the oxide layer has been disrupted and has not healed, the material usually has very little corrosion resistance. Consequently, these materials can simultaneously exist in both active and passive states, sometimes adjacent to each other. The potential difference between the anodic active state and the cathodic passive state acts to galvanically drive the corrosion cell. In addition, the anode area in such cells is typically much smaller than the cathode area. This difference acts to further accelerate the corrosion rate.

Crevices and deposits can accelerate corrosion in metals such as carbon steel, which does not exhibit both active and passive states. However, the rate of corrosion is much slower in such materials because they lack the galvanic driving force of the active-passive metals.

Anodes are occasionally associated with the residual stress fields of welds or with weld metal, weld fusion zones or heat affected zones. Figure 2-2 provides an example of this type of problem. It shows "knife-edge" attack in the weld of an

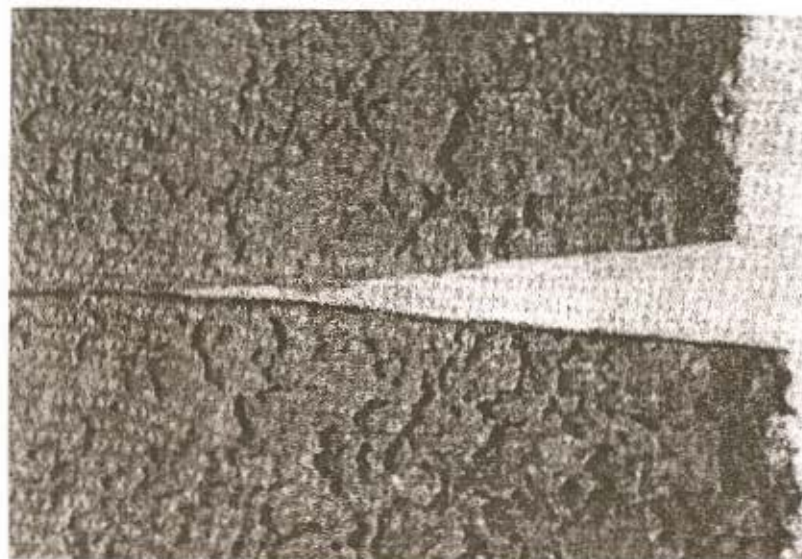


Figure 2-2 An example of "knife-edge" attack in ERW (electric resistance welded) pipe. This localized corrosion was shown to be caused by excessive sulfur concentrating in the fusion zone of the weld.

ERW (electric resistance-welded) pipe. This example illustrates the rapid rate of localized metal loss that can occur when the cathode, in this case the parent metal, has a much larger area than the anode, in this case the thin weld.

Similarly, a welding-induced sensitized area in a stainless steel may be anodic with respect to the unaffected adjacent metal. Refer to Part 2 of Chapter 3 for a discussion of sensitization.

C. CORROSION CONTROL

The rate of corrosion at the anode is directly proportional to the anode current density (expressed as amps per unit area). This bit of theory opens the way to understanding how to prevent or control corrosion: use methods that eliminate or reduce anode current density. What follows are some of the more common methods used to prevent or control electrolytic corrosion.

1. Barrier Coatings: Interrupt or Reduce the Flow of Current

The primary function of a barrier coating is to prevent gross contact between the corrodent and the metal surface. This is usually done by a paint coating or a lining. In some applications, a chemical inhibitor is used.

Inhibitors

Chemical treatment by inhibitors is a frequently used corrosion control measure, particularly for piping systems. In essence, most inhibitors function by laying down a very thin (sometimes monomolecular) adsorbed layer that acts as a barrier coating. Film-forming amines are a common example. Because such inhibitors can be easily disturbed and thereby lose their barrier function, inhibitors are usually continuously injected. In some applications such as large-diameter pipelines, batch inhibition may be necessary. Inhibition is usually not permitted in processes intended to produce high-purity products.

Corrosion control by chemical inhibitors can be effective, particularly in clean systems in which turbulent flow does not interfere with the adsorption of the inhibitor. Chemical inhibition is usually not an effective mitigation measure in components subject to turbulent flow (such as pumps and control valves). It is also usually ineffective in systems having deposits that prevent the inhibitor from contacting the metal surface to be protected. In "dirty" systems, particularly in plants, chemical cleaning is sometimes a regularly scheduled measure. In most pipeline systems using inhibitors, regular cleaning by means of "pigging" is used. Pigging is done by using pipeline pressure to push a mechanical cleaning device through the pipeline.

Coatings and Linings

In addition to acting as barrier coatings, most coatings and linings are dielectric, that is, they act as electrical insulators. By providing electrical insulation on the cathode, the total cathode current available to concentrate at the anodes is reduced. The theory here is based on the fact that the total cell current must balance to zero: the total anode current equals the total cathode current. By reducing the total cathode current, the anode current density is reduced.

In immersion services, this technique can still result in large anode current densities if the coating has "holidays," the name sometimes given to pinholes. Holidays act as very small anode areas. With thick linings, pinholing is not regarded as a problem. Such holidays are usually quickly plugged with corrosion products. The subsequent very slow corrosion rate is controlled by diffusion and polarization. However, thin film coatings, such as most paint coatings, do have a fairly high risk of either initial or age-induced holidays. Holidays in these coatings may be subject to sustained high rates of corrosion, since all of the current concen-

trates at the holidays. Even though the cathode current density may be low, the very large cathode/anode area ratio dominates the corrosion rate. Thin-film coatings can generate high anode current densities in tanks and vessels and therefore should not be used without the backup of a cathodic protection system. Thick dielectric linings such as rubber virtually eliminate cathode current. Backup by cathodic protection is usually unnecessary.

Thin-film coatings in immersion service should be used with caution in situations involving galvanic couples, unless the couple is cathodically protected. In such situations, coating the anode without also doing something to control the cathode can lead to very unfavorable anode/cathode area ratios. For example, coating the carbon steel channel/channel cover in a seawater heat exchanger having a more noble aluminum bronze tubesheet. In such a case, any holiday in the anode coating could result in an enormous anode current density. There are at least two proper mitigation responses for this example:

- Coat the tubesheet as well as the channel/channel cover, perhaps with sacrificial anodes used to handle holiday problems.
- Coat only the cathode, without requiring the use of supplemental cathodic protection.

Galvanically noble metal coatings such as electroless nickel plating or chromium plating are sometimes recommended as barrier coats on anodic substrates such as carbon steel. Such recommendations should be regarded with great caution because these coatings are electrically conductive, permitting unrestricted participation of the cathode in supplying current to available anodes. Also, the coatings themselves are cathodic with respect to the substrate, making any pinhole an anode with a very large cathode/anode area ratio. The current density at such anodes can be enormous.

Such coatings, being galvanically noble, generate a significant electrical potential between the anode and the cathode. For high-conductivity fluids such as seawater, resistivity is small. Ohm's law indicates why such couples have increased current densities at the anode: $I = V/R$.

Note that such coatings are successfully used on substrates such as stainless steel, primarily for improving wear resistance. In such cases, the substrate is usually galvanically neutral with respect to the coating.

The galvanic series in seawater is often used to judge the risk of galvanic corrosion in other media, for which the series may not be available. Refer to Appendix 10 for an illustration of the galvanic series in seawater. The risk of galvanic corrosion depends as much on the corrosivity and conductivity of the medium as on the separation of the two metals in the galvanic series. In most cases, fresh waters have neither the corrosivity nor the conductivity to support galvanic activity. Seawater often actively supports galvanic corrosion.

In rare cases, the relatively small heat affected zone area of a weld will be an anode to the relatively large cathodic surface area of the parent metal. In moderately corrosive media, the heat affected zone may corrode much faster than either the weld metal or the parent metal. In such cases, postweld heat treatment is usually helpful. In some instances, normalizing (or even solution annealing in the case of an austenitic stainless steel) the weldment is necessary, a measure that can cause significant distortion problems. In most cases, the weld metal, heat affected zone and parent metal do not have significant galvanic differences.

2. Cathodic Protection: Make Everything into a Cathode

This can be done in either of two ways:

1. The piece to be protected can be electronically and electrolytically connected to an inert material such as graphite or silicon iron. A power supply imposes a voltage that makes the inert material an electron donor, i.e., an anode. This is an *impressed current* cathodic protection system. Such systems are frequently used to protect buried pipelines and submerged structures, and in plants to provide external cathodic protection to tank bottoms, buried piping runs, etc.
2. The piece to be protected can be electronically and electrolytically connected to a more reactive material. For example, iron can be protected by connecting it to zinc or aluminum. The less noble material (zinc or aluminum) is a *sacrificial anode*. Galvanized carbon steel is a common example of this application.

Sacrificial anodes are usually used to provide cathodic protection to offshore structures and pipelines. Onshore, they are typically used for small applications and in situations in which impressed current systems are not cost effective. Onshore examples include short buried piping runs and internal cathodic protection for tanks and vessels.

3. Anodic Protection: Make Everything into an Anode

Anodic protection uses an impressed current to protect alloys that can exist in both active and passive states. These materials are typically oxide-stabilized. Examples include stainless steels and titanium. The procedure uses a power supply, an inert impressed current electrode and a potentiostat to provide a potential that keeps the material in the passive state. The most common application is for stainless steel tanks in strong mineral acids and for coolers in sulfuric acid plants. Since severe corrosion rates can occur if potentials are not kept in the passive region, the technique should not be used without expert assistance.

A similar application, without an impressed current system, involves spreading the cathode current over a very large anode area, forcing the anode current density to be small. This also minimizes the cathode area and thus minimizes the total cathode current available for corrosion. An example is the repair of a carbon steel internal tank bottom in a location where painting is not practical. In such cases, it has been shown that turning the entire tank bottom into an anode, by abrasive blasting, slows down local pitting rates.

4. Passivation

Carbon steel and stainless steels are among the common alloys that can be passivated. *Passivation* consists of exposing the clean metal surface to an oxidizing environment. The resulting passivated surface is much more corrosion resistant than it would be in an unpassivated state. Passivation is thought to be associated with the formation of an oxide film. In materials such as carbon steel, which form relatively weak oxides, passivation can be destroyed rather easily. In oxide-stabilized alloys such as the stainless steels, passivation-induced corrosion resistance is not easily destroyed, especially in oxidizing environments.

Passivation is most often associated with chemical cleaning. The chemical cleaning process should include a "passivation" procedure as the final step. A sodium nitrite solution is normally used to passivate carbon steel. (Chromates were widely used but are now considered to be too toxic.) Austenitic stainless steels are usually passivated in air after pickling and neutralization. Note that some authorities regard the principal benefit of passivation to be the removal, by chemical cleaning, of surface contaminants.

Pickling is a chemical process often used to descale or clean new stainless steel materials, components or assemblies. (See ASTM A380 for recommended procedures.) For heavily oxidized materials, the pickling process should be of a duration long enough to remove the chromium-depleted surface beneath the layer of scale. The acid solutions used to pickle stainless steels usually contain sufficient nitric acid (a good oxidizer) that a subsequent passivation step is unnecessary.

5. Polarization

Polarization occurs because of ion concentration buildup in the vicinity of the anode and/or cathode. Once the ion concentration reaches saturation, corrosion slows to a virtual stop. Polarization can occur when:

- Hydrogen ions concentrate at an active cathode in the absence of a cathodic depolarizer. Dissolved oxygen is an example of a cathodic depolarizer.

- Soluble $\text{Fe}(++)$ saturates the electrolyte around an anode in carbon steel, perhaps as the result of the precipitation of an insoluble iron salt which inhibits diffusion of $\text{Fe}(++)$.

The anode current density, which is directly proportional to the corrosion rate, decreases because of polarization. The rate of corrosion becomes limited by diffusion, and in many cases, corrosion ceases, for all practical purposes.

- We see the effects of polarization in deaerated, but otherwise corrosive, water. Without dissolved oxygen, hydrogen polarization all but shuts down the corrosion mechanism. For example, seawater deaerated to less than about 10 ppbw is non-corrosive to carbon steel.
- Many waters form insoluble dense scales on the corroded substrate. The result is polarization from the presence of ion-saturated water at the scale-substrate interface. In addition, the dense scale acts as a barrier to the diffusion of new corrodent and dissolved oxygen to the substrate surface. Refer to Appendix 9 for a discussion of the Ryznar and Langelier indices, which are used to predict the corrosivity and/or scaling tendencies of water.

Polarization is encouraged by any phenomenon that promotes the buildup of ion concentrations at anodes or cathodes. Conversely, polarization is retarded by phenomena that reduce such ion concentrations.

Polarization		
	Anodic	Cathodic
Encouraged by	Formation of dense, adherent, insoluble salts Low-velocity flow Appropriate cathodic protection	Low-velocity flow Appropriate cathodic protection
Reduced by	Formation of soluble salts instead of scale Formation of soft scale that is easily removed by high-velocity flow Particulate erosion High-velocity flow	Presence of hydrogen scavengers such as dissolved oxygen Cathodic poisons High-velocity flow

Ions such as sulfides and cyanides can act as "cathode poisons." Instead of the hydrogen ions recombining to form hydrogen gas, which in turn can act to polarize the cathode, they form nascent hydrogen atoms. The nascent hydrogen then diffuses into the substrate material. In ferritic steels, the result can be hydrogen

embrittlement and/or hydrogen stress cracking, and various forms of hydrogen-induced cracking, including blistering.

Electrolytic corrosion is the most common form of corrosion in chemical and hydrocarbon plants. The problem and the various countermeasures it requires will be referred to often in subsequent sections.

In addition to electrolytic corrosion, the selection of materials must also take into account various oxidation/reduction processes that can occur in the absence of an aqueous electrolyte. Examples include various forms of sulfidation, destructive oxidation of alloys in air or steam at high temperatures, carburization, nitriding, fuel ash corrosion and high-temperature hydrogen attack, all of which are discussed in Chapter 3, "Failure Modes."

PART 2: MATERIALS

A. METALLURGICAL DEFINITIONS

Metallurgical descriptions usually contain jargon and arcane words that baffle the uninitiated. Here we offer clear, useful explanations of some of the most frequently encountered terms.

1. Heat Treatments

Annealing

For carbon and low alloy steels, full annealing requires heating the steel to a temperature in the range of 1350 to 1750°F (730 to 955°C). 1650°F (900°C) $\pm 25^\circ\text{F}$ (14°C) is the typical target temperature for annealing. After holding this temperature for a period long enough to ensure through-thickness heating, the material is furnace cooled. This produces a "dead soft" carbon steel (Figure 2-3). This condition is often unacceptable, since carbon and low-alloy steels can be very brittle in the fully annealed condition. Such steels are usually subsequently normalized. Figure 2-4 shows the microstructural effects of normalizing. The heating portion of this heat treatment is sometimes referred to as "austenitizing."

For austenitic stainless steels, annealing usually means heating to about 2000°F (1095°C), followed by either a water quench or a rapid air cool. This procedure is more properly called a "solution anneal," since the objective is to redissolve any chromium carbides that may have formed during prior processing.



Figure 2-3 A typical microstructure in carbon steel that has been furnace annealed. (Courtesy of Dr. E. V. Bravenec, Anderson & Assoc.)

Normalizing

In this process, a carbon or low-alloy steel is heated to about 1650°F (900°C) and is then air cooled. The process partially relieves stresses retained from prior processing and “refines” the material. The term “refining” means that the grain size is reduced and the grain structure becomes more homogeneous, thereby producing a tougher, more ductile product. Comparing Figure 2-4 to Figures 2-3 and 4-12 illustrates the microstructural benefits of normalizing.

Preheating

Many steels are susceptible to various forms of cracking during or after welding. Examples include high-strength carbon steels and low-alloy steels such as the air-hardenable Cr-Mo steels. Preheating the base metal or substrate is beneficial in reducing the risks of such cracking. The common engineering codes contain guidance for preheat temperatures and procedures.

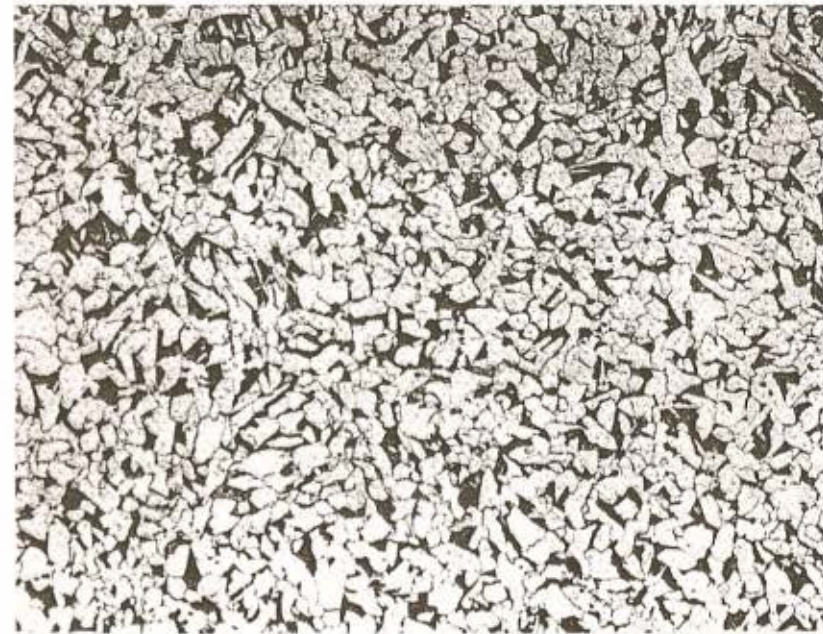


Figure 2-4 A typical normalized ferrite-pearlite microstructure in carbon steel. (Courtesy of Dr. E. V. Bravenec, Anderson & Assoc.)

Stress Relief/Postweld Heat Treatment

Residual stresses can be introduced into a metal by fabrication processes such as forging or rolling, by uneven heating or cooling, or by welding. The magnitude of such stresses is usually on the order of the yield strength but may in some cases approach the tensile strength of the metal.

In order to stress relieve or postweld heat treat carbon and low-alloy steels, it is necessary to heat them, typically to a temperature in the range of 1100 to 1350°F (595 to 730°C). They are then held at this temperature for some period of time, followed by air cooling. The minimum holding time is specified by the relevant engineering code. The holding temperature must be less than the lower transformation temperature of the steel. The lower transformation temperature is the lowest temperature at which austenite starts to form. For example, 1333°F (720°C) is the lower transformation temperature for plain carbon steels.

Metals and alloys weaken as they become hotter, that is, their yield strengths decrease. Residual stresses in excess of the reduced yield strength are eliminated via plastic deformation. Upon cooling, the maximum residual stress possible is the yield strength at the holding temperature. For carbon steels, this heat treatment process reduces residual stress by about two-thirds. When done for the purpose of removing residual stresses caused by cold work, the process is termed *stress relief*.

When the liquid metal in a weld solidifies, it becomes at least partially constrained by the surrounding metal. As the weld metal cools to ambient temperature, this restraint interferes with contraction. The resulting residual stress in the weld is approximately equal to the ambient temperature yield strength of the parent metal. Stress relief heat treatment for welds is called *postweld heat treatment*. An additional benefit of postweld heat treatment is a reduction in weld metal and heat affected zone hardnesses, which can be beneficial in reducing the risk of some forms of stress corrosion cracking.

Incidents of stress corrosion cracking in postweld heat treated weldments indicate that postweld heat treatments are sometimes ineffective in reducing residual stresses and/or hardnesses associated with welds. Sometimes this result can be attributed to microalloying. The effects of microalloying on heat affected zone hardnesses is discussed in Section D (p. 39). In some cases, subsequent stress corrosion cracking can be traced to an improperly executed postweld heat treatment, for example, where the postweld heat treatment temperature was too low. In other cases, it has been speculated that even the lowered level of residual stress was sufficient for the initiation of stress corrosion cracking. In such cases, a change in the process or the material of construction is indicated.

Some design and construction codes allow low-temperature postweld heat treatments if the weldment is held at the lower temperature for an extended time. Such postweld heat treatments should not be permitted if postweld heat treatment was specified in order to avoid or minimize the risk of stress corrosion cracking.

Austenitic stainless steels are not usually stress relieved or postweld heat treated. When they are subjected to such heat treatments, they are held at a temperature of 1600 to 1650°F (870 to 900°C), followed by rapid cooling. The rapid cooling is necessary to avoid sensitization. (See Part 2 of Chapter 3 for a discussion of sensitization.) Stress relief or postweld heat treatments of ordinary austenitic stainless steels at less than 1600°F (870°C) can grossly sensitize the alloy. For this reason, local stress relief of unstabilized austenitic stainless steel is usually impractical, since the "runout" areas immediately adjacent to the region being heat treated will be grossly sensitized. An exception is stress relief of low-carbon grades of thin-section products such as tubing. These can be stress relieved fast enough to avoid gross sensitization. Stabilized grades of austenitic stainless steels such as Type 321 SS are much less susceptible to sensitization if they have

been stabilization annealed. Stabilized grades are usually selected if local stress relief or postweld heat treatment is required.

Quenching and Tempering

This procedure is used to produce materials with improved strength and/or toughness. It is restricted to alloys whose microstructures are transformed upon cooling. In this procedure, a ferritic steel is first heated to a temperature of about 1650°F (900°C) or higher, then quickly cooled in air, water, water spray, oil or salt bath. The cooling step is the "quench" part of the procedure. The required rate of cooling, and consequently the choice of quenchant, depends on alloy chemistry and section thickness.

Normally, the objective of the procedure is to develop a very strong, tough material. The quenching part of the procedure produces a hard and strong—but brittle—phase called *martensite*. Tempering is usually done at 1100 to 1300°F (595 to 705°C). The tempering procedure is very similar to that used for stress relief or postweld heat treatment. Tempering is performed to promote some carbon diffusion from the martensite, thereby greatly improving the ductility and toughness of the quenched steel.

Thick sections of many ferritic steels cannot be cooled quickly enough in air to obtain the desired normalized microstructure. In such cases, quenching is often used to hasten the cooling rate. The objective is to produce the same sort of microstructure that would be obtained from normalizing a thinner section of the same material. In thick sections of such materials, even quenching does not ordinarily generate the cooling rates necessary to develop martensite. Hence, tempering is primarily intended for stress relief rather than for softening martensite. Many engineering codes such as the ASME Boiler and Pressure Vessel Code, Section VIII [1] and materials specifications such as ASTM A516 permit such thick sections, when properly quenched and tempered, to be equivalent to normalized material.

Tempering is also sometimes done in conjunction with other heat treatments such as normalizing. The purpose is usually to promote carbon diffusion, with the intention of softening and/or toughening the steel. In some cases, stress relief may be a secondary or even a primary objective.

Fabricators will occasionally propose to use multiple heat treatments or heat treatments having unusually long holding times or unusually high holding temperatures. The user should be wary of such proposals. Some multiple heat treatments will cause degradation of the common materials of construction. Loss of strength and/or loss of toughness may result. If permitted, the fabricator should be required to demonstrate, by testing, that the proposed procedure will not result in material degradation.

2. Microstructural Terms

Austenite

Austenite is a high-temperature form of carbon steel, having a face-centered cubic crystal structure. The lowest temperature at which ordinary carbon steel can be fully austenitic is 1333°F (720°C). During normalizing heat treatments, the holding temperature and time is specified so that the alloy becomes fully austenitic. For the common carbon steels, the austenitizing temperature is typically specified as 1650°F (900°C).

Austenite has a much higher solubility for carbon than do the lower temperature forms of steel. Heating the steel to an austenitizing temperature causes any carbides that may have formed (as a result of lower temperature transformations or materials processing) to dissolve. Alloys capable of forming austenite at high temperatures, but that transform to other crystal structures at lower temperatures, are said to be hardenable by heat treatment. Martensitic steels are an example. Most of the carbon and low-alloy steels are hardenable by heat treatment.

By adding alloying elements such as nickel or manganese to carbon steel, the austenitic microstructure can be made to be stable at low temperatures. For example, most austenitic stainless steel and high-nickel alloys exhibit stable microstructures at temperatures approaching absolute zero. These alloys have excellent low-temperature fracture toughness and are immune to hydrogen embrittlement from causes other than cathodic charging. Most austenitic alloys are not hardenable by heat treatment, the major exception being a few precipitation hardenable types.

Ferrite

Ferrite is essentially pure iron at temperatures less than approximately 1675°F (915°C). It has a body-centered cubic crystal structure. Ferrite forms from austenite as the austenite cools from a normalizing heat treatment. Because ferrite does not contain enough carbon to permit the formation of martensite, it is not hardenable by heat treatment. Accordingly, steels composed only of ferrite are not hardenable by heat treatment. The most common example of a truly ferritic steel is Type 405 SS, a ferritic stainless steel.

Please note that the generic term "ferritic steel" is used to refer to carbon or low-alloy steels that contain other phases in addition to ferrite. Such steels are usually hardenable by heat treatment.

Ferritic steels become brittle at low temperatures. This phenomenon is reversible, that is, the steels regain their former toughness after being warmed up. Ferritic steels are also susceptible to hydrogen embrittlement.

Martensite

Martensite is formed from high-temperature austenite, in heat-treatable alloys, by cooling the austenite fast enough to prevent the formation of ferrite. For some

heat-treatable alloys, quenching in water or some other liquid such as oil or a molten salt is required to obtain the cooling rate necessary to produce martensite. Some steels have sufficient alloying additions that quenching is not necessary to produce martensite. Air cooling produces the martensitic microstructure in Type 410 SS and other martensitic stainless steels. Since martensite is usually a brittle material, it is normally subsequently tempered. The tempering temperature should be colder than the austenite transformation temperature. The primary purpose of tempering is to permit some carbon to diffuse from the martensite. The subsequent tempered martensite is significantly stronger and tougher than the parent ferritic alloy. Note that a tempered material should never be stress relieved or postweld heat treated at a temperature exceeding the final tempering temperature. Such heat treatments can seriously degrade the mechanical properties of the alloy.

Although properly heat-treated martensitic steels have superior fracture toughness, they do become brittle at low temperatures. Most martensitic steels are very sensitive to hydrogen embrittlement.

Martensitic alloys find widespread use in the hydrocarbon and chemical process industries. Examples include high-strength bolting such as ASTM A193 Type B7, high-strength quenched and tempered plate such as ASTM A543 and martensitic stainless steels such as Type 410 SS.

Pearlite

Most carbon and low-alloy steels contain enough carbon to be hardenable by heat treatment. However, carbon steels usually are not intended to be hardened by heat treatment. Instead, carbon steels are normally produced with a more ductile, lower strength microstructure which forms during cooling from austenitic temperatures. This microstructure is composed of a mixture of ferrite and pearlite. During cooling, ferrite starts to form from austenite. The ferrite contains essentially no carbon. As the ferrite forms, it leaves behind an increasing concentration of carbon in the remaining austenite. The excess carbon is eventually ejected from austenite. Under normal circumstances, the excess carbon combines with iron to form iron carbide (Fe_3C), called "cementite." If the austenite cools relatively slowly, as in air cooling, pearlite forms. Pearlite consists of a binary mixture of ferrite and cementite. The structure of pearlite is lamellar, consisting of very fine, alternating layers of ferrite and cementite. Thus, the gross microstructure of normal carbon steels consists of a mixture of ferrite and pearlite. See Figure 2-4 for the microstructure of a typical ferrite-pearlite carbon steel in the normalized condition.

3. Metallurgical Terms

The terms defined in this section are frequently used in this book and in many purchasing specifications. Other, less frequently used terms are defined as

necessary in the text. For a more complete dictionary of metallurgical terms, see reference [2].

Base Metal

Used interchangeably with the term *parent metal*, this term refers to the material of the components in a weldment, to differentiate such material from the *weld metal* and the *heat affected zone* of the base metal.

Carbon Equivalent

Carbon equivalence is used in evaluating the weldability of a carbon steel. There are many different formulas used to calculate the carbon equivalent (CE) value, the most common being:

$$CE = C + Mn/6 + (Cr + Mo + V)/5 + (Ni + Cu)/15$$

where the concentration of each element is expressed in wt. percent.

The primary uses of CE values are for evaluating the risk of developing hard, heat affected zones and the susceptibility of the weldment to delayed hydrogen cracking. Table 2-1 shows typical limits for carbon steels.

When the maximum allowed CE value is exceeded, additional fabrication measures such as preheat, postweld heat treatment and/or inspection for the effects of delayed hydrogen cracking are usually necessary.

Cold Working

When a metal is stressed above its yield strength, plastic deformation occurs. Such deformation raises the internal energy of the material. The mechanism of energy storage involves creation of distortions in the crystal structure of the material. In terms of thermodynamics, this is an increase in unit entropy. Cold working involves plastic deformation at relatively low temperatures. (In reference to cold work, "low" refers to ambient temperatures up to several hundred degrees for most of the common materials of construction.) The effects of deformation are irreversible, unless the material is subsequently subjected to heat treatments such as

Table 2-1 Typical carbon equivalent limits for carbon steels

Wall Thickness	1/2" 12.7 mm	5/8" 15.9 mm	3/4" 19 mm	7/8" 22 mm	1.0" 25.4 mm
Max. CE Value	0.40	0.39	0.37	0.35	0.34

normalizing or solution annealing. The term *cold working* has been given to this phenomenon. Cold-worked materials have increased yield strengths and reduced ductilities; such materials are sometimes said to have been *strain hardened*.

In some applications such as bolting that will not be exposed to crack-inducing agents, cold working is deliberately used to obtain increased yield strengths. However, cold worked areas are typical sites for the development of strain ageing (see Part 1 of Chapter 3 for a discussion of strain ageing, an embrittlement mechanism). In addition, cold worked areas can be susceptible to corrosion pitting, stress corrosion cracking, hydrogen embrittlement and other damaging phenomena. For applications in which excessive cold working may be harmful, it is normal practice to stress relieve materials that have received more than five percent permanent strain.

Elastic and Plastic Deformation

Plastic deformation is caused by a stress that exceeds the yield strength of the material. Deformation at stresses less than the yield strength is called elastic deformation. Elastic deformation is reversible, that is, the deformation disappears with the removal of the stress. Plastic deformation (sometimes called *permanent strain*) is permanent, i.e., the deformation remains after removal of the stress that caused it.

Galling

Galling is related to adhesive wear. When two metals of similar chemistry and hardness are in moving contact and under pressure, in the absence of lubrication, surface asperities tend to momentarily weld together. Continued movement ruptures these very local welds, resulting in metallic particles being torn from one or both surfaces. The welding, generation of particle debris trapped between the two surfaces and small cavities produced by tearing results in rapidly increasing friction.

Austenitic stainless steels are the most common materials susceptible to galling. Examples include threaded fasteners (galling occurs in the threaded region) and valve closures.

Hardenability

Hardenability is used to describe the ability of an alloy to be hardened and strengthened, usually by heat treatments such as quenching and tempering. The term is also used to describe alloys that can be hardened and strengthened by cold working, for example, strain-hardened bolting.

Heat Affected Zone

A heat affected zone (HAZ) is a volume of the parent metal in which the mechanical properties and/or the microstructure have been changed by the heat of

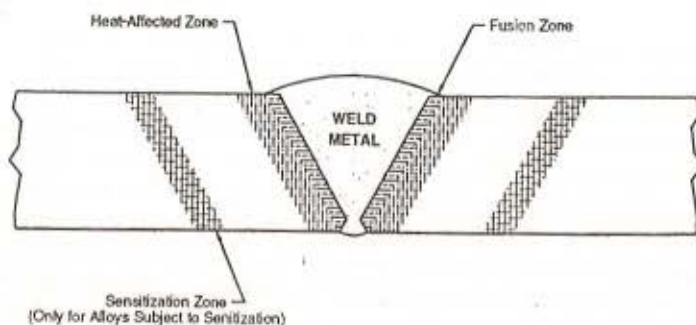


Figure 2-5 Illustrating the typical features of a weld.

welding, or thermal cutting. For most welds in carbon and low-alloy steels, the HAZ is a band, usually about 1/8" (3 mm) wide, adjacent to the fusion line of the weld. In austenitic stainless steels, a narrow, secondary HAZ may be generated at some distance from the fusion line, as a result of welding-induced sensitization. This effect is illustrated in Figure 2-5.

Hot Working

Hot working describes plastic deformation occurring at a temperature hot enough to prevent the material from becoming strain hardened. Instead, it spontaneously "recovers" plastic deformation. Hot-worked materials therefore do not have the stored energy characteristic of cold-worked materials.

The academic definition of the temperature necessary to spontaneously recover plastic deformation is unusable. In the real world, hot-work temperatures are dictated by factors such as tool life. These temperatures range from as low as 350°F (175°C) for aluminum alloys to as high as 2300°F (1260°C) for steels and nickel alloys. Such temperatures exceed the academic definition of the temperature needed to recover plastic deformation spontaneously.

Product Form

The common product forms are plate, strip, sheet, wire, pipe, tubing, bolting, bars, forgings, extrusions and castings.

Toughness

Toughness is the ability of a material to deform plastically and absorb energy before fracturing. It can be thought of as the energy per unit area necessary to create a fracture. Obviously, a material that requires a great deal of energy to create fracture surfaces is very resistant to fracture.

Toughness is usually measured by the energy absorbed during an impact test. The most common example of such a test is the Charpy V-notch impact test (see ASTM A370).

Weldment

A weldment is an assembly whose component parts are joined together by welding.

B. ALLOY DESIGNATIONS

It is common practice to refer to alloys by a standardized numbering system, called the Unified Numbering System [3,4]. The UNS numbering system incorporates many earlier alloy identification systems which were developed for particular alloy families such as those for aluminum and copper alloys. Use of the UNS permits one to discuss and/or recommend an alloy without becoming entangled with the rules and regulations that surround proprietary alloys. This system will be referred to extensively. However, in cases where the ordinary alloy designation is nonproprietary and is in common use, such as the 300-series stainless steels, the ordinary alloy designation is used instead of the UNS number.

Without referring to the specific UNS listing, one cannot easily determine the composition of an alloy simply from its UNS number. In order to assist the reader, the nominal composition of the alloy is listed the first time the alloy is mentioned in a chapter. All alloys referenced by UNS number are listed in Appendix 12, which also lists the nominal composition of each alloy.

C. MANUFACTURING EFFECTS

Metals and alloys are available in two primary forms: *wrought* and *cast*. Products created by other methods such as powder metallurgy are not common enough in chemical and hydrocarbon plants to warrant inclusion in this discussion.

Wrought products are formed from solid metal, usually while hot. Wrought processes generally employ compressive forces, which may be either continuous or cyclic, with or without dies. Examples of wrought processes include rolling, forging, extrusion and drawing. Product forms include plate, pipe, tubing, sheet, wire, forging, extrusions, and bars.

Wrought products may or may not be heat treated as part of the manufacturing process. Note that terms such as "hot finished" or "hot rolled" are usually not regarded as substitutes for heat treatment. If the materials selection process indicates a heat treatment requirement, check the purchasing specification to see if the product is supplied in the heat-treated condition or if heat treatment must be indicated as a supplemental requirement.

Castings are products formed by solidification of a liquid in a mold. (Welds are an unusual form of casting.) Virtually all wrought products begin as castings, usually in the form of ingots. Castings dominate product lines such as pump cases, where geometry favors the simplicity of castings.

Almost all castings are heat treated as part of the manufacturing process. Occasionally, a casting requires repair welding, as part of either a fabrication or maintenance procedure. Postweld heat treatment (or solution annealing in the case of austenitic stainless steels) may be indicated. However, such heat treatments can warp previously machined surfaces. Special welding procedures, hardness controls, shot peening, etc., may be used to avoid heat treatment. In some cases, heat treatment cannot be avoided. To avoid or minimize warping, special fabrication measures such as use of strong-backs or bracing are employed.

Most metals and alloys are available in either wrought or cast form. However, the cast chemistry is often somewhat different, usually containing more silicon than the wrought form. Silicon improves the "pourability" of the liquid alloy; there may be other minor differences between the two chemistries. Some alloys are available only in cast form, as they are too unstable or brittle to be formed by wrought methods. There are a few alloys that are provided only in wrought form. Typically, an alloy in cast form has a different name from its wrought counterpart, for example, Grade CF-8 is the cast version of Type 304 SS.

Wrought products are usually preferred to castings. The hot-forming procedures characteristic of wrought products tend to break up and weld shut defects in the ingot, while such defects remain present in castings. In addition, the plastic deformation used to form wrought products, plus the reheating involved in hot processing, tends to produce a uniform, fine, partially isotropic grain structure. However, wrought products are normally more expensive than their cast counterparts, reflecting the fabrication costs of hot working, machining, welding, etc.

Castings typically have lower strength, lower toughness, higher defect concentrations and coarse anisotropic grain structures. Their advantages include relatively low cost, ease of obtaining complex shapes and minimal machining. In some alloys, the silicon addition and/or cast grain structure produces exceptional corrosion resistance. For example, austenitic stainless steel castings are more resistant to chloride stress corrosion cracking than are their wrought equivalents.

Castings are often less weldable than their wrought equivalents, usually because of their greater silicon and/or carbon contents. Thus, repairability may be an issue in materials selection for castings. In some cases, repairability may be enhanced by careful chemistry selection. A common example is the use of CA-6NM (12Cr-4Ni-Mo; UNS J91540) instead of CA-15 (13Cr; UNS J91150) for 12 Cr castings.

Choosing between wrought and cast components is rarely an issue. When the issue does arise, the decision will usually favor either the greater safety or repairability of the wrought product or the lower cost or a unique property of the cast product.

D. METALS AND ALLOYS

1. Cast Irons

Cast irons differ from cast carbon steels primarily in carbon content. Cast irons typically contain at least two wt. percent carbon, while the cast carbon steels commonly used for plant construction rarely contain more than 0.35 percent. The high carbon content of cast iron makes the material difficult, at best, to weld. Two types of cast iron are commonly used:

1. *Gray cast iron* such as ASTM A48 material is plain cast iron. These materials are composed of ferrite containing graphite stringers, with no intentional alloying additions. Figure 2-6 shows the microstructure typical of gray cast iron. This material is brittle and is usually restricted to applications in which toughness is not a concern. Gray cast iron is rarely used in most plant processes.

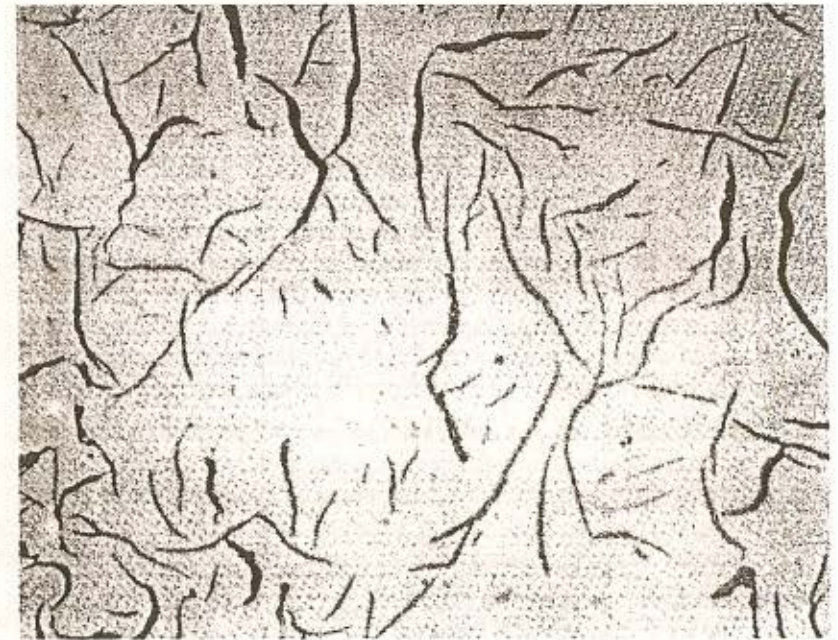


Figure 2-6 A typical gray cast iron microstructure. (Courtesy of Dr. E. V. Bravenec, Anderson & Assoc.)

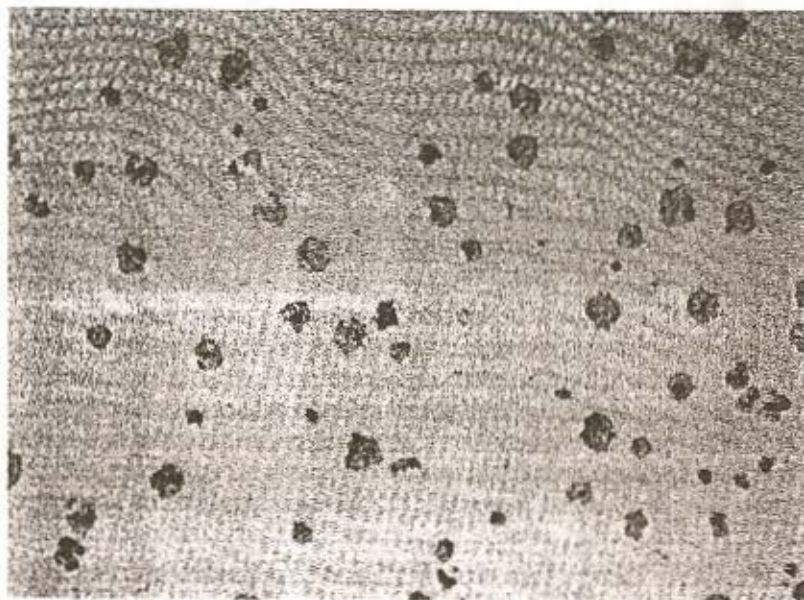


Figure 2-7 A typical ductile cast iron microstructure. (Courtesy of Dr. E. V. Bravenec, Anderson & Assoc.)

2. Ductile cast iron (also known as nodular or spheroidal iron) contains a small magnesium addition, which greatly improves ductility and toughness. An example is ASTM A536. The magnesium addition is responsible for the nodularity of the graphite. Figure 2-7 shows the microstructure typical of ductile cast iron. Nodular cast iron is occasionally used in valve bodies and in pumps in various utility services, and in large reciprocating compressors. Malleable cast iron such as ASTM A47 material is a related alloy. The graphite nodules are formed as a result of heat treatment.

Mildly acidic water can *graphitize* both gray and ductile cast irons. Used in this context, graphitization is a corrosion mechanism in which the iron is slowly leached from the casting, leaving behind a network of graphite (Figure 2-8). The graphitized casting loses almost all of its mechanical strength and eventually leaks or ruptures. Many old underground cast iron water mains eventually require replacement because of graphitization.

Three specialty cast irons are occasionally employed. Corrosion- and erosion-resistant *silicon* cast irons such as those of ASTM A518 find use in acid and abrasive services. *White* cast irons such as those of ASTM A532, containing up to 25 percent chromium, are used in highly abrasive services such as pumping abras-



Figure 2-8 "Graphitization" of a gray cast iron pipe, caused by long-term service in slightly acidic water.

ive slurries. Nickel-rich cast irons, known as *Ni-Resist* cast irons (such as those of ASTM A436), find use in both low- and high-temperature applications, services requiring resistance to wear and as seawater alloys.

Cast iron is normally not permitted for pressure containment components in hydrocarbon processing streams because of its brittleness, especially in areas where it could be quenched during the course of fighting a fire. However, cast irons are routinely used in many services for internal components such as pump impellers.

Most cast irons cannot be repaired by welding. Thus, repairability sometimes precludes the selection of cast irons as materials of construction.

2. Carbon Steels

Carbon steel is the most widely used material of construction in most plants. Unalloyed carbon steels typically contain nominal amounts of manganese, silicon, phosphorus and sulfur. They do not contain deliberate alloying additives such as nickel, chromium or molybdenum, or microalloying elements such as niobium, titanium or vanadium. These steels are normally supplied with a pearlitic-ferritic microstructure (see Figure 2-4). This microstructure is produced by air cooling a hot-formed product (e.g., hot-rolled plate) or by a normalizing heat treatment.

Carbon steel is commonly available in two forms: killed carbon steel or plain carbon steel.

Killed Carbon Steel

Raw liquid steel is saturated with oxygen in the form of both dissolved gas and as iron oxides. The oxygen can combine with carbon, also dissolved in the liquid steel, to form carbon monoxide. This reaction can cause violent boiling during the pouring and solidification processes. By adding an oxygen scavenger such as silicon to the liquid steel before it is poured, the excess oxygen can be removed as slag. The resulting material does not boil during pouring and cooling, thereby producing a more homogeneous "killed" steel. Such steels are cleaner and contain fewer defects than "unkilled" or "wild" steels. ASTM A106 pipe, A105 forgings and A516 plate are examples of killed carbon steel products. Cast carbon steel products are also killed, even though typical ASTM specifications for castings do not mention the requirement.

Killing with an oxygen scavenger such as silicon is the primary method of deoxidation. A less common method is vacuum degassing, which is usually a secondary measure, employed when very clean steels are required. Vacuum degassing not only assists in controlling oxidizing gases such as oxygen and carbon dioxide, but will help to limit non-oxidizing gases such as nitrogen and hydrogen.

Steels killed with silicon, such as ASTM A515 plate, tend to have a coarse grain structure. Such steels usually have silicon present in the range of 0.15 to 0.30 wt. percent. These steels characteristically have relatively high brittle-ductile transition temperatures, making them unsuitable for applications requiring low-temperature toughness. However, the coarse grained steels are more resistant to creep, graphitization and some forms of corrosion, making them preferred for some applications.

Steels killed with a combination of silicon and aluminum or aluminum alone have a fine austenitic grain size. They are preferred for applications requiring low temperature toughness; ASTM A516 (plate) is an example. Such steels are usually described in ASTM specifications as being made to "fine grain practice." Although ASTM specifications for steel products usually do not indicate a requirement for aluminum content, steels killed with aluminum will have aluminum present in the range of 0.02 to 0.05 wt. percent.

Plain Carbon Steel

The terms *semikilled*, *rimmed* and *capped* are used to refer to steels that have been partially deoxidized or not deoxidized at all. Many product forms are available for such steels. Examples of specifications include ASTM A53 and API 5L [5] for pipe and ASTM A36, a structural steel specification.

Although plain carbon steels are often permitted in benign services such as chemically treated utility water or air lines, killed carbon steel is generally used instead. There are at least three reasons for this preference:

1. There is virtually no cost difference between the killed carbon steels and plain carbon steels used in plant construction. Killed carbon steel is usually preferred because of its lower defect density and higher maximum code-allowable stress at higher service temperatures.
2. Commonly used purchasing specifications such as ASTM A53 for pipe permit the substitution of killed for plain carbon steel. Such substitution is becoming increasingly common.
3. Many construction projects want to avoid the unintentional substitution at the job site of unkilled for killed steel. By stocking only killed steel at the job site, such unintentional substitutions are avoided.

3. Microalloyed Steels

Microalloyed steels (sometimes called high-strength, low-alloy steels, or HSLA steels) form a family that is intermediate between carbon steels and low-alloy steels (discussed in the following section). These are killed steels that contain small amounts of elements such as vanadium, titanium and niobium. The combined total of such additions is usually about 0.1 wt. percent or less. These elements modify the microstructure and refine grain size, that is, they encourage the formation of a relatively small and uniform grain size. The microalloying additions improve toughness and strength (typical specified minimum yield strengths are 60 ksi (410 MPa), or higher). These steels are usually used in applications where section thickness or gross weight is a concern, for example, in large-diameter, long pipelines where pipe tonnage is a major cost factor. Such steels are also sometimes selected for applications in which improved toughness is a requirement. Most such applications are for plate steels used for improved piping and vessel toughness. Microalloyed steels require some care in selecting weld joint geometries and welding procedures.

Microalloyed steels have a tendency to produce excessively hard heat affected zones, increasing their susceptibility to various forms of hydrogen stress cracking. If the intended service does not involve the threat of hydrogen stress cracking, hard heat affected zones are usually not regarded as a concern. The risk of producing a hard heat affected zone is determined to some extent by the geometry of the weld joint. Double-sided welds such as those preferred for vessels are much more likely to produce hard heat affected zones than single-sided welds such as those normally used in piping and pipelines. In multiple-pass, single-side welds, the previously deposited bead weld is subsequently tempered by the following bead(s). Thus, pipe welds are usually much less likely to retain hard heat affected zones than are vessel welds.

The common carbon steels used in piping and vessel construction are permitted by ASTM specifications to contain unreported levels of microalloying elements that are capable of producing excessive heat affected zone hardnesses. Thus, it occasionally happens that a carbon steel weldment of a conventional carbon steel will contain small regions in the heat affected zone having excessive hardness. The present state of the art in hardness testing is incapable of detecting

hard heat affected zones in production welds. At present, there is no effective means to address this problem other than to require weld procedure testing on materials intended for actual construction. Even this requirement does not totally eliminate the problem unless all heats of steel intended for welded construction are so tested. This measure can be costly and can affect delivery schedules; it is therefore rarely used. Experience supports accepting the present situation, since few incidents of harmful effects have been reported.

Some users either prohibit the purchase of deliberately microalloyed carbon steels or place limits on both the carbon equivalent and the microalloying content of such steels. The permitted microalloying limits vary from user to user, but usually fall in the range of 0.03 to 0.10 for the sum of the concentrations of Ti, V and Cb¹ (each expressed in weight percent). Alternatively, as mentioned above, weld procedure qualification tests can be required to show that excessive weld hardness is not a problem. However, satisfactory results may require preheat and/or postweld heat treatment. Refer to NACE RP0472 [6] for a discussion of the effects of microalloying additions and mitigation measures. ASTM A737 plate and ASTM A714 pipe (and API 5L pipe, grades X56 and higher) are examples of microalloyed products.

4. Low-Alloy Steels

Low-alloy steels are defined as iron-based alloys containing less than 12 percent intentional alloying elements. Note that all low-alloy steels are killed. Alloying is used to either enhance mechanical properties or improve corrosion resistance.

Alloying for Improved Mechanical Properties

Alloying can substantially improve mechanical properties such as strength, toughness and fatigue resistance. Such steels are normally heat treated to enhance their properties. Note that welding on these alloys can degrade their properties unless the weldment is properly heat treated.

Low alloy Cr-Mo steels such as 1Cr-½Mo and 1¼Cr-½Mo steels are often used instead of carbon steel for temperatures above 800°F (425°C). (Carbon steels become susceptible to creep at temperatures above about 750°F (400°C). In addition, carbon steels weaken by carbide spheroidization and/or graphitization if exposed to sustained temperatures exceeding about 850°F (455°C). Refer to Part 2 of Chapter 3 for a discussion of these phenomena.

The mechanical properties of several of the Cr-Mo low-alloy steels have been improved with the addition of vanadium. Examples include vanadium-enhanced

¹The element niobium is often called columbium (Cb) in engineering applications.

1Cr-1Mo for turbine rotors and vanadium-enhanced 1Cr-½Mo bolts, widely used for temperatures up to 1100°F (595°C).

Alloys such as AISI 4140 steel (1Cr-0.2Mo, with carbon between 0.37 and 0.49; UNS G41400) are widely used as rotating equipment shafts, bolts, high-strength forgings, etc.

Ni-Mn (with either 3½ or 9 Ni) alloys are used for moderately low temperature services, in the range of -50 to -320°F (-46 to -195°C). They are commonly used in liquefied petroleum gas (LPG) and liquefied natural gas (LNG) plants. (See ASTM A203, A333, A334, A350, A352 and A420 for various product forms of these materials.)

Note that 3½ Ni steel forgings have a reported history of welding problems in which the parent metal adjacent to the heat affected zone tends to develop crack-like fissures after welding. The cause has not been determined. Prudence suggests avoiding this material. Type 304L SS, while more costly as a material, may result in a lower fabricated cost by avoidance of welding problems.

A variety of enhanced strength plate steels are used primarily in pressure vessels for high-pressure applications in which the use of conventional carbon steels would require excessive wall thickness. Postweld heat treatment is usually mandatory for these materials. See ASTM A302, A537, A542 and A543 for examples of plate materials of this class.

Alloying for Improved Corrosion Resistance

The most common family of corrosion-resistant low-alloy steels in use in chemical and hydrocarbon plants is based on chromium and molybdenum additions. The lowest of these alloys, 1Cr-½Mo and 1¼Cr-½Mo, are often used instead of carbon steel for temperatures above 800°F (425°C). In addition, the low-alloy Cr-Mo steels (with Cr ≥ 5 percent) are useful for their resistance to high-temperature sulfidic corrosion. However, the Cr-Mo alloys find their most critical use in high-temperature, high-pressure hydrogen service. The Cr and Mo additions stabilize the carbides against attack by dissolved high-temperature hydrogen. The most commonly used of these alloys for high-temperature, high-pressure hydrogen service are the 1¼Cr-½Mo, 2¼Cr-1Mo and 3Cr-1Mo steels. Vanadium-enhanced versions of the 2¼Cr-1Mo and 3Cr-1Mo alloys have been developed for heavy-wall vessels. The vanadium-enhanced alloys are finding increasing acceptance for severe services, since they can provide substantially reduced wall thicknesses.

9Cr-1Mo is available as piping but is not commonly used in vessel construction. A vanadium-enhanced version has been developed for use in heavy-wall vessels, primarily intended for use in high-pressure, high-temperature hydrogen service.

- ASME B31.3 [7] provides maximum allowable stresses for 9Cr-1Mo tubing, piping, fittings, plates and castings.

- ASME Section VIII, Div. 1 and Div. 2 [1] does not provide maximum allowable stresses for 9Cr-1Mo plate material. Div. 1 does provide maximum allowable stresses for 9Cr-1Mo-V plate material, but it is rarely used for pressure vessels.

All of the Cr-Mo alloys are air hardenable; they usually require postweld heat treatment. (See ASTM A182, A199, A217, A335, A336, A387, A541 and A739 for various product forms of these materials.)

- Another relatively common class of low-alloy steels employed for their corrosion resistance is "weathering" steels, many of which are also classified as HSLA steels. These steels commonly have small chromium and copper additions that help the steel to form a stable patina-type rust in mildly corrosive atmospheres. These steels find use primarily in structural applications. See ASTM A242, A588 and A618 for various product forms.

5. High Alloys

Stainless Steels

Straight Chromium Stainless Steels

The cheapest alloys in this class are the 12 Cr stainless steels. Typical examples are Type 405 SS and Type 410 SS. They are used for their corrosion resistance, particularly in wet CO₂ and in hot (>500°F (>260°C)) services containing organic sulfur compounds or hydrogen sulfide.

Types 405, 410S and 410 SS are the most commonly used grades of straight chromium stainless steels in the hydrocarbon and chemical process industries. Type 410 SS (a martensitic alloy) is used only when welding is not required. When welding is required, either Type 405 SS or Type 410S SS is specified.

All of the 400-series stainless steels are subject to grain coarsening in weld heat-affected zones. Martensitic grades, being air hardenable, can also produce very brittle heat-affected zones. Consequently, none of the straight chromium stainless steels are usually recommended for primary pressure containment. Their major use is in heat exchanger tubing, valve and pump internals, vessel internals and as clad or weld overlayed linings in pressure vessels and heat exchangers.

All of the 400-series alloys are essentially immune to chloride stress corrosion cracking. Unfortunately, none of the straight chromium stainless steels are very resistant to chloride pitting. Accordingly, these alloys are rarely used in systems subject to chloride pitting. However, a series of "superferritic" stainless steels, containing up to 29 percent chromium and 4 percent molybdenum, are now available. Some of these alloys also contain up to about 4 percent nickel without affecting their ferritic microstructure. One example is 25Cr-4Ni-4Mo (UNS S44635). These alloys have satisfactory resistance to chloride pitting and chloride stress corrosion cracking in all but the most severe services.

Stabilized superferritic alloys, resistant to sensitization, are also available, for example, 26Cr-3Ni-3Mo, stabilized with niobium and titanium (UNS S44660).

The higher chromium grades such as Type 430 SS are susceptible to "885°F (475°C) embrittlement" at temperatures above about 750°F (400°C). Refer to Part 1 of Chapter 3 for a discussion of this form of embrittlement. 885°F (475°C) embrittlement is usually mild in the straight 12 Cr grades but can become severe in grades having a chromium content of 15 percent or more. It has become industry practice to avoid the use of any of the straight chromium stainless steels for pressure containment at temperatures exceeding 650°F (345°C). The higher chromium grades should not be used for any purpose at temperatures above 650°F (345°C) unless their subsequent embrittlement is of no concern.

All of the ferritic and martensitic stainless steels are susceptible to hydrogen stress cracking phenomena such as sulfide stress corrosion cracking. In addition, these steels are susceptible to both hydrogen embrittlement and low-temperature embrittlement. If sensitized, these steels can also be susceptible to intergranular corrosion. For a discussion of this problem, refer to Part 2 of Chapter 3.

Austenitic Stainless Steels

The 200-series austenitic Cr-Mn-Ni stainless steels (exemplified by Types 201, 202 and 216) are generally as corrosion resistant and are stronger than their better-known 300-series Cr-Ni cousins. While these alloys may find occasional use, usually as vessel internals, the 200-series alloys are uncommon in chemical process or hydrocarbon plants, reportedly because of fabrication problems. In addition, they are not commonly available from alloy suppliers and have very limited availability in product forms other than bar, plate and sheet. In addition, most fabricators have little or no experience with them. As a consequence of the lack of use of the 200-series, the term "austenitic stainless steel" has come to mean the 300-series Cr-Ni alloys such as Type 304 SS. Sometimes called the "18/8s" (representing a nominal 18Cr-8Ni composition), the 300-series austenitic stainless steels are the workhorses for corrosion resistance in industry. Figure 2-9 shows a typical austenitic stainless steel microstructure. These alloys provide superior corrosion resistance and are capable of higher temperature service than are the straight chromium grades. The 300-series find extensive use as internals, cladding and overlays in vessels exposed to corrosive services. They are also widely used in pumps, valves and piping.

The austenitic stainless steels do not air harden and thus do not require postweld heat treatment as a hardness control measure. They are sometimes stress relieved or postweld heat treated to reduce residual stresses, thereby improving their resistance to stress corrosion cracking. In some cases, the austenitic stainless steels are chosen in preference to the Cr-Mo low-alloy steels because postweld heat treatment can be avoided. (Note that dissimilar metal welds involving austenitic stainless steel may be air hardenable.)

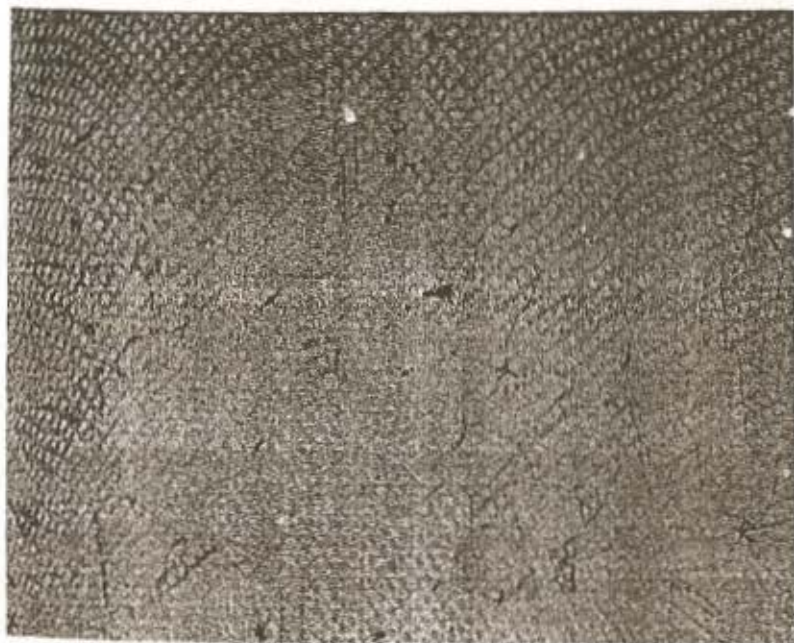


Figure 2-9 A typical solution annealed austenitic stainless steel microstructure.

The low-carbon grades such as Type 304L are preferred for welded construction. In addition, the low-carbon grades or the stabilized grades such as Types 321 SS and 347 SS are specified if sensitization is expected to be a problem.

Type 316 SS (its small molybdenum addition differentiates it from Type 304 SS) is specified when increased resistance to chloride pitting or crevice corrosion is desired. Type 316 SS also has a higher maximum allowable stress than does Type 304 SS. The high carbon H grades such as Type 304H SS are specified for high temperature use ($>1000^{\circ}\text{F}$ ($>540^{\circ}\text{C}$)), since they have a maximum code-allowable stress advantage over the conventional grades. The H grades should be used with caution in services subject to carburization.

Higher chromium-nickel austenitic alloys are used extensively in high-temperature applications such as heaters, in both cast and wrought form. Examples include Type 310 stainless steel (25Cr-20Ni), the Alloy 800 series (20Cr-32Ni, with Ti and Al; UNS N08800, N08810 and N08811), HK-40 (a casting, 25Cr-20Ni; UNS J94204) and many proprietary alloys such as the "HP-Mod" materials. These alloys can suffer a variety of problems such as weldment cracking, embrittlement, carburization, nitriding, oxidation and metal dusting. (These

phenomena are discussed in Chapter 3, "Failure Modes.") Their selection should be undertaken only if one is familiar with industry experience.

Galling is sometimes a problem with austenitic stainless steels. Aside from the use of lubricants and coatings (TFE is effective), the most common way to avoid the problem is to require that the two mating surfaces have a hardness difference of at least 50 BHN. In components such as valve closures, the hardness differential is usually obtained by using a hard face weld overlay or electroless nickel plating on one of the two components. In threaded connectors, the hardness differential is usually obtained from cold working one of the components. Sometimes the hardness differential is obtained by specifying the two components in different materials having appropriately different hardnesses. Galling may also be mitigated by specifying one component to be a free machining grade such as Type 303 SS. Note that NACE MR0175 [8] does not allow free machining grades in wet sour service.

The major difficulty with conventional austenitic stainless steels is that they are susceptible to chloride stress corrosion cracking. In many cases, the risk of chloride stress corrosion cracking is too large to permit the use of an ordinary austenitic stainless steel. In such cases, the following specialty alloys are usually selected:

- Ferritic stainless steels such as Type 430 SS; note that such materials are subject to chloride pitting. Accordingly, they are selected only for services in which the risk of such pitting is low, for example, clean, flowing saline waters. Alternatively, superferritic grades may be selected.
- Ni-Cu alloys such as Alloy 400 (67Ni-30Cu; UNS N04400).
- "Superaustenitic" alloys; these are austenitic alloys with high chromium and nickel, as well as 2–6 wt. percent molybdenum. Alloy AL-6XN (21Cr-25Ni-6.5Mo-N; UNS N08367) is an example of a superaustenitic stainless steel.
- Nickel alloys such as Alloy 825 (22Cr-42Ni-3Mo, Ti stabilized; UNS N08825).
- Duplex austenitic-ferritic alloys such as Alloy 2205 (22Cr-5Ni-3Mo-N; UNS S31803).

Note that cast austenitic alloys are much less susceptible to chloride stress corrosion cracking than are their wrought equivalents. Accordingly, cast austenitic stainless steel valve bodies and pump casings are often useful in services in which higher alloys are necessary for the wrought components (pipe, tubing, fittings, plate, etc.).

Unless heavily cold worked, the austenitic stainless steels are essentially immune to hydrogen stress cracking such as that caused by hydrogen sulfide. They are also relatively immune to hydrogen embrittlement caused by phenomena other than cathodic charging. If sensitized, austenitic stainless steels can also be

susceptible to intergranular corrosion. For a discussion of this problem, refer to Part 2 of Chapter 3.

Duplex Stainless Steels

These steels contain both ferrite and austenite in approximately equal amounts; Alloy 2205 is an example. Figure 2-10 illustrates the microstructure of a duplex stainless steel microstructure. Typically, such steels contain 17 percent or more chromium and less than 7 percent nickel. The more corrosion-resistant types contain a molybdenum addition of at least 2 percent. They are much stronger than the austenitic stainless steels, permitting a thinner section thickness. Thus, while they may cost more per *pound*, they may cost less per *piece*.

With the desired microstructure, these alloys have great resistance to hydrogen stress cracking. They are much more resistant to chloride stress corrosion cracking than are the conventional austenitic stainless steels. (The threshold temperature for chloride stress corrosion cracking of duplex alloys in neutral pH aqueous chlorides is on the order of 300°F (150°C).) Some data indicate that the chloride stress resistance of the duplex alloys is about the same as that of the superaustenitic alloys



Figure 2-10 The microstructure of a typical duplex stainless steel. (Courtesy of Dr. E. V. Bravenec, Anderson & Assoc.)

such as Alloy AL-6XN. However, the threshold values for hydrogen stress cracking and chloride stress corrosion cracking have not been defined as well for the duplex alloys as they have for the austenitic stainless steels. Because they contain about 50 percent ferrite, the duplex stainless steels are susceptible to hydrogen embrittlement.

Experience has shown that special precautions must be taken when welding duplex stainless steels, as the welds can vary considerably from the desired microstructural balance. When they do vary, they can become susceptible to chloride stress corrosion cracking and/or to hydrogen stress cracking. Because of welding and other manufacturing problems, duplex stainless steel construction is usually more costly than construction with conventional austenitic stainless steels.

Precipitation-Hardening Stainless Steels

The designations of these alloys end with the suffix "PH" (i.e., Precipitation Hardening), for example, 17-4 PH (17Cr-4Ni-4Cu; UNS S17400). These alloys are hardenable by heat treatment and are relatively easy to fabricate. They are most often used for springs, valve stems, the internals of rotating equipment and other applications where both high strength and superior corrosion resistance are desirable. These alloys offer corrosion resistance superior to the 12Cr stainless steels but are somewhat inferior to Type 304 SS. The precipitation hardening alloys can be susceptible to both chloride stress corrosion cracking and hydrogen stress cracking.

Nickel Alloys

Nickel and nickel alloys are commonly used in a wide variety of services including acids, caustics, corrosive waters, numerous corrosive process applications and for low- and high-temperature applications. Many of these alloys are available in most, if not all, product forms. Nickel alloys are frequently used for applications in which product contamination cannot be tolerated.

Many nickel alloys have been developed for special applications:

- Commercially pure nickel (Alloy 200; UNS N02200) is resistant to high-purity hot caustic. The low-carbon version (Ni 201; UNS N02201) has a lower maximum code-allowable stress but is code-permitted at higher temperatures.
- Electroless nickel plating (often referred to as ENP) is sometimes used in process industries to avoid product contamination by substrate carbon steel. It is also used to prevent galling and to enhance tight sealing in valve closures. Refer to the section entitled "Thin Metallic Barrier Coatings" (p. 103) for a discussion of ENP.
- Even a few percent nickel profoundly improves toughness. Examples: 3½Ni, a low-alloy steel, is routinely used for service temperatures down to

-150°F (-100°C); the 300-series stainless steels (18Cr-8Ni family) are used for cryogenic applications, to temperatures approaching absolute zero.

- Alloys containing a minimum of about 45 percent nickel are regarded as being essentially immune to chloride stress corrosion cracking even under severe conditions.
- Alloy 400, a nickel alloy containing about 30 percent copper and a small amount of iron, is a premium alloy for seawater, brine, alkalis and reducing acid services. It is available in a precipitation-hardenable form (UNS N05500), which is often used for high-strength applications such as pump shafts. Alloy 400 is commonly used in processes that include dilute, reducing hydrochloric acid, for example, the overhead system in atmospheric crude distillation units.
- Ni-Resist is a family of austenitic cast irons containing 13-35 percent nickel, usually with copper and/or chromium additions; see UNS F41000 for an example. They are widely used for wear resistance, corrosion resistance, and both low- and high-temperature services.
- Nickel-molybdenum alloys, such as Alloy B-2 (Ni-28Mo; UNS N10665), are resistant to severe reducing acids such as concentrated hot hydrochloric acid.
- In combination with chromium and molybdenum additions, nickel alloys are resistant to a wide variety of oxidizing acids. Alloy C-276 (15Cr-54Ni-16Mo; UNS N10276) is an example. Derivative alloys containing a tungsten addition are regarded as premium alloys for such applications. Alloy C-22 (22Cr-58Ni-13Mo-3W; UNS N06022) is an example.
- Stabilized nickel alloys such as Alloy 625 (22Cr-58Ni-9Mo; UNS N06625) and Alloy 825 are useful in applications requiring resistance to both chloride stress corrosion cracking and polythionic acid attack.
- High-temperature wrought alloys such as Alloy 800 are used in applications such as furnace tubing and crossover piping. Cast alloys such as the proprietary HP-modified alloys (25Cr-35Ni, with niobium and often with other microalloying agents) are also widely used in high-temperature applications such as furnace tubes. The key advantages of these high-temperature alloys are their creep resistance and relatively large high-temperature maximum code-allowable stresses.

Nickel alloys are subject to a variety of failure mechanisms, including sulfidation, high-temperature intermetallic phase embrittlement, stress corrosion cracking and various forms of corrosion. Failure mechanisms and their corresponding threshold values tend to be alloy-specific.

From this brief description, it can be seen that nickel alloys are useful for a very wide variety of purposes. Some of their uses are indicated in subsequent sections on high-temperature effects and corrosion. However, a complete description of the available alloys is well beyond the scope of this book. The user

is advised to contact an alloy specialist or the Nickel Development Institute for further information regarding specific applications.

Nickel Development Institute
214 King Street West, Suite 510
Toronto, Canada M5H 3S6
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Copper Alloys

Brasses and bronzes find extensive use in heat transfer systems exposed to corrosive waters (primarily brackish or saline waters). Naval brasses such as UNS C46400, usually as a cladding on carbon steel, are used for tubesheets and plate components. Inhibited admiralty alloys such as UNS C44300 and the 70/30 (UNS C71500) and 90/10 (UNS C70600) Cu/Ni alloys are often used for piping and heat exchanger tubes. The Cu/Ni alloys are usually preferred, as they have better impingement resistance and can tolerate higher velocities. Aluminum bronzes such as UNS C60800 are relatively high-strength alloys, finding use as pump and valve components. These alloys are available in most, if not all, product forms.

Most copper alloys are unsuitable for processes that contain ammonia, sometimes in even trace amounts. Copper alloys are not suitable for wet sour services because of their lack of corrosion resistance and susceptibility.

Note that many of the brass alloys contain zinc in excess of 15 percent. Unless properly "inhibited" by arsenic, antimony or phosphorus, such alloys can "dezincify" in brackish or saline waters. Some users avoid inhibited alloys; instead, they limit zinc content to less than 15 percent.

For assistance in evaluating copper alloys, contact an alloy specialist or the Copper Development Association for further information.

Copper Development Association
260 Madison Ave., 16th Floor
New York, NY 10016
Tel. (212) 251-7200

Cobalt Alloys

The primary use of cobalt alloys is in hard face applications, in which they are regarded as premium materials; Stellite 6¹ (60Co-29Cr-5W; UNS R30006) is an example. The usual purpose of hardfacing is to improve resistance to abrasion, friction, galling and/or impact. The most common uses of these alloys are in closure

¹Registered Trademark of Deloro Stellite Inc.

applications such as valve seats, where both galling resistance and leak-tightness are required and in abrasive services such as mixers and nozzles. Grinding, requiring wear resistance, is also a common use. Cobalt hard face alloys are typically about as corrosion resistant as the 300-series stainless steels.

Cobalt hard face alloys usually contain 30 to 60 percent cobalt, typically with additions of carbon, nickel, chromium, tungsten, and/or molybdenum. They are applied, usually in one or two layers, by welding or thermal spray processes. The harder, more wear-resistant alloys are difficult to apply without their developing cracks (called "crazing" or "check" cracks). Applied hardnesses are typically in the range 20 to 50 HRC. Some of the alloys can be further hardened by cold work. Hard face alloys can be applied to almost any metallic substrate. Typical finished thicknesses range from 1/16" to 1/4" (1.5 to 6.4 mm).

Selection of hard face alloys is best done by consulting with technical representatives of the manufacturers of these products. Their recommendations are usually based on experience and are tailored for specific applications.

Cobalt-base alloys, in both wrought and cast forms, have also been developed for various high-temperature applications such as gas turbine components and for parts in high-temperature furnaces and kilns. Alloy 25 (55Co-20Cr-10Ni-15W; UNS R30605) is an example.

Reactive and Refractory Metals

These metals and their derivative alloys are oxide stabilized. All of the oxide-stabilized metals are reactive, that is, they become susceptible to oxidation or corrosion if the oxide layer is disrupted. Because of this behavior, these metals and their alloys can display both active and passive behavior. Similarly, they are all subject to catastrophic oxidation under extreme conditions.

The definition of a refractory metal is somewhat arbitrary. For the purposes of this book, refractory metals are defined as metals with melting points greater than that of iron (2795°F (1535°C)).

The most common reactive, non-refractory metal is aluminum. Reactive, refractory metals such as zirconium and tantalum are less commonly used, but they do find applications in severe services such as hot concentrated inorganic acid processes. Most of these metals are relatively immune to corrosion attack in oxidizing environments. However, each of these materials is subject to attack by specific corrodents and/or crack-inducing agents. Accordingly, materials selection should be done on the basis of successful prior experience or as justified by a testing program.

Aluminum (melting point: 1221°F (660°C))

Aluminum is a reactive (but not a refractory) metal. Aluminum alloys are available in a large number of variations, emphasizing properties such as strength, fatigue resistance, toughness and enhanced corrosion resistance. Some aluminum alloys

are hardenable (i.e., strengthened) by heat treatment. Aluminum and most of its alloys have excellent low-temperature toughness, permitting its use in cryogenic applications such as liquefied natural gas (LNG) and liquefied air. Aluminum and its alloys are available in most, if not all, product forms.

Many aluminum alloys have useful corrosion resistance to clean seawater and, in mildly corrosive atmospheres, in applications such as cable trays and as fins on air cooler tubes. They are compatible with a wide range of organic chemicals such as acetic acid. Aluminum alloys are also used for the storage and transportation of many refined chemicals. However, care should be taken in organic applications, since some compounds can vigorously attack some of the aluminum alloys.

There are many applications in which aluminum and its alloys are not suitable materials of construction.

- Because it forms an amphoteric hydroxide, aluminum and aluminum alloys should not be exposed to alkalis. (Amphoteric hydroxides are soluble in alkaline solutions.)
- Aluminum is usually susceptible to aggressive corrosion by acids at a pH of 4.5 or less. A major exception is aerated acetic acid, for which aluminum tankage is used for concentrations up to about 99 percent.
- Many aluminum alloys are susceptible to severe liquid metal embrittlement by mercury, which can be a significant risk in some LNG operations. Liquid metal embrittlement causes cracking very similar to that generated by stress corrosion cracking. Refer to the section entitled "Stress Corrosion Cracking" (p. 177) in Part 3 of Chapter 3 for a discussion of liquid metal embrittlement.
- High-strength aluminum alloys are rarely used in plant operations because of their susceptibility to environmental cracking.
- In common with many oxide stabilized materials such as conventional stainless steels, aluminum and its alloys are susceptible to chloride pitting. Similarly, aluminum and its alloys are also susceptible to concentration cell problems such as crevice corrosion and under-deposit corrosion.

Due to its galvanic activity (aluminum is anodic to most other common metals), aluminum is often used as the sacrificial anode in distributed anode cathodic protection systems. However, for the same reason, care must be taken when using aluminum or its alloys in combination with other metals and/or alloys in corrosive environments. Aluminum components will corrode preferentially to protect less active components such as carbon steels. For example, aluminum fins will corrode to protect steel air cooler tubes if exposed to a wet corrosive environment.

Chromium (melting point: 3375°F (1857°C))

Chromium is regarded as a refractory metal. Neither chromium metal nor chromium-based alloys find much use in the hydrocarbon or chemical process

industries. Chromium plating is useful for aesthetic purposes and finds some use in hard face applications. Chromium is extensively used as an alloy addition to low-alloy steels (usually for the purpose of stabilizing carbides), in cast irons (to produce wear-resistant products) and in nickel alloys (for increased corrosion resistance). Chromium is the main alloying addition in the 400-series stainless steels and is used extensively as a primary alloying addition in the 200- and 300-series stainless steels.

Titanium (melting point: 3034°F (1668°C))

Titanium is a reactive, refractory metal. The most common use of titanium and its alloys in the hydrocarbon and chemical process industries is in heat transfer applications. It is resistant to a wide range of both organic and inorganic corrodents. It finds relatively widespread acceptance as heat exchanger tubing for corrosive processes on one side and corrosive cooling water such as seawater on the other side. Titanium is also commonly used for wet chlorine and for concentrated hot caustic solutions. Titanium usage is becoming more common as it becomes more cost competitive with conventional corrosion resistant alloys such as the 300-series stainless steels.

Titanium can be useful in mildly reducing applications such as wet alkaline sour overhead condensing systems, if they are properly designed and fabricated. However, titanium (and the other reactive and refractory metals) can be unstable in strongly reducing environments. Selection should be based on experience or should be justified by a testing program.

Titanium can become unstable in the presence of powerful oxidizers. Examples include dry chlorine, red fuming nitric acid and liquid oxygen. In addition, titanium can be embrittled by the formation of hydrides (see Part I of Chapter 3 for a discussion of titanium hydriding).

Zirconium (melting point: 3365°F (1852°C))

Zirconium is a reactive, refractory metal. Zirconium and its alloys can be relatively difficult to work, are sensitive to relatively minor welding problems and are expensive. Nevertheless, they can be useful in severe applications. Their most common use is in the chemical process industries, where they are valued for their resistance to hot concentrated alkalis and inorganic acids and in processes in which contamination cannot be tolerated. Zirconium is not suitable for hydrofluoric acid, even in dilute applications.

Zirconium is one of the better metals for handling reducing mineral acids, such as hydrochloric acid and sulfuric acid, where it is resistant up to 70 percent at the boiling point and up to 75 percent at 265°F (130°C). Note, however, that this metal is susceptible to stress corrosion cracking in 64 to 69 percent sulfuric acid at elevated temperatures. Zirconium also resists attack by organic acids such as formic and acetic acids. An advantage of zirconium over nickel alloys is that it can

handle these acids when oxygen or other oxidants are present. Corrosion of zirconium, when it does occur, may produce compounds that are pyrophoric. This can be an ignition source when equipment is taken out of service.

Zirconium is resistant to oxidizing acids such as nitric acid. Its corrosion rate is less than 5 mpy¹ (0.1 mm/yr) in 0 to 70 percent acid at temperatures up to 500°F (260°C). However, it is susceptible to stress corrosion cracking in concentrations exceeding 70 percent.

Zirconium finds its largest use in processes that involve severe formic, acetic, sulfuric, nitric, hydrochloric and phosphoric acid applications. One such application uses 5 percent sulfuric acid at 420°F (215°C) in a process that converts wood chips to ethanol. Another application involves a slurry of aluminum chloride in 36 percent hydrochloric acid at 590°F (310°C). For best corrosion resistance, welded construction should be heat treated at 1425°F (775°C) and cooled rapidly.

Zirconium has greater resistance to caustics than does tantalum. It can be used in batch processes that range from acidic to alkaline over the course of the batch.

Because of its expense, solid metal zirconium construction is used only if no other suitable metals or alloys are suitable. Utilization of zirconium and its alloys is generally confined to clad plate and to thin-wall applications such as heat exchanger tubing or sheet used for "strip lining" or "wall papering." Refer to the section entitled "Thick Metallic Barrier Coatings," (p. 100) for a discussion of these techniques.

Tantalum (melting point: 5425°F (2996°C))

Tantalum is the most expensive refractory metal widely used for corrosion resistance. It is used primarily in chemical process industries. The corrosion resistance of tantalum is often compared to glass, except that it can tolerate higher temperatures. Although it is attacked by hydrofluoric acid and caustics as well as by oleum, sulfur trioxide and chlorosulfonic acid, it is resistant to most other chemicals.

Tantalum is even more expensive than zirconium. Accordingly, its use is mainly in thin-section applications such as bayonet heaters, heating coils, plate heaters or sheet used for strip lining or wall papering. Typical applications include heaters and condensers for organic acid recovery, ammonium chloride concentrators, hydrochloric acid absorbers, bromine condensers and ferric chloride heaters.

E. NON-METALLIC MATERIALS

1. Plastics

Introduction

While metals and alloys remain the primary materials used for construction of chemical and hydrocarbon plants, plastics are used in a number of applications.

¹mpy: mils per year, where a mil is 0.001".

Use of reinforced thermoset plastic (RTP) for vessels is an example. Acceptance of these materials, also known as fiber-reinforced plastic (FRP), was hindered for a long time by lack of an industry standard for the design and fabrication of equipment. This led to a number of vessel failures, which gave the material a reputation for unreliability. In recent years this problem has largely been overcome by the adoption of ASME RTP-1, "Reinforced Thermoset Plastic Corrosion Resistant Equipment" [9] for atmospheric pressure equipment and Class II design rules in Section X of the ASME Boiler and Pressure Vessel Code [1].

Plastic pipe, including thermoplastic, reinforced thermoset plastic and plastic lined steel, has a number of advantages over metal pipe. Very good corrosion resistance can be achieved if the proper plastic is selected. Installation may be less expensive than for ordinary steel construction. Where double containment is required for environmental reasons, plastic pipe is almost always the choice.

Plastics Used in the Chemical and Hydrocarbon Industries

Plastics used in the industries of interest may be classified as thermoplastics or thermosets. Thermoplastics solidify by cooling and may be remelted repeatedly. In contrast, thermosets solidify by cross-linking between reactive groups on adjacent polymer chains, thereby forming a three-dimensional network. Once solidified, they cannot be restored to their liquid form. Typical thermoplastics include polyethylene, polyvinyl chloride and polypropylene. Typical thermosets include epoxy, phenolic and vinyl ester.

The primary reasons for using plastics are their good chemical resistance, light weight and low cost compared with high-performance alloy alternatives. Their flammability is one factor that limits their use. In addition, they are relatively fragile compared to metals and they have relatively low strength, especially at elevated temperatures. Some plastics are susceptible to damage by the ultraviolet light component of sunlight. Their relatively low thermal conductivity is an advantage in some applications, but is a distinct disadvantage for heat exchanger applications.

Examples of plastics applications are given in Table 2-2. This compilation is neither an exhaustive list of the plastics available nor of their applications. However, it does illustrate that these materials are widely used. A summary of the corrosion resistance of these plastics is given in Table 2-3, and the maximum operating temperature for many of these plastics is given in Table 2-4. A word of caution is in order. The corrosion resistance indicated in Table 2-3 may not correspond with the maximum operating temperature, which is based on mechanical properties. Before selecting a plastic for a specific application, the behavior of the materials being considered should be evaluated for operating conditions.

Table 2-2 Examples of plastics applications

COMPONENTS	PLASTIC TYPES									
	FRP	PE	PP	PVC	PS	PC	PA	PMMA	PTFE	Other
Pressure vessels	•									
Storage tanks	•									
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
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Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						
Storage tanks	•	•	•	•						
Process piping	•	•	•	•						
Heat exchangers	•	•	•	•						
Distillation columns	•	•	•	•						
Reactor vessels	•	•	•	•						

Table 2-3 Corrosion resistance of common plastics

	Strong Acids	Weak Acids	Caustics	Aliphatic Solvents	Aromatic Solvents	Alcohols	Halogenated Solvents	Ketones	Deionized Water
THERMOSETS									
Epoxy	2	2	1	1	1	2	3	3	1
Polyester (Isophthalic)	3	2	3	1	3	2	3	3	1
Polyester (Chlorendic)	1	1	3	1	2	1	2	3	1
Polyester (Bisphenol A Fumarate)	2	1	1	1	3	2	2	3	1
Vinyl Ester	2	1	2	1	3	1	3	3	1
Vinyl Ester (High Temp.)	1	1	2	1	2	1	3	2	1
Furan	2	1	1	1	1	1	2	2	1
THERMOPLASTICS									
LDPE	3	1	1	2	3	1	3	2	1
HDPE	3	1	1	2	3	1	3	3	1
UHMWPE	2	1	1	2	3	1	3	3	1
PP	3	1	1	2	3	1	3	1	1
PVC	2	1	1	2	3	2	3	3	1
CPVC	2	1	1	2	3	1	3	3	1
PVDC	2	1	1	2	3	2	3	3	1
PVDF	1	1	2	1	1	1	3	3	1
PTFE	1	1	1	1	1	1	1	1	1
FEP	1	1	1	1	1	1	1	1	1
PFA	1	1	1	1	1	1	1	1	1
ECTFE	2	1	1	2	3	3	3	3	1
ABS	3	3	3	3	3	3	3	3	2
Polyamide	3	3	2	1	1	1	1	1	2
PEEK	2	2	2	1	3	*	2	2	*

1 = Resistant; 2 = Marginal; 3 = Not resistant; * = No data

Table 2-4 Maximum operating temperatures^{1,2} of common plastics, coatings and elastomers

MATERIAL	MAXIMUM OPERATING TEMPERATURE, °F (°C)
THERMOPLASTICS	
Polyolefins	
Polyethylene (PE)	180 (80)
High-Density PE (HDPE)	194 (90)
Ultrahigh-Molecular-Weight PE (UHMWPE)	200 (93)
Polypropylene (PP)	250 (120)
Chloropolymers	
Polyvinyl Chloride (PVC)	150 (66)
Chlorinated PVC (CPVC)	212 (100)
Polyvinylidene Chloride (PVDC)	250 (120)
Fluoropolymers	
Polyvinyl Fluoride (PVF)	230 (110)
Polyvinylidene Fluoride (PVDF)	300 (150)
Ethylene Chlorotrifluoroethylene (ECTFE)	330 (165)
Polytetrafluoroethylene (PTFE)	525 (275)
Fluorinated Ethylene Fluoride (FEP)	400 (205)
Perfluoroalkoxy (PFA)	500 (260)
Polychlorotrifluoroethylene (PCTFE)	380 (190)
Engineered Polymers	
Polyamide (Nylon)	250 (120)
Polyaryl Ether Ether Ketone (PEEK)	450 (250)

Table 2-4 (Continued)

MATERIAL	MAXIMUM OPERATING TEMPERATURE, °F (°C)
THERMOSETTING PLASTICS	
Epoxies	400 (250)
Polyesters	
Isophthalic	180 (82)
Chlorendic	350 (175)
Bisphenol A Fumarate	250 (120)
Vinyl Esters	
Common (Bisphenol A)	250 (120)
High Temperature (Epoxy Novalac)	350 (175)
REINFORCED THERMOSETTING RESIN CONSTRUCTION	
Vinyl Ester	450 (230)
Polyester	350 (175)
Epoxy	300 (150)
COATINGS AND LININGS	
Vinyl Ester	355 (180)
Epoxy	250 (120)
ELASTOMERS	
Perfluoroelastomer (FFKM ³)	500 (260)
Silicone (VMQ ³)	450 (230)
Fluoroelastomer (FPM ³)	400 (205)
Ethylene Propylene (EPM ³ , EPDM ³)	400 (205)
Polyacrylate (ACM ³ , ANM ³)	350 (175)

Table 2-4 (Continued)

MATERIAL	MAXIMUM OPERATING TEMPERATURE, °F (°C)
ELASTOMERS (cont.)	
Fluorosilicone (FVMO ³)	350 (175)
Neoprene (CR ³)	300 (150)
Epichlorohydrin (CO ³ , ECO ³)	275 (135)
Nitrile Rubber (NBR ³) (high-temperature type)	250 (120)
Chlorosulfonated Polyethylene (CM ³)	250 (120)
Polysulfide (PTR ³)	225 (105)
Nitrile Rubber (NBR ³) (low-temperature type)	225 (105)
Butyl Rubber (BR ³)	225 (105)

¹These temperatures are typical of the maximum operating temperatures for these materials in non-corrosive environments. The maximum temperature for specific applications depends on the environment and may be much lower than indicated in the table.

²See reference [14]. © Copyright ASTM. Reprinted with permission.

³Standard designation per ASTM D1418.

The primary limitation of polyethylene is its relatively low maximum allowable temperature. For example, while PE can handle most chemicals at room temperature, its upper temperature limit is about 180°F (80°C). HDPE may be attacked by aromatic, aliphatic and chlorinated hydrocarbons. Stress corrosion cracking of HDPE may occur in some detergents and organic solvents.

UHMWPE has a polymer chain 10 to 20 times longer than HDPE. The increased chain length improves toughness, abrasion resistance and resistance to stress cracking. It has excellent chemical resistance as well with an upper temperature limit of 200°F (93°C). It is used for chemical resistant gears and pump impellers.

Cross-linked polyethylene can be produced by exposure of ordinary polyethylene to radiation. Cross-linking causes networks to form between the polymer chains, making a stronger, more impervious material. This greatly increases its resistance to hydrocarbons. It has excellent resistance to most chemicals at room temperature. Cross-linking is also used to produce heat

shrinkable material for applications such as protecting cable connections and the girth welds in piping or pipelines.

Polypropylene (PP). In many ways PP is similar to PE, but it has greater rigidity and heat resistance. It has enhanced resistance to environmental stress cracking. Nevertheless, it has been reported to crack in 93 percent sulfuric acid at room temperature. It has good resistance to caustics, solvents, acids and organic chemicals. It is not resistant to oxidizing acids, detergents or chlorinated organic compounds. As with other thermoplastics, it can be blended with fillers, reinforcements and elastomers to enhance toughness and flexibility.

Chloropolymers

The chloropolymers most frequently used in the hydrocarbon and chemical process industries include polyvinyl chloride (PVC), chlorinated polyvinyl chloride (CPVC) and polyvinylidene chloride (PVDC).

Polyvinyl Chloride (PVC). PVC is popular in the form of plastic pipe because of its easy-working properties. The material may be joined by either solvent bonding or hot-air welding. Because of its relatively poor solvent resistance and thermal stability, its service is usually restricted to handling water solutions, inorganic chemicals and specific organic compounds such as alcohols and straight-chain hydrocarbons. PVC has excellent resistance to inorganic acids and alkalis, and is one of the most resistant plastics for strong inorganic oxidizing agents such as chlorine water and dilute nitric acid. Its upper temperature limit is about 150°F (66°C).

PVC sheet is available for use in linings and solid fabrications. PVC-lined pipe is widespread, although it is unsuitable as a stand-alone material for many other applications because of its relatively low strength.

Chlorinated Polyvinyl Chloride (CPVC). CPVC's chemical resistance is similar to, but usually better than, that of PVC. Its primary advantage over PVC is a higher use temperature, nearly 212°F (100°C). Its primary use is for hot water piping and for inorganic aqueous solutions. Because of its high chlorine content, it has considerable flame resistance.

Polyvinylidene Chloride (PVDC). PVDC is commonly known as Saran.¹ Its most important property is resistance to permeation by both gases and liquids. Its chemical resistance is similar to that of PVC. A special formulation, having enhanced chemical resistance, is used in lined pipe.

Fluoropolymers

As a group, these polymers have high chemical resistance at relatively high temperatures. Their primary drawback is cost, except where they replace more

costly metals. One way to decrease overall cost is to use the fluoropolymers as linings in reinforced thermoset plastic equipment. This will be discussed in greater detail later in this section.

Polyvinylidene Fluoride (PVDF). Common trade names for PVDF include Kynar¹ and Sygef.² Its working properties, appearance and mechanical properties are similar to those of PVC. However, it has superior heat stability (300°F (150°C)) and chemical resistance. While it has good chemical resistance, it can be attacked by organic acids, amines, aromatic compounds, aldehydes, ketones and esters at elevated temperatures. It resists oxidizing agents well, including the halogens, and is used extensively in chlorine service. PVDF is used in lined pipe and valves, as tower packing and a number of other applications in the chemical process and hydrocarbon industries.

Polytetrafluoroethylene (PTFE). PTFE, also referred to as TFE, is best known by the trade name Teflon.³ (Teflon is a family of fluoropolymers, one of which is PTFE.) It has almost universal chemical resistance. Only fluorine, a few exotic chlorinated solvents and molten alkali attack it, even at elevated temperatures. The continuous temperature limit is about 525°F (275°C), although cold flow can occur at lower temperatures. PTFE has good impact strength and a low coefficient of friction. However, its tensile strength, wear and abrasion resistance, and resistance to creep and permeation are not as good as that of some other thermoplastics.

PTFE has a very high melt viscosity that prohibits conventional processing. Components are manufactured by compression and isostatic molding, ram and paste extrusion and dispersion coating techniques that include a sintering heat treatment at about 680–715°F (360–380°C) to fuse the components into an integral whole.

PTFE is widely used in the chemical process and hydrocarbon industries in applications such as envelope gaskets, hose, lined pipe and valves, and non-lubricated valve seats.

Fluorinated Ethylene Propylene (FEP). FEP, also sold under the trade name of Teflon, has substantially the same chemical resistance as PTFE, but the maximum temperature limit is lower, 400°F (205°C). The primary advantage of FEP over PTFE is that it is melt processible. This permits the molding of complex geometries not easily obtained with PTFE. Common applications include liners for valves, lined pipe and liners for process equipment.

Perfluoroalkoxy (PFA). PFA, also sold under the trade name of Teflon, is very similar to FEP except that it has a higher continuous service temperature, 500°F (260°C). It is melt processible, with essentially the same universal chemical resistance as PTFE.

¹Registered Trademark of Atochem Inc.

²Registered Trademark of George Fischer Signet, Inc.

³Registered Trademark of E. I. du Pont de Nemours & Company.

¹Registered Trademark of Atochem Inc.

Polychlorotrifluoroethylene (PCTFE). PCTFE has less chemical resistance than PTFE, FEP and PFA. It is subject to swelling in some chlorinated solvents at elevated temperature and is attacked by the same chemicals that attack PTFE. PCTFE has better mechanical properties than PTFE, and it has the lowest water transmission rate of all the thermoplastics. Its continuous service temperature limit is about 380°F (190°C).

Ethylene Chlorotrifluoroethylene (ECTFE). ECTFE, also known as Halar,⁴ is essentially a co-polymer of ethylene and chlorotrifluoroethylene. It has a useful temperature range from cryogenic to about 330°F (165°C). Its strength and wear resistance are substantially better than that of PTFE, FEP and PFA. At ambient temperatures the material may be attacked by aromatics, chlorinated solvents, esters, ketones, aldehydes and amines.

Engineered Polymers

These polymers find limited use in the industries of interest.

Acrylonitrile-Butadiene-Styrene (ABS). ABS plastic has good resistance to paraffinic hydrocarbons, is easily joined by threading or solvent bonding and is a cost-effective material for transfer lines. It is used in plumbing applications and in compressed air and instrument air piping systems. It has limited chemical resistance and is attacked by acids, alkalis and many of the common aromatic and aliphatic solvents.

Polyamide (Nylon). Polyamides have good dimensional stability and are used as gears in washing machines, sewing machines and other home appliances. Their toughness encourages their use in mechanical applications such as lubrication reservoirs and chemical-resistant fan blades and housings. Good heat stability is observed up to about 250°F (120°C). Nylon is resistant to most organic solvents and alkalis at ambient temperature. It has poor resistance to acids and oxidizing agents.

Polyaryl Ether Ether Ketone (PEEK). PEEK retains its high-temperature strength for extended times and has a maximum allowable working temperature of 450°F (250°C). PEEK is used in machine components in chemical applications such as compressor valves, safety valve seats, oxygen sensors, pump sleeves, filters and gaskets. It has excellent chemical resistance in a wide range of organic and inorganic compounds. However, it is attacked by strong oxidizing agents. It undergoes surface crazing when stressed and exposed to short-chain organic solvents such as acetone, ethyl acetate and chloroform.

Thermosets

Thermoset plastics are used as impregnants in graphite equipment and in reinforced laminate and composite construction. They are also used in some paint and coating

⁴Registered Trademark of Ausimont.

products. In section entitled "Laminate and Composite Structures" (p. 68), thermoset plastics are discussed.

Epoxies

Glass fiber-reinforced epoxy laminates are one of the most attractive plastics for use in the industries of interest. Sections of plastic are laminated with glass cloth or roving to produce articles with attractive mechanical properties. While this construction is not inexpensive compared with steel, it features relatively easy joining and has a broad range of chemical resistance.

Standard epoxy resins are the reaction product of bisphenol A and epichlorohydrin. They have good resistance to alkalis, hot and cold mineral acids (except nitric acid) to about 20 percent concentration and most organic solvents. Epoxy pipe can be joined by a number of methods including bell and spigot joints with epoxy resin in the joint, resin-saturated glass cloth-wrapped joints and use of proprietary fittings. No matter what design is used, close attention to joint details is required for a reliable assembly.

The upper chemical limit for standard epoxies is about 400°F (204°C). They have poor resistance to strong oxidizing agents, amine compounds and some chlorinated solvents.

Epoxy Novalacs

Epoxy novalacs are formed by the reaction of a novalac resin such as *o*-phenol, or *o*-phenol plus formaldehyde, with epichlorohydrin. The novalacs have better heat and chemical resistance than the standard epoxies when cured with appropriate hardeners.

Polyester

More storage tanks and duct work have been constructed from fiberglass-reinforced polyester resin laminates than from any other plastic material. This is the result of the favorable cost/strength ratio and the generally good chemical resistance of these resins.

Three types of polyester are commonly used in the hydrocarbon and chemical process industries: isophthalic, chlorendic and bisphenol A fumarate grades.

Isophthalic. These resins have good tensile and flexural strength but only fair chemical resistance to acids and caustics up to 180°F (82°C). They are widely used for applications such as the external casings, fan plenums and inlet louvers in cooling towers.

Chlorendic. This resin has low elongation and is inherently brittle, but it has good elevated temperature resistance to 350°F (175°C). It can be used in aggressive oxidizing environments to contain concentrated acids such as chromic acid (30 percent to 140°F (60°C)) and nitric acid (20 percent to 140°F (60°C)) and some solvents such as naphtha. It has poor resistance to caustic.

Bisphenol A Fumarate. Bisphenol A fumarate resins have better resistance to acids than the isophthalic polyesters and better resistance to alkalis than vinyl esters. Temperature resistance is acceptable to 250°F (120°C). Typical applications include glass fiber-reinforced tanks and pipe.

Vinyl Esters

The vinyl esters encompass a wide range of chemical compounds. The common vinyl esters are based on bisphenol A epoxy and have an upper temperature limit of about 250°F (120°C). The high-temperature resins, which have superior chemical resistance and an upper operating temperature of about 350°F (175°C), are based on epoxy novolacs. These resins have excellent resistance to most acids but poor resistance to strong alkalis. They are resistant at ambient temperatures to all but a few aggressive solvents and oxidizers.

Furan

Furan resins are formed by the partial condensation of furfural alcohol. One of the reaction products is water, which can have a negative effect on the final product unless special procedures are followed to remove the water. Examples are heat curing or a post-cure heat treatment carefully controlled to avoid formation of steam that could cause the product to disintegrate.

Furan and phenolic resins are used to impregnate graphite to make it impervious. Since the furan resins are brittle and continue to grow more so with time, they should always be reinforced with glass or other suitable material. They are widely used in fiberglass-reinforced plastic equipment. They have broad chemical resistance. Limitations include poor resistance to oxidizing chemicals such as chromic and nitric acids, peroxides and hypochlorites.

Laminate and Composite Structures

With the exception of such specialized applications as impregnants for graphite equipment and coatings, thermoset plastics are almost always made into laminates or composites. The addition of reinforcing fibers, most often made of glass, adds strength and rigidity and permits the fabrication of equipment of considerable utility in the industries of interest. For cylindrical equipment such as vessels, tanks, columns and scrubbers, there are two basic fabrication methods: hand lay-up and filament winding. Pipe can be fabricated by either of these methods as well as by centrifugal casting. Plastics can also be made into useful shapes by injection molding, extrusion, pultrusion, compression molding and machining shapes from stock material.

Hand lay-up is generally used where maximum corrosion resistance is required. In most cases, a resin-rich "corrosion barrier" is created on the inner surface while the structural wall is created from layers of resin-impregnated glass mat and woven roving. A variation is to apply layers of chopped glass fibers and

resin. Filament winding is used when the greatest strength for a given wall thickness is required.

ASME standard ASME RTP-1, "Reinforced Thermoset Plastic Corrosion Resistant Equipment" [9], describes in considerable detail the materials to be used for corrosion resistant equipment, design methods, fabrication procedures, inspection requirements and tests and shop qualification. This provided a much-needed industry standard for atmospheric pressure equipment. About the same time, ASME revised Section X (entitled "Fiber-Reinforced Plastic Pressure Vessels") of the Boiler and Pressure Vessel Code [1], to provide design and construction rules for plastic pressure vessels. The combined use of these two standards provides a sound basis for design and fabrication of reinforced thermoset plastic equipment.

Plastic Pipe

Plastic pipe is not as rigid as metal pipe and a properly designed support system is required for reliable service. Failure to properly support plastic pipe has been a major cause of problems in plastic piping systems. In addition, plastic pipe has greater thermal expansion than does metal pipe. Failure to take these two factors into consideration during design has resulted in almost immediate failures. Such results have given plastic pipe an undeserved reputation for unreliability in some plants.

Plastic pipe is usually easy to join. Joining is frequently done with solvent welding. However, ease of fabrication has sometimes resulted in too little attention being given to joint quality. Since the finished joints are difficult to inspect, care must be taken to ensure that the joints are properly made. Personnel installing plastic pipe should be thoroughly trained in proper joining techniques and the consequences of poor workmanship. All too often, the installation crews are inexperienced and must undergo "learning curve" training before they can perform effectively. This, too, has contributed to some undeserved criticism of plastic piping.

Reinforced thermoset plastic (RTP) pipe can be built to withstand high pressures. For example, one pipeline has been used to transport crude oil at 2,500 psig (17,240 Mpa) for more than a decade. A major advantage of this application is that the material needs no external corrosion protection.

Plastic-lined steel pipe offers the advantages of high mechanical strength from the steel pressure retaining component and optimal corrosion resistance for the application from the thermoplastic liner. Thus, relatively soft liners such as polypropylene and PTFE can be selected for their chemical resistance. This permits designing a system that can withstand most chemical processes as long as the liner's temperature limits are not exceeded. A limitation to the use of lined steel pipe has been the need for frequent flanges, which are potential points for leaks. Recent developments include a process for fabricating complex customized piping

systems as a single unit. Such pipe sections may contain several elbows and straight runs between flanges.

Dual Laminate Construction

Dual laminate construction is a valuable system for chemical-resistant equipment. This construction consists of a thermoplastic lining in a fiber-reinforced thermoset structural body. It is used for pipe, tanks, ducts, reactors, scrubbers and the like. The thermoplastic material can be selected for its chemical resistance while the thermoset resin can be selected for its mechanical properties.

Almost any thermoplastic can be used for lining. The materials most commonly used are PVC, CPVC, PP, PVDF and FEP. The selected material should have good resistance to chemical attack, including dissolution and solvation. It should also resist permeation. Permeation can result in disbonding between the thermoplastic and the fiber-reinforced thermoset body if there are air bubbles at the interface. The permeating molecule can condense at these bubbles and generate high pressures if the unit is heated. The permeating species may also degrade the thermoset resin or the bond between the resin and the reinforcing fibers. The fact that the permeating species usually can continue on through the thermoset resin without serious damage is a major advantage of dual laminate construction over plastic-lined steel construction. In the latter case, the permeating species is blocked at the steel-plastic interface and creates disbonding.

The bond strength between a thermoplastic lining and the structural body must be strong enough to maintain structural integrity during temperature cycles and mechanical abuse. Thermoplastics have higher coefficients of thermal expansion than fiber-reinforced thermosets. If there is thermal cycling, this mismatch can produce failure of the bond at the interface between the thermoplastic and the thermoset. It also produces a tensile stress in the thermoplastic during cooling. Such stresses can result in lining failure, especially if the thermoplastic is sensitive to environmental stress cracking in the process fluid. If the thermoplastic liner material is bonded to the thermoset resin by the use of solvents or a special bonding resin, no intermediate backing is needed. PVC and CPVC fall into this category. If the liner is of the polyolefin or fluorocarbon families, an intermediate backing is needed to provide a bond. This backing is usually a double knit or non-woven fabric that permits forming the lining into the desired shape. The backing should be treated to provide good wettability by the thermoset resin to minimize air bubbles at the interface.

The dual laminate is constructed by first fabricating the thermoplastic lining by thermoforming and welding. It is common practice to apply a conductive strip of carbon-filled resin behind the thermoplastic welds to permit spark testing for weld integrity. Welding can be accomplished either by using a hot air gun and filler rod or by butt welding.

The fabricated lining becomes the form for the fiber reinforced thermoset body. The latter is then fabricated in much the same manner as with an unlined unit except there is no need for the resin-rich "corrosion barrier."

2. Elastomers

Elastomers are defined as any polymeric material which at room temperature can be stretched to at least twice its original length and upon release of the stress will immediately return to approximately its original length. Thus, elastomers include rubber as well as many synthetic polymers which have been developed for special properties. Also of interest, although not an elastomer as described above, is "hard rubber," or ebonite.

Elastomers are used primarily in three applications in hydrocarbon and chemical process plants:

- Hoses
- Seals, including O-rings and gaskets
- Linings for vessels, tanks, ponds, bins, etc.

This discussion focuses on the properties of elastomers and on their application as linings.

Elastomer Chemistry

Most elastomers are "compounded" to achieve specific properties. The most important additive is sulfur, which promotes vulcanization (i.e., cross-linking) of the linear polymeric chains. Peroxides alone, or mixed with sulfur, are used as vulcanizing agents for some elastomers. Vulcanization increases hardness, decreases elongation and usually increases corrosion resistance.

Natural rubber can be vulcanized to three levels:

1. "Soft" rubber, which has 0.5 to 4.0 wt. percent sulfur and achieves a hardness of 30 to 70 Shore Durometer A. (The various hardness scales for elastomers are discussed in the next section.)
2. "Semi-hard" rubber, which has 5 to 25 wt. percent sulfur and reaches a hardness level of 50 to 90 Shore Durometer A.
3. "Hard" rubber, often known as ebonite, which contain 25 to 45 percent sulfur and has hardnesses exceeding 90 Shore Durometer A.

Additives are incorporated for a number of purposes.

- *Carbon black* is added to rubbers to increase strength; however, elongation is reduced by this addition. Carbon black is the most common strengthening additive, although finely divided silica, china clay, or

titanium dioxide are also used. Normal amounts of carbon black are in the range of 20 to 40 percent by weight.

- *Mineral oil* is added to decrease viscosity and make forming and shaping easier before vulcanization.
- *Accelerators* may be added to promote vulcanization. Retarders may be added to retard the onset of vulcanization until the rubber is formed or shaped. Retarders may be necessary if warm forming is used.
- *Oxygen*, especially ozone, promotes progressive vulcanization, resulting in a loss of resiliency.
 - *Anti-oxidants* such as amines are often used to resist aging and weathering.
 - *Wax* is added to some formulations. The wax migrates to the surface and forms a thin coating that effectively prevents oxygen from degrading the rubber. Of course, if the rubber is to be repaired, patched or lapped in the process of making a lining, the wax must first be completely removed from the area where bonding is to be accomplished.

Elastomer Hardness

Hardness indicates the degree of vulcanization or cure. There are many applications which require a specific hardness level such as gaskets or O-rings, where sealability depends, in part, on elastomer hardness.

Hardness is measured according to ASTM D2240, "Test Method for Durometer Hardness," and ASTM D1415, "Test Method for International Hardness." The Durometer instrument measures the indentation depth when the instrument is pressed onto a flat surface of the elastomer. One instrument is used for soft materials (Shore Durometer A scale) and another for harder materials (Shore Durometer D scale). Figure 2-11 shows the relationship between the Durometer scales and the Rockwell R scale used for plastic materials.

Elastomer Properties

Table 2-5 shows some of the properties of a few of the more commonly used elastomers.

Natural Rubber (NR)

These materials (including their synthetic "isoprene" equivalents) are still the most common elastomers in general service. They are the first choice for abrasion-resistant linings and for hoses for acid service. Soft natural rubber liners are used in hydrochloric acid service. Semi-hard rubbers are suitable for water services in which metal ion contamination is important. Natural rubbers are not affected by alkalies and non-oxidizing acids; however, they can be very vulnerable to many organic solvents. Oxidizing environments such as nitric acid, concentrated sulfuric acid, permanganates, and even aerated solutions over extended periods cause embrittlement.

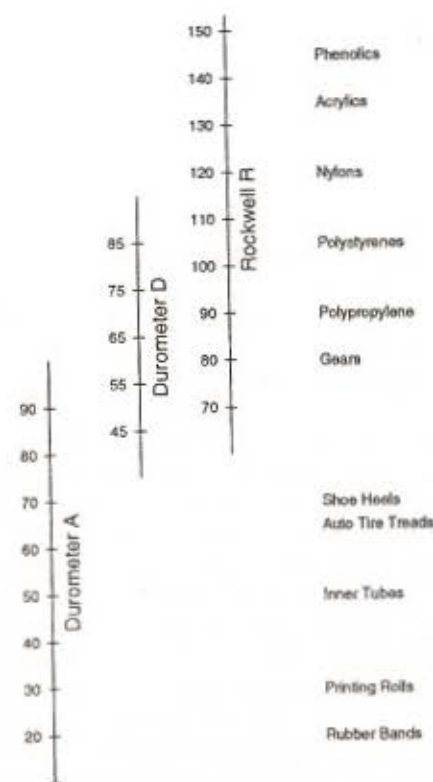


Figure 2-11 Approximate comparison of hardness scales for elastomers and plastics.

Very hard rubber (called ebonite) is considerably more corrosion resistant to organic solvents as well as to oxidizing environments. Ebonite will swell and crack when in contact with the more effective rubber solvents such as benzene, chlorobenzene and carbon disulfide. Also, ebonite is much less resilient and is subject to mechanical damage from impacts, dents in metal backing, etc., which can occur during shipping and handling. Because of its brittleness, ebonite should not be used in applications involving thermal cycling and/or thermal stresses.

Nitrile Rubber (NBR)

Nitrile rubber, also known as Buna N, is a copolymer of butadiene and acrylonitrile. Normal levels of acrylonitrile are 20 to 40 percent. As the

Table 2-5a Mechanical properties of commonly used elastomers

Class	Code ¹	Hardness Durometer A	Abrasion Resistance	Temp. Range - °F	Oxidation Resistance
Natural Rubber	NR				
Soft		30–50	E	–22 to 212	P
Semi-hard		50–90	G	40 to 180	G
Hard		>90	P	50 to 160	G
Buna N	NBR	40–95	G	–4 to 221	G
Chloroprene	CR	40–95	G	–4 to 158	G
Chlorobutyl		50–60	E	–60 to 260	G
Hypalon ²	CSM	45–95	E	14 to 230	E
Fluorocarbon	FPM	40–75	P	14 to 230	E
Kalrez		80–90	F	–22 to 212	E
Silicone	VMQ or SIL	30–90	P	–178 to 450	E
Ethylene Propylene	EDPM	30–90	G	–40 to 312	E

¹In accordance with ASTM D1418.²Registered Trademark of E. I. du Pont de Nemours & Company.

VP = Very Poor; P = Poor; G = Good; E = Excellent.

Table 2-5b Chemical resistance of commonly used elastomers

Class	Acids	Alkalis	Aliphatic Solvents	Aromatic Solvents	Chlorinated Solvents
Natural Rubber					
Soft	G	G	P	P	P
Semi-hard	G	G	G	P	P
Hard	G	G	G	P	P
Buna N	G	G	F	P	P
Chloroprene	E	E	G	P	P
Chlorobutyl	G	G	P	P	P
Hypalon ¹	E	E	F	P	P
Fluorocarbon	E	G	E	E	E
Kalrez	E	E	E	E	E
Silicone	G	G	P	P	P
Ethylene- Propylene	G	G	VP	P	VP

¹Registered Trademark of E. I. du Pont de Nemours & Company.

VP = Very Poor; P = Poor; G = Good; E = Excellent.

acrylonitrile content increases, the resistance to petroleum products and fuels increases, but low-temperature flexibility decreases.

Nitrile rubber is significantly better than natural rubber for use with fuels and oils. It is attacked by strong oxidizing agents and by ketones, ethers and esters. It is used in linings, hoses, diaphragms and seals, especially those for lubricating oils.

Chloroprene Rubber (CR)

Chloroprene rubber, also known as Neoprene, is often used instead of Buna N, since it is stronger (3 to 4 ksi (20 to 27 MPa) for CR versus 0.5 to 0.9 ksi (3.4 to 6 MPa) for Buna N.) It is more resilient and resists heat, oxidation and ozone better than Buna N. It is four to ten times as impermeable to gases as natural rubber. It is not compatible with strong oxidizing agents such as nitric acid, peroxides and potassium dichromate.

Chloroprene rubber is used extensively for linings, hoses and seals in oil services. It has become the standard elastomer for hydraulic services because of its durability.

Butyl (IIR) Rubber

Butyl rubbers are noted for their extremely low permeability to gases such as oxygen and nitrogen. They find use in acid, alkali and animal and vegetable oil services, but should not be used with most solvents. Both butyl and chlorobutyl rubbers tend to soften at temperatures above 140°F (60°C), while natural rubbers tend to harden. This characteristic makes butyl and chlorobutyl rubbers much better for abrasive services at high temperatures.

Chlorobutyl Rubber

Chlorobutyl rubber is chlorinated butyl rubber, which is a copolymer of isoprene (synthetic "natural" rubber) and isobutylene. This rubber is essentially impervious to gases.

Chlorobutyl rubber has found service as a container material for very strong hydrofluoric acid and superphosphoric acid. It is better than natural soft rubber for containing hydrochloric acid at temperatures up to 200°F (93°C), which is above the 170°F (77°C) maximum use temperature of natural rubber in this service.

A limitation to the use of butyl and chlorobutyl rubber rubbers is their very poor adhesion to steel. In many cases, using chlorobutyl with a natural rubber backing ply is an acceptable approach to adhering these materials to steel. However, this combination has caused failures. In one case, a chlorobutyl liner disbonded from a filter feed tank, without any visible damage to the liner. The natural rubber ply used for adhering the chlorobutyl lining to the steel showed swelling and lack of adhesion. Apparently, an organic constituent diffused through the chlorobutyl liner to the natural rubber bonding layer, where it eventually

attacked and disbonded this layer. Subsequent laboratory testing confirmed that natural rubber was not resistant to the contents of the tank.

Chlorosulfonated Polyethylene (CSM)

Chlorosulfonated polyethylene, also known as Hypalon,¹ can be compounded and vulcanized. The properties can be slightly varied by the degree of chlorination, which is normally in the range of 25 to 30 percent chlorine. Hypalon finds use in acids and alkalis. It is useful in oxidizing environments, both for chemicals such as concentrated sulfuric acid as well as oxygen or ozone atmospheres. It is also used with concentrated hydrochloric acid.

Significant advantages are its excellent resistance to ultraviolet radiation and atmospheric oxidation. Since it is also highly resistant to prolonged immersion in water, it serves well in outdoor applications where weathering resistance is necessary.

Hypalon has poor resistance to organic solvents and should not be used where there is a possibility that organic materials may contaminate the system.

Fluorocarbon Rubber (FPM)

Fluorocarbon rubbers were first introduced in the mid 1950s. Viton A¹ is typical of this class of elastomers. It is a copolymer of vinylidene fluoride and hexafluoropropylene.

These fluorocarbon elastomers have superb resistance to aliphatic hydrocarbons, fuels and oils and to dilute acids and alkalis. They have poor resistance to alcohols, aldehydes, ketones, esters, ethers, oxygenated solvents, acrylonitrile and freons. They have low permeability to air and extremely low water absorption. Abrasion resistance is poor and applications involving abrading solids should be avoided. High-temperature resistance is excellent.

Perfluoroelastomer

Perfluoroelastomers, also known as Kalrez¹ and Chemraz,² are probably the most chemically resistant of all the elastomers. The chemistries of these elastomers are based on tetrafluoroethylene, the monomer in TFE Teflon,¹ and contain two or more copolymers. Kalrez is described as a copolymer of tetrafluoroethylene and perfluoromethyl vinyl ether, with small amounts of a perfluorinated comonomer, which provides sites in the polymer for chemical cross-linking. To be useful, these elastomers must contain fillers and be cross-linked.

There are a number of compounds for special applications. For example, Kalrez 1050 has a high ratio of Teflon to vinyl ether and has better chemical resistance than some of the other Kalrez products. The chemical resistance of

¹Registered Trademark of E. I. du Pont de Nemours & Company.

²Registered Trademark of Green, Tweed & Company.

Table 2-6 Standards for elastomers and rubber-lined equipment

ASTM D-1418	Classification of Elastomers
ASTM D-2000	Automotive Use Classification of Elastomers
ASTM D-471	Rubber Immersion Testing
ASTM D-429	Adhesion Testing
ASTM D-418	Adhesion Testing
ASTM D-3486	Installation of Rubber Linings
CP 3003	British Code of Practice CP 3003, Part I, 1967
Rubber Manufacturers Association	Protective Linings Technical Bulletin

Kalrez is similar to that of Teflon, except that fully halogenated freons and uranium hexafluoride cause considerable swelling. Above 100°F (38°C), Kalrez may not have long service life in high concentrations of some diamines, nitric acid and basic phenol.

These elastomers are very expensive. However, in many applications the cost is justified by reduced downtime, reduced repair costs and increased safety.

Silicone Rubber (VMQ)

Silicone rubber is an organo-silicone oxide polymer, specifically, dimethyl siloxane polymer. The linear chains may be "vulcanized" by using benzoyl peroxide to promote cross-linking.

Silicone rubber is used for high-temperature applications. Its performance up to 450°F (232°C) is exceptional; it retains strength, flexibility and resiliency at these temperatures. It can withstand intermittent service to 600°F (316°C).

Silicone rubbers are not resistant to aromatic solvents nor to steam at high temperatures. They have excellent ozone and weathering resistance. They are used primarily as high-temperature seals, gaskets, ducts, etc.

Ethylene-Propylene (EPDM)

There are two ethylene-propylene elastomers: EPDM and EPR. EPDM is a sulfur-curing terpolymer, while EPR is a saturated copolymer.

EPDM is a much better material than polyethylene, natural rubber, or polypropylene for general-purpose outdoor service. It resists weather and sunlight, oxidation and ozone. It is resistant to acids, bases, water and alcohol but is attacked by solvents such as hydrocarbons and chlorinated hydrocarbons. EPDM elastomer does not show the stress cracks that plague polyethylene.

EPDM is used for loose linings outdoors, for instance as a liner for waste treatment lagoons.

Standards for Elastomers and Rubber-Lined Equipment

Table 2-6 lists some of the standards associated with elastomers and rubber-lined equipment. The first two standards deal with the classification of elastomers, the next three with testing and the last three with rubber lining.

3. Carbon and Graphite

Commercial carbon and graphite are produced from carbon particles bonded with materials that carbonize during subsequent processing. Carbon is usually produced below 2250°F (1230°C). Graphite is a crystalline form of carbon produced by processing at temperatures in excess of 3600°F (1980°C).

Carbon

Carbon is usually used for its chemical inertness. It is primarily used in the form of brick and for packing rings. Carbon has a broad temperature capability and may be used to 660°F (350°C) in an oxidizing environment or 5000°F (2760°C) in inert or reducing environments.

Carbon has very good chemical resistance, even greater than that of graphite. Concentrated sulfuric acid, bromine and fluorine can be handled in carbon, but not in graphite.

Carbon brick is porous and must be used with a membrane such as asphalt, rubber or plastic. In a typical tower or tank application, carbon brick serves three functions:

1. It thermally insulates the membrane and vessel wall from the temperature of the fluid.
2. It holds the membrane in place.
3. It protects the membrane from mechanical damage such as abrasion and impact.

Carbon is also used in mechanical seals. To obtain greater wear life, the contact surface of carbon components can be converted to silicon carbide by high-temperature exposure to silicon monoxide. Alternatively, they may be impregnated with a phenolic resin or metals such as antimony or Babbitt. (Babbitt is the name of a family of tin-based bearing alloys.)

Impervious Graphite

Normal fine-grain graphite is porous. To make it impervious, it is usually impregnated with organic resins such as phenolic or furan prior to the final heat

treatment. A phenolic resin is used for resistance to most acids, salt solutions and organic compounds. A furan resin is used for materials to be used in alkaline and oxidizing services.

Impervious graphite has high heat transfer capability and is chemically stable in many environments. It can be used at temperatures up to 338°F (170°C). Above this temperature spalling can occur, due to a thermal expansion mismatch between the graphite and the resin. Other impregnating resins such as PTFE are available for higher-temperature applications. Also, the surface can be treated to form silicon carbide in order to seal porosity and increase the resistance to erosive wear.

Chemical Resistance

Table 2-7 shows the chemical resistance of graphite for a number of common corrosives.

Heat Exchangers

A major application for impervious graphite is in heat exchangers. Shell and tube and block designs have been used for a number of years. Both forms benefit from the high heat transfer rate characteristic of this material. More recently, a fluorocarbon-impregnated plate and frame heat exchanger has become available.

In shell and tube heat exchangers, the corrosive process fluid is normally contained in the tubes. In some cases, the shell can also be fabricated from graphite, but a steel shell is the more typical construction. Pressure is limited to about 100 psig for small units and 50 psig for large units.

Block heat exchangers are made from a block of graphite with a series of holes drilled perpendicular to each other. One fluid flows through one set of holes and the other fluid through the other set of holes. Block exchangers can be operated at higher pressures than shell and tube exchangers, since they are more robust.

Plate and frame heat exchangers made with graphite are similar in design to metallic plate and frame heat exchangers. The individual plates are mounted on a rack and are manifolded to permit the hot and cold fluids to flow on opposite sides of each plate.

Mechanical shock is the primary cause of failure for all types of graphite heat exchangers. Care during transporting and installing the heat exchangers is an obvious requirement. This is especially critical with shell and tube designs. The primary sources of in-service failures are from:

- Mechanical shock during startup. If the hot side comes up to temperature faster than the cool side, fluids having a high vapor pressure may flash, causing breakage.
- Vibration caused by excessive velocity flow across the tubes. This can result in breakage.

Table 2-7 Chemical resistance of impervious graphite in common chemicals^{1,2}

Corrosive	Concentrations	Maximum Temperature	Recommended Impregnant
Amines	All	Boiling point	Phenolic
Ammonium hydroxide	All	Boiling point	Phenolic
Calcium hydroxide	All	Boiling point	Furan
Hydrofluoric acid	to 48%	Boiling point	Phenolic
	48–60%	185°F (85°C)	Phenolic
	Over 60%	Not recommended	
Hydrogen sulfide-water	All	Boiling	Phenolic
Nitric acid	10–20%	140°F (60°C)	Phenolic
	Over 20%	Not recommended	
Organic acids	All	Boiling point	Phenolic or Furan
Phosphoric acid	0–85%	Boiling point	Phenolic
Sodium hydroxide	6–67%	Boiling point	Furan
	67–80%	275°F (135°C)	Furan
Sulfuric acid	0–70%	Boiling point	Phenolic
	70–85%	340°F (170°C)	Phenolic
	85–90%	300°F (150°C)	Phenolic
	90–93%	160°F (70°C)	Phenolic
	93–96%	75°F (25°C)	Phenolic
	Over 96%	Not recommended	

¹For a more complete listing of chemical compatibility, see Ref. [13] or literature from the manufacturers of impregnated graphite equipment.

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- Erosion of the graphite caused by high-velocity flow. With clean fluids, the maximum velocity should be 8 ft/sec (2.5 m/s). With dirty fluids, the velocity should be limited to 5 ft/sec (1.5 m/s).

Impervious graphite is also used in:

- *Pumps.* All of the wetted parts may be made of impervious graphite. To provide greater abrasion resistance, the surfaces of pump parts may be converted to silicon carbide.
- *Vessels* such as absorbers, evaporators, reactors and distillation columns. Impervious graphite can be used for pressure containment, for vessel internals, or in attachments such as rupture disks.
- *Piping.*

Flexible Graphite

Flexible graphite is available as both a foil and a fiber. Considerable use is made of graphite fibers as a reinforcement for composites in a number of special applications ranging from golf clubs to high-performance aircraft. However, only limited use has been made of these fibers in the process industries. One example is the use of graphite reinforcement for polyester and vinyl ester composite vessels. Another is the common use of graphite fibers that have been impregnated with PTFE (polytetrafluoroethylene) colloidal graphite. This material is used as packing in valves and seals.

Graphite foil is used extensively as a gasket material (e.g., Grafoil¹). For this application, the graphite is generally pure carbon without any binders or fillers. It can be used up to its oxidation temperature which is about 825°F (400°C) in air. Graphite foil has the same good chemical resistance as impregnated graphite.

Care must be taken in using graphite gaskets and packing, since the material is an electrical conductor and is cathodic to most metals. Under some circumstances, a galvanic cell can be established that can result in corrosion of the metal adjacent to the graphite.

4. Glass

Glass has a long history of providing barrier protection in very hostile chemical environments, often involving strong inorganic acids (hydrofluoric acid being the major exception). It is also used for processes that must be protected from corrosion-induced contamination. Being a dielectric material, glass does minimize the anode/cathode area effect at a holiday. In addition, glass linings are sometimes

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selected for their smoothness and non-stick surface, which promote drainability. However, glass is usually a less desirable selection because it:

- Is susceptible to mechanical damage.
- Is difficult and expensive to repair.
- Must be holiday free.

5. Cement

Cement (usually Portland cement) is the key ingredient in the slurry used to make concrete, the composite material that finds widespread use as a structural material. Conventional concrete is a mixture of cement, sand and, usually, an additional aggregate such as crushed stone.

The term "cement" is often used instead of the more proper term "concrete," to describe cement-based linings in tanks, vessels and pipe. Such "cements," used for lining, are mixtures of Portland cement, sand and, for some applications, pozzolanic material. The mixture is formulated so that it has an excess of free lime after it has cured. While Portland cement is the normal base material, special cements resistant to low pH, acid gases, sulfates, erosion, etc., are available.

As a lining, cement acts as a barrier in the sense that it impedes fluid flow towards the substrate surface. In aqueous environments it also provides protection by modifying the environment of the substrate surface. As free water migrates to the substrate surface via cracks and other voids, it becomes saturated with hydroxide, raising the local pH to 11 or more. At this saturation level pH, carbon steel is passivated and will not corrode.

Cement linings applied internally to vessels and tanks are usually sprayed on ("gunited"). Internal cement linings for pipe may be either mill-applied (centrifugally cast) or may be applied *in situ*. The choice is usually based on commercial considerations, but mill-applied cement linings are by far the most common. (*In situ* linings are generally adopted for existing pipelines in need of repair.)

Fluid velocities in cement lined pipe are usually limited to 5-10 ft/sec (1.5-3 m/s) because of erosion concerns at changes in direction such as elbows. The upper limit of 10 ft/sec (3 m/s) is usually satisfactory for saline waters such as seawater. The lower limit is favored for fluids involving suspended abrasive solids.

There are a variety of girth weld jointing systems used for mill-applied cement-lined pipe. Each system provides for continuous lining across the pipe joint. Most users prefer the bell-and-spigot joint, which utilizes external girth fillet welds. The internal joint is sealed with a special slurry that expands upon curing. This system provides reliable protection across the joint area and permits a relatively strong weld. Other alternatives include:

- *Gaskets with butt welds.* The gasket is inserted just before the butt weld is made. Slippage, misalignment and gasket loss are relatively common problems.
- *Cement with butt welds.* A slurry-type compound that expands upon curing is smeared on the butt surface of the cement adjacent to the weld preparation just before welding.

Note that the above two methods usually produce butt welds with serious defects due to porosity and lack of penetration. It is probably impossible to obtain full penetration welds to the quality standards of most cross-country pipeline or plant piping codes.

- *Gaskets with flanged connections.*
- *Hand repair.* A worker can enter large-diameter pipe and hand-repair the weld joint area, using a slurry that expands upon curing. This type of system usually produces a successful joint.

Fittings and branch connections for cement lined pipe are usually weak points. If the diameter is large enough, the fitting and joint can be hand lined, but the quality is inferior to the centrifugally cast pipe lining. The same is true for miter joints made from cement-lined pipe; these are often used instead of elbows that cannot be otherwise lined or are unavailable. The most difficult connections are lateral branch connections such as vents and drains, where the cement lining has broken out of the pipe run. Suitable repairs are virtually impossible unless the site is essentially stagnant while in operation.

6. Refractories

Refractories are available in several forms including fiber blankets, bricks and blocks, and castables. The last group, which includes both castable ceramics and plastic refractories, is usually employed to make monolithic linings. In some applications, refractories are used to provide corrosion protection to the substrate pressure-retaining material, for example, the use of refractory liners in sulfuric acid plants. However, the major function of the refractory is to keep the pressure-containing material cool enough to avoid high-temperature degradation problems.

Local gross failure of a refractory can cause "hot spots" that will locally degrade the pressure-containing metal. Eventually, failure will usually occur because of some high-temperature degradation phenomenon such as creep. Refer to Chapter 3, "Failure Modes," for a discussion of these phenomena. If the process contains a corrodent such as high-temperature hydrogen or hydrogen sulfide, rapid failure may occur, leading to a rupture. Thermochromic paints, which change color after crossing a high-temperature threshold, are often used as a means of monitoring refractory-lined equipment for local failures of the refractory. When using thermochromic paints, the painted surface obviously must be left uninsulated.

Monolithic Linings

Castable Ceramics

Castable ceramics are the most commonly used of the monolithic lining materials. They consist of a refractory concrete that contains both a binder and an aggregate. The mixture typically contains 60 to 80 percent aggregate. The binder may be either a hydraulic type such as Portland or calcium aluminate cement, or it may be chemically setting type such as the silicates or phosphates. Of these, the calcium aluminates are probably the most commonly used in the industries of interest.

Castables are placed by casting, gunning or hand packing. The addition of stainless steel fibers into castable formulations was introduced in the early 1980s and is reported to promote the formation of a number of fine cracks during the drying and firing cycles, rather than a few large cracks.

Gunning is the most common method of application for castables. It generally provides better properties than are obtained with casting, since it usually uses much less water in the mix. After application, the concrete must be cured before it is put into service. Details of the curing process depend on the type of castable being used and the application. Proper curing is essential to successful service.

Plastic Refractories

A plastic refractory is similar to unfired fire brick; it requires a high-temperature heating or curing process to develop the ceramic bonding necessary to become mechanically stable. Plastic refractories are composed of a calcined clay plus a binder of unfired clay. The mixture is generally very stiff and is applied with an air hammer. Until it is fired, a plastic refractory remains soft and can be easily damaged. To improve their resistance to incidental mechanical damage before firing, some plastic refractories use an alkaline silicate to provide some air hardening. Plastic refractories are used in processes with service temperatures in excess of 1800°F (980°C), in order to develop adequate ceramic bonding.

Refractory Brick

Brick is useful for chemical resistance applications and erosion resistance as well as for thermal insulation. The construction processes for chemical resistance applications may differ considerably from those used for other applications.

Chemical-Resistant Construction

Three components are necessary for a chemical-resistant masonry construction:

1. *A chemical-resistant membrane lining is applied to the substrate material.* This membrane may be any of a number of materials ranging from a hot-applied asphaltic pitch to some sort of sheet lining. Sheet lining materials may be rubber or thermoplastic. The membrane is chosen for its resistance

to attack by the chemicals present in the process at the temperature expected at the location of the lining.

2. *A chemically resistant brick or tile.* The role of the brick or tile is to provide thermal and mechanical protection to the membrane and the substrate material. The brick or tile must be resistant to the process chemicals at the expected temperature.

A number of brick and tile compositions are available for use in chemical-resistant applications. These include bricks made of red shale or fireclay. Other brick materials are carbon, foamed glass, silica and silicon carbide. Like brick, tile is made from a variety of materials. The most common tiles are quarry tile, paver tiles and glazed tiles. Tile thickness varies from about $\frac{1}{4}$ in. (6 mm) for glazed tile to $1\frac{3}{16}$ in. (3 cm) for paver tile. Quarry tile is usually either $\frac{1}{2}$ in. (13 mm) or $\frac{3}{4}$ in. (19 mm) thick.

3. *Chemical resistant mortar and grout for bedding and joining bricks and tiles.* The mortars and grouts used for this construction may be either organic or inorganic, depending on the operating temperature and the chemicals to be encountered. Organic mortars and grouts are used for floors, trenches, walls, etc., where high temperatures are not expected. Typical materials are furans, phenolics, epoxies, polyesters and vinyl esters. Inorganic mortars and grouts are used in applications where the expected temperatures are too high for the organic materials. Inorganic mortars and grouts are usually sodium or potassium silicates or sulfur.

Insulation and Erosion Resistance

In most cases, construction for insulation and erosion resistance does not include the use of a membrane layer. For applications in which both insulation and erosion resistance is necessary, a two-layer construction is often used. The layer adjacent to the substrate is made of a less dense material that provides insulation, while the layer exposed to the process is made of a dense brick that is more erosion resistant.

Ceramic Fibers

Ceramic fiber insulation is available in a number of product forms including blankets, modules, paper, bulk fiber, boards and shapes. This material is used in applications where its light weight, ease of installation and extremely good insulating capacity can be used to advantage. The primary disadvantage of the material is its poor resistance to high-velocity gas (50 ft/sec (15 m/s) or greater). It can be eroded at even moderate velocities (10 ft/sec (3 m/s)) by gases containing particulates. Such erosion problems are partially overcome by using boards made of ceramic fibers.

Chemical Stoneware and Other Shaped Ceramics

Chemical stoneware is a term used to describe bodies that have been more highly vitrified than ordinary vitrified clay pipe and shapes. This material is used in applications where a higher density is required to improve resistance to chemicals.

Other ceramic shapes are widely used to applications such as tower packing and heat exchanger ferrules.

As can be seen from the above discussion, the technology of refractories is highly specialized. The reader should contact a refractory specialist or a manufacturer's technical representative for materials selection advice for specific applications.

7. Wood

Wood is still used extensively as a structural material in applications such as pilings, decks, etc. However, wood is no longer a primary material of construction for most process equipment (a notable exception being cooling towers). Nevertheless, in some applications it may be a cost-effective alternative. Wood occasionally finds service in a wide range of equipment including materials handling (e.g., chutes), tanks, vessels, vats and pipe.

Sometimes wood is not considered for an application because it is considered to be old fashioned or obsolete. Siebert [10] reports a number of cases where wood had given good service, but where it was not considered sufficiently modern when a replacement was required. For example, a small wooden tank had been maintenance-free for 18 years. When a spare tank was required to expand the process capacity, a nickel-molybdenum alloy tank was specified. A wooden tank would have been much less expensive.

Wood deteriorates from two principal causes, chemical and biological attack. The chemical resistance of wood depends primarily on the resistance of the wood's cell walls to chemical action and on the extent the chemical penetrates into the wood. Wood generally provides durable service for any solution that is not actively destructive to the wood fiber. In water, wood swells without degradation. Long-term service is usually determined by the resistance of the wood to delignification.

Unfortunately, wood shrinks when it dries out. If the wood is kept wet, dimensional stability is good. This swelling action is used to seal wooden tanks, buckets, pipes and the like. Similar behavior is seen in dilute aqueous solutions and solvents such as alcohol.

Woods give their best service in the pH range of 2 through 9 and can be used at up to pH 11. Wood is resistant to weak acids, but concentrated mineral acids tend to hydrolyze the cellulose and hemicellulose constituents. Alkalis and oxidizing agents such as ozone attack the lignin that binds the fibers together.

Strong oxidizing agents can also oxidize the cellulose, forming a brittle oxycellulose. For this reason nitric acid, chromates, potassium permanganate and chlorinated water attack wood.

Biological deterioration of wood is caused primarily by aquatic organisms, insects and fungi. Mitigation of biological deterioration is often based on pressure-treating the wood with preservatives such as creosote. Such treatments can be effective for many years in services that are not severe. Extended life can sometimes be obtained by jacketing the wood. For example, jacketed piles are used to extend pile life in seawater service. In some cases, jacketing is part of original construction, but in many cases it is done after several years in service. Jacketing while in service restricts the flow of oxygen and nutrients to aquatic life that has colonized the wood. Resident populations are killed and repopulation is prevented by the barrier effects of the jacketing. In recirculating systems such as cooling towers, biocides and/or fungicides are used to help control biological attack. Protection from insects is usually provided by preservatives and/or treating adjacent soils with insecticides.

Unlined wood can be used to handle dilute (<5 percent) hydrochloric and sulfuric acids at ambient temperature, phosphoric acid up to 30 percent at ambient temperature, organic acids, aldehydes, alcohols and acid salts. Wood tanks can be lined with bituminous materials, coatings, plastic or elastomers to extend their usefulness. Wood can also be impregnated with various resins to increase its resistance. Phenolics provide increased resistance to acids and furans provide resistance to alkalis. Other impregnants promote resistance to weathering and fire. Treated wood is not generally used in contact with food, potable water or where contamination of the product is objectionable.

A common application of wood is the oak tanks and barrels used to store and age wine and whiskey. It is used in food preparation applications such as making vinegar and preparing pickles, olives and cherries. Wood pipes are used for handling corrosive slurries and waste waters. A major application of wood is in the handling of bulk fertilizers. Easily replaced wood liners and impingement plates are used in abrasive services such as receiving tanks or vats taking abrasive feed from conveyers.

Redwood, red cedar, Douglas fir and various pines are usually chosen for cooling towers and for many chemical exposures. Redwood and fir are used in sulfite liquors from the pulp and paper industry. Pine serves reasonably well in acid mine waters, dilute mineral acids and mildly alkaline solutions. Maple is used for more abrasive slurries, because of its hardness. Heartwood that has been kiln dried is preferred. Cypress is an excellent wood for general chemical service.

Structural members of solid timbers or glue-laminated timbers are used extensively in architectural applications and are candidates for greater use in process applications. Laminated members start with commercially available lengths of seasoned lumber. By arranging the joints at staggered intervals,

structural components of virtually any dimension and shape can be created. Laminated wood members maintain their shape when exposed to fire, until being destroyed by combustion. They can withstand thermal conditions that would cause steel members to buckle.

F. COATINGS AND LININGS

1. Introduction

Coatings and linings are used for many reasons. They:

- Act as a physical barrier to corrodents to protect the substrate material from contact with a corrosive process fluid or environment. Examples include alloy cladding, most weld overlays and most paint coatings.
- Reduce the amount of cathode current by using the coating as a dielectric barrier. For example, coating the more noble metal tubesheet of a heat exchanger helps protect the less noble channel or channel cover.
- Provide the substrate surface with cathodic protection such as galvanizing.
- Modify the surface environment of a substrate material to prevent corrosion in an otherwise corrosive environment. One of the most common applications of this approach involves cement-lined piping, in which the free lime in the cement creates a high-pH, non-corrosive aqueous layer at the surface between the cement lining and the carbon steel pipe.
- Create a smooth surface for mixing and/or draining.
- Modify the surface of the substrate material. Examples include providing protection from galling by use of a hard face plating or weld overlay and the use of peening to place the surface under compression, thereby inhibiting stress corrosion cracking.
- Restore lost thickness. A common application is the use of a plasma-sprayed coating to repair a worn rotating equipment shaft. In many cases, a coating or lining may serve more than one beneficial purpose. For example, a paint coating may act as both a physical barrier to the process fluid as well as a dielectric barrier.
- Provide thermal protection when used as refractory linings for the pressure-containing metal or alloy.

In other cases, a coating or lining intended to solve one problem can generate an unexpected problem. For example, holidays in a coating may concentrate the anodic current, causing extremely high local pitting rates, which lead to early leaks.

To ensure success in using coatings and linings, the choice of type and product must be based on a firm understanding of what is to be accomplished. Lack of such understanding may lead to an unpleasant surprise.

2. Thick Dielectric Barrier Coatings

Thick dielectric barrier coatings and linings depend on their integrity to ensure protection, usually because cathodic protection cannot be relied on to protect the substrate from flaws or pinholes in the coating. Thickness provides one and sometimes two advantages:

- Fewer pinholes and other through-thickness flaws (holidays).
- Virtual elimination of cathode current from the substrate, thereby limiting the anodic current at any pinholes or other holidays. Since the pitting corrosion rate is directly proportional to the anode current density, limiting the anodic current density limits the pitting corrosion rates at pinholes and other holidays.

Rubber, polymers and composites, typically $\frac{1}{8}$ " to $\frac{1}{2}$ " (3 to 12.7 mm) thick, are used for a variety of applications, none of which can depend on cathodic protection.

On offshore structures, the splash zone caused by wind and wave action is not continuously wetted. The splash zone therefore cannot be reliably protected by the cathodic protection system used to protect the submerged sections of platforms and pipelines. In splash zone areas subject to the risk of impact damage by boats or debris, high-reliability systems such as thick rubber coatings are usually specified.

In some splash zone services not subject to mechanical damage, catalytically cured polymeric products (generically called "splash zone compound") are used. Because of the difficulties involved in cleaning in place, such products are often smeared on over wet and/or unclean surfaces. Successful application limits access and/or flow of corrodents.

Rubber is also commonly used as a coating or lining. Rubber is frequently selected for coating the internals of butterfly valves and some types of tanks and pumps for services such as seawater, in many chemical services and in some abrasive slurry services. Note that many rubber compositions are susceptible to deterioration by organic solvents. Consult the manufacturer for specific composition recommendations.

Thick polymers such as PVC and TFE are often specified in lieu of rubber. They also see service as liners in chemical service piping and equipment in which carbon or stainless steel is used for pressure containment. Such systems are commonly used to handle inorganic acids. This type of piping system is particularly useful in situations where internal holidays cannot be tolerated and internal joint protection is required. Providing such protection with thin-film paint coatings is virtually impossible.

Thick polymers, sometimes "filled" with inorganic or metallic reinforcing fibers or particles, are marketed as temporary repair materials for internally corroded equipment such as pumps, vessel shells and tanks. Such products usually

do extend equipment life, sometimes very successfully. These products are also sometimes used in mildly abrasive services, with good results.

Polymer tapes, with a combined adhesive-backing thickness of about 0.050" to 0.075" (1.3 to 1.9 mm), have been extensively used as tapewrap for external protection. These wraps are fixed to the cleaned surface with an adhesive. Tapewraps have worked well in applications where properly applied tape is not subsequently subject to age-induced embrittlement, rock damage in the ditch, impact damage, soil stress, etc.

For buried pipelines (a major application), tapewraps have an erratic history. Even though tapewraps are sometimes provided with a protective covering (often referred to as a "rock guard") to help prevent tearing of the tape during and after lowering the pipe into the ditch, tapewraps have proved to be fragile. Even when supplemented with a cathodic protection system, a badly deteriorated tapewrapped system usually continues to corrode, because the cathodic protection system was never designed to accommodate large-scale tape damage. In addition, disbonded tapewrap and/or rock guard may interfere with cathodic protection through "shielding."

Tapewrap can be seriously damaged during the construction phase of a pipeline. Pipeline construction, which is normally schedule driven, employs over-the-ditch tapewrapping. Examples of construction-related problems include inadequate cleaning, insufficient overlap, and improper tensioning and priming difficulties.

Yard-applied tapewrapping is occasionally employed. This technique also has potential damage problems, including those due to transportation, laydown, fit-up and welding.

Early failures can also occur because of tearing due to soil stressing, penetration by rocks in the ditch, or embrittlement of tape by excessive pipeline operating temperatures. Some tapewrap products become very soft if exposed to high temperatures, making them especially sensitive to penetration problems. In soils known to be corrosive, tapewrapped pipelines should be provided with suitable cathodic protection.

Composite reinforced plastics such as blown-in-place chopped fiberglass/epoxy resin are sometimes used as liners in tanks and large vessels in which water condensation can occur but in which the water will not form a continuous phase. In such situations, cathodic protection is ineffective. For example, in crude oil storage tanks, tar-like deposits may cause the formation of isolated "pockets" of saline water.

Rubber Linings

As mentioned above, rubber linings are used extensively in chemical process plants, in abrasive services and in many severely corrosive services such as mineral

acids. A discussion of some of the important elements of the process of rubber lining will illustrate many of the features of other lining processes as well.

Rubber linings combine the chemical resistance of rubber with the strength of steel or concrete. These linings may be directly exposed to the environment or used as a membrane for brick-lined equipment. Typical rubber lining applications are shown in Table 2-8.

Only a few elastomers are used for lining applications. The most common are:

- Natural and synthetic natural rubber (soft, semi-hard, hard)
- Chloroprene rubber (Neoprene)
- Butyl and chlorobutyl rubbers

Linings for equipment require modification of the basic polymer by the addition of fillers, vulcanizers and other agents. As a result, the composition of

Table 2-8 Rubber lining applications

Storage, day and weigh tanks
Reactors
Columns
Towers
Crystallizers
Evaporators
Filters
Centrifuges
Agitators
Pumps
Pipes
Valves
Transportation: rail and truck
Membranes for brick linings

Table 2-9 Composition of natural rubber linings

Ingredient	Soft	Semi-Hard	Hard
Rubber	~80%	55-65%	55-65%
Filler	~20%	35-40%	34-40%
Vulcanizers	1-2%	1-2%	1-2%
Durometer A Hardness	30-50	50-90	>90

rubber sheet stock may be only 50 percent basic resin, as illustrated in Table 2-9. Note the effects of filler (usually carbon black) and vulcanizer (sulfur) on the hardness of the sheet stock: increased hardness generally results in increased chemical resistance.

Since rubber lining sheet stock is made from many raw materials (resins, fillers, accelerators, vulcanizers, etc.), there are many formulation variations within a given generic type. No two manufacturers make identical linings. Tests should be conducted with the same sheet material being considered for an application. The results may not be applicable to an "equivalent" formulation.

The rubber sheet stock should be of the proper thickness. There are some common guidelines for sheet thickness before vulcanization are:

- Minimum: $\frac{1}{8}$ " (3 mm)
- Preferred: $\frac{3}{16}$ " (4.7 mm)
- Maximum in one layer: $\frac{1}{4}$ " (6 mm)
- If more than $\frac{1}{4}$ " is required, the rubber should be applied in two or more layers.

Sheet stock for lining can be made of a single rubber or of more than one composition. For example, it is common to have a natural rubber ply on the underside of a synthetic rubber lining to facilitate bonding to the steel. Another common practice is to use triple ply linings in which the inner layer is a soft rubber for good adhesion, the middle layer is a semi-hard rubber for improved chemical and permeation resistance and the outer layer is soft rubber for abrasion resistance. Other combinations can be used for special applications.

Considerations for Rubber-Lined Equipment

There are a number of factors that should be taken into account when rubber lined equipment is being considered. The first factor is the size and complexity of the equipment to be lined. The more fittings, nozzles, baffles, coils, etc., in the

equipment, the more difficult it is to get a defect-free rubber lining. The number of these internals also increases the lining cost since each fitting must be lined unless it is made of a corrosion resistant material.

Another consideration is where the lining is to be installed. In most cases, it is preferable to line a vessel in a shop where it can be vulcanized in an autoclave. However, this can present a problem in the winter since transportation of hard or semi-hard rubber-lined equipment in cold weather can result in cracking.

A further consideration is the vulcanization method, which must be appropriate for the equipment and rubber. Alternatives include:

- *Vulcanizing in an autoclave.* This produces the best bond and lowest porosity and is the preferred alternative in most cases. However, large equipment may exceed the size limitations of the available autoclaves.
- *Using the equipment as its own autoclave.* If the equipment is designed to withstand the pressures involved, and if high-pressure steam is available, this may be a viable alternative. Temporary insulation may be required to obtain the desired wall temperature.
- *Vulcanizing with steam or hot air at ambient pressure.* This requires the use of rubbers designed for this curing method since the temperatures obtained are lower than with autoclave curing. Again, the vessel should be insulated to get the highest possible wall temperature.
- *Self-vulcanization or chemical vulcanization.* This is usually the best choice when concrete equipment is lined. The high heat capacity of concrete equipment usually precludes the use of other curing methods. These rubbers have a more limited range of chemical resistance than rubbers vulcanized by heating.

Design, Fabrication and Preparation of Equipment to Be Lined

Metal Equipment

Most problems with rubber-lined equipment can be traced to either inadequate design or improper application. For a discussion of these topics, including detailed drawings that illustrate many important design and fabrication features, refer to reference [11]. The following discussion highlights key elements in the design of equipment to be rubber lined.

Since fully cured rubbers are often somewhat brittle, equipment to be lined must be rigid enough to avoid deformation or deflections that could result in damage to the lining during transportation, installation, or operation. This often requires a more robust construction than would be used for normal fabrication. Where stiffeners are required, they should be attached to the exterior side of the equipment.

Failure to consider the brittle nature of cured rubber linings has resulted in equipment failures. In one case, semi-hard natural rubber-lined equipment was

shipped during the winter. The combination of thermal stresses and mechanical stresses from shipping and handling in cold weather resulted in the equipment having many lining cracks when it arrived at its destination.

Rubber lining requires that the lined surfaces be accessible and that there be adequate ventilation to carry off solvent fumes from the adhesive. In enclosed vessels there should be at least one manway at least 24" (600 mm) in diameter and one additional nozzle of not less than 3" (75 mm), to permit adequate air circulation.

It is important that the rubber adhere to the surface, with no air pockets, which may subsequently cause blisters during curing. In addition, there should be no sharp edges, which promote cracking. Therefore, surfaces to be lined should have a smooth contour and be manually accessible.

Discontinuities, crevices and sharp projections will result in poor linings. Therefore, riveted construction should not be used. Bolted joints should be used only if they can be dismantled for lining.

All attachments to adjacent equipment should be flanged since welding is not permitted on lined equipment. To facilitate lining, nozzles should be as short as possible. Flange faces should be designed to allow the lining to continue over the face in order to eliminate an edge exposure of the lining to the process fluid.

Rubber gaskets of 30-50 Durometer A should be used when the rubber on the flange faces exceeds 65 Durometer A. An anti-stick material should be applied to the rubber surface before tightening the flange to avoid tearing the rubber when the flange is disassembled. It may be necessary to limit the compression of the rubber in a bolted joint. In such cases, torque settings for the bolts should be specified or suitable spacers designed and provided. Torque values should not exceed 40 ft-lbs (55 N-m).

For vessels, internals such as heating coils, immersion heaters, sparger pipes and other unlined parts should be installed after completion of the lining. These parts should be designed so that local overheating is not possible. They should not be closer than four in. (100 mm) from a lined surface.

Pipework and Fittings

Lining pipework and fittings is similar to lining vessels except that access is a greater concern. For pipework and fittings too small for physical access, mechanized methods must be used. Activities such as dressing the welds, preparing the surface for lining and applying the lining itself become more difficult to inspect. It is best to use straight lengths of pipe. The lengths of pipe may contain tees or a single bend provided that the nominal size is six in. (150 mm) or above and the leg length of the tee or bend does not exceed the dimensions of a standard tee or bend. Use separate standard (1.5D) bends and standard tees. Bends should not exceed 90 degrees.

Refer to Table 2-10 for guidance on maximum pipe length.

Table 2-10 Maximum lengths of pipe recommended for lining^{1,2}

Nominal Bore		Length of Pipe	
in.	(mm)	ft	(mm)
1.0	(25)	6.5	(2000)
1.3	(32)	8.25	(2500)
1.6	(40)	10.0	(3000)
2.0	(50)	11.5	(3500)
2.6	(65)	13.0	(4000)
3.2-24	(80-600)	19.5	(6000)

¹Refer to Ref. [11].

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Fabrication of Metal Equipment

Metal equipment intended for rubber lining must be fabricated to special standards to ensure that a sound lining can be applied. The welds must be continuous and butt welds must be used for the main seams. Lap seams and the like are not consistent with sound linings. The side of the weld to be lined must be free of porosity.

Weld surfaces should be ground smooth, with sharp edges and weld ripples removed. The weld should be free from undercutting, cracks, porosity, surface cavities of any type and lack of fusion. All weld defects should be repaired and the surface reground. Welded attachments such as insulation cleats and lifting lugs should be completed before the equipment is prepared for lining.

Castings must be smooth with no slag and slag inclusions, shrinkage cavities, scabs, cracks, porosity, or burrs.

Surface Preparation of Metal Equipment

The surfaces to be lined must be smooth and should have large radius contours. External corners should be finished to a radius at least equal to the thickness of the rubber, while internal corners should be finished to a radius of at least twice the rubber thickness. All surface defects such as weld spatter, scores and pits should be removed as should all foreign material such as grease, oil and chalk. All carbon steel or cast iron surfaces to which linings are to be applied should be abrasive blasted to a "white metal" quality per NACE Standard No. TM0170 (equivalent to

Steel Structures Painting Council SSPC No. 5). After blast cleaning, all dust and other residues should be removed and the surface primed within four hours, before any visible rusting occurs.

Inspection of Metal Equipment

It is important that equipment be inspected before, during and after the rubber is applied and cured. Vulcanization is not a reversible process. Repair of defects after vulcanization is not as satisfactory as when defects are found and corrected earlier. Inspection should take place at the following stages:

- As the equipment is fabricated, to ensure that the equipment meets the specified requirements.
- After the welds and edges are prepared.
- After the equipment is blast cleaned. The surface should be clean, with no dust or rust stains present. It should meet the specified "white metal" standard.
- After the lining is fitted but before vulcanization. Lining defects are easier to repair at this point than at any later time.
- After the first stage of vulcanization (when the process is done in two steps). The lining can still be effectively repaired at this point.
- After vulcanization is complete.
- After the equipment has been installed but before it has been put into service. If the lining is very hard, it may be desirable to inspect it after it has been transported but before it is installed.
- Periodically during the life of the equipment and whenever any remedial work is done on the equipment.

Inspecting the lining normally involves:

- A visual examination for blisters and to ensure that the lining joints are properly made. Generally, blisters are repaired since they can lead to lining failure. Small blisters between rubber plies are sometimes left in place if the expected service permits this. It is best if the number and size of blisters that will be permitted is spelled out before the job is started.
- A test of the lining continuity. This is done with a high-frequency AC spark-testing instrument typically set between 20 and 55 kV, depending on the thickness and type of rubber and the joint design.
- A test of the hardness of the cured rubber.
- A test of the lining adhesion, especially if there is reason to suspect that it is inadequate. However, this test is destructive and requires lining repair. Therefore, it is not normally done on actual equipment. If the owner requires a high level of adhesion, the more common practice is to have the fabricator prepare test panels of the same type and thickness of rubber that is cured at the same time as the equipment.

Concrete Equipment

Concrete equipment should be designed to eliminate structural cracking. The equipment should not have expansion joints unless absolutely necessary. Therefore, special attention should be given to thermal stresses. Extra reinforcement may be required.

Pipes and fittings should be provided with flanges and cast into the concrete. They will normally be rubber lined before being cast into the concrete.

All corners in the concrete equipment should be designed to be formed with a 45 degree fillet and with a minimum leg length of 0.8 in. (20 mm). After the concrete has cured, all surfaces to be lined should be treated to remove laitance and residual release agents. Blast cleaning is recommended; however, blast cleaning must be controlled so that laitance is removed without exposing the aggregate profile. Cold acid etching with hydrochloric acid is an alternative cleaning method.

Failures in Rubber Linings

A common cause of failure of rubber-lined equipment is mechanical abuse. This can take the form of abrasion and wear from slurries and crystals. Cuts, gouges and tears at stress points and excessive vacuum and/or exposure to excessive temperatures that causes blistering and disbonding are sources of failure. Deflections of vessel shells during transportation or erection or by impact can also cause cracks in semi-hard and hard rubber linings.

Chemical attack can result in surface hardening or softening of the rubber lining. Another mode of attack is diffusion and permeation of chemicals through the lining, resulting in attack on the bond between the rubber and the steel or concrete surface. This can result in disbonding, with no apparent attack of the lining itself. Permeation was the cause of failure in a waste acid storage tank that handled sulfuric acid and ammonium sulfate at 150°F (65°C). During upset, it was possible for a chlorinated hydrocarbon to enter the tank. After eight months of operation, the acids permeated the lining and attacked the steel, resulting in a disbonded lining. The unanticipated organic contaminant apparently caused the lining to swell, which then permitted permeation of the vessel's inorganic contents through the lining.

Storage, Transport and Installation

Lined equipment should be stored away from direct sunlight, heat and outdoor seasonal weathering. Piping and equipment lined with soft rubber may be stored outdoors provided the equipment is covered and not subjected to extreme temperature conditions such as temperatures below freezing or warmer than 120°F (49°C). Sudden changes in temperature should be avoided. Equipment stored or used outdoors should be painted a light color to reflect heat.

Semi-hard and hard rubber linings are more fragile. They should be stored indoors and should never be exposed to freezing. These linings are subject to cracking caused by thermal stresses.

Rubber-lined vessels and tanks may be protected during storage by filling them one-quarter full with a liquid such as five percent sulfuric acid or five percent sodium carbonate. This will keep the lining flexible and thus minimize expansion and contraction. It will also prevent ozone in the air from causing the lining surface to deteriorate. The liquid should not be permitted to freeze. Exposed rubber at openings such as nozzles should be covered with plywood or other material.

3. Thin Dielectric Barrier Coatings

Most paints and coatings provide protection because of their barrier and dielectric properties. The major exception is inorganic zinc paint, which is not a dielectric product. In fact, inorganic zinc paint provides cathodic protection to the substrate, rather than serving as a dielectric barrier.

Coatings used for atmospheric protection must have good resistance to their environment and to problems caused by through-thickness flaws. This is because cathodic protection cannot be used to supplement the protection such coatings provide. Tests for adhesion, resistance to undercutting, etc., can be used to rank the probable performance of such coatings for specific applications. Data are usually available from the technical representatives of paint and coating manufacturers to assist in making choices.

When choosing coatings for immersion service, some thought should be given to providing supplementary cathodic protection. Even though the coating may be dielectric, some cathode current does pass through the coated areas. If concentrated at pinholes, this current can generate a relatively large anode current density, hence a high pitting rate, at such flaws.

A rule of thumb is that the maximum effective linear distance that a cathode can interact with an anode is three to five diameters. When considering thin-film coatings for corrosion protection, keep in mind that, for immersion service, the practical upper limit of service temperature is about 200°F (93°C) for catalytically cured coatings and about 400°F (205°C) for baked-on products. Each generic coating usually has a fairly well defined upper limit for successful performance. However, there is usually some variation among particular products within a generic family. Manufacturers should be contacted for their recommendations and advice on service condition limitations unless the user has prior successful experience with a particular product.

Piping

Supplementary internal cathodic protection is usually not necessary in piping if the internal coating does not have a high density of holidays. Holidays should occur at

a frequency of no more than one holiday per three to five pipe diameters of line length.

Because of the beneficial effect of cathode current reduction, internal pipe coatings can extend the life of piping systems in electrolytically corrosive services. However, the method is not widely used in plants. Non-metallics, plastic liners, bimetallic piping and alloy piping are usually employed as they are more reliable and provide a much longer useful life. In addition, internally coating girth welds and branch connections in small-diameter plant piping is usually not possible.

Internal coatings are successfully used in large-diameter pipelines in corrosive water service. The primary usage is in water injection pipelines used for oil field reservoir pressure maintenance. For lines over about 12" (30 mm) diameter, crawlers have been developed that will properly clean and coat girth welds. *In situ* coating techniques have been developed that provide a continuous coating in the pipeline. This practice is usually used to salvage a pipeline that has developed internal corrosion problems, but it has also been used to internally coat new pipelines. A number of proprietary polymer internal liner systems have been developed for the salvage of corroded pipelines.

Vessels and Tanks

The three- to five-diameter rule of thumb requires that thin-film internal coatings in immersion service be supplemented with cathodic protection. Both impressed and sacrificial systems have been successfully used. In the event that cathodic protection is not practical, thick dielectric coatings, weld overlays or some other mitigation measure should be used.

4. Thick Metallic Barrier Coatings

Since metallic barriers such as cladding, weld overlays and metallic plating are anything but dielectric, they depend solely on their barrier ability for protection of the substrate. When they are used in electrolytically corrosive applications, the user should be alert to possible galvanic activity and potential problems involving unfavorable anode/cathode area relationships.

Cladding and Weld Overlays

In many reactors, vessels and heat exchangers, clad construction is the most cost-effective way to achieve both pressure containment and corrosion resistance. In this technology, a relatively thin clad or weld overlay layer is used to withstand process-induced corrosion while the pressure shell is made of a higher-strength, lower-cost material such as carbon or low-alloy steel. Such services, because they do not operate with a continuous electrolytically conductive phase, cannot depend on cathodic protection.

Unlike most sprayed metal coatings (discussed later), neither clad nor most overlayed products are likely to have pinholes. Thus, even if the cladding or overlay is cathodic with respect to the substrate, there is usually no danger of developing an unfavorable anode/cathode area problem.

The two-layer construction approach has the added advantage of eliminating the risk of externally induced chloride stress corrosion cracking, which would accompany the use of solid austenitic stainless steel.

The choice between clad and weld overlay may be determined by either of two criteria:

1. Roll bond clad plate is available only in relatively thin substrate thicknesses; the practical limit is about 3½" to 4" (90 to 100 mm). Thicker substrate thicknesses are available as an explosion-bonded product. Clad plate is usually cheaper than overlayed plate.
2. Weld overlays are thought to resist interlayer disbonding better, particularly in hydrogen service.

The recommended minimum thickness of cladding depends on both its susceptibility to mechanical damage in service and on economics. For vessels in which the risk of mechanical damage is small, cladding can be as thin as 0.050" (1.3 mm). Cladding is specified to be as thin as practical for expensive cladding materials such as tantalum or zirconium. For vessels subject to in-service mechanical damage, such as heat exchanger shells subject to bundle removal/insertion, the clad layer should be at least 1/8" (3 mm) thick.

The recommended minimum thickness of a weld overlay depends on two considerations:

- As with cladding, the service susceptibility to mechanical damage.
- The concern, if any, about weld dilution. (Weld dilution occurs when the material being welded mixes into the molten weld metal.)

For mild services, a single-layer overlay, using a consumable with a composition that at least partially accommodates weld dilution, is often specified. Current technology can usually supply a consumable that provides the metal surface with a composition that is, for practical purposes, unaffected by dilution. The thickness of a single layer overlay is usually specified to be 1/8" (3 mm) minimum.

For severe services, a two-layer overlay is often specified, with each layer being a minimum of 1/8" (3 mm) thick. In two-layer overlays, the first layer is usually made of a consumable that partially compensates for weld dilution. In one common example, Type 309L-Cb SS is used for the first layer and Type 347 SS for the second layer.

Hard Facing

Weld overlays are frequently used as "hard face" layers on valve internals, integral wear rings in pumps, etc. Such overlays are frequently used to establish a hardness difference of at least 50 BHN to prevent galling. Hard face overlays are most frequently used to reduce wear, friction and/or impact damage.

Hard face overlays are frequently thin, typically about 0.050" (1.3 mm) finished thickness. For wear resistance, however, they are often thicker (typically 1/4" (6.4 mm)). The overlay material is often much more brittle than the substrate material. In cooling from the welding process, the brittle weld overlay sometimes forms a crack network (called "crazing" or "checking") that extends through the thickness of the overlay. Since the overlay material may be more noble than the substrate, an unfavorable cathode/anode area relationship may develop in a corrosive medium.

If the substrate will not be resistant to corrosion by the process, consider the possible beneficial effects of weld dilution. In the event that dilution by the weld metal will not be adequate, choose a substrate material that will be resistant to the process fluid. In evaluating the beneficial effects of dilution, one will generally depend on case histories.

Strip Lining

This technique is not normally used in the fabrication of new equipment, the major exception being the use of expensive refractory metals such as tantalum, used as liners for some chemical process vessels. Normally, strip lining is used for the purpose of salvaging the pressure shell of a vessel that has undergone internal corrosion. The technique involves welding thin strips (usually about 4" x 30" (100 mm X 750 mm)) circumferentially to the vessel wall using either butt-welded or overlapped strips. Some users require one or more plug welds to strengthen the weldment. Each finished strip is usually subjected to a vacuum test to ensure weld integrity.

A related technique, "wall papering," is sometimes used to install corrosion-resistant liners in corrosive flue gas desulfurization systems, ducts and stacks. NACE has published an excellent recommended practice for wall papering; many of its guidelines are applicable to strip lining as well (see NACE RP0292 [12]).

These techniques provide true barrier protection. Since the barriers are usually quite noble with respect to the substrate material, they in fact form a galvanic couple with the substrate. In practice, accelerated corrosion due to a failed strip is rare. This may be due to the lack of a cathodic depolarizer such as oxygen. In some cases, the low rate of subsequent corrosion may be due to the rate being controlled by diffusion. This is the case when the size of the tear or hole is small enough that it restricts the flow of corrodent behind the failed strip. In other cases,

the absence of accelerated corrosion is due to the lack of a liquid electrolyte condensing in the pocket formed by the perforated strip.

Splash Zone Protection

Some companies prefer to use Ni-Cu alloys such as Alloy 400 sheathing in the splash zones of offshore structures. This practice has a long history of success. Even when penetrated, Alloy 400 sheathing is usually effective. Apparently, the penetrations are usually too small to provide flow of sufficient aerated seawater. Oxygen depletion by either the entrained marine life or by corrosion may contribute to maintaining the passivity of the carbon steel.

5. Thin Metallic Barrier Coatings

The most common of the thin-film metallic coatings are:

- Electroplated chromium, usually for wear and/or galling resistance
- Electroless nickel plate (ENP), usually for galling resistance or to assist in making a tight seal in a valve closure
- Vapor-deposited surfaces, usually employing aluminum for deposition

Thin film metallic coatings should never be used for protection from electrolytic corrosion if the substrate material is anodic with respect to the coating. In the presence of a strong corrodent and/or an effective cathodic depolarizer such as dissolved oxygen, a pinhole or holiday has a very unfavorable anode/cathode area relationship. With the cathode being covered with a good electrical conductor, no reduction in cathode current density occurs. The high anode current density generates high local pitting rates. It is not uncommon, after a relatively short time in service, to find that large sections of the substrate have dissolved, leaving the pinhole and the metallic barrier intact. This phenomenon is particularly common with chromium plate and ENP sold to the user as a form of corrosion protection. In one notable case, an ENP applicator advertised that its product protected carbon steel valve internals from corrosion by seawater. The advertising did not mention that the seawater had been deaerated to less than 10 ppbw.

Thin film metallic coatings, particularly ENP, are occasionally used to reduce product contamination in process streams of already low corrosivity. The base material is usually carbon steel and the applications usually involve components that can be coated without holidays in services that are not likely to generate scratches or pinholes. Such applications are occasionally used in food and drug processes.

Vapor deposition coatings find limited use in most plants. Very specialized products are used as protective coatings on high-temperature steam and combustion gas turbine components. Such applications are outside the scope of this book.

Aluminum vapor deposition coatings are sometimes used to protect carbon steel, Cr-Mo steels and high-alloy tubes from sulfidic corrosion, carburization and nitriding. They are also used in some hydrocarbon plants to minimize downstream contamination that could result in plugging or degradation of catalysts or product streams. These coatings are about 3–5 mils (0.075–0.13 mm) thick. They consist of a metallurgically bonded layer containing various aluminides and an outer layer that is virtually pure aluminum. Their long-term success in protecting against high-temperature corrosion generally depends on their freedom from through-thickness defects and the development of service-induced, through-thickness flaws. Given the brittle nature of the coating, its susceptibility to impact damage, cracks due to bending and the absence of protection at welds, such coatings have a mixed history of success.

Aluminum vapor deposition coatings have gained a reputation for improving heat transfer performance by reducing fouling. In general, however, they do not extend the time between decoking runs or equipment inspection, which are usually determined by other factors. These coatings have been used successfully to protect downstream equipment from sulfide scale fouling. Upstream carbon steel, low-alloy steel and 12 Cr SS components, subject to mild to moderate rates of sulfidic corrosion, have been coated to essentially prevent scale formation.

In high-temperature applications of aluminum vapor deposition coatings involving austenitic stainless steels and high alloys, in-service diffusion adjacent to the substrate interface has caused potentially damaging changes in microstructures. In some cases, failures were due to operating temperatures in excess of the temperatures used to form the coating. Nevertheless, some case histories of success can be cited for using vapor-deposited aluminum to protect austenitic and high-alloy steels from high-temperature attack.

Given the mixed history of service for aluminum vapor deposition coatings, the user is well advised to verify with other users any claims of successful applications.

6. Sprayed Metal Coatings

Sprayed metal coatings (the process is often called "metallizing") are in common use. Various heat sources are used such as flame, arc and plasma. In this process, molten metal is sprayed onto the surface to be protected. Sprayed metal coatings are subject to several disadvantages:

- Very little metallurgical bonding takes place in most such coatings; the coating "sticks" to the substrate via a "mechanical" bond. Some metallurgical bonding is claimed for a few of the processes.

- Some coatings are porous, being made up of as much as 50 percent voids. Such coatings usually contain some fraction of oxidized metal, which act as additional embedded defects.
- Many sprayed metal coatings are subject to disbonding induced by tensile stresses such as bending and by thermal stresses, and may be subject to undercutting in corrosive environments.

As a result of the shortcomings of sprayed metal coatings, hot-dip products are usually preferred. However, sprayed metal coatings are useful for several purposes, usually involving applications where hot-dip application is not feasible.

Corrosion Protection

Sprayed metal coatings are useful for shop and fabrication yard applications, for situations in which it is impractical to hot dip fabricated components. A good example is the use of such coatings for platforms and structures to be used offshore. In selecting metal spray coatings intended for corrosion protection, choose coatings that are anodic with respect to the substrate. Aluminum, zinc or an aluminum-zinc alloy are usually selected for coating carbon steel. It is usually possible to select a coating that is not only anodic but is also resistant to the contacting fluid. For example, aluminum is very resistant to wet CO₂ corrosion and is therefore a good choice for coating carbon steel that would otherwise be in contact with the wet CO₂.

Note that because some sprayed metal coatings are quite porous, applicators will sometimes recommend that they be "sealed." In this process, a sealant such as a paint coating is subsequently applied to the sprayed metal coating. Since many sprayed metal coatings can be applied with very little porosity, the user should regard such recommendations with some caution. Low-porosity sprayed metal coating technologies should be preferred.

Cathodic products such as stainless steels are sometimes marketed as corrosion coatings to protect anodic substrate materials. However, potential porosity and relatively poor adhesion of the coating provide a significant risk that a very unfavorable anode/cathode area relationship could develop, leading to rapid failure by pitting. Even if the porosity is sealed, any through-thickness nick, spall or unsealed pore could either destroy the substrate or undercut the metal coating. Sealed or unsealed, such coatings should be considered with caution.

Erosion and Wear Protection

Some sprayed metal coatings, usually applied by the plasma spray method or by detonation spraying, have been successfully used to enhance resistance to erosion and wear. Be careful when loading these coatings in bending. They may be quite brittle and may readily disbond or spall if subjected to tension or impact loading.

Thermal stresses, caused by rapid or nonuniform heating or cooling, also may disbond such coatings.

Metal Restoration

Worn shafts, rolls, etc., are often metal sprayed to restore thickness, then machined to original dimensions. If not loaded in bending, such restorations are usually successful.

7. Galvanizing

Galvanizing is a coating process that deposits zinc on a substrate metal. It is commonly used to protect carbon steel from either atmospheric corrosion or corrosion from mild to moderately corrosive immersion service. Galvanizing provides cathodic protection to the carbon steel. It can be applied by any of four methods, after first degreasing and pickling the product form to be galvanized:

- *Hot-dip galvanizing (carbon steel dipped in molten zinc).* This is the most common method of application. It is used extensively for structurals, piping and water tanks. For piping, galvanizing may be either internal, external or both. The process is also used for structural bolting. The outer surface is essentially pure zinc, with the inner layers composed of Fe-Zn intermetallic compounds and a diffusion layer metallurgically bonded to the steel. Coating thicknesses typically range from about 3 to 5 mils (0.075 to 0.13 mm).
- *Zinc plating.* The coating is essentially pure zinc. The advantage of this process is the accuracy with which the thickness can be controlled. Its major disadvantage is the potential of the process to hydrogen-embrittle ferritic steels. Adequate coating of edges can also be a problem. Coating thickness is on the order of 0.5 to 1 mils (0.01 to 0.025 mm).
- *Metal spraying (metallizing).* This is not a common zinc coating. The major advantage is the ability to coat in place. Sprayed zinc has a typical thickness of about 5 mils (0.13 mm).
- *Sheradizing (mechanical galvanizing).* This process is commonly used to galvanize nuts and bolts. In the process, zinc dust is heated to just below its melting point. Nuts and bolts are tumbled with the dust in a rotating drum, generating a cementation-type coating. Thickness can be readily controlled, ranging from about 0.3 to 2 mils (0.0075 to 0.05 mm).

Some users are sensitive to galvanized products being adjacent to austenitic stainless steel piping, vessels and/or equipment. Refer to Part 3 of Chapter 3 for a discussion of zinc embrittlement.

8. Other Metallic Coatings

Cadmium is often supplied as a coating on small hardware items such as light-duty screws, nuts and bolts. It is adequate for mild service but should not be allowed to substitute for galvanizing.

Other metals such as nickel and chromium, and alloys such as brass, are occasionally offered as corrosion-resistant coatings. They should never be accepted if they are intended for service in corrosive electrolytes and are cathodic with respect to their substrate. Refer to the previous section, "Thin Metallic Barrier Coatings," (p. 103) for a discussion of the risks of such applications.

Electroplated products are sometimes embrittled by hydrogen generated during the plating process. The embrittlement phenomenon is occasionally called "cathodic charging." Materials subject to this problem include ferritic or martensitic steels. Austenitic alloys are relatively immune to this type of embrittlement, except under the most severe conditions. In particular, this mechanism has been a recurrent source of failure in medium- to high-strength bolts. Low- to medium-strength bolts, with tensile strengths up to about 70 ksi (480 MPa), are relatively immune to hydrogen embrittlement caused by electroplating. To restore ductility, susceptible plated products should receive an appropriate postplating hydrogen bakeout prior to use. Refer to Part 1 of Chapter 3 for a discussion of hydrogen embrittlement and bakeouts. It is particularly important to require such bakeouts for embrittled materials subject to impact, tensile or bending loads.

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3

FAILURE MODES

The procedure used to select materials of construction must include consideration of various forms of materials degradation, including electrolytic corrosion, high-temperature corrosion and stress corrosion cracking. In addition, embrittlement by high- and low-temperature phenomena, as well as by various chemicals, must be properly addressed. The avoidance or control of such degradation measures is necessary to achieve the desired design life. In this chapter, the most common forms of degradation phenomena, and the methods of mitigation that are usually adopted, are discussed.

PART 1: EMBRITTLEMENT PHENOMENA

A. INTRODUCTION

Before discussing the effects of embrittlement, we must first define several terms and concepts that involve crack propagation.

- **Brittleness.** A "brittle" crack propagates with little or no macroscopic plastic deformation. Characteristically, brittle crack propagation absorbs little energy, is rapid and results in ruptures. The various engineering codes contain specific guidance on avoiding brittle fractures via impact testing rules.
- **Ductile.** "Ductile" crack propagation is accompanied by gross plastic deformation. Such propagation absorbs significant energy and is typically very slow. Fast ductile fractures can result when the remaining ligament is too small to support the gross load. However, fast ductile fractures exhibit the gross tearing typical of ductile crack propagation.
- **Risk of Fracture.** A distinction should be made between brittleness and the risk of fracture. A brittle material will not fracture as long as the applied stress is below the crack propagation threshold. In practice, brittle materials such as gray cast iron and glass can be used safely if the applied stresses are kept small enough that inherent flaws do not propagate into unstable cracks (i.e., brittle fracture).
- **Fracture-Safe design.** Brittle fracture can occur in most metals and alloys due to a thickness effect; this subject is the focus of *fracture mechanics*. It turns out that for each metal and alloy there is a combination of critical crack size, stress intensity and thickness above which cracks will no longer propagate in a ductile manner. Brittle fractures of this type are rarely encountered in the low- to medium-strength carbon and low-alloy steels utilized in ordinary chemical and hydrocarbon plants. These materials typically have tensile strengths of 70 ksi (480 MPa) or less. As a result, fracture mechanics has not been commonly used in most plant designs, though it is used with some frequency by the chemical and hydrocarbon industries for high-pressure processes in which relatively high-strength materials of construction are employed. In the near future, the ASME Boiler and Pressure Vessel Code, Section VIII [1], is expected to issue the rules for Division 3, which uses fracture mechanics as the design basis for high-pressure vessels.
- **Leak-Before-Break.** A common application of fracture-safe design is to ensure that a pressure system will "leak-before-break." This design procedure utilizes fracture mechanics to ensure that the applied stress is insufficient to cause a through-thickness crack to propagate in a brittle manner. Propagation of a through-thickness crack will be ductile. The material will be of adequate toughness to ensure that the through-thickness crack will be easily detectable before it becomes susceptible to brittle propagation. Hence, a pressure system will start leaking at the through-thickness crack long before there is any danger of brittle crack propagation.

- **Ten Percent Rule.** One application of leak-before-break involves piping and equipment in low-pressure services. For carbon and low to medium-strength low-alloy steels, fracture control experimentation has established that brittle fracture will not occur as long as the combined stress in tension is less than about ten percent of the material's tensile strength. (This will hereafter be referred to as the "ten percent rule".) Thus, in carbon and low-alloy steel applications in which the applied stress in tension is less than ten percent of the tensile strength, the design will inherently provide for leak-before-break. The ten percent rule principle has been incorporated into the major domestic vessel and piping engineering codes. Note that while low-stress conditions do not permit brittle fracture, stable crack propagation by other mechanisms such as stress corrosion cracking can still be active.

Embrittlement refers to a loss of ductility and fracture toughness. A material in which crack growth is ordinarily by a ductile mechanism becomes susceptible to brittle crack propagation. In most cases, brittle or embrittled materials have a threshold temperature range above which they respond to crack propagation stresses in a ductile manner. Cracking that occurs below the threshold temperature is at least partially brittle. Such cracking is often catastrophic. Cracking that occurs above the threshold temperature is by a ductile mechanism.

Often, the term *embrittlement* is applied to the ambient temperature ductility of an alloy that has become embrittled by high-temperature service and which remains ductile at high temperature. In some cases, process fluids can embrittle a material. Hydrogen embrittlement is an example of this effect. In carbon and low-alloy steels the term sometimes refers to the brittleness that develops in the material at temperatures below the brittle-ductile transition range. There are in fact several different causes of embrittlement. Only the relatively common forms of embrittlement will be discussed.

B. CARBON AND LOW-ALLOY STEELS

1. Temper Embrittlement

Temper embrittlement occurs in 2½Cr-1Mo and 3Cr-1Mo steels. These alloys are used for the pressure shells of heavy walled reactors such as hydrotreaters. Temper embrittlement occurs at 700–1100°F (370–595°C); it is reversible by exposure to higher temperatures. In the 700–1100°F (370 to 595°C) range, tramp elements such as tin, phosphorus and arsenic segregate at the grain boundaries. In addition, silicon and manganese contribute to grain boundary embrittlement. While tramp elements cannot be completely eliminated from the

alloy during steel making, modern mills can now control the tramp elements, and silicon and manganese, such that temper embrittlement of these alloys is no longer a major concern.

Temper embrittlement does not affect high-temperature ductility. Its effect is limited to temperatures less than about 250°F (120°C). Accordingly, components suspected to have suffered temper embrittlement can be safely operated if they are not pressurized at temperatures less than 250°F (120°C).

2. Creep Embrittlement

Creep embrittlement can occur in 1Cr-½Mo and 1¼Cr-½Mo steels exposed to sustained temperatures exceeding 850°F (455°C). Note that creep embrittlement is not really embrittlement in the sense that the metal has lost inherent ductility. The loss of ductility is mostly due to a loss in load-bearing capacity because of the formation of gross cracks in the structure.

The effect of creep embrittlement usually takes at least 10–15 years to become evident, but there are reports of such embrittlement in as little as eight years. The mechanism is unpredictable, as there are many vessels and piping systems operating above 850°F (455°C) that have not experienced creep embrittlement. Cracking due to this phenomenon occurs mainly in heat affected zones, usually at nozzles having sharp changes in cross section. Such cracking has also been seen in base metals adjacent to heat affected zones. Once cracking has occurred, embrittlement is irreversible.

The mechanism of creep embrittlement seems to involve the formation of very fine intragranular precipitates which strengthen the metal. The strengthening effect of the grains is thought to force deformation to be confined to the grain boundaries. The residual stresses and plastic constraint of the weldment contribute to the initiation and growth of cracks, called creep cracks.

At this time, there is no consensus on steel-making improvements that can effectively prevent or control this type of embrittlement. We do not know how to prevent or minimize creep embrittlement, or even if it will occur, in 1Cr-½Mo or 1¼Cr-½Mo steels. In low-stress applications, the consequences of creep embrittlement are usually acceptable, since leak-before-break will govern. For higher stress applications, the best policy is to present the user with two choices:

1. Select the less expensive 1Cr-½Mo or 1¼Cr-½Mo material with the risk of replacement or repair; the anticipated life is at least 15–20 years.
2. Select 2¼Cr-1Mo, a more expensive alloy, with chemistry controlled to prevent temper embrittlement.

3. Strain Ageing

Strain ageing occurs in most carbon and low-alloy steels. In this mechanism, a cold-worked material that is allowed to age at ambient or relatively low-temperatures will develop an anomalously high-strength and hardness, accompanied by reduced ductility. This type of embrittlement is relatively rare, since cold-worked materials are usually stress relieved before being placed in service. Typically, a limit of five percent cold work (defined in terms of outer fiber strain) is permitted without subsequent heat treatment. Since cold work is sometimes used to straighten or repair dented or bent structurals or equipment, the user should be aware of the risk of strain-ageing embrittlement caused by such procedures.

4. Hydrogen Embrittlement

Hydrogen embrittlement can occur in carbon and low-alloy steels, in ferritic and martensitic stainless steels and in duplex stainless steels. It is normally not a problem in either the austenitic stainless steels or nickel-based high alloys. Atomic (i.e., nascent) hydrogen does not diffuse very well in austenitic stainless steels, although it is more soluble in the austenitic alloys than in most other steels. In contrast, nascent hydrogen diffuses readily in non-austenitic steels, although it has a lower solubility in such steels. A general rule of thumb is that the lower the solubility, the more susceptible the material will be to hydrogen embrittlement.

Hydrogen can dissolve in steel as a result of a number of phenomena:

- A chemical or corrosion reaction can create nascent hydrogen, usually in the presence of a cathodic poison. Refer to Part 1 of Chapter 2 for a discussion of cathodic poisons. Any corrosion reaction that can cause hydrogen stress cracking can provide enough dissolved hydrogen to cause hydrogen embrittlement in susceptible alloys.
- High-temperature, high-pressure gaseous hydrogen service (discussed on p. 133 in this chapter) can saturate a steel with dissolved hydrogen.
- Exposure to excessive cathodic protection or cathodic charging can saturate a steel with nascent hydrogen. The most common example of this problem is hydrogen embrittlement due to an electroplating procedure. The most common product form affected is bolting. Some of the austenitic stainless steels and nickel-based high alloys have been shown to be susceptible to hydrogen embrittlement by cathodic charging.
- Welding with moist consumables is a well-known source of hydrogen embrittlement in carbon and low-alloy steels.

At temperatures less than about 250°F (120°C), dissolved hydrogen inhibits the dislocation mechanisms responsible for plastic deformation in metals, resulting in loss of ductility. The effect is particularly evident at slow strain rates. Hydrogen embrittlement is reversible; dissolved hydrogen is driven from the material by a "bakeout" at high-temperature. One practice is baking at 600°F (315°C) for four hours.

Hydrogen embrittlement is temperature dependent, occurring from subambient temperatures to about 250°F (120°C). The maximum effect is in the range of 0 to 100°F (-18 to 38°C). The risk of hydrogen embrittlement rapidly diminishes at temperatures above 175°F (80°C). For this reason, low-alloy steels such as the Cr-Mo steels used in gaseous hydrogen service are usually not pressurized until the operating temperature is brought up to 250°F (120°C) or warmer.

The ordinary low- to medium-strength steels (with specified minimum tensile strengths of up to 70 ksi (480 MPa)) are moderately susceptible to hydrogen embrittlement. Between 70 and 90 ksi (480 and 620 MPa) specified minimum tensile strength, steel is susceptible to hydrogen embrittlement. Higher-strength steels (with specified minimum tensile strengths in excess of about 90 ksi (620 MPa)) can be severely embrittled. This strength relationship is the reason that bolting is the product form with which one most commonly encounters hydrogen embrittlement problems in plants. Often, the embrittlement of bolting is due to the bolts being electroplated without a subsequent hydrogen bakeout.

For carbon and low-alloy steels, the relationship between susceptibility to hydrogen embrittlement and strength is very similar to the relationship between susceptibility to hydrogen stress cracking and strength. In fact, one of the major risks of hydrogen embrittlement occurs in carbon steels, low-alloy steels and ferritic or martensitic stainless steels subject to hydrogen stress cracking environments. Examples include sulfide stress corrosion cracking and hydrofluoric acid cracking. The mitigation measures used to minimize the risk of hydrogen embrittlement are essentially the same as those used to minimize the risk of stress corrosion cracking: hardness controls, control of microalloying additions, postweld heat treatment, etc. These recommended mitigation measures are discussed later in this chapter, in the section entitled "Wet Sour Service" (p. 196).

Hydrogen embrittlement is normally not a problem in most chemical process and hydrocarbon plants, probably because the material strengths are too low and the stresses below 250°F (120°C) are insufficient to propagate cracks. However, there are at least four situations which should be given special attention:

1. The rate and extent of hydrogen embrittlement are affected by the amount of residual cold work. Accordingly, it is good practice to stress-relieve components that have been cold worked. Examples include pressed or spun heads and U-bends in heat exchanger bundles. Five percent cold work is often used as the threshold for requiring stress relief.

Designs should avoid stress concentration sites such as sharp notches, as these can subsequently become cold worked as a result of hydrotesting or service and thus become sites for accelerated hydrogen embrittlement.

2. Components charged with hydrogen during high-temperature, high-pressure hydrogen service can become hydrogen embrittled. This can pose an operating risk, especially upon cooldown. Such components (usually Cr-Mo low-alloy steels) may be subject to brittle fracture if exposed to inadvertent tensile or bending stresses due to activities such as maintenance, revamp fabrication, etc.
3. Hard heat affected zones are susceptible to both hydrogen embrittlement and hydrogen stress cracking. Conventional welding processes and joint configurations normally produce heat affected zone hardnesses that are immune to these phenomena. However, if the carbon steel parent metal has excessive microalloying or if the weld cools too rapidly, excessive heat affected zone hardness can be created. This is a common problem when a thin section is welded to a thick section, as in tube-to-tubesheet welds. Heat affected zone hardnesses of 200 BHN or less are regarded as being immune to the effects of dissolved hydrogen.
4. *Delayed hydrogen cracking* (also called *underbead cracking* or *cold cracking*) is sometimes associated with hydrogen embrittlement; it is a form of hydrogen stress cracking. The problem occurs in freshly made welds, usually because of hydrogen generated during the welding process. The most common cause is moist welding consumables. However, such cracking can occur in repair welds because of hydrogen dissolved in the steel due to prior service. In this case, the problem involves either a hydrogen stress-cracking environment or a high-temperature, high-pressure hydrogen service. Such cracking in repair welds can be prevented by a suitable bakeout.

The delayed hydrogen cracking mechanism requires an incubation period before cracking occurs. Thus, this type of cracking may not be visible if the weld is inspected immediately after it has been finished. In the event that this mechanism is of concern, inspection should be delayed until at least three days after completion of the weld. The primary mitigation measures are:

- Bakeout, if necessary
- Preheat
- Control of welding consumables to avoid moisture absorption

5. Caustic Embrittlement

The term *caustic embrittlement* is a misnomer. The loss of ductility characteristic of caustic embrittlement is due to the reduction in load-carrying

capability caused by the formation of a network of cracks. In this case, the cracks are caused by alkaline stress corrosion cracking.

6. Low-Temperature Embrittlement

Low-temperature embrittlement occurs in carbon and low-alloy steels when they are exposed to temperatures below their brittle-ductile transition temperatures. The effect is reversible: as soon as the alloy is warmed to a temperature above the transition range, the alloy behaves in a ductile manner. This type of embrittlement is the subject of Charpy impact testing in accordance with relevant engineering codes. The need for such testing depends primarily on the section thickness and the minimum design temperature. Refer to Figure A1-1 and Table A1-1 for materials selection guidance for low-temperature services.

C. STAINLESS STEELS

1. Ferritic Stainless Steels: 885°F (475°C) Embrittlement

Most of the ferritic stainless steels are straight chromium stainless steels, containing 12 percent or more chromium. These steels can become embrittled in the range 750–975°F (400–525°C). The mechanism is called *885°F (475°C) embrittlement*. This embrittlement is reversible by exposure to higher temperatures.

There is widespread industry agreement that pressure-containing alloys subject to this form of embrittlement should not be exposed to service temperatures exceeding about 650°F (345°C). However, ferritic stainless steel non-pressure components such as vessel trays or internal shell cladding are sometimes used for resistance to corrosion. In refineries, a common example of such an application is coke drums, which are often internally clad with a ferritic stainless steel to protect the substrate carbon steel shell from sulfidic corrosion.

885°F (475°C) embrittlement is not normally a problem in the 12 Cr alloys such as Type 405 SS. For ferritic stainless steels containing 15 percent or more chromium, embrittlement can become severe. One should be very cautious of accepting "upgrades" of straight chromium stainless steels without first checking on their thermal history and the intended service temperature.

The higher chromium grades of the ferritic stainless steels such as Type 446 become susceptible to embrittlement by the formation of intermetallic phases, such as sigma or chi phases, at temperatures exceeding about 1050°F (565°C). Most of the straight chromium grades are also susceptible to sensitization-induced corrosion problems. Refer to Part 2 of this chapter (p. 121) for a

discussion of sensitization. Normal practice avoids the use of these alloys for pressure containment at temperatures exceeding 650°F (345°C). Therefore, the practical effects of their high-temperature embrittlement and sensitization are confined to non-pressure components such as valve trim, vessel internals and pressure boundary liners such as weld overlays. These applications are, however, common in the processing of high-temperature sulfur-containing streams such as refinery coke drums and crude units processing sour crudes.

Similar to carbon and low-alloy steels, the ferritic stainless steels are susceptible to low-temperature embrittlement. The engineering codes typically require such steels to be qualified for low-temperature service by impact testing.

2. Martensitic Stainless Steels

The martensitic stainless steels are susceptible to low-temperature embrittlement. The engineering codes typically require such steels to be qualified for low-temperature service by impact testing.

3. Austenitic Stainless Steels: Sigma Phase Embrittlement

The 300-series stainless steels can be subject to *sigma phase embrittlement*, a high-temperature embrittlement mechanism. Occurrence depends primarily on service temperature and is accelerated by the presence of ferrite. While the normal austenitic grades such as Type 304 SS can develop sigma phase embrittlement, this type of embrittlement is more common in austenitic products that contain small amounts of ferrite. Examples include austenitic weld metal and castings.

Sigma phase formation occurs in the range 1050–1700°F (565–925°C). The upper temperature limit for sigma phase formation varies from about 1600 to 1800°F (870 to 980°C), depending primarily on alloy chemistry. The upper limit is somewhat academic for ordinary austenitic stainless steels, since it is near or exceeds the oxidation limit of most of these alloys. Embrittlement usually occurs very slowly. Type 304 SS will usually show only two to three percent sigma phase in its microstructure after 10 years at 1200°F (650°C). When exposed to temperatures near the upper limit of the embrittlement range, embrittlement may develop in a few weeks. The rate of embrittlement is increased by cold work prior to exposure to embrittling temperatures. The non-stabilized alloys such as Type 304 SS embrittle more rapidly than do the stabilized alloys, typically represented by Types 321 and 347 SS. Sigma phase embrittlement is reversible by solution annealing.

The effect of sigma phase embrittlement on toughness depends somewhat on both temperature and alloy chemistry. For non-stabilized austenitic stainless steels, a sigmatized alloy can be brittle at temperatures as high as 1400°F

(760°C). Above this temperature, sigma phase embrittlement has little effect on toughness. The behavior of the stabilized grades is less clear, but they appear to recover some ductility as a function of increasing temperature.

The austenitic stainless steels are essentially immune to the effects of low-temperature embrittlement. Most of these alloys are exempt from impact testing for design temperatures down to -320°F (-195°C). Some types such as Type 304 SS are exempt down to -425°F (-255°C). Note that the exemption temperatures for weld metal are usually warmer than those for parent metal.

4. Duplex Stainless Steels

These steels are susceptible to 885°F (475°C) embrittlement and to sigma phase formation. They are usually not selected for service temperatures exceeding about 650°F (345°C). Because of their ferrite content, the duplex stainless steels are susceptible to low-temperature embrittlement. However, the duplex stainless steels tend to have relatively low brittle-ductile transition temperatures. The engineering codes typically require the duplex stainless steels to be qualified for low-temperature service by impact testing.

D. HIGH ALLOYS

Virtually all high alloys will suffer some form of embrittlement if exposed to sustained high-temperature service. Such embrittlement is due to the formation of intermetallic compounds. Conditions and rates of embrittlement vary from one alloy to another. Check with alloy manufacturers for specific information.

High alloys containing enough nickel to ensure an austenitic microstructure are, like the austenitic stainless steels, essentially immune to low-temperature embrittlement.

E. HYDRIDING

All of the refractory metals, including Ti, Zr, Nb and Ta, are sensitive to hydriding. Galvanic cells that promote hydriding can be particularly damaging. Instances of iron sacrificial anodes causing hydriding in titanium heat exchanger components have been reported.

Hydriding is related to hydrogen embrittlement. Hydrides are brittle, thermodynamically stable compounds. Once they form, the metal or alloy is irreversibly embrittled. Re-refining is required to destroy the hydrides.

Titanium is the most common material of construction that can be hydrided. In the case of titanium, hydriding can be caused by either hydrogen gas or by a

corrosion reaction. The threshold temperature for diffusion and hydride formation is about 175°F (80°C).

- Titanium can absorb hydrogen directly from anhydrous process streams containing hydrogen gas. This form of embrittlement is relatively uncommon since only a small amount of moisture is necessary for its inhibition.
- Nascent hydrogen generated by a corrosion reaction involving cathodic poisons (such as sulfides, cyanides, and arsenic or antimony compounds) can diffuse into titanium to form hydrides.
- Cathodic protection of titanium can charge the metal with hydrogen. Most cases are caused by inadvertent cathodic protection being provided by a galvanic couple such as an alloy tubesheet with titanium tubes.

PART 2: HIGH-TEMPERATURE EFFECTS

A. MECHANICAL EFFECTS

1. Introduction

High-temperature tends to force the selection of expensive materials of construction. Whenever possible, the materials selection engineer should review the design data or design basis to see if there is opportunity to justify reducing the maximum design temperature.

2. Creep

Most metals and alloys exhibit a temperature above which the grain boundaries become weaker than the grains themselves. This temperature is the threshold temperature above which the material is susceptible to *creep*.

For metals and alloys at temperatures less than their creep thresholds, strain is not time-dependent for constant stress. However, at temperatures above the creep threshold, creep can occur. Creep is defined as time-dependent strain at constant stress—or, stated another way, the strain rate is greater than 0 for a stress rate of 0. In the creep range, stresses above the creep threshold cause the nucleation and propagation of grain boundary voids. Figure 3-1 shows an idealized representation of the three stages of creep.

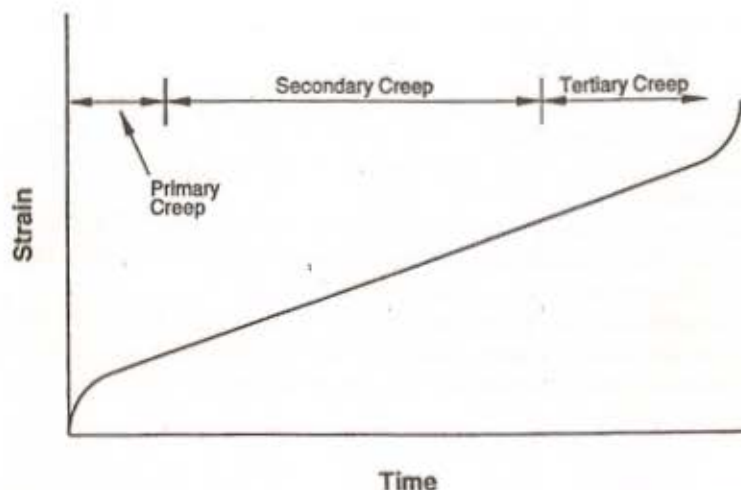


Figure 3-1 The three stages of creep.

In primary creep, the material plastically deforms while undergoing rapid work hardening. No significant damage is generated. During secondary creep, grain boundary yielding produces local work hardening and the nucleation of grain boundary voids. During tertiary creep, the grain boundary voids link up and gross necking or thinning develops. Tertiary creep ends in an exponentially accelerating strain rate, rapidly leading to fracture. Fracture by this phenomenon is called *stress rupture*.

The lower (threshold) end of the creep temperature range for carbon steel is about 750°F (400°C). The Cr-Mo steels have creep threshold temperatures of about 900°F (480°C) and higher. The conventional austenitic stainless steels have creep threshold temperatures of 1050 to 1100°F (565 to 595°C). A safe estimate for the creep threshold temperature of a material is the upper temperature limit permitted by ASME Section VIII, Div. 2 [1].

Piping and equipment engineers are not ordinarily concerned with accommodating for creep. However, some engineering codes such as ASME B31.3 [2] for piping and ASME Section VIII, Div. 1 [1] for vessels contain provisions for creep design. If creep is a concern, coarse-grained materials are favored. Carbon steels killed with silicon are usually recommended for temperatures where creep is a concern. Examples include ASTM A106 for pipe and ASTM A515 for plate.

3. Stress Rupture

If sustained maximum operating temperatures will create significant creep strain, the component is at risk of failure by *stress rupture*, typically associated with tertiary creep. Stress rupture design includes "safety" factors intended to define inspection intervals and/or schedule replacement before the onset of tertiary creep. In typical stress rupture designs, the design life of the component is the expected period of secondary creep. During secondary creep, component dimensions such as tube diameter and length slowly increase. In wrought materials, secondary creep strains of 10 to 20 percent are not uncommon. In the high-temperature cast materials such as HK-40 (25Cr-20Ni; UNS J94204), secondary creep strains are usually on the order of 2 to 3 percent.

When operating in the creep range, care must be taken to avoid temperature or stress excursions; of the two, temperature excursions are by far the more damaging. A 50°F (28°C) excursion can easily reduce the operating life by 50 percent or more. Furnaces and heaters are about the only equipment having both temperatures and stresses high enough to require creep to be taken into account during plant design. Refer to the section "High-Temperature Alloys" (p. 140) for a discussion of creep design.

Thermal fatigue produces fractures that are virtually identical to creep failures. Maximum code-allowable stresses are high enough to permit thermal fatigue. Accordingly, if thermal cycles are a feature of equipment design (such as for coke drums), thermal fatigue analysis is usually recommended.

B. METALLURGICAL EFFECTS

1. Sensitization

Conventional stainless steels, both austenitic 300-series alloys and the straight chromium grades such as Types 405 and 410 SS, can be subject to intergranular corrosion or cracking as a result of a phenomenon called *sensitization*. Sensitization refers to the precipitation of chromium carbides in the grain boundaries of the alloy as a result of exposure to temperatures in the range of 800 to 1600°F (425 to 870°C). As the chromium carbides develop, the nearby metal becomes depleted in dissolved chromium. This creates a zone adjacent to the grain boundary of locally corrosion susceptible iron-nickel alloy. In the case of the straight chromium grades, the local composition may approach that of plain carbon steel. Not only does a chromium-depleted zone have less corrosion resistance than the adjacent unaffected alloy, but the two can interact galvanically. Such action can significantly accelerate intergranular corrosion rates. See Figure 3-2 for an example of sensitization.



Figure 3-2 Sensitized Type 304 stainless steel. (Courtesy of Dr. E. V. Bravenec, Anderson & Assoc.)

There is some controversy over the lower threshold temperature that causes sensitization. However, for solution-annealed austenitic stainless steels, sensitization at temperatures less than about 850°F (455°C) appears to require extremely long exposure times. Cold-worked austenitic stainless steels are reported to sensitize at temperatures as low as 700°F (370°C). Sensitization occurs most rapidly when the temperature is about 1500°F (815°C). For example, welding alone can sensitize the heat affected zones in non-stabilized stainless steels that are not of a low-carbon composition. Sensitization can be caused in non-stabilized alloys by cooling too slowly from a solution-annealing or stress relief heat treatment.

Sensitization can cause two types of corrosion problems: weld rusting and intergranular corrosion.

Weld Rusting

Mildly acidic liquids can cause the locally chromium-depleted iron-nickel alloy to slowly rust. An example of this problem is weld metal rusting of stainless steel by dew (containing dissolved CO₂) condensing on the outside of a pipe. While normally this is only an aesthetic problem, in some contamination-sensitive processes or aesthetic applications, such rusting is unacceptable. If

chlorides are involved, such corrosion may become aggressive due to the formation of ferric chloride.

Intergranular Corrosion

Some fluids, including most oxidizing acids, will cause intergranular corrosion in the chromium-depleted region of sensitized grain boundaries. For sensitized welds in austenitic stainless steels, this form of corrosion is sometimes called "weld decay." See Figure 3-3 for an example of this problem. In some cases, intergranular attack is stress related and is more properly referred to as *intergranular stress corrosion cracking*.

The most common fluid causing intergranular corrosion in hydrocarbon plants is *polythionic acid*. Both austenitic and straight chromium grades of stainless steels can be attacked by polythionic acid. This phenomenon is usually an internal problem, occurring on the process-exposed side of a piping run, vessel shell, exchanger bundle, heater tube, etc. The phenomenon usually starts with the stainless steel surface forming a thin iron sulfide film, because of exposure to small amounts of sulfur, usually from hydrogen sulfide, in the process stream. During a shutdown, in the presence of air and liquid water, often

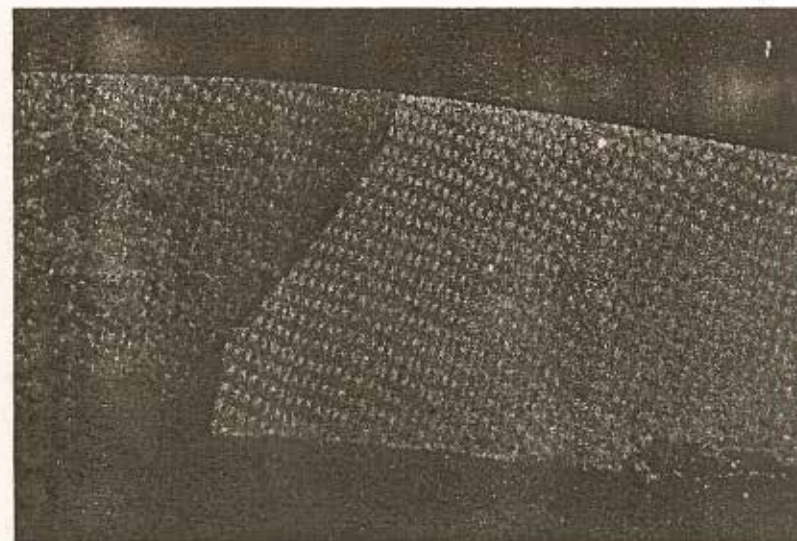


Figure 3-3 Intergranular corrosion in a sensitized stainless steel, caused by welding ("weld decay"). Note that the sensitized zone is relatively remote from the weld, a feature typical of welding-induced sensitization.

dew point water, the sulfides convert to polythionic acid. The polythionic acid then corrodes the chromium-depleted grain boundaries of the sensitized alloy. Since stainless steels are usually supplied to fabricators in the solution-annealed condition, sensitization is usually confined to weld heat affected zones. See Figure 3-4 for an example of polythionic acid attack. Upon subsequent startup, leaks may develop. Sometimes the leaks take two or more shutdowns to develop fully. In some cases, the problem becomes obvious during a shutdown while repair welding. Repair welding on stainless steel that has been damaged by stress corrosion cracking or polythionic acid usually causes growth of a massive crack network.

Process controls can be used to protect sensitized equipment from polythionic acid attack:

- *Prevent air ingress.* The system is kept sealed and at a positive pressure to ensure that any leaks that do occur are from the inside to the outside
- *Prevent the formation or ingress of liquid water.* Prior to shutdown, the system is usually purged with a dry inert gas such as nitrogen and is then kept under a slightly positive pressure to ensure that any leaks are from the inside to the outside.

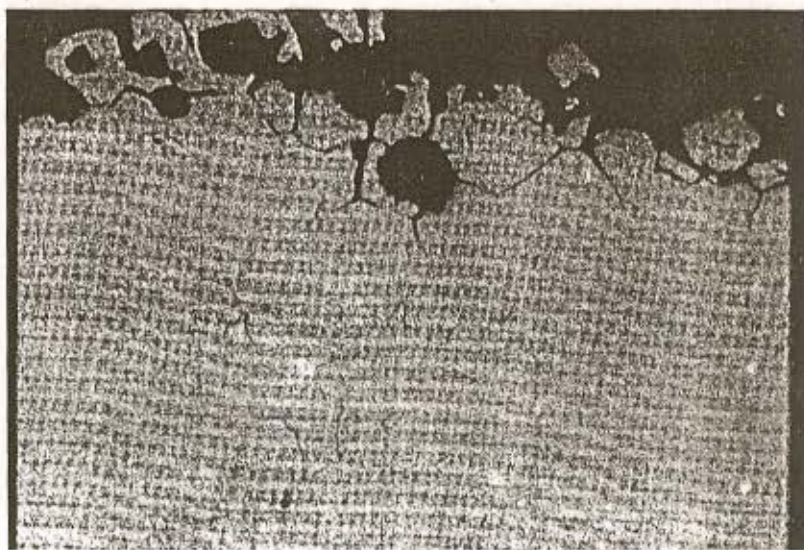


Figure 3-4 Polythionic acid attack on Type 316 stainless steel. (Courtesy of Mr. C. P. Dillon, C. P. Dillon & Assoc.)

- *Use a neutralizing wash.* Both ammonia and soda ash solutions are used, with the latter the more common. Refer to NACE RP0170 "Protection of Austenitic Stainless Steel from Polythionic Acid Stress Corrosion Cracking During Shutdown of Refinery Equipment" [3] for details of recommended practices.

External polythionic acid attack has been observed to occur in plants having atmospheric sulfide pollution. However, the problem does not usually occur externally in fired equipment, because excess combustion air causes sulfates, instead of sulfides, to form.

Note that the iron sulfides necessary to form polythionic acids can be transported by process streams to sensitized stainless steel equipment. In wet sour systems containing even small amounts of dissolved iron, a large amount of iron sulfide is formed and deposited. Such systems should never be flushed or drained into stainless steel piping or equipment prior to a shutdown unless appropriate precautions are taken.

Several metallurgical methods have been developed to address the problem of intergranular corrosion caused by sensitization:

Low-Carbon Grades

The "L" grades such as Type 304L SS have their carbon contents controlled in order to limit the degree to which they can be sensitized. However, these alloys have lower maximum code-allowable stresses than either the conventional grades or the stabilized grades. The low-carbon grades are typically chosen for services in which welded fabrication is required, but the operating temperatures will be less than the sensitization threshold. For the purposes of materials selection, this is usually taken to be less than about 800°F (425°C). The low carbon content slows the rate of sensitization. The postweld cooling rate in the heat affected zone is fast enough to avoid significant sensitization. Low-carbon grades of ferritic stainless steels are also available; 29Cr-4Mo, UNS S44700 is an example.

Chemically Stabilized Alloys

Types 321, 347 and 348 SS and their H grades, and Type 316Ti SS are generally regarded as relatively immune to sensitization. They contain carbon scavengers (titanium in Type 321 and Type 316Ti and niobium in Type 347 and Type 348) that inhibit chromium depletion. Note that not all of these materials are available in all product forms or, for some product forms, with corresponding code-allowable stresses. The niobium grades are regarded as being more resistant to sensitization than the titanium-stabilized grades. In general, Type 347 is preferred for heater tubes and as the cladding or overlay material for vessels and heat exchangers because of its superior resistance to sensitization. Type 321 is normally specified

for tubing and piping. Type 321 is preferred for welded construction because Type 347 has a greater tendency to crack during welding. Stabilized ferritic stainless steels such as Types 409 and 439 SS have also been developed.

ASTM specifications used to purchase austenitic stainless steels, including the stabilized grades, generally require that the product form be furnished in the solution-annealed condition. In this condition, the stabilized grades are not resistant to sensitization caused by long-term high-temperature service. Accordingly, many of these ASTM specifications warn the user that solution-annealing the stabilized grades may result in inferior resistance to intergranular corrosion. These specifications permit the user to require that the mill solution anneal be followed by a *stabilization anneal*. The ASTM specifications do not describe a recommended procedure. A widely used procedure is to hold the alloy at about 1650°F (900°C) for two to four hours, followed by air cooling. This procedure encourages the formation of stable carbides, formed either from titanium for Types 321 and 316Ti SS or from niobium for Types 347 or 348 SS, without chromium depletion. Note that the purchaser must specify stabilization annealing or else the mill will furnish the alloy in the solution-annealed condition.

Special alloy composition requirements may be required to assure the effectiveness of stabilization annealing [4]. These requirements place limits on the ratios of Ti/C in Type 321 SS and of Nb/C in Type 347 SS. There is no industry consensus on utilization of these limits. ASTM specifications permit alloy compositions that do not satisfy the proposed ratio limits.

The protection provided by a stabilization anneal can be partially destroyed by subsequent welding. For full protection, any welds made after the stabilization anneal should be restabilized. Type 321 SS is more susceptible to this welding effect than is Type 347. It should be noted that even without benefit of stabilization annealing, the chemically stabilized alloys are much more resistant to sensitization than are the regular grades.

A number of stabilized Cr-Ni high alloys such as Alloy 825 (22Cr-42Ni-3Mo, Ti stabilized; UNS N08825) have been developed to provide resistance to sensitization. These alloys are usually furnished in the stabilization-annealed condition and may be made susceptible to sensitization by subsequent postweld heat treatments. The alloy manufacturer should be consulted before undertaking postweld heat treatments.

Virtually all non-stabilized Cr-Ni high alloys are susceptible to sensitization and intergranular corrosion. If fabrication will involve aggressive pickling or if the alloy will be exposed to polythionic acid attack, the user should consider sensitization and resistance to intergranular corrosion. Check the technical literature about the alloy or consult with the alloy manufacturer regarding resistance to intergranular corrosion in the event the alloy may be sensitized by either fabrication practices or high-temperature service.

Materials selection designed to address sensitization requires the following considerations:

- Alloys susceptible to sensitization are acceptable if not welded and if the maximum design temperature does not exceed 800°F (425°C). For these alloys in the cold-worked condition, the upper temperature limit is usually taken to be 700°F (370°C).
 - The low-carbon "L" grades are acceptable in weldments for which the maximum design temperature does not exceed 800°F (425°C). For these alloys in the cold-worked condition, the upper temperature limit is usually taken to be 700°F (370°C).
 - Stabilized alloys should be selected for processes in which the maximum design temperature exceeds 800°F (425°C).
 - Types 316Ti and 321 SS are acceptable in weldments and in processes for which the maximum design temperature does not exceed 900°F (480°C).
 - Type 347 SS is acceptable in weldments and is usually selected for processes in which the maximum design temperature exceeds 900°F (480°C). In processes with maximum design temperatures less than 975°F (525°C), this material is essentially immune to sensitization.
- Note that, while Type 347 SS is more resistant to sensitization than is Type 321 SS, the latter is favored whenever possible. Type 321 SS is less susceptible to welding problems than is Type 347 SS.
- Stabilized ferritic stainless steels may be substituted for higher grades in services that do not demand the superior corrosion resistance of the higher grades. However, as mentioned earlier, these alloys are susceptible to 885°F (475°C) embrittlement.
 - Stabilized Cr-Ni alloys are available for processes in which the corrosion resistance of the 300-series is inadequate.

Heat Treatment

Solution annealing will dissolve carbides formed by sensitization. This is usually impractical for welded components because of distortion problems. If a welded austenitic stainless steel is subjected to subsequent solution annealing, the assembly will still be susceptible to sensitization if exposed to sustained service temperatures exceeding 800 to 850°F (425 to 455°C).

As discussed above, the chemically stabilized grades are sometimes specified to be stabilization annealed before and/or after welding.

2. Spheroidization and Graphitization of Carbon Steels

Spheroidization and *graphitization* can occur in carbon and C-½Mo steels at high-temperature. Low-alloy steels with chromium contents of about 0.7 wt. percent or more are considered immune to these effects. Spheroidization and graphitization occur at temperatures above 850°F (455°C). Since most users avoid the selection of carbon steels for use above 800°F (425°C), the effects of these two mechanisms are often not considered. However, many plants use carbon steel lined with refractory for high-temperature services. Refractory failures occasionally expose these carbon steels to temperatures substantially in excess of 800°F (425°C). Selecting carbon steel for such services does carry a risk, so understanding what could happen is important.

Iron carbide (cementite: Fe₃C), one of the primary components of carbon steel, is thermodynamically unstable. However, its rate of decomposition in carbon and C-½Mo steels is negligible at temperatures less than 850°F (455°C). The rate of decomposition begins to accelerate at temperatures exceeding 850°F (455°C). Like most high-temperature, diffusion-controlled phenomena, the rate is exponentially related to temperature. At 900°F (480°C), 50 percent conversion to graphite occurs in about 10,000 hours. At 1100°F (595°C), the conversion time is only about 1000 hours.

The process of iron carbide decomposing to form iron and graphite is called *graphitization*. Decomposition is accompanied by a moderate reduction in the strength of the steel. This reduction will accelerate the formation of creep damage if the applied stress is large enough to cause creep. Decomposition of the iron carbide can "embrittle" the steel if the graphite that develops forms a continuous (or closely spaced discontinuous) band. Ruptures have occurred from this cause, most frequently in C-½Mo steels. This alloy is no longer being recommended as a material of construction for high-temperature services.

Aluminum-killed steels are more susceptible to graphitization than are silicon-killed steels such as ASTM A515. Silicon-killed steels are preferred for high-temperature services.

Spheroidization refers to the formation of spheroids of iron carbide from the normal microstructure, pearlite. The mechanism occurs at temperatures above 900°F (480°C), again at rates which are exponential with temperature. However, for sustained high-temperatures, graphitization becomes the dominant mechanism.

Unless carried to extremes by prolonged exposures at high-temperatures, spheroidization is often regarded as beneficial, since it greatly improves the impact toughness of carbon steel with only a minor loss of strength. Normalizing a pearlitic carbon steel causes partial spheroidization, resulting in improved toughness. Too much spheroidization will cause an unacceptable loss

of strength. The user should be wary of requests to allow multiple normalizations and/or postweld heat treatments.

Above 850°F (455°C), prolonged exposure causes carbon steels to lose strength; they can become susceptible to stress rupture if the stress is large enough. Above 1000°F (540°C), oxidation and spalling can occur, further enhancing the risk of early failure. In general, it is safe to tolerate short-term excursions to 1000°F (540°C) if the applied stress is less than the maximum code-allowable stress. Even short-term excursions above 1000°F (540°C) should be avoided unless the applied stresses are very small.

3. Welding

Welding can cause several problems related to high-temperature effects including:

- *Microstructural problems.* Examples include grain coarsening in the heataffected zone, which can result in reduced toughness and, in the case of stainless steels, sensitization. Postweld heat treatments such as normalizing for ferritic steels, and stabilization annealing or solution annealing for austenitic stainless steels, are useful in mitigating these problems.
- *Residual stresses,* which can contribute to stress corrosion cracking. Stress relief by postweld heat treatment is usually required in processes that can cause stress corrosion cracking.
- *Thermal gradients,* which can generate thermal stresses. Accordingly, they can cause mechanical distortion. Thermal stress problems are usually addressed by a combination of mechanical stabilization such as bracing, slow heating and cooling, and cold straightening. Recall that cold straightening can be a cause of strain ageing.

Welds between dissimilar metals can generate several subsequent problems:

- Warping, buckling and/or excessive residual stresses. These affects are often due to differences in the coefficients of thermal expansion during the heat of welding (or subsequent cooling). Heat treatments of weldments containing dissimilar metals can also cause such problems.
- Galvanic effects.
- Formation of "hard spots" in heat affected zones and fusion zones. These "hard spots" may subsequently act as initiation sites for hydrogen stress cracking. Mitigation measures include preheat and postweld heat treatments. Another mitigation method is the use of a "butter" layer of high-alloy weld metal. This layer is deposited first in order to minimize the effects of weld dilution.

Lamellar tearing is an unusual type of failure associated with damage that can be caused as a weldment cools. This type of failure usually involves plate and/or plate products and is associated with a restrained weld joint geometry (see Figure 3-5). As the weldment cools, restraint causes the region just below the weld to be in tension. If this region has inadequate through-thickness (often referred to as the "short transverse" direction) toughness, tearing can occur. Lamellar tearing is normally not a problem in plate less than 1" (25 mm) thick.

The cause of poor through-thickness toughness is usually the presence of a relatively high density of non-metallic inclusions, that is, a "dirty" steel. The rolling process used to produce plate flattens the non-metallic inclusions and orients them parallel to the direction of rolling. The surfaces of the flattened non-metallic inclusions are perpendicular to the through-thickness direction. Since the inclusions are poorly bonded to the surrounding metal, they reduce the through-thickness strength as well as acting as stress risers.

Several methods can be used, usually in combination, to avoid lamellar tearing.

- Materials control
 - Purchase plate with a low concentration of non-metallic inclusions. This can be done by using the purchasing specifications developed for plate resistant to hydrogen induced cracking (HIC). Refer to the discussion of HIC resistance in the section entitled "Wet Sour Service" (p. 196).
 - Use ASTM A435 "Standard Specification for Straight-Beam Ultrasonic Examination of Steel Plates" to ensure that the plate manufacturer or vendor has inspected the plate for the presence of injurious non-metallic inclusions.

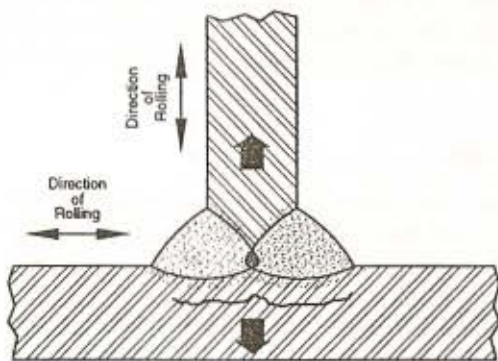


Figure 3-5 Lamellar tearing in a T-joint.

- Consider ordering plate with proven through-thickness properties (see ASTM A770 "Standard Specification for Through-Thickness Tension Testing of Steel Plates for Special Applications").
- Welding technique
 - Use a "butter" layer of low-strength weld metal on the surface of the plate for which lamellar tearing is to be avoided. This technique may require adjusting the weld joint efficiency if the minimum specified tensile strength of the filler metal is less than that of the base metal.
 - Modify the joint design or type of weld to minimize restraint. For example, using fillet welds rather than full penetration welds is sometimes useful.

Post-weld inspection for lamellar tears is difficult unless the tear penetrates to the surface (usually at the toe of the weld). In such cases, dye penetrant techniques are reliable. For embedded tears, ultrasonic inspection is sometimes used, but tear indications are difficult to differentiate from indications caused by non-injurious inclusions.

C. CHEMICAL EFFECTS

1. Carburization

Carburization refers to the development of a carbide-rich layer on the surface of a material exposed to a reducing hydrocarbon environment. This phenomenon is associated with high-temperature service or, in some cases, to high-temperature excursions. Carburization of carbon and low-alloy steels is rare since they are not normally subjected to operating temperatures high enough to induce carburization. Mild carburization of ordinary 300-series austenitic stainless steels is sometimes observed since they can be used at temperatures high enough to see low rates of carburization. In refineries it is sometimes observed in the plenum of a fluid catalytic cracking unit. Special alloys such as the Alloy 800 series (20Cr-32Ni, with Ti and Al; UNS N08800/8810/8811) or HP-Mod. are usually specified for use in carburizing atmospheres at high-temperatures, for example, the cracking tubes in an ethylene furnace.

Carburization can cause premature failures or contribute to such failures. Failure is often caused by cracking due to the large difference in the coefficients of thermal expansion between the parent alloy and the carburized layer. Such cracking causes the carburized layer to disbond, thereby exposing fresh material to subsequently carburize. Thermal cycling is the normal cause of such failures.

Metal loss is the form of failure in a carburization mechanism known as *metal dusting*, which can occur very rapidly. This very limited mechanism involves process streams with CO/CO₂ ratios on the order of 3 to 5, at

temperatures in the range 1200–1550°F (650–845°C), usually involving Fe-Cr and Fe-Cr-Ni alloys having a chromium content of 25 percent or less [5]. Metal dusting usually causes smooth, circular pits, typically worst in stagnant areas. In some cases, pitting damage is general, resulting in overall surface wastage.

When selecting materials for high-temperature hydrocarbon services, the potential for carburization should be determined. Process licensors usually provide excellent guidance for materials selection. Alloy manufacturers can also provide excellent advice. If carburization is anticipated, it is normal practice to provide a nominal *carburization* allowance. Do not attempt to mitigate metal dusting with a corrosion allowance; a change in alloy or in the process is required for this mechanism.

2. Fuel Ash Corrosion

Some fuels, particularly low-grade fuel oils, contain elements that can cause accelerated high-temperature corrosion. The major culprits are vanadium and sodium. At temperatures above about 1200°F (650°C), vanadium oxide vapor and sodium sulfate react to form sodium vanadate, which in turn can react with metal oxides on the surfaces of heater tubes, hangers, tubesheets, etc. The resulting slag can become a low-melting eutectic mixture, acting as a flux. (A flux is a molten solvent for metal oxides.) The slag dissolves protective metal oxides and prevents their reformation. The mechanism is further accelerated by the presence of sulfur in the fuel. Sulfur contributes to the problem both by sulfidation and by an additional lowering of the melting point of the vanadium oxide flux. Failures generated by this mechanism tend to be rapid.

Concentration thresholds for fuel ash attack are not well defined. However, concentrations less than 5 ppmw vanadium appear to have little effect. Concentrations up to about 20 ppmw are safe as long as the maximum metal temperature is less than about 1550°F (845°C). The safe maximum metal temperature for concentrations in excess of 20 ppmw vanadium appears to be 1200°F (650°C).

Virtually all alloys are susceptible to fuel ash corrosion. However, alloys rich in nickel and chromium (50Cr-50Ni) offer good protection. Reducing the amount of excess air to less than 5 percent has been used to control fuel ash corrosion successfully. The rate of corrosion decreases dramatically at very low excess air concentrations.

A wide variety of complex vapor deposition coatings have been developed for protecting components such as turbine blades from this type of attack. Vapor deposition coatings of aluminum and chromium have been tried as tube coatings with some success.

3. Hydrogen Gas

For the purpose of materials selection, hydrogen service is defined as any service in which the partial pressure of the hydrogen gas exceeds 100 psia (0.7 MPa). Hydrogen gas can cause two types of problems: hydrogen embrittlement and hydrogen attack.

Hydrogen Embrittlement

As discussed earlier, hydrogen gas can cause carbon and low-alloy steels to be hydrogen embrittled at temperatures ranging from subambient to about 250°F (120°C). However, hydrogen gas itself is not a problem, since it cannot dissolve or diffuse in metal. The problem is nascent hydrogen. At even ambient temperatures, carbon and low-alloy steels can dissolve nascent hydrogen from hydrogen gas. The amount of nascent hydrogen capable of dissolving from gaseous hydrogen is normally quite small, since its concentration in the metal must be in equilibrium with the concentration of nascent hydrogen in the gas. The latter concentration is very small except at high-temperatures and high hydrogen partial pressures. As a rule of thumb, gaseous hydrogen at temperatures less than about 430°F (220°C) cannot provide enough nascent hydrogen to embrittle carbon or low-alloy steels.

As is discussed in the following section, carbon steels are not selected for high-temperature, high-pressure hydrogen services. Accordingly, they are not susceptible to hydrogen embrittlement by hydrogen gas, unless they are improperly exposed. As a result, postweld heat treatment is normally not required for carbon steels in hydrogen service.

Gaseous hydrogen service can cause hydrogen embrittlement in straight chromium stainless steels and low-alloy steels (including the Cr-Mo steels, which are favored for high-temperature, high-pressure hydrogen gas service). Hydrogen that dissolves in the steel at high-temperatures can embrittle the steel upon cooldown, if cooling is too fast to permit the escape of excess hydrogen as the metal cools. Note that such steels have a very low solubility for hydrogen at temperatures below about 400°F (205°C). Weld repair requires bakeout and preheat.

Hydrogen Attack

Hydrogen gas can cause surface decarburization as well as internal decarburization and fissuring. (The latter is called *hydrogen attack* in carbon and low-alloy steels.) These types of deterioration involve exposure to high-temperature services having high hydrogen partial pressures. See Figure 3-6 for an example of the damage caused by hydrogen attack on carbon steel. Since

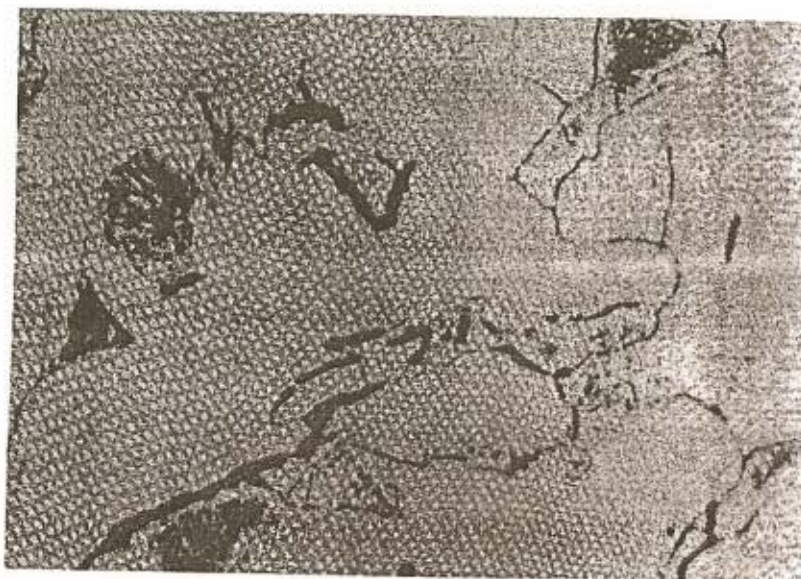


Figure 3-6 Surface decarburization and grain boundary cracking in carbon steel, caused by hydrogen attack.

surface decarburization causes only a slight reduction in material strength, it is not normally regarded as a problem.

Hydrogen attack can occur at temperatures above about 430°F (220°C). Dissolved hydrogen can attack iron carbide (Fe₃C-cementite), generating methane gas (CH₄), which is trapped in the metal because the methane molecule is too large for diffusion. Attack is usually at grain boundaries. As the concentration of methane gas increases, increasing pressure begins to tear the grain boundary apart, causing first fissures, then cracks, then networks of cracks. Simultaneously, the loss of carbides lowers the strength of the material. Combined, the two effects can substantially reduce the expected life of a component. Both chromium and molybdenum form more stable carbides, leading to a preference for Cr-Mo alloy steels in hydrogen service. Unless severely cold worked, austenitic stainless steels are unaffected by hydrogen attack.

The Nelson curves are used to select materials that will be immune to hydrogen attack in gaseous hydrogen service. Refer to Appendix 4 and API Publication No. 941 "Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants" [6]. Because of the "scatter" in the Nelson curve data, it is common to use the maximum operating temperature plus a 25°F (14°C) margin when selecting materials using the

Nelson curves. Some users and process licensors specify the use of a 50°F (28°C) margin. Make sure that the maximum design temperature is large enough to include the maximum operating temperature plus the selected margin. (Note that if the maximum design temperature is used for materials selection, the use of an additional operating temperature margin should be unnecessary.)

For the vertical portion of the curves, it is customary to use a 25 or 50 psia (170 to 345 kPa) margin on the maximum operating hydrogen partial pressure. Make sure that the maximum design pressure is large enough to include the maximum operating pressure plus the selected margin.

Hydrogen attack is accelerated by inclusions and slag-type defects. Therefore, killed steels are selected. Inclusion-free welds are often specified. To further protect materials exposed to hydrogen service, it is common industry practice to impose weld metal hardness controls. Postweld heat treatment is recommended for all Cr-Mo alloy steels. Components cold worked more than 5 percent should be stress relieved. Welded attachments such as reinforcing pads should be vented.

Except at high-temperatures and high hydrogen partial pressures, there is a significant incubation time before hydrogen damage becomes detectable. Thus, in situations where the metal is exposed to infrequent and short-term transient combinations of high-temperature and moderate hydrogen partial pressure, there may be a significant incubation time before the effects of such attack become detectable. Investigation of incubation times can often justify the choice of a lower-cost material of construction. Refer to API Publication No. 941 [6] for details on incubation times.

To summarize, when selecting materials for hydrogen service:

- The Nelson curves utilizing the maximum operating temperature plus 25°F (14°C) should be used.
- Carbon steels should be fully killed or otherwise deoxidized.
- Low-alloy steels such as the Cr-Mo steels should be postweld heat treated.
- Cold-worked materials should be stress relieved.
- Seamless tubing and pipe are preferred, as they avoid potential problems associated with longitudinal welds.
- Hardness controls should be employed:
 - NACE RP0472. The maximum weld metal hardness permitted for carbon steel is 200 BHN. Weld procedure qualification testing is done to ensure that heat-affected zone hardnesses do not exceed 248 VHN [7].
 - NACE MR0175. It is industry practice to limit the weld metal hardness of Cr-Mo low-alloy steels (225 BHN for Cr < 3 and 241 BHN for 3 < Cr < 9). NACE MR0175 [8], which limits the hardnesses of parent metals and heat affected zones, should be required.

Heat affected zone hardnesses should be shown to be satisfactory in the Welding Procedure Qualification Record via a hardness traverse across the weld metal-parent metal interface.

Since proper use of the Nelson curves will prevent hydrogen attack on materials of construction, hydrogen gas is regarded as a crack-inducing agent rather than as a corrodent. As discussed in Part I of this chapter, hydrogen gas service involving the Cr-Mo steels is a major concern because of:

- The hydrogen embrittlement that could occur at operating temperatures less than about 250°F (120°C). This concern is usually addressed by not pressurizing at operating temperatures colder than 250°F (120°C).
- The potential for delayed hydrogen cracking that could occur in weld repairs subsequent to service. This concern is addressed by an appropriate bakeout prior to repair welding.

4. Nitriding

Stainless steels and many higher alloys such as Alloy 800 will slowly develop a brittle nitride layer if exposed to a nitriding atmosphere at temperatures exceeding about 750°F (400°C). By far the most common nitriding atmosphere is ammonia or a mixture of gases rich in ammonia. Nitriding of stainless steels has also been reported in high-temperature chemical process streams utilizing nitrogen-bearing organic compounds such as urea. Gaseous nitrogen is not regarded as a nitriding atmosphere.

Nitriding usually occurs at a much slower rate than carburization. Special alloys and/or aluminum including aluminum vapor-deposited coatings are used to resist nitriding. Materials selection often accommodates nitriding by providing a nominal *nitriding* allowance such as 1/16" (1.5 mm).

5. Oxidation

Virtually all metals and alloys have threshold temperatures above which they become susceptible to rapid scale formation and spalling when heated in air or steam. Table 3-1, developed from data in Appendix 1, shows the oxidation/scaling threshold temperatures for commonly used materials.

Materials in applications subject to thickness losses due to oxidation are usually provided with a nominal *oxidation* allowance; 1/16" to 1/8" (1.5 to 3 mm) is typical.

Most often, hot lines and equipment are thermally insulated to conserve energy. Properly insulated and jacketed, hot lines and equipment can be kept in safe service at temperatures above the oxidation limits of the materials of construction. Care must be taken to ensure that the process stream chemistry is

Table 3-1 Oxidation/scaling temperatures for common materials of construction

MATERIAL	SCALING TEMPERATURE
Carbon Steel	1000°F (540°C)
1¼Cr-½Mo	1050°F (565°C)
2¼Cr-1Mo	1075°F (580°C)
3Cr-1Mo	1100°F (595°C)
5Cr-½Mo	1150°F (620°C)
9Cr-1Mo	1200°F (650°C)
12 Cr	1500°F (815°C)
3½ Ni	1000°F (540°C)
9Ni	1000°F (540°C)
18Cr-8Ni	1650°F (900°C)
Types 309 & 310 SS ¹	2000°F (1095°C)

¹Nickel content increases spalling resistance. Thus, the higher Ni grades (such as Type 310 SS instead of Type 309 SS) are favored, particularly in cyclical services, where thermal stressing will encourage spalling.

either non-oxidizing or that the process-side surface is protected by an insulating or refractory liner. In such cases, the limiting factor will be the availability of a code maximum allowable stress.

Alloys containing significant amounts of molybdenum are potentially subject to *catastrophic oxidation*. The superaustenitic stainless steels such as Alloy AL-6XN, a 21Cr-25Ni-6.5Mo-N alloy (UNS N08367) are an example. This problem is associated with the formation of a heavy molybdenum oxide scale, usually as a result of an improper heat treatment or a severe thermal excursion while in service. Experience has shown that removal of such scales prior to service (or return to service) will prevent the problem. Removal usually requires a pickling treatment.

Heat tinting, such as the blue tinge often seen on welds, is a common condition associated with welds and thermally cut surfaces. For carbon and low-alloy steels, such tinting is usually ignored. However, the subsurface areas of heat-tinted stainless steels may be significantly depleted of chromium. For demanding environments, heat tinting is usually removed by mechanical methods such as grinding or by chemical cleaning or both.

6. Sulfidation and Sulfidic Corrosion

Sulfur and sulfur compounds may attack carbon and low-alloy steels at temperatures above 500°F (260°C) and nickel base alloys such as Alloy 600 (15Cr-72Ni-8Fe; UNS N06600) at temperatures above about 600°F (315°C).

Sulfidic Corrosion

Sulfidic corrosion is most often associated with sulfur in crude oil (as organic sulfides and/or as H₂S). It can cause severe pitting and general wastage in carbon and alloy steels at temperatures exceeding 500°F (260°C). Corrosion rates can be estimated using the McConomy and the Couper-Gorman curves.

McConomy Curves

Use the McConomy curves for services that do not contain hydrogen. Refer to Appendix 5 [9].

These curves were developed from empirical data, obtained from crude oil heaters used to preheat sour crudes feeding atmospheric crude units. Experience has shown that the total sulfur content (in wt. percent) is not a precise indicator of the corrosivity of a crude oil, at least partly because not all organic sulfur compounds are corrosive to carbon and alloy steels, even at elevated temperatures. Nevertheless, the McConomy curves are generally used to estimate corrosion rates for carbon and low-alloy steels in sour crude streams, without the addition of hydrogen, at elevated temperatures. There is no better nonproprietary method available.

Long-term experience with the McConomy curves indicates that they often predict excessive corrosion rates. Appendix 5 includes a discussion of how to use the McConomy curves and how to use adjustments that can be employed to obtain more realistic corrosion rates.

Note that many hydrocarbon plants have successfully operated 5Cr-½Mo and 9Cr-1Mo piping and equipment with sour crude streams at temperatures exceeding 850°F (455°C). There appear to be two reasons for this success:

1. Heated sour oil, at temperatures exceeding about 850°F (455°C), becomes less corrosive due to the liberation of corrosive species. Note that the

McConomy curves show a maximum corrosion rate at about 850°F (455°C). At higher temperatures, the residual sour oil is less corrosive.

2. Coke builds up on the process surfaces, protecting those surfaces from sulfur corrosion.

Couper-Gorman Curves

Use the Couper-Gorman curves for services that contain hydrogen gas having a partial pressure of at least 50 psia (345 kPa). Refer to Appendix 6 [10].

When the use of carbon steel is indicated by either the McConomy or Couper-Gorman curves, silicon-killed carbon steels are generally preferred, as they seem to be more resistant to sulfidic corrosion than are the aluminum-killed carbon steels. The choice of coarse-grained silicon-killed steels may be precluded by a requirement for the low-temperature toughness provided by the fine grain practice steels killed with aluminum.

In sulfur plants, mixed sulfur-hydrogen sulfide streams are usually handled in carbon steel for temperatures up to about 575°F (300°C). Many users consider it safe to use carbon steel to about 600°F (315°C). Corrosion rates estimated from the McConomy curves are generally regarded as excessive for sulfur plants.

For temperatures at which sulfidic corrosion rates would be excessive, two alternatives can be used to extend the useful limits of carbon and low-alloy steels:

1. Refractory linings are often used in both vessels and piping. A low iron-containing refractory is required, since spalling of the refractory has been associated with iron oxide contaminants in the refractory.
2. An aluminum diffusion coating is sometimes employed to extend the usefulness of carbon steel. This coating is applied by a proprietary process for vapor-diffusing aluminum on and into the steel. An important example is heater tubing, extending the useful temperature range to 800°F (425°C). Such coatings have also been used on low-alloy steels for protection of heater tubes from external sulfidic corrosion. The effectiveness of this type of coating is inconsistent. It appears that an imperfect coating can lead to early failures.

Pure liquid sulfur is stored in pits made of Type V concrete. Piping for liquid sulfur is usually carbon steel. Heating, normally by steam tracing, is employed to keep the sulfur molten. Liquid sulfur in the presence of air can be very corrosive to carbon steel. Nitrogen blanketing or alloys such as Alloy 20 Cb-3 (20Cr-35Ni-2.5Mo-Cb; UNS N08020) or Type 310 SS are employed.

Sulfidation

Sulfur and sulfur compounds may attack nickel-base alloys at temperatures above about 600°F (315°C). See Figure 3-7 for an example of the damage

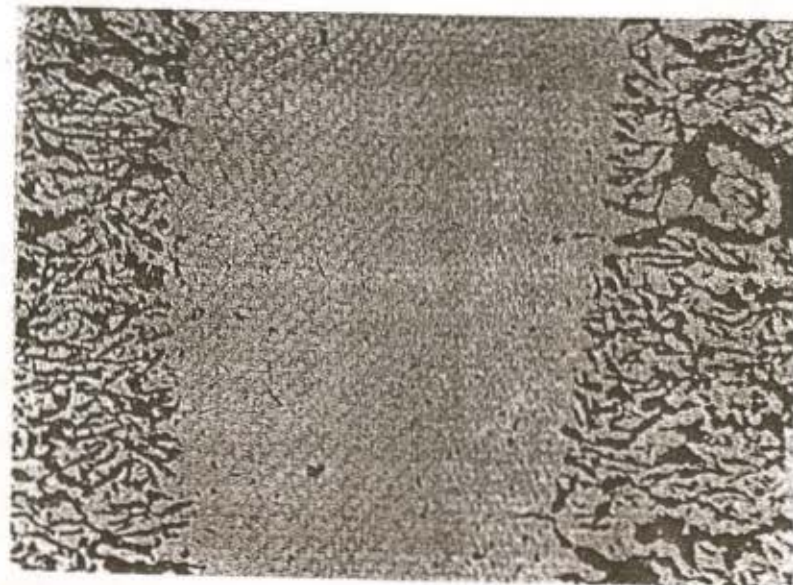


Figure 3-7 Sulfidation of Alloy 20 Cb-3.

caused by sulfidation. The threshold temperature for this attack depends on both the process and the alloy composition. At least one user regards the threshold to be as low as 300°F (150°C) for Alloy 400 (67Ni-30Cu; UNS N04400) in reducing hydrogen sulfide. Sulfur attack can assume several forms and can be quite severe, particularly under reducing conditions. While pitting can occur, severe sulfidation usually involves either intergranular attack or fluxing due to molten sulfides. Ordinary austenitic stainless steels are also subject to fluxing by molten Fe-Ni sulfides. Since the threshold temperature for sulfidation depends on both alloy and process compositions, the literature or technical assistance of alloy manufacturers should be sought for differentiating among alloys.

D. HIGH-TEMPERATURE ALLOYS

Conventional 300-series stainless steels are useful in many services up to about 1500°F (815°C). Above this temperature, their maximum code-allowable stresses are too low for most practical long term non-creep designs. Higher chromium-nickel conventional austenitic stainless steels such as Types 309 and 310 SS do find use in low-stress applications such as shrouds used as refractory liners and flare tip applications, up to about 2000°F (1095°C).

In addition to having less than adequate maximum allowable stresses at high-temperatures, the 18Cr-8Ni stainless steels become susceptible to oxidation and spalling at temperatures above about 1650°F (900°C). At higher temperatures the minimum chromium content for reliable resistance to oxidation is 25 to 28 percent, depending on alloying additions such as aluminum and silicon.

In this section, the term *high-temperature alloys* is taken to mean alloys intended for service temperatures above 1500°F (815°C). For moderate stress service, there are several high-nickel alloys for which conventional engineering codes provide maximum allowable stresses useful for non-creep design. The Alloy 800 series is an example. However, many high-temperature applications such as furnace tubes involve stresses that will generate creep.

There are a few conventional alloys that can withstand oxidation at temperatures up to about 2200°F (1205°C), usually because of relatively high silicon content. However, for most applications above 2050°F (1120°C), either ceramics or engineered materials are required. An example of the latter are the coated and internally cooled alloy blades that are used in high-performance combustion gas turbines.

Most designs for temperatures exceeding 1500°F (815°C) must allow for creep and/or stress rupture. Such designs take into account material behavior not normally encountered in conventional design. It is normal practice to use an "operating margin" when designing a high-temperature system. Often, the operating margin is 50°F (28°C), that is, the design temperature is taken to be 50°F above the maximum operating temperature. In the creep range, this margin amounts to a design life extension, often 50 to 100 percent or more. Needless to say, design life guarantees are easily achieved unless the system is abused by operation at excessive temperatures.

For most applications, the maximum allowable stress of a high-temperature alloy is taken as the 100,000 hour stress rupture value. API Recommended Practice No. 530 "Recommended Practice for Calculation of Heater Tube Thickness in Petroleum Refineries" [11] is a good source of stress rupture data for conventional high-temperature alloys such as the 300-series stainless steels, HK-40 and Alloy 800. This reference also includes stress rupture data for carbon steel and the Cr-Mo low-alloy steels. However, most of the modern alloys preferred for high-temperature service are not included in API 530. These are proprietary alloys and their design data are provided by the manufacturer. Experience has shown that most manufacturers provide reliable data. Nevertheless, it is prudent to compare the data of different manufacturers for the same type of alloy in order to detect anomalies.

While there are a few wrought alloys on the market, such as the Alloy 800 series, most of the alloys used in high-temperature furnace and heater applications are available only in the form of castings. Examples include tubes,

tubesheets and hangars. Centrifugal castings are preferred for tubulars. This restriction is due to their chemistries, usually because of their high carbon and silicon content. Various alloying additions impart greater resistance to creep, oxidation, nitriding, carburizing, etc. However, these alloys do have some disadvantages:

- Even when new, they are usually brittle, preventing their being used in fabrication procedures requiring forging, rolling, drawing, etc.
- In service, most of them become even more brittle as they age, the result of the formation of brittle intermetallic compounds. Aged alloys are often impossible to repair by welding.
- They usually require special welding procedures, as they are unusually prone to cracking induced by welding.

Some users insist that components external to the heater or furnace be made of a wrought alloy. This insistence is based on the belief that the cast alloys are too brittle and are therefore unsafe for use outside the fired area. This belief is changing as some of the newer cast alloys show both improved initial ductility and improved resistance to in-service embrittlement.

Conventional alloys such as the HKs, per ASTM A297 and ASTM A608, have been largely displaced by a number of proprietary alloys. Some of these alloys are marketed as variants of "HP-Mod." This is a generic alloy family with compositions based on a 25Cr-35Ni content, with varying microalloying additions of Ti, Cb, W, etc. While the HP-Mod alloys are probably the most widely used of the modern cast high-temperature alloys, there are numerous other alloys of different chemistries offering advantages in cost or extended operation. The newer alloys have a number of advantages, particularly for furnace or heater tubes:

- Because of their higher strength, they need less section thickness. This reduces the thermal gradient (i.e., thermal stress) across the tube wall thickness. The reduced thermal gradient is a real benefit, since it substantially extends the creep life. Less section thickness often does not translate into less cost, since the improved alloys are usually more costly than the older alloys.

"Corrosion" allowance, including allowances for carburization, nitriding, oxidation, etc., should be kept to a minimum. Such increases in thickness also increase the thermal gradient, thereby decreasing the creep life. Similarly, the ID surfaces of centrifugally cast tubulars should be bored and honed to a smooth finish, as this reduces thermal stresses as well as improves resistance to degradation processes such as carburization.

- From a process standpoint, reducing the section thickness without reducing the tube diameter allows more mass flow. In the case of catalyst-based applications such as reformer furnace tubes, reducing section thickness

results in a larger catalyst charge. In both cases, the result is improved production rates.

- Most of the newer alloys have a higher useful maximum design temperature, permitting greater process efficiency.

Materials selection among the available alloys is a complex process. All of the high-temperature alloys undergo various temperature- and process-induced degradation phenomena such as various forms of embrittlement, sensitization, carburization, oxidation, sulfidation and creep. Most alloys are quite sensitive to cyclic operation, which accelerates both creep damage accumulation and degradation mechanisms such as carburization.

In many cases, materials selection is based on the recommendations of process licensors, as they have the experience necessary to optimize the selection of materials. In other cases, the user must depend on the alloy manufacturers' data base, past plant experience and/or in-plant or laboratory testing. In situations where adequate information is not available, the user is advised to either obtain the assistance of a competent specialist or survey the advice of a variety of manufacturer technical representatives.

PART 3: CORROSION

A. CORRODENTS

1. Acids, General

Acids are often classified as *oxidizing* or *non-oxidizing* (the latter are sometimes referred to as *reducing* acids). Some acids can show more than one kind of behavior, depending on concentration and/or temperature. Materials selection for acids and their derivative compounds depends in part on whether they are reducing or oxidizing. In addition, the corrosivity of the solution often depends on the presence of strong oxidizing salts such as ferric chloride (FeCl_3) or cupric chloride (CuCl_2). Both salts are also strong pitting agents. Such oxidizers are sometimes present as contaminants. Particularly in reducing acids, corrosivity can be dominated by aeration and/or the presence of oxidizing contaminants.

In general, oxide-stabilized corrosion resistant materials perform well in the presence of oxidizing acids. Examples include the refractory metals such as titanium, the austenitic stainless steels and Ni-Cr-Mo alloys such as Alloy 20 Cb-3, Alloy C-276 (15Cr-54Ni-16Mo; UNS N10276), Alloy 625 (22Cr-60Ni-9Mo-Cb; UNS N06625) and Alloy 825. For alloys, it is a general rule that the higher the alloying content, particularly for chromium, the higher the

concentration and temperature limits for which the alloy will be suitable. Increasing the Ni content increases resistance to chloride pitting and to chloride stress corrosion cracking. Increasing the Mo content reduces susceptibility to localized corrosion phenomena such as pitting and crevice corrosion. Alloys such as Alloy C-276 find use in both oxidizing and reducing acids. They are usually specified for reducing acids which contain or can become contaminated by oxidizing agents.

Alloys designed to operate well in reducing acids may perform poorly in such acids if they are aerated or contain oxidizing contaminants. Alloy 400 and Alloy B-2 (65Ni-28Mo-Fe; UNS N10665) are examples. Accordingly, it is important to determine if reducing acids will contain oxidizing contaminants or will be aerated.

When austenitic stainless steels are selected for acid service, it is conventional to specify the low carbon grade, that is, the "L" grade. Many acids will attack the sensitized band in the weld heat affected zones of the conventional grades.

If pilot plant testing is required to select materials or verify materials selection, the program should include testing in all applicable phases. Consider vapor phase coupons and partially submerged coupons in addition to normal immersion testing. The coupon rack should include weld metal, heat affected zone and deliberately sensitized specimens. If fabrication or construction will include cold work, stress relief and/or postweld heat treatment, appropriate coupons should be included in the test program.

In surveying materials for a specific application, keep in mind the following alternatives:

- Non-metallic materials such as fiber-reinforced plastics are available for both piping and for most equipment such as vessels, tanks and pumps.
- Liners such as rubber, polymer or glass are frequently cost effective. Plastic-lined piping is a common choice in acid systems.
- Cladding and/or weld overlays, using carbon or low-alloy steel for pressure containment and a corrosion resistant alloy for corrosion resistance, are sometimes used.

In the following sections, conventional selections of materials of construction are described for a variety of inorganic and organic acids. This information is provided to allow the reader to select materials for simple systems or to provide some background which can be used to review proposed materials for suitability. The user should investigate alloy manufacturer and process licensor experience, review available literature and seek expert assistance if the process involved will include complicating issues such as contaminants, temperatures or pressures outside the conventional range, or complex equipment items such as distillation towers or heat exchangers.

2. Inorganic Acids

Hydrochloric, hydrofluoric, nitric, sulfuric and phosphoric acids account for most of the strong inorganic acids encountered in hydrocarbon and chemical process plants. Hydrochloric, hydrofluoric and phosphoric acids are non-oxidizing. Nitric acid is a strong oxidizer. Sulfuric acid can be either oxidizing or non-oxidizing, depending on temperature and concentration. Sulfuric acid becomes increasingly oxidizing at concentrations of about 25 wt. percent and higher. Below 25 percent, the uncontaminated acid is regarded as non-oxidizing.

Because of their relatively severe corrosiveness, many of the inorganic acids are difficult to handle with alloys. In addition, use of highly alloyed materials substantially increases both capital and installed costs. For these reasons, it is common for materials selection to include plastics (including fiber-reinforced plastics), elastomers, linings and coatings. Carbon and graphite also find use in some severe applications. Fluoropolymers such as PVDF are usually very resistant to most inorganic acids, but may be permeable. Often, less expensive plastics are suitable. Equipment constructed of lined carbon steel is often selected. Candidate linings include rubber, plastic, resistant paint coatings (if backed up with cathodic protection) and glass. Plastic lined piping is regarded as the normal choice for many industrial applications.

Industrial users of inorganic acids are served by a very competitive component and equipment supply industry. Many equipment fabricators offer proprietary as well as conventional alloys, plastics and liner materials. Many companies provide excellent technical assistance in the selection of materials. When using such sources, be aware that the recommended materials, while satisfying the technical selection criteria, may not be the most cost effective. Also, do not overlook information available from trade organizations. The Nickel Development Institute and the Copper Development Association (see p. 53) are good sources. References [12], [13] and [14] are also useful.

Sulfuric Acid

Carbon steel is normally used for storage tanks and sometimes for piping for sulfuric acid at concentrations of 70 wt. percent and above, at temperatures up to 104°F (40°C). Typical industrial concentrations are 93 and 97 percent. The selection of carbon steel depends on controlling velocities to less than about three ft/sec (0.9 m/s). The velocity limitation is critical, since successful use of carbon steel depends on not disturbing the protective, but non-adherent, soft, insoluble iron sulfate scale layer. Linings and anodic protection are also specified, sometimes from concerns over product purity. Note that some design and construction details can be important. Examples include avoiding accidental entry of water and proper precommissioning cleaning. Refer to NACE RP0391

"Materials for Handling and Storage of Concentrated (90 to 100 percent) Sulfuric Acid at Ambient Temperatures" [15] for further details.

Hydrogen damage can occur in carbon steels in sulfuric acid services.

- Hydrogen induced cracking (HIC) damage, including blistering, has been observed in tanks and other components built of plate. Both of these phenomena can be minimized by using clean carbon steels of the type recommended for HIC resistance. [For a discussion of HIC resistance, see the section entitled "Wet Sour Service" (p. 196).]
- *Hydrogen grooving* has been observed in carbon steel tanks in sulfuric acid service. This phenomenon is caused by bubbles of H_2 eroding the protective scale covering from the steel, permitting continued attack of the substrate. This problem is usually associated with manholes or nozzles and can be minimized by use of corrosion-resistant linings or alloys.
- Type 316L SS, rather than carbon steel, is becoming the standard metallic material of construction for piping concentrated sulfuric acid for temperatures up to about 80°F (27°C). Alloy 20 Cb-3 is usually specified for valves. 14 wt. percent silicon cast iron (see ASTM A518) or cast Alloy 20 Cb-3 (see ASTM A351, A743 or A744, Gr CN-7M) is usually recommended for pumps. The 14 percent silicon cast iron material is not recommended for fuming sulfuric acid.

Where low velocities or occasional upset-induced higher corrosion rates cannot be accepted, corrosion-resistant alloys are specified for concentrated sulfuric acid. Corrosion-resistant alloys are also usually required if better reliability or low maintenance is a project objective. Alloy 20 Cb-3 is a commonly specified material.

Lower concentrations of acid or higher operating temperatures require the use of more resistant materials. Type 316L SS can be used, in conjunction with anodic protection. However, applications are limited because of the possible consequences of failure or disruption of the anodic protection system.

- Lead has been widely used in both the manufacture and use of sulfuric acid. As with carbon steel, the successful use of lead depends on not disturbing the protective, insoluble lead sulfate layer. Velocities should be limited to three ft/sec (0.9 m/s). Lead is resistant to sulfuric acid at temperatures up to 275°F (135°C) for concentrations up to about 60 wt. percent. Above this point, lead is useful at higher concentrations, but at lower temperatures. The use of lead in sulfuric acid service is being curtailed by environmental and disposal concerns. In addition, lead is not competitive with many non-metallic materials.
- Alloy 20 Cb-3 performs well in sulfuric acid in the concentration range 0 to about 60 wt. percent at temperatures up to about 175°F (80°C).

Corrosion rates are usually on the order of 10 to 15 mpy (0.25 to 0.38 mm/yr).

- Alloy C-276 is resistant at all concentrations at maximum temperatures ranging from about 125°F (52°C) to 200°F (93°C).
- Alloy 825 offers corrosion resistance similar to that of Alloy C-276, but at a lower temperature range (about 100 to 200°F (38 to 93°C)).
- Alloy 400 is used for temperatures up to about 200°F (93°C) for concentrations up to about 60 wt. percent in the absence of aeration and/or oxidizing contaminants.
- Alloy B-2 is resistant to boiling sulfuric acid up to a concentration of about 70 wt. percent. In concentrated acids, it is resistant at temperatures up to about 225°F (107°C). Note that this alloy is sensitive to aeration and/or the presence of oxidizing contaminants.
- Zirconium is useful up to at least 60 wt. percent concentration at temperatures up to the boiling point. For concentrations between 60 and 80 percent, zirconium is useful for temperatures up to about 200°F (93°C).
- Tantalum is essentially inert to all concentrations of sulfuric acid at temperatures up to about 300°F (150°C). Above this temperature, concentrated acid corrodes tantalum at very moderate rates up to about 500°F (260°C). Tantalum is highly resistant to dilute acid up to the boiling point.

In common with most mineral acids, sulfuric acid in various concentrations and temperatures can be handled by fiber-reinforced plastics, liners such as rubber (e.g., neoprene), polymers such as polypropylene and glass and plastic-lined pipe.

Refer to Appendix 11 for a materials selection graph for sulfuric acid.

Hydrochloric Acid

This acid is destructive to all conventional carbon, low-alloy and stainless steels, unless it is inhibited. Inhibited 5 to 15 wt. percent acid is used at low velocities for cleaning carbon steel piping and equipment. Nickel and nickel alloys are required for even moderate corrosion resistance. In common with other reducing acids, aeration and/or the presence of oxidizing impurities can profoundly change the corrosivity of the acid.

- Alloy 200 (commercially pure Ni; UNS N02200) and Alloy 400 are used at concentrations up to 20 wt. percent at room temperature for non-aerated processes. These alloys can be used to concentrations of only 10 percent if the acid is aerated. Alloy 400 is generally preferred because of its superior tolerance at higher concentrations and temperatures. Both alloys are very sensitive to oxidizing contaminants such as the ferric ion, that is, Fe^{+++} .

- Alloys 825 and C-276 can be used at concentrations up to 37 wt. percent at ambient temperatures. These alloys are usually chosen for aerated acids or acids containing oxidizing contaminants.
- For higher-temperature service, Alloy B-2, zirconium or tantalum may be required.
 - Alloy B-2 will tolerate aeration, but it is sensitive to oxidizing contaminants such as the ferric ion.
 - Zirconium is only slightly corroded by hydrochloric acid at all concentrations, for temperatures up to about 275°F (135°C). However, it is sensitive to oxidizing impurities.
 - Tantalum is regarded as resistant to all concentrations of hydrochloric acid at temperatures up to about 300°F (150°C). However, tantalum and its alloys are very susceptible to hydriding, requiring careful design. Refer to Part 1 of this chapter for a discussion of hydriding.
- Titanium alloys have a wide range of response to variations in concentration, oxidizing contaminants and temperature for hydrochloric acid service. The Ti-Pd alloy (Gr 7) is regarded as the most resistant of the Ti alloys for hydrochloric acid service. These alloys find use in relatively dilute acids, particularly if the acid contains oxidizing impurities. Titanium should not be selected for hydrochloric acid service unless the application has a proven history or the selection is justified by adequate testing.

Hydrochloric acid in various concentrations and at various temperatures can be handled by fiber-reinforced plastics, liners such as rubber, polymers and glass- and plastic-lined pipe. Polymeric materials are the normal choice for handling and storing hydrochloric acid.

Refer to Appendix 11 for a materials selection graph for hydrochloric acid.

Hydrofluoric Acid

NACE Technical Committee Report SA171 entitled "Materials for Receiving, Handling and Storing Hydrofluoric Acid" [16] provides detailed guidelines on selection of both metallic and non-metallic materials for both hydrofluoric acid and anhydrous hydrogen fluoride.

- Carbon steel is commonly used for the storage and piping of non-aerated hydrofluoric acids, at concentrations of 70 wt. percent or more, for temperatures up to 90°F (32°C). The resistance of carbon steel in this service depends on the formation of a stable surface film of non-adherent iron fluoride. Consequently, control of velocities, to a maximum of 2 ft/sec (0.6 m/s), is required. Hydrofluoric acid can cause hydrogen embrittlement, hydrogen stress cracking, hydrogen induced cracking damage and stress oriented hydrogen induced cracking in carbon steels. The mitigation measures used for carbon steels in "wet sour" service also apply to carbon

steels in hydrofluoric acid service. [For a discussion of wet sour service mitigation measures, see the section entitled "Wet Sour Service" (p. 196).]

- Lead has been a conventional material of construction for non-aerated hydrofluoric acid service process equipment. It is useful for concentrations up to about 60 wt. percent, at ambient temperature. Use of lead is becoming less common, as it generates environmental concerns and is not competitive with many non-metallic materials.
- Alloys 400 and C-276 are usually specified if an alloy is required. These alloys are useful for all concentrations of acid, at temperatures up to about 175°F (80°C).
 - Alloy 400 is very sensitive to the aeration and/or the presence of oxidizing contaminants.
 - Cold-worked components of Alloy 400 should be stress relieved.

Hydrofluoric acid in various concentrations and temperatures can be handled by fiber-reinforced plastics, liners such as rubber and polymers and by plastic-lined pipe. Fiber reinforcements must be of materials other than glass.

Refer to Appendix 11 for a materials selection graph for hydrofluoric acid.

Nitric Acid

Carbon and low-alloy steels are not suitable materials of construction for nitric acid service. Fourteen wt. percent silicon cast iron (see ASTM A518) is very resistant to concentrations exceeding about 45 percent, up to the boiling point. This material is useful for pumps (CF-3M, the cast version of Type 304L SS, and titanium are also commonly used for pumps). Use of Types 316 or 316L SS is generally avoided, since these alloys are susceptible to intergranular attack.

The standard material of construction is Type 304L SS, for temperatures up to about 250°F (120°C). This alloy should not be used for concentrations exceeding 90 wt. percent. Aluminum alloys are used in the 90 to 100 percent concentration range for temperatures up to about 100°F (38°C).

Titanium is resistant to nitric acid concentrations below about 20 wt. percent or between 70 and 90 wt. percent, at temperatures up to the boiling point. It may be specified instead of Type 304L in processes that are sensitive to product contamination. Titanium should not be used in fuming nitric acid.

Zirconium is used for severe, high-temperature services for concentrations up to about 70 wt. percent. Tantalum is resistant to all concentrations of nitric acid.

Nitric acid corrosion of Type 304L SS can be accelerated by the presence of hexavalent chromium ions. The process chemistry should be reviewed to prevent conditions that could lead to the production and/or deposition of this contaminant.

Nitric acid in various concentrations and temperatures can be handled by fiber-reinforced plastics, liners such as rubber, polymers and glass- and plastic-lined pipe.

Phosphoric Acid

Type 316L SS is the conventional material of construction for pure phosphoric acid at concentrations up to 85 wt. percent and temperatures up to 200°F (93°C). Higher alloys such as Alloy 20 Cb-3 and Alloy 825 are resistant to concentrations up to 85 percent of the pure acid, up to the boiling point.

In the manufacture of phosphoric acid, contaminants dominate materials selection. Higher alloys such as Alloy 20 Cb-3, Alloy 625 and Alloy C-276, are commonly used. The high chromium duplex stainless steels such as Alloy 2507 (25Cr-7Ni-4Mo; UNS S32750) also find extensive use in this service.

There are numerous non-metallics such as fiber reinforced plastics and liners such as rubber, polymers and glass, as well as plastic-lined pipe, available for phosphoric acid service.

3. Organic Acids

Organic acids and their derivative compounds can pose serious corrosion problems in plant piping and equipment. Organic acids are electrolytes; they do not require free water to be corrosive. Organic acids, their esters and anhydrides are common commodities in many chemical process plants; they range in corrosivity from mild to aggressive. Organic acids and/or their derivative compounds are created as byproducts or contaminants in many chemical process and hydrocarbon plant operations. Naphthenic acids are occasionally a corrodent in crude oils, primarily as they move through the atmospheric and vacuum distillation columns in refineries.

Most organic acids are weak and non-oxidizing. Nevertheless, some can be quite corrosive. The corrosivities of organic acids usually increase with aeration and the presence of oxidizing contaminants. However, the presence of oxidizing contaminants (such as air) usually improves the corrosion resistance of the most common material of construction, Type 316 SS.

The corrosivity of most organic acids increases at elevated temperatures; naphthenic acid is an example. Also, anhydrous organic acids are reported to be generally much more corrosive than if they contain even traces of water. In general, the corrosivity of an acid family decreases as the molecular weight increases.

Corrosion rates are usually moderate to severe for carbon and low-alloy steels exposed to organic acids, unless the acid is inhibited. (Note that it is common practice to clean carbon steel plant piping systems with inhibited citric acid.) Type 316 SS and CF-3M castings are the standard materials of construction for most

organic acids and their derivatives. Chloride contaminants are usually avoided due to the risk of chloride stress corrosion cracking or chloride pitting. For higher temperatures, nickel alloys are often useful.

- Be alert to potential problems with nickel alloys that do not contain oxide formers such as chromium. Examples include materials such as Alloy 200 (commercially pure Ni), Alloy 400 and Alloy B-2. Such alloys usually do not perform well in the presence of oxidizing contaminants such as FeCl₃ or dissolved oxygen. In the event that this type of alloy is a candidate, make sure that the process stream will not contain oxidizing contaminants.
- The oxide-stabilized alloys such as Alloys C-276, 625 and 825 usually perform well in the presence of oxidizing contaminants.

The following organic acids are common enough in chemical process and hydrocarbon plants to justify individual discussion. Note that because many applications involving organic acids are in proprietary processes, the user should be able to depend on the process licensor for guidance in materials selection. If process licensor assistance is not available, alloy manufacturer assistance and/or references [12], [13], [14], [17] and [18] may be useful.

Acetic Acid

Type 304L SS is often specified for the storage of pure acetic acid in concentrations up to 90 wt. percent, at temperatures up to 60°F (16°C). Type 316L SS is usually specified for process equipment. It is suitable for all concentrations and for temperatures up to the normal boiling points. Zirconium is often used for severe applications, at temperatures up to about 575°F (300°C), particularly if product contamination is a concern.

Higher alloys such as Alloy 20 Cb-3, Alloy C-276, or titanium are sometimes specified for high-temperature services or applications involving contaminants. High-strength titanium alloys may be susceptible to stress corrosion cracking in hot acetic acid. Alloy B-2 is specified for hot, highly concentrated solutions under reducing conditions.

Aluminum tankage is used for aerated acetic acid for all concentrations up to about 99 wt. percent, at ambient temperatures. Type 316L SS is usually specified for heating coils in acetic acid storage tanks. Rubber-lined carbon steel is useful, but product discoloration can be a problem. Resistant fiber-reinforced plastics are available, primarily for vessels and piping. A number of polymers are used for plastic lined pipe.

Formic Acid

Type 304L SS is generally specified for the storage of all concentrations of formic acid at ambient temperature. Type 316L SS is usually specified for

process equipment. Type 316L SS is also used at all concentrations for temperatures up to at least 200°F (93°C) if moderate corrosion can be tolerated. Corrosion rates can approach 50 mpy (1.3 mm/yr) under severe conditions.

Copper and 90/10 Cu/Ni alloy (UNS C70600) have been used at temperatures up to the boiling point, at all concentrations, where moderate corrosion can be accepted (non-aerated conditions must be maintained).

Several higher alloys are resistant at elevated temperatures, including Alloy 825, Alloy 20 Cb-3, Alloy 28 (27Cr-31Ni-3.5Mo; UNS N08028) and Alloy 904L (21Cr-25Ni-4.5Mo; UNS N08904). These alloys are resistant at temperatures up to 150°F (65°C). Alloy C-276 has been used at all concentrations, up to the boiling point, with only minor corrosion reported.

Titanium is reported as being very resistant to formic acid. However, it is known to be susceptible to rapid attack by anhydrous formic acid. The use of titanium in high concentrations of formic acid at elevated temperatures should be based on an adequate testing program.

Zirconium and tantalum have been reported in successful use at temperatures up to 200°F (93°C) and 300°F (150°C), respectively.

As with acetic acid, fiber-reinforced plastics, rubber and polymeric liners are useful.

Fatty Acids

The fatty acids such as lauric and oleic acids are generally regarded as very mild acids. Type 316L SS is generally used. Type 317L SS may be needed if product purity is a concern, particularly for high-temperature processes. Alloy C-276 and Alloy 625 are usually specified for the most severe services.

Di- and Tricarboxylic Acids

Most of these acids such as oxalic, maleic and phthalic acids are only mildly corrosive. Type 316L SS is the normal material of construction. Oxalic acid is an exception. It is aggressive to the austenitic stainless steels, including Type 316L SS, at virtually all concentrations and temperatures. Alloys such as Alloy 400 are useful to about 90°F (32°C) while Alloy B-2 and Alloy C-276 are useful up to at least 200°F (93°C). There is a wide range of rubber and polymeric materials resistant to oxalic acid.

Naphthenic Acids

Naphthenic acid is the collective name given to organic acids contained in some crude oils and crude oil fractions. It can cause corrosion at temperatures as low as 350°F (175°C). However, serious corrosion, observed as severe

pitting and/or grooving, usually does not occur until the temperature exceeds 450°F (230°C).

Naphthenic acid corrosion occurs in crude distillation units, but is usually worst in vacuum distillation units. Corrosion is most aggressive in areas of high velocity, impingement or turbulence. Naphthenic acid corrosion is not regarded as a problem in modern thermal or catalytic cracking units, probably because the feed heaters operate at temperatures that thermally decompose the acids (900 to 950°F (480 to 510°C)).

The concentration of naphthenic acid is usually reported as the total acid number (TAN) and is stated in units of mg KOH per gram of oil. A TAN value of less than 0.5 mg KOH per gram of oil is considered to be relatively harmless. TAN values between 0.5 and 1.5 are regarded as being slightly to moderately corrosive. Severe attack can occur for TAN values exceeding 1.5. There is no reliable correlation among the TAN, operating temperatures and corrosion rates. While the TAN value is a general guide to corrosivity, experience has shown that corrosion activity tends to be crude-specific. Accordingly, the best indication of the corrosivity to be expected of a crude oil containing naphthenic acids is operating experience.

One should be alert to the fact that refining a crude oil containing naphthenic acids will concentrate the acid fraction in the heavy end draws such as gas oils and in distillation tower bottoms. Even in a crude oil with a TAN less than 0.5, concentrations with TANs of 1.5 or more may occur in distillation products.

Experience indicates that the entrained chloride content can accelerate corrosion, while H₂S can slow the rate of corrosion. Typically, naphthenic acid corrosion is worst in the vacuum distillation unit of a refinery, where the hydrogen sulfide concentration is minimal. Serious corrosion has been reported at temperatures as low as 350°F (175°C). Corrosion rates are lower in the atmospheric distillation column, which has a higher concentration of hydrogen sulfide. Naphthenic acid in hydrotreater feeds is destroyed by the addition of hydrogen. Thus, naphthenic acid is not considered to be a problem downstream of the point of hydrogen injection.

Velocity and turbulence are known to accelerate naphthenic acid corrosion. Furnace tube and transfer line velocities should not be allowed to exceed 200 ft/sec (62 m/s). Some refiners limit velocities to 130 ft/sec (40 m/s). Long-radius piping elbows and bends should be specified.

In most refineries, naphthenic acid corrosion is mitigated by use of austenitic stainless steels containing at least 2.5 wt. percent molybdenum. Type 316 SS can be used, but it must be specified to have a minimum of 2.5 wt. percent molybdenum. ASTM specifications permit a range of 2.0 to 3.0 wt. percent molybdenum for Type 316 SS. With modern steel-making processes, alloy manufacturers can routinely target the molybdenum content of Type 316

SS towards the lower limit, 2.0 wt. percent. This concentration of molybdenum is insufficient for protection from naphthenic acid corrosion. Type 317 SS is sometimes specified, since the molybdenum content of this grade ranges from 3.0 to 4.0 wt. percent. Type 317 SS may be required for severe combinations of TAN, temperature, and velocity or turbulence. The "L" grades of Types 316 and 317 are preferred for welded construction.

Controlling naphthenic acid attack illustrates one of the classic compromise situations in refinery materials selection. Naphthenic acids do their damage in a refinery during removal of sulfur from the crude oil. Normally, stabilized grades of stainless steel such as Type 321 SS would be used to prevent polythionic acid attack. However, Types 321 and 347 SS are susceptible to naphthenic acid attack, thereby requiring the use of a molybdenum-bearing grade. The refining industry has developed different approaches to the dilemma.

- Some users and process licensors choose to accept the risk of polythionic acid attack; Type 316L SS is usually specified. Polythionic acid attack is controlled by operational measures such as preventing air ingress, or by the use of neutralizing washes [3].
- Some users and process licensors are more concerned about polythionic acid attack than they are about naphthenic acid corrosion. This concern dictates the use of stabilized alloys such as Type 321 SS. Concern for naphthenic acid attack is addressed by both onstream inspection, usually by ultrasonic thickness testing, and visual inspections during shutdowns.
- In some applications, Type 316 SS is used for "nonreplaceable" items such as weld overlays, while a stabilized grade is used for a "replaceable" item such as heat exchanger tubing.
- For plate and plate products, Type 316Ti, a stabilized grade, may be specified. This material mitigates both polythionic acid attack and naphthenic acid corrosion.

Naphthenic acid corrosion can be mitigated by inhibitors. However, inhibitors are ineffective in areas of excessive velocity and/or turbulence. Consequently, inhibitors are of marginal value for the control of naphthenic acid corrosion. For new equipment, selection of a molybdenum-bearing stainless steel is recommended.

4. Acid Salts

Any salt that is the product of a weak base and a strong acid, such as NH_4Cl and Fe_3Cl , will produce an acidic solution when dissolved in water. Acid salts can cause a variety of corrosion problems.

- In systems where acid salt deposits can form and absorb water, such deposits can cause under-deposit corrosion such as pitting and may cause stress corrosion cracking.
- Most of the destructive acid salts are highly soluble in water and can form acidic solutions which may be concentrated.
 - If the anionic species is a sulfide or other cathodic poison, cracking mechanisms such as hydrogen stress cracking or hydrogen induced cracking can be significantly accelerated.
 - Acidic chloride salts such as NH_4Cl are particularly damaging to stainless steels. They can cause not only under-deposit pitting, but also cause chloride stress corrosion cracking of austenitic stainless steels under conditions that would normally be considered benign. A wet chloride acid salt deposit can reduce the under-deposit pH to very acidic values, with a very high chloride concentration. In addition, the deposit acts as a diffusion barrier, leading to oxygen depletion beneath the deposit. Galvanic effects from the active-passive cell can accelerate corrosion mechanisms. This situation can cause stress corrosion cracking at temperatures well below the 140°F (60°C) threshold characteristic of the austenitic stainless steels in neutral saline waters.
 - Acidic salt solutions will act as weak mineral acids, causing accelerated general pitting corrosion. These solutions also tend to destabilize otherwise protective scale formations. In non-turbulent regions, this phenomenon usually causes localized accelerated pitting, with the production of large quantities of loose, soft scale. In turbulent areas, erosion corrosion is usually the destructive mechanism.

Most acid salts are hygroscopic, that is, they can absorb water vapor. This results in two conditions under which salt deposits may cause corrosion problems in nominally "dry" systems.

1. In a water-saturated vapor system, salt deposits may absorb enough water vapor to produce a wet spot under the deposit, leading to severe under-deposit pitting. This phenomenon is a cause of pitting failures in carbon and low-alloy steels, but is particularly common with oxide stabilized alloys such as stainless steels. In austenitic stainless steels, this can also cause accelerated chloride stress corrosion cracking, as described above.
2. Particularly in heat exchangers, the metal temperature under the deposit may be below the water dew point of the otherwise "dry" system. A hygroscopic salt deposit may form an aggressive corrosion cell under such conditions.

Neutralization, via injection of a neutralizer such as caustic soda or a neutralizing amine, is sometimes used to control the problems caused by acid

salt solutions. However, water washing is probably the most common mitigation method used to dilute and dispose of harmful acid salt solutions and deposits. Note that the wash water must be free of dissolved oxygen, or destructive corrosion will occur. A concentration of 50 ppbw dissolved oxygen is usually an acceptable limit. In a refinery, stripped sour water is often used as wash water because of its very low oxygen content.

A typical example of an acid salt problem is ammonium bisulfide (NH_4HS) in hydroprocessing effluent systems. It corrodes numerous materials, in a number of ways:

- Erosion corrosion of carbon steel can occur when fluid velocity exceeds about 20 feet per second. For the higher alloys, including the austenitic stainless steels, erosion corrosion is not a problem at velocities up to at least 30 feet per second.
- Under-deposit corrosion such as pitting occurs at wet salt deposits on carbon and stainless steels. Wash water (oxygen free) is often used for mitigation.
- Rapid pitting corrosion can occur with copper alloys and Ni-Cu alloys such as Alloy 400. These alloys therefore are not recommended. In addition, the copper alloys are usually susceptible to ammonia-induced stress corrosion cracking.

For carbon steels, the recommended concentration threshold for safe operation is usually on the order of 2 to 3 wt. percent. Some users accommodate up to 8 wt. percent in carbon steel. Concentrations exceeding 10 percent are considered destructive to carbon steel even at low velocities.

Corrosion susceptibility for common materials is as follows:

- *Carbon steel*: most susceptible
- *Aluminum*: susceptible
- *Stainless steel (300-series)*: velocity sensitive; can be stress corrosion cracked by chloride excursions
- *Alloy 825*: resistant
- *Titanium*: resistant, but not recommended for streams containing hot hydrogen
- *Alloy C-276*: resistant

When preparing the template, indicate the concentrations of the expected acid salts. Consider whether they are corrodents or crack-inducing agents or both. In the Notes section of the materials selection template, indicate if acid solutions or salt deposits are anticipated. If deposits are expected, show the deposition threshold temperature. For vapor systems, show the water dew point temperature. For materials selection, consult the process licensor, pertinent literature such as references [13] and [14], or plant experience.

5. Amines

The primary use of amines is in acid gas (CO_2 and/or H_2S) removal systems. Amines are also used as neutralizing agents and as film-forming inhibitors. Materials selected for amine systems in which the H_2S concentration is less than five mole percent may be different from systems in which the H_2S content is five mole percent or greater. For systems used to remove CO_2 , stainless steels are usually required unless the amine system is inhibited. Inhibited systems built of carbon steel have been shown to work well but are subject to severe corrosion in CO_2 -rich vapor spaces if the system is not carefully designed and operated.

For systems in which the acid gas is composed of at least five percent H_2S , carbon steel is commonly used. The iron sulfide surface scale that forms on carbon steel usually protects it from CO_2 corrosion. Refer to the section "Carbon Dioxide" (p. 158) for a discussion of the combined effects of H_2S and CO_2 .

Amine solutions can cause pitting and stress corrosion cracking in carbon steels. Postweld heat treatment is usually recommended for amine services, in which the amine concentration exceeds two wt. percent, to avoid stress corrosion cracking. Exceptions are equipment and piping in uncontaminated (i.e., fresh) amine service, in which stress corrosion cracking does not occur. Rich amines (amines saturated with acid gas) can cause erosion corrosion in carbon steel tubing and piping. A maximum velocity of 6 ft/sec (2 m/s) is recommended.

Type 304L SS is used for heat transfer services operating above 230°F (110°C) and for all services for which the metal temperature exceeds 300°F (150°C). Type 304L SS is also used for piping downstream of control valves in rich amine service to prevent corrosion damage caused by flashing. A 10-ft spool piece is usually sufficient. In the event that the control valve is at a vessel inlet, specify the use of a Type 304 SS (304L if welded) splash plate in the vessel. The inlet nozzle may require a lining. Type 316 SS is usually specified for valve trim.

Lean amine pumps are usually supplied with carbon steel casings and either carbon steel or cast iron internals. Hot lean amine (>175°F (>80°C)) and rich amine pumps should be supplied with a minimum of 12 Cr SS casing and 12 Cr SS internals. CA-6NM is the recommended material for 12 Cr SS castings.

Refer to API Recommended Practice 945 "Avoiding Environmental Cracking in Amine Units" [19] for a detailed discussion of materials of construction of amine units.

6. Ammonia

Dry ammonia is non-corrosive to most materials of construction. The major exception is carbon steel, which can undergo stress corrosion cracking in truly

anhydrous ammonia. For a discussion of ammonia-induced cracking, see the section "Stress Corrosion Cracking" (p. 177).

Wet ammonia (ammonium hydroxide) causes pitting in copper-base alloys. In addition, most such alloys are susceptible to stress corrosion cracking by wet ammonia. Pitting is also a risk in all but very dilute solutions for nickel-copper alloys such as Alloy 400. Carbon steel and stainless steels are the common materials of construction for wet ammonia. Stainless steels and nitriding-resistant specialty alloys or aluminum vapor deposition coatings are used for hot ammonia.

7. Carbon Dioxide

Wet carbon dioxide (carbonic acid, a weak inorganic acid) can cause severe pitting and/or grooving in carbon and low-alloy steels. A rule of thumb is that carbon steel is usually acceptable for wet CO_2 if the CO_2 partial pressure is less than about 4 psia (27 kPa). A corrosion allowance of up to $\frac{1}{4}$ " (6.4 mm) is usually specified. However, it is easy to estimate the corrosion rate of carbon steel, using the de Waard-Milliams nomograph [20, 21] (see Appendix 2). If the estimated corrosion rate is unacceptable, consider the use of corrosion inhibitors, increase the corrosion allowance or use alloys such as 12 Cr or Type 304L SS.

The de Waard-Milliams nomograph is based on corrosion rates measured in carbonic acid, for clean steel surfaces. Surfaces protected by scales such as mill scale (Fe_3O_4) or other surface deposits are usually at least partially protective. In addition, these rates are valid only for non-turbulent systems. Thus, the rates predicted by the nomograph can be influenced by several factors.

- Surface scales produced by carbonic acid corrosion such as FeCO_3 can result in significantly reduced corrosion rates. Protection by such scales is influenced by several factors, including temperature, pH and velocity. The user should review the paper by de Waard and Lotz [21] to determine if reduced corrosion rate estimates are justified.
- Experimental and field data indicate that nomograph rates are unreliable for systems in which the carbonic acid is condensing, that is, in systems involving the formation of dew point water. The nomograph rates are too large; de Waard and Lotz [21] suggest derating the nomograph rates by a multiplier of one-tenth.
- At higher temperatures, the wet CO_2 corrosion rate begins to decrease due to the formation of a protective corrosion scale. Hence, the rates estimated for design conditions may actually be less than the rates estimated for operating conditions. Thus, the user should check the rates under operating conditions before determining the basis for materials selection.

- Carbon steel protected by mill scale or other surface deposits may corrode at rates substantially less than those predicted by the de Waard-Milliams nomograph. However, such scales (particularly mill scale, Fe_3O_4) may be susceptible to slow dissolution by carbonic acid, eventually resulting in accelerated corrosion at rates in accordance with the de Waard-Milliams diagram. During the dissolution of mill scale by carbonic acid, the carbon steel surface usually develops a characteristic appearance, leading to the descriptive term "mesa" corrosion.
- In process streams containing oxygen or other cathodic depolarizers, carbonic acid pitting rates may be much higher than predicted by the de Waard-Milliams nomograph.
- In turbulent systems, the rate may be greater than 1 in. per year (25 mm/yr).

Wet liquid-vapor process streams that contain both H_2S and CO_2 are usually substantially less corrosive than CO_2 alone at the same CO_2 partial pressure. A commonly used rule of thumb is that carbon steel construction is suitable if the vapor stream contains at least five mole percent H_2S . Exposed carbon steel will usually form an adherent sulfide coating. Unless the process stream dissolves or erodes the sulfide coating, further corrosion is at very low rates. In such systems, the de Waard-Milliams nomograph does not apply.

Some hydrocarbon streams, including many produced crudes, contain a substantial concentration of dissolved acid gases, including CO_2 . Such streams frequently also contain entrained free water. The medium and heavy crude oils are usually effective inhibitors. Light crudes with sufficiently high gas-oil ratios are produced in the form of a foam, which acts as a corrosion inhibitor. In many streams, the water may be at least partially emulsified, making the stream either less corrosive or non-corrosive. Prolonged shutdowns in such streams tend to promote corrosion because the fluid will gradually partition into separate phases. It is good practice to take into account the inhibiting and emulsifying properties of the hydrocarbon phase when determining the materials of construction and the corrosion allowance in such systems.

It is not unusual to inject demulsifiers into crude streams upstream of desalters and water knockout vessels. The downstream crude will retain some demulsifier. If the downstream crude stream is subsequently pipelined or shipped to storage, it will often continue to drop out free water. Water slugs and/or corrosion can occur because of the subsequent water dropout.

8. Caustics

Corrosion-induced metal loss by caustics is uncommon. However, a localized form of pitting, called *caustic gouging*, can occur with carbon steel, particularly in high-temperature services such as boiler systems. Such systems typically

have some form of caustic-based water treatment program. Debris or deposits permit the formation of under-deposit solutions of hot concentrated sodium hydroxide, which attack the substrate steel. The key to preventing this form of pitting is to chemically clean the caustic-exposed system before commissioning and then keep the system clean during operation. Modern phosphate-based treatments avoid this problem.

Metals and alloys that can form amphoteric hydroxides are subject to accelerated corrosion in alkaline environments. (Amphoteric hydroxides are soluble in alkaline solutions.) Aluminum and zinc are the most common metals exhibiting this behavior. Their use in alkaline processes is usually not recommended. Likewise, their use in buried or submerged alkaline environments can lead to rapid metal loss.

The most common corrosion problem involving caustics is alkaline stress corrosion cracking [discussed in the section "Stress Corrosion Cracking" (p. 177)].

9. Chlorides

Aqueous chlorides provide an excellent electrolytic environment for corrosion. However, ambient temperature neutral chloride solutions are not particularly aggressive to carbon and low-alloy steels. Acid aqueous chlorides, below a pH of about 4.5, can be very aggressive to such steels.

Carbon steel, unprotected by coatings or cathodic protection, usually provides a useful life of at least several years in seawater, which contains chlorides at concentrations of 3.5 to 5.5 wt. percent. Pitting rates in aerated saline waters are usually on the order of 3–5 mpy (0.08–0.1 mm/yr). Rates can approach 25 mpy (0.64 mm/yr) in turbulent saline water such as the unprotected splash zones of offshore structures. Saturated chloride solutions (i.e., brines) are not as corrosive and are often used as chemical inhibitors for carbon steel. These brines are less corrosive because of their lower solubility for oxygen.

Carbon steel is the normal material of construction for saline or brine solutions unless the pH is below about 5 or the solution is highly aerated; in either case, pitting can occur. Two different phenomena are involved.

1. When the pH is below about 4.5, general corrosion in the form of small, closely spaced pitting is the normal form of attack. The mechanism is essentially one of mild acid attack. See Figure 3-8 for an illustration of the dependence of the corrosion rate of carbon steel on the pH of the corrodent.

The presence of aeration (at least 1 ppmw dissolved O_2) accelerates corrosion due to the action of dissolved oxygen as a cathodic depolarizer. Under-deposit corrosion, which is a form of concentration cell corrosion, can be very severe in aerated waters with low pH and chlorides. Velocity can also accelerate the rate of metal loss due to erosion corrosion.

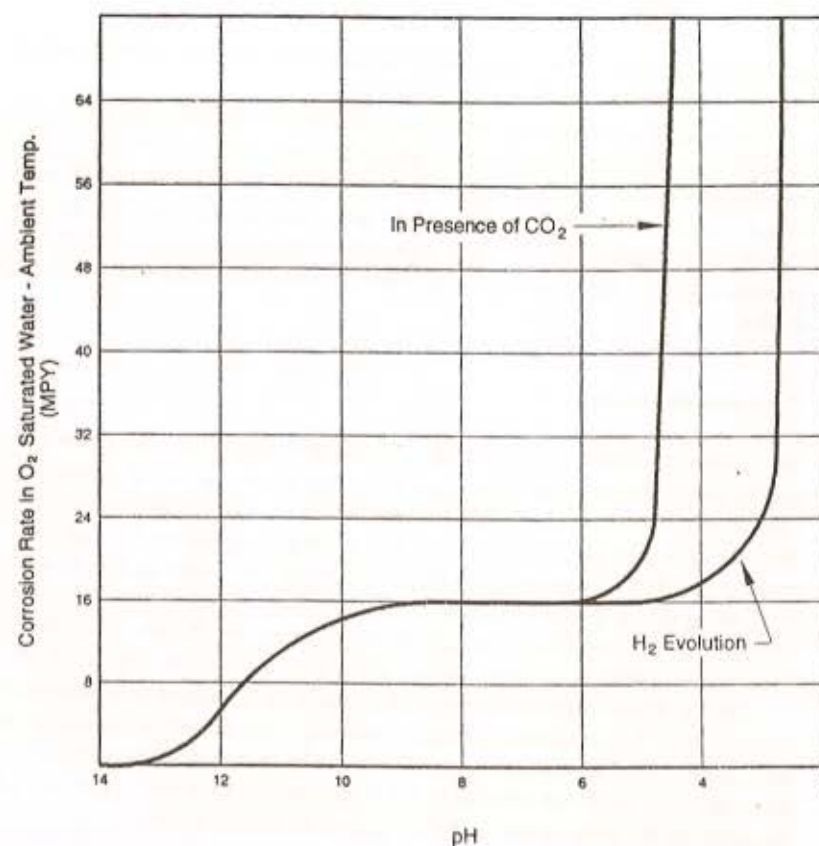


Figure 3-8 Illustrating the dependence of the corrosion rate of carbon steel on the pH of the corrodent. (Reprinted from [31]. Published 1924 by the American Chemical Society.)

2. Chlorides in water can disrupt scales that would otherwise protect the substrate steel. Pitting corrosion, sometimes producing "carbuncles," is the normal form of attack. If the scale is mill scale (Fe_3O_4), pitting rates can be quite severe, since mill scale is both cathodic with respect to the substrate steel and is a relatively good conductor. (Unlike most scales, mill scale is not dielectric.)

The threshold concentration for disruption is somewhere between about 50 and 500 ppmw chloride. The threshold is affected by stream

velocity, with 15 ft/sec (4.6 m/s) being considered safe for even concentrated brines.

Aeration greatly accelerates pitting rates. Aeration in chloride-bearing waters poses a high risk of under-deposit pitting corrosion. Consequently, a minimum flow velocity of at least 2.5 ft/sec (1.5 m/s) should be maintained to keep entrained debris from settling to form a deposit. The minimum flow velocity may have to be increased in streams having settled debris. Designs should avoid deadlegs.

Stainless steels, both the 12 Cr and austenitic grades, can be susceptible to pitting, under-deposit and crevice corrosion in aerated chloride-containing waters. Free-flowing, clean chloride solutions such as seawater permit the use of Type 316 SS (Type 316L SS if welded; CF-3M for castings) if the temperature is not allowed to exceed 140°F (60°C). The latter temperature is the threshold temperature for chloride stress corrosion cracking of Type 316 SS in neutral saline waters.

Nickel-rich alloys such as Alloy 825 and Alloy C-276, the superaustenitic stainless steels, duplex stainless steels (especially those with enhanced molybdenum content) and titanium are often chosen for severe chloride services and chloride services subject to stress corrosion cracking.

The chloride content of water used for hydrostatic testing is often a concern. Most users require that hydrotest water contain no more than 50 ppmw chloride. The concern is usually about pitting in carbon steel components or bacterial corrosion, pitting, crevice corrosion and/or chloride stress corrosion cracking in austenitic stainless steels.

In most carbon steel systems, serious corrosion damage due to improper hydrotesting is rare. When it does happen, the cause is usually a long period of idleness between hydrotesting and commissioning. Pockets of residual hydrotest water cause pitting and sometimes large volumes of rust. In addition, some processes can be seriously contaminated with residual chlorides from the hydrotest water. In general, however, small amounts of residual water left over after draining usually evaporate before they can cause serious corrosion problems.

Austenitic stainless steels are much more susceptible to chloride damage as a result of improper layup after hydrotesting. Because of the potential galvanic couple that can exist between active and passive stainless steel surfaces, chloride-induced damage can occur rapidly in stainless steel, for example, crevice corrosion. Microbiologically induced corrosion is also a threat in improperly layed-up stainless steel piping and equipment. Chloride stress corrosion cracking is usually not a concern, since the exposure temperature is less than 140°F (60°C).

The 50 ppmw chloride concentration threshold, as with many rules of thumb, can be misleading.

Low-chloride water (<50 ppmw) can cause serious corrosion if it is not properly drained and dried. Pockets of such water can concentrate chlorides by evaporation. In the presence of air, which acts as a cathodic depolarizer, such pockets can cause corrosion problems. Properly executed, equipment can be safely hydrotested with high-chloride water by one of the following means.

- Test with high chloride water, then drain and flush with a low chloride water. Proper drying is needed, especially if austenitic stainless steels are involved.
- Test with high chloride water, drain and then thoroughly dry the system. Sometimes this method includes physical entry to perform manual drying. Often, hot air (<140°F (<60°C) for austenitic stainless steels) is used to dry the system, with the discharge air monitored for dew point. Occasionally, a flushing solvent (usually methanol) is used for drying.
- Wet layup is probably the simplest solution. Drain the hydrotest water, whether of high or low chloride content. Then seal the system and purge it of air. Lay up the system with a low-pressure inert gas blanket (typically nitrogen) until it is ready to be commissioned.

The wet layup procedure, particularly in stainless steel systems, must properly address the risk of microbiologically induced corrosion. This is usually accomplished by either making sure that the residual hydrotest water does not contain nutrients or is treated with a sufficient dose of biocide.

10. Flue Gas

Flue gases often contain potentially corrosive compounds such as SO₂. Severe corrosion problems can occur, most of which are associated either with wet flue gas or with zones in which the temperature falls below the water or acid gas dew point. The dew point condensation temperature should be calculated [22, 23] before making a materials selection.

In some cases, corrosion is caused by the condensation of hygroscopic acid salts which may become very corrosive when wet. Note that a dry condensing salt will not cause corrosion. The salt deposit can become wet because of an upset that introduces water or if it is cooled by the substrate metal to a temperature below the process stream dew point. An example of the latter is a salt deposit on the OD of a cool heat exchanger tube. Such conditions should be avoided by design, since they are difficult to mitigate by either materials selection or operation/maintenance.

Materials used to control corrosion damage include alloys, "wall papering" with thin sheets of alloy, polymeric coatings and linings and corrosion-resistant ceramics/refractories. Plant-specific measures are usually selected on the basis

of previous plant experience or are provided by process licensors and/or alloy manufacturers.

11. Hydrogen Sulfide

Hydrogen sulfide can cause severe pitting and general corrosion in carbon and low-alloy steels at temperatures exceeding about 500°F (260°C). [For a discussion of corrosion by high-temperature sulfur, see the section "Sulfidation and Sulfidic Corrosion" (p. 138).] Wet hydrogen sulfide can cause several types of problems:

- Usually mild pitting and/or mild general corrosion in carbon and low-alloy steels. However, there are conditions in which wet H₂S can cause severe pitting, grooving and/or general corrosion. Such conditions usually involve the presence of cyanides or high concentrations of NH₄HS.
- Extremely high pitting rates for carbon and low-alloy steels and even for the 12 Cr and austenitic stainless steels when there is 1 ppmw or more dissolved oxygen. Normally, oxygen ingress is avoided by keeping systems pressurized or by process controls. If oxygen ingress cannot be avoided, mitigation measures are usually necessary. Such measures include use of coatings, cathodic protection and highly alloyed materials (e.g., the 6 Mo superaustenitic stainless steels).
- Hydrogen embrittlement of carbon and low-alloy steels. Similarly, it can also cause sulfide stress corrosion cracking, hydrogen induced cracking and stress oriented hydrogen induced cracking. [For a discussion of these phenomena, see the section "Stress Corrosion Cracking" (p. 177).]

Iron sulfide can be pyrophoric, that is, it can spontaneously ignite. Proper safety precautions must be provided for those process streams in which pyrophoric iron sulfide can form or deposit. For formation to occur:

- A layer of iron oxide (rust) must be present
- The rust layer must be water wet
- The process stream must provide hydrogen sulfide at a vapor concentration of at least 0.2 mole percent
- The oxygen concentration must be less than about one mole percent

Criteria for spontaneous ignition are:

- The iron sulfide mass must be dry of water
- The ignition atmosphere must contain at least 11 percent oxygen
- There must be sufficient sulfide mass to store the heat of the exothermic reaction that converts iron sulfide to iron oxide. Without sufficient mass, the heat of reaction will be dissipated by radiation and the sulfide will not heat up enough to initiate spontaneous ignition.

Mitigation measures include using coatings and adjusting the process conditions to prevent the formation of iron sulfide.

In the event that pyrophoric iron sulfide is suspected, an effective measure is to keep it either blanketed with inert gas or water wet until it can be either neutralized or disposed of.

12. Insulation

Corrosion under insulation has been and continues to be a major problem in plants. Both metal loss corrosion such as pitting and environmental cracking such as chloride stress corrosion cracking occur. Problems have occurred in piping and equipment insulated for both low- and high-temperature services, for virtually all types of insulation, including products used for personnel protection and fireproofing. Some of the worst problems have occurred in insulated piping and equipment subject to periodic "deluge" testing of fire water systems. Bypass loops, typically hot only during startup or shutdown, are frequent locations of aggressive external corrosion. Improperly "mothballed" plants typically suffer their worst corrosion under insulation that should have been removed.

Often, a "vapor barrier" is relied upon to prevent liquid water from penetrating the outermost layer of insulation. However, even the best such barriers only slow down the penetration rate. They are permeable to water vapor and are subject to punctures, slippage, ageing, delamination, etc. The best position to take with vapor barriers is that they are not barriers, particularly in cold services where vapor penetration can cause the formation of destructive ice lenses.

Experience has taught that insulated piping and equipment with operating temperatures less than about 250°F (120°C) should be carefully coated with a high-performance coating prior to being insulated. NACE has published a report that gives guidance on the selection of coatings for under-insulation protection. Refer to Publication 6H189: "A State-of-the-Art Report of Protective Coatings for Carbon Steel and Austenitic Stainless Steel Surfaces Under Thermal Insulation and Cementitious Fireproofing" [24].

In addressing this old and well-known problem of corrosion under insulation, it is important to give attention to the chemistry of insulation products to be used on austenitic stainless steel. Insulation products should not be permitted to contain leachable chlorides.

13. Oxidants

Strong oxidants such as chlorine and oxygen are usually handled in carbon steel at ambient temperatures, if dry. They require special alloys for higher

temperature use. Carbon steel is permitted at temperatures up to 300°F (150°C) for chlorine and for temperatures up to 150°F (65°C) for oxygen. However, greases, oils and other hydrocarbons can spontaneously ignite in such services. Accordingly, aspects such as precommissioning cleaning, lubrication, seals and packing require special attention. Use the Notes section of the materials selection template to document special requirements.

14. Water

Pure water is non-corrosive to ordinary engineering materials. However, most waters contain dissolved salts and may contain dissolved oxygen and/or acid gases such as CO₂ or H₂S. Such waters are often quite corrosive.

Anaerobic water (water without dissolved oxygen) may become corrosive due to the presence of anaerobic microbes such as sulfate-reducing bacteria (SRB) or similar bacteria. Sulfate-reducing bacteria metabolize dissolved sulfates and generate H₂S as a metabolic product. SRB activity is most commonly observed in anaerobic seawater. [Refer to the section "Microbiologically Induced Corrosion" (p. 173).]

Dissolved oxygen plays a key role in determining the corrosivity of a water. Oxygen acts as a cathodic depolarizer, not as a corrodent. Experience has shown that water that contains less than about 10 ppbw dissolved oxygen is essentially deaerated. Waters containing less than about 200 ppbw are usually not corrosive unless they contain acid gases or have pHs less than about 5. Neutral waters containing from 200 ppbw to about 1 ppmw are mildly corrosive to carbon steel. Corrosion rates are usually on the order of 3–5 mpy (0.08–0.1 mm/yr). Waters containing oxygen in excess of one ppmw should be considered corrosive and subject to chemical treatment or some other mitigation measure.

Clean aerated seawater can be aggressive to carbon steel, with corrosion rates of 25 mpy (0.64 mm/yr) or more under turbulent conditions.

Deaerated seawater is essentially non-corrosive to carbon steel. However, because of its sulfate content, deaerated seawater can become very corrosive in the presence of SRB. Once inoculated with SRB, a non-piggable piping system is almost impossible to sterilize, unless it is chemically cleaned.

Stagnant seawater exposed to carbon steel becomes deaerated as the iron corrodes. SRB can become aggressive as soon as the seawater is deaerated. However, the long-term corrosivity of deaerated seawater depends on the surface-to-volume ratio. In systems such as piping, the high surface-to-volume ratio leads to rapid exhaustion of the available sulfate nutrient. Such systems usually become dormant because they quickly consume the available nutrients. Stagnation prevents nutrient replenishment. Accordingly, carbon steel in

stagnant seawater often has very low corrosion rates, on the order of 2 to 5 mpy (0.05 to 0.08 mm/yr). If the surface-to-volume ratio is low, as in large storage tanks, or if the seawater is cyclically stagnant, deaerated seawater can cause significant long-term damage to carbon steel.

In many facilities, the source water for the fire water system is aerated. However, if the fire water system is stagnant, the dissolved oxygen is soon scavenged by the carbon steel piping, making the water non-corrosive. Again, if this water contains dissolved sulfates (such as seawater), SRB can become a major problem.

In aerated waters, dissolved salts and/or velocity control corrosivity. If the dissolved salts promote the formation of a dense scale, the water is usually non-corrosive. (The scale layer acts as a barrier to oxygen diffusion and promotes rapid polarization of the anode surface by anion saturation.) The Langelier index and the Ryznar stability index [25] are commonly used to determine the corrosivity of waters based on their chemistries. Refer to Appendix 9 for a discussion of how such indices are used to estimate water corrosivity.

While scale formation may favorably reduce corrosivity, it can cause other serious problems such as plugging and "hot spots" in heat transfer equipment. If a water is determined to be "scaling," the process should be analyzed to determine if the side effects are acceptable.

The velocity of an aerated water affects its corrosivity. Some alloys such as admiralty brass are limited in their use because of their sensitivity to velocity in corrosive waters. In some systems, low-velocity components such as piping may be made of carbon steel. Higher velocity components such as pumps and control valves may require alloys such as 12 Cr SS. Table 3-2 provides guidance on the recommended limits for water velocities. The recommended lower limit is to prevent fouling by the formation of deposits.

Waters with low total dissolved solids (TDS) have a wide range of corrosivities. Very pure waters, such as distilled and totally deionized waters, are non-corrosive if uncontaminated. They can be very corrosive if they absorb an acid gas such as carbon dioxide, which can rapidly reduce the pH of the water. This problem can be severe in boiler systems if the steam condensate is allowed to absorb CO₂ in the condensate handling and storage system. (The source of CO₂ is usually carbonate salts in the boiler feed water, which decompose in the steam system and carry over into the condensate system.)

Partially deionized waters such as waters that have anions but no cations (other than hydrogen) can be very corrosive. Such waters are uncommon.

Waters containing high concentrations of dissolved salts also become more corrosive if they absorb acid gases. However, the presence of the dissolved salts buffers the water, preventing a rapid reduction in the pH value. Thus, high-TDS

Table 3-2 Recommended limits for water velocity for some common materials of construction

MATERIAL	MAXIMUM VELOCITY (ft/sec)/(m/s)	MINIMUM VELOCITY (ft/sec)/(m/s)
Carbon Steel	12/3.7	2.5/0.77
Cement-Lined Carbon Steel	10/3.1	None
Fiberglass	8/2.5	None
Inhibited Admiralty Brass	6/1.8	2.5/0.77
Inhibited Aluminum Bronze	10/3.1	2.5/0.77
90/10 Cu/Ni	10/3.1	2.5/0.77
70/30 Cu/Ni	12/3.7	2.5/0.77
Type 316 SS	30/9.2	2.5/0.77

waters containing dissolved CO₂ are much less corrosive than low-TDS waters that have absorbed CO₂.

Waters that have absorbed both oxygen and an acid gas such as CO₂ or H₂S can be very aggressive, whether the water is hard or soft. Such waters must be chemically treated if they are to be rendered non-corrosive to carbon steel. In some cases, other measures such as alloys, paints, coatings, linings or cathodic protection are employed.

Galvanic couples or crevices can aggravate the local corrosivity of water. In such cases, the key issue is the presence or absence of dissolved oxygen. If there is insufficient oxygen to act as a cathodic depolarizer, the couple or crevice will polarize and will not be a serious problem. Galvanic couples in aggressive water should be examined to ensure that unfavorable anode/cathode area problems are mitigated. Galvanic couples that are also crevices can be particularly vulnerable to accelerated corrosion. For example, titanium tubes have caused severe crevice corrosion in alloy tubesheets in aerated seawater.

Materials selection for waters can be a real challenge. In most plants, it is safe to assume the cooling, utility and fire waters to be non-corrosive, because of either chemical treatment or because of design. An example of the latter is a fire

water system that is stagnant and not subject to SRB. However, prudence requires the determination the corrosivity of the various waters to be handled. In the event that corrosivity is a concern, mitigation measures include chemical treatment, cathodic protection, alloys, linings such as cement-lined pipe, and paints or coatings. Some general rules for materials selection follow.

For non-corrosive, mildly corrosive or chemically treated water, carbon steel is the normal material of construction. Galvanized carbon steel is often recommended for moderately corrosive waters.

For corrosive, untreated waters, the common alternatives are:

- Carbon steel with corrosion protection such as the use of coatings, linings and/or cathodic protection.
- Corrosion-resistant alloys.
 - The austenitic stainless steels are usually not employed in corrosive waters because of the dangers of chloride-induced pitting and stress corrosion cracking. However, Type 316 SS (Type 316L if welded; CF-3M for castings) has found extensive successful use in freely flowing, clean aerated seawater for temperatures below 140°F (60°C). Type 316 SS is a common material of construction for the internals of seawater pumps.
 - 12Cr steels such as Type 410 SS and CA-6NM are often used for pump and valve casings and internals in clean, moderately corrosive and brackish waters. However, these alloys are quite susceptible to chloride-induced pitting and crevice corrosion in saline services such as seawater. Also, the 12Cr stainless steels can be susceptible to hydrogen embrittlement if subject to a cathodic protection system.
 - Cu-Ni alloys are often used in corrosive waters or relatively low velocity applications such as heat exchanger tubes.
 - Alloys such as the nickel-rich cast irons, the superaustenitic stainless steels and the high-molybdenum duplex stainless steels or titanium may be required for severely corrosive waters or for critical services.
- Corrosion-resistant non-metals such as polyethylene, PVC, or fiberglass.
 - Fiberglass is commonly used for piping and vessel shells in corrosive water service. Note that none of the non-metallic materials are suitable for services in which they are likely to be mechanically abused. Examples include pipe movement, water hammer and hydraulic surges.
 - PVC, CPVC and polyethylene piping are commonly used in corrosive waters.

- Concrete is a common material of construction for sumps and for cement-lined carbon steel pipe. Check on the nature of pH swings before selecting concrete or the cement from which it is to be made.

There are other measures that can be used to prevent corrosion:

- Cement linings are usually successful. Select the cement with due regard for the pH expected of the water. Note that cement linings are usually not recommended for waters with $\text{pH} < 6$.
- Coatings (e.g., coal tar) are often used, in conjunction with internal cathodic protection, for tanks and vessels in corrosive water service.
- In deaerated water storage tanks, inert gas blanketing can be used.

15. Seawater

Protection against seawater, while addressable by the guidelines given above, is such a common aggressive water that it warrants special discussion. Seawater is normally used on a once-through basis and is usually chemically treated to control colonization by and growth of marine organisms. If uncontrolled, colonies of marine organisms such as mollusks can slough, causing plugging and/or severe pressure loss in downstream piping or components such as exchanger tubing. Biocides are used in both continuous and slug treatments. Chlorination, with hypochlorites, from bottled chlorine or from electrolytic chlorine, is the most common biocide chemical used for aerated seawater. Biocides such as glutaraldehyde are generally used for non-aerated (i.e., anaerobic) seawater.

Even aerated seawater systems often develop colonies of SRB, which shield themselves from aeration by generating protective slime coverings. In order to control these colonies, occasional mechanical cleaning or aggressive chemical treatments may be necessary. Such chemical treatment programs may include acid cleaning or surfactants. Provision for such treatments should be included in the design of seawater piping systems.

Some seawater systems are anaerobic. Examples include stagnant systems and systems in which the seawater is deliberately deaerated by either chemicals such as sodium sulfite or processes such as stripping with an inert gas. In evaluating stagnant systems, consideration should be given to the following concerns:

- Volume-to-surface ratio. In systems having a small volume-to-surface ratio, such as most piping systems, dissolved oxygen is quickly consumed by a combination of corrosion of unprotected steel and biological activity.

The volume contains insufficient sulfate nutrient to support significant SRB activity.

For systems with large volume-to-surface ratios, such as large storage tanks, stagnant conditions can cause significant corrosion damage to unprotected steel. The dissolved oxygen content is sufficient to sustain relatively long-term conventional corrosion. Once activity begins, it can cause extensive H_2S corrosion because of the relatively large amount of available sulfate nutrient.

- Cyclic systems. Systems in cyclic service, such as ballast lines, are periodically replenished with dissolved oxygen and sulfate nutrient. Even in nominally stagnant services, cyclic operation can cause significant corrosion damage. Such systems should be carefully evaluated since they may require materials resistant to both aerated and anaerobic conditions.

For the purposes of materials selection, seawater should be considered anaerobic if the oxygen content is less than 10 ppbw and aerated if the oxygen content is at least 1 ppmw. These thresholds are based on the observation that SRB are active at oxygen concentrations less than 10 ppbw and are inactive at concentrations exceeding 1 ppmw. For the intermediate range, there are no hard rules regarding aeration. Fortunately, the intermediate range seems to be rare. This is at least partly due to the fact that when SRB activity begins to generate H_2S , the H_2S acts as an oxygen scavenger. This activity quickly reduces the residual dissolved oxygen content to virtually zero.

Carbon steel is the normal material for anaerobic seawater periodically treated for SRB control. Carbon steel is much cheaper than the materials normally chosen for aerated seawater. Accordingly, it is sometimes worthwhile to avoid or minimize the aerated seawater option. Seawater can be deaerated with chemicals such as sodium sulfite or by processes such as stripping with an inert gas. Alternatively, if the main usage of the seawater is for cooling, one can adopt a closed-loop freshwater cooling system that is heat exchanged against seawater, thus minimizing the amount of equipment necessary for handling aerated seawater. Copper alloys should not be specified for anaerobic seawater, since they can be severely corroded by H_2S generated by SRB.

Materials selection guidelines for aerated seawater include the following:

- Polluted seawater is usually more corrosive than clean seawater. Hydrogen sulfide and ammonia are the most common pollutants. Hydrogen sulfide causes pitting and fouling in carbon and low-alloy steels and in copper alloys. Hydrogen sulfide can also cause stress corrosion cracking and hydrogen induced cracking problems in carbon and low-alloy steels. Ammonia can cause stress corrosion cracking in copper-containing alloys.
- Unprotected carbon steel is usually not recommended for flowing seawater, which can generate pitting rates of 20 to 30 mpy (0.5 to 0.76

mm/yr). Extreme pitting rates can be on the order of 50 mpy (1.3 mm/yr).

Carbon steel is often recommended for stagnant seawater. However, the recommendation is usually limited to piping (or similar applications) where the oxygen and sulfate availability are too small to sustain corrosion. Carbon steel is usually avoided if such systems are in cyclic service.

- Concrete construction, including cement linings, is usually successful. Type V or other sulfate-resisting cement should be specified. Reinforcing for concrete structures should be designed to resist corrosion. Use of cathodic protection and/or coatings should be considered.

In tropical climates, concrete construction may be susceptible to destruction by boring mollusks. Concrete exposed to tropical seawater should be protected by liners, jacketing or other means to control this form of attack.

- Coated carbon steel, in conjunction with cathodic protection, is often used in immersion services such as tankage. Coal tar epoxies are commonly used for seawater service.
- Rubber linings on carbon steel are usually successful in services such as splash zones and valve internals.
- Type 316 SS (Type 316L if welded; CF-3M for castings) is used in clean, flowing seawater, particularly for pumps. This material is normally not recommended for seawater service if:
 - The maximum design temperature is 140°F (60°C) or warmer.
 - The flow velocity is less than 5 ft/sec (1.5 m/s).
 - The service will include long periods of shut-in, during which severe crevice corrosion could occur. In some applications, crevice corrosion can be prevented by other, less noble, components providing cathodic protection, for example, cast iron pump case with Type 316 SS internals.

Note that any condition that diminishes or prevents oxygen-rich seawater from contacting the stainless steel surface will usually cause localized pitting. Sources include deposits, marine fouling, stagnant seawater and crevices.

- Cu/Ni alloys such as 90/10 Cu/Ni are usually successful in applications such as heat exchanger tubes. Alloy 400 or titanium tubes are required for severe services.
- Brasses provide moderate corrosion resistance to seawater and are often specified for noncritical services in applications such as valves. Avoid

the use of uninhibited brasses containing more than 15 percent zinc, as they are subject to *dezincification*.

- Ni-Al bronze, aluminum bronze and inhibited admiralty brass are often used as the standard materials of construction for seawater services subject to intermittent non-flowing conditions. These materials are used for applications such as pumps, valves, tubing and tubesheets. Ni-Resist (a nickel-rich cast iron) is sometimes recommended for pump casings in such services.
- Alloy 400, Alloy 20 Cb-3, the superaustenitic stainless and duplex stainless steels (especially those with enhanced molybdenum content) and titanium are often specified for critical or severe services. Examples of such services include pumps and pump internals, stagnant conditions, heat exchanger tubing subject to hot spots and components subject to under-deposit corrosion. These materials are also useful in applications where Type 316 SS is subject to chloride stress corrosion cracking.
- Dual metallurgy pipe is an option in applications where weight is a consideration, such as on offshore platforms. Such pipe uses carbon steel for pressure containment and corrosion-resistant alloy as a liner.
- Non-metallics, such as fiberglass, HDPE, PVC and CPVC, are widely used in low-pressure seawater applications. As discussed earlier, such materials are not suitable for service where they may be subject to mechanical abuses such as pipe movement or water hammer.

B. MICROBIOLOGICALLY INFLUENCED CORROSION

1. Introduction

Microbiologically influenced corrosion (MIC) is defined as the corrosion of materials caused by microorganisms. MIC is an underestimated problem. Some estimates place the cost of MIC at \$30 to 50 billion per year. The combination of unexpected attack and rapid failure makes MIC a matter of considerable concern in many applications.

Most MIC occurs in stagnant water systems or the water legs of mixed-phase, quiescent process streams. A typical example would be the pitting corrosion that occurs in the bottom of a pipeline, before commissioning, due to microbial activity in residual hydrotest water. It generally occurs at ambient temperatures but may occur at temperatures as high as 200°F (93°C). Most materials of construction are susceptible.

The microorganisms responsible for MIC are primarily bacteria and fungi. They may be anaerobes (which will not function in the presence of oxygen) or

aerobes (which require oxygen, usually dissolved, in order to function). Often, MIC is caused by a mixture of several microorganisms living in colonies. It should be noted that while strictly anaerobic environments are not common in nature, anaerobes are commonly found within the anaerobic microenvironments that can develop in even highly aerated systems. For example, anaerobic conditions can be established under the slime film formed by some aerobic types of microbes.

A number of organisms are commonly associated with MIC, including sulfate-reducing bacteria (SRB), sulfur/sulfide-oxidizing bacteria, iron/manganese-oxidizing bacteria, aerobic slime formers, methane producers and acid-producing bacteria and fungi.

- Sulfate-reducing bacteria (SRB) are anaerobes. They reduce sulfate to hydrogen sulfide or, in the presence of iron, ferrous sulfide. In the absence of sulfate, they can become fermenters and use the resulting organic compounds to produce acetate, hydrogen and carbon dioxide. Some of these bacteria are capable of consuming hydrogen and thereby act as cathode-depolarizing agents.
- Sulfur/sulfide-oxidizing bacteria are aerobes. They can form bulky deposits that may develop into anaerobic sites suitable for the growth of SRB. Some types reduce sulfur to sulfuric acid, forming areas with pH values as low as 1. These bacteria are usually found with SRB, where they are able to draw energy from a synergistic sulfur cycle.
- Iron/manganese-oxidizing bacteria derive energy from the oxidation of Fe^{++} to Fe^{+++} . They are found in tubercles covering pits in the surfaces of carbon steel, low-alloy steel and stainless steel.
- Aerobic slime formers produce extracellular polymers, commonly referred to as slime. Slimes create an excellent environment for anaerobic SRB organisms.
- Methane producers consume hydrogen and are capable of cathodic depolarization. They often exist in symbiotic relationship with SRB. The SRB produce hydrogen, carbon dioxide and acetate by fermentation, and methanogens consume these compounds, thus permitting the fermentation to continue.
- Acid-producing bacteria and fungi have been reported to be involved with corrosion of gas lines and aluminum fuel tanks.

The organisms that produce MIC usually form discrete biodeposits—either nodules or flat shiny deposits. An exception is when the organisms exist in high concentrations in anaerobic soil environments, where they do not need to form either a film or a deposit to become active. Under such conditions, these

organisms can still produce metabolic products in sufficient concentration to promote corrosion.

There are four prerequisites for MIC:

1. Microbes must be present in the environment.
2. The service temperature range must support microbial metabolism. Most organisms are most active in a narrow temperature range (10 to 20°F (5 to 11°C)). However, certain organisms can be active from below freezing to above 200°F (93°C).
3. The environment must support microbial activity by supplying appropriate nutrients and providing the aerobic or anaerobic conditions required for sustaining microbial life.
4. The material of construction must be susceptible to MIC. Most materials, with the possible exception of titanium, are susceptible to some form of MIC.

2. Effect on Materials of Construction

Steels and stainless steels are the materials that seem to support the greatest amount of MIC activity in the hydrocarbon and chemical process industries. This may very well be because of the extensive use of these materials in these industries. The results of a four-year study reported by Felder and Stein [26] showed that stainless steels have variable susceptibility to MIC (Table 3-3). There is some lack of agreement over whether sensitization increases susceptibility to MIC. Accordingly, it is prudent to avoid sensitization, since it can lead to selective attack from other causes.

Attack morphologies seem to be related to the organisms involved. Pinhole openings under nodules, accompanied by extensive tunneling, may be typical of *Gallionella* bacteria on stainless steels, while shallow surface attack beneath nodules or open pits may be typical of SRB on stainless and carbon steels.

Aluminum alloys also have been attacked by microorganisms. For example, there have been MIC problems with aluminum fuel tanks and transfer lines. In this case, microorganisms grow in the water layer under the fuel to produce volcano-shaped tubercles with frequent evolution of gas. Pitting occurs under the tubercles.

Copper has been believed to be toxic to any microorganisms that cause corrosion. Hence, MIC of copper alloys has been considered insignificant. But there are copper-resistant organisms that have been associated with the corrosion of copper. Corrosion of copper condenser tubes by microbially produced

Table 3-3 Percent colonization after four years¹

ALLOY	PERCENT COLONIZATION
Type 304 SS	100
Type 316 SS	21
Type 316L SS	15
6 % Mo SS	2
Ti	0

¹Refer to Ref. [26].

Source: Reprinted with permission of NACE International.

ammonia has been reported. In addition, sulfuric acid produced by microbial activity has been associated with corrosion of underground copper pipes.

There are no reported cases of MIC on *titanium*.

Some *non-metallic* materials such as coatings and plastics are known to be susceptible to microbial degradation. Glass-reinforced thermoplastics are colonized by bacteria. However, the resins (typically epoxy or vinyl ester) are resistant to attack by most microbes. SRB can selectively attack the organic surfactant used on the glass fibers. As a result, the glass-resin bond can be disrupted and the composite damaged. Also, hydrogen-producing bacteria can disrupt the glass fiber-resin bond.

Some anaerobes oxidize sulfide or sulfur to sulfuric acid. These bacteria proliferate inside sanitary sewer lines and can be responsible for rapid corrosion of *concrete* mains.

3. Mitigation Methods

The best mitigation measure is to prevent microbiological activity. A major step in the right direction is to avoid the development of stagnant or quiescent water legs. This objective requires the combined commitment of design, construction and operation. Other measures include using barrier materials such as those discussed in Part 2 of Chapter 2 or using materials resistant to damage by MIC.

Once an MIC problem develops, the common control methods include:

- Mechanical cleaning using brushes, pigs, sponge balls, water or gas jets. Operational procedures such as backwashing or flow jogging are also used. These methods are intended to disrupt and disperse microbial colonies. However, they are ineffective at killing microbes. Consequently, these methods are usually used in conjunction with a subsequent chemical treatment.
- Chemical methods such as acid cleaning and the use of biocides or biostatic agents, inhibitors, surfactants and dispersants.

Acid cleaning is in a class by itself in terms of effectively killing microbial colonies. Other chemical treatment methods such as biocide treatment, by themselves, may not be very effective. The problem is the protection provided to the colonies by their slime barriers or by occlusion due to corrosion products such as tubercles. Consequently, other chemical treatment programs are usually used in combination with some sort of mechanical or chemically assisted cleaning.

C. STRESS CORROSION CRACKING

1. Introduction

Failures due to stress corrosion cracking (SCC), while not common, may occur without warning, and when they do occur, they may have catastrophic consequences. In evaluating the risks of stress corrosion cracking, keep in mind that safety may be a central issue.

Each type of stress corrosion cracking requires very specific coincident conditions in order for the mechanism to produce cracks. Such conditions include a susceptible material and the appropriate combination of stress, temperature, crack-inducing agent, pH, aeration, etc. For example, chloride stress corrosion cracking of austenitic stainless steels can be quite dependent on the presence of dissolved oxygen. Sometimes, stress corrosion cracking can be avoided simply by applying practical knowledge of the mechanism, for instance, keeping oxygen out of saline waters that could otherwise cause chloride cracking of austenitic stainless steel.

There are at least three types of stress corrosion cracking:

- *Hydrogen stress cracking* (e.g., sulfide stress cracking).
- *Anodic stress cracking* phenomena such as alkaline stress cracking of carbon steels and chloride stress cracking of austenitic stainless steels.
- *Intergranular stress cracking* such as that caused by polythionic acid stress corrosion cracking.

Stress corrosion cracking is usually associated with the residual stress fields of welds, although cracking can occur in stressed or cold-worked parent metal. It has been shown that the development of a stress corrosion crack requires the presence of a *tensile* stress. Such cracking does not occur with shear or compressive stresses. Most forms of stress corrosion cracking depend on the presence of an electrolyte, usually liquid water, containing the crack-inducing agent.

It is common practice to specify special metallurgical and fabrication requirements to prevent or minimize the risk of stress corrosion cracking in pressure retaining services. The three most common measures are hardness controls, normalizing, and postweld treatment.

Hardness Controls

Hardness controls should be required for any stress cracking mechanism involving hydrogen embrittlement or hydrogen stress cracking.

Hardness controls are used primarily to reduce the risk of *crack initiation*. *Crack propagation* risks can be reduced either by increasing the fracture toughness of the material or by reducing stresses. With either method, the objective is to eliminate crack propagation or to ensure that it is slow and stable. Stable crack growth results in "leak-before-break" (i.e., it is not catastrophic).

The following measures are recommended when hardness controls are indicated:

- NACE RP0472 ("Methods and Controls to Prevent In-Service Cracking of Carbon Steel Welds in P-1 Materials in Corrosive Petroleum Refining Environments" [7]) limits the hardness of carbon steel weld metal to 200 BHN or less. Weld procedure qualification testing is required to ensure that the heat affected zone hardnesses do not exceed 248 VHN.

It is common industry practice to limit the weld metal hardness of air hardening (e.g., Cr-Mo) low-alloy steels as follows. Hereafter, whenever the hardness limitation of NACE RP0472 is referenced, it is also the intent to reference the following limits:

- 1 < Cr < 3: 225 BHN
- 3 < Cr < 9: 241 BHN (approximately RC 22)

Be especially alert to potential hardness problems in welds involving dissimilar metals and in welds involving unusually different thicknesses at the weld joint. Tube-to-tubesheet welds and thin fillet welds used to attach tray support rings are examples of the latter problem.

- In the absence of a better specification, materials subject to hydrogen stress cracking mechanisms should be required to meet the limitations of NACE MR0175 ("Sulfide Stress Cracking Resistant Metallic Materials for Oilfield

Equipment" [8]. Refer to the section "Wet Sour Service" (p. 196) for a discussion of MR0175.)

Normalizing

Normalizing, or normalizing and tempering, are used to increase the fracture toughness of carbon and some low-alloy steels. Other heat treatment methods such as quench and tempering may be used for materials such as some of the Cr-Mo steels.

Note that NACE MR0175 [8] requires that all carbon and low-alloy steels in wet sour service have a toughness-enhancing heat treatment. Normalizing is conventional. Hot rolling is acceptable for carbon steel in wet sour service.

Postweld Heat Treatment (PWHT)

Postweld heat treatment is primarily a stress reduction technique. It is the primary mitigation measure for avoiding alkaline stress corrosion cracking in carbon steels. It is also useful for minimizing crack propagation for carbon and low-alloy steels. However, PWHT can soften hard welds and heat affected zones, making them more resistant to crack initiation in services subject to hydrogen stress cracking. PWHT is required by many users, some domestic recommended practices and some foreign engineering codes for services that promote stress corrosion cracking.

Hardness control, PWHT and normalizing may be unnecessary if the combined stress in tension is less than the "ten percent rule." Examples of such applications are small day tanks, many atmospheric vessels, low-pressure equipment and piping, and drains. Under such conditions, the residual stresses and/or untempered hardnesses of welds and/or heat affected zones may indeed initiate cracking and may even eventually produce through-thickness cracks. However, the combined stresses are too low to generate catastrophic cracking. Since development of through-thickness cracks usually takes many years of service exposure, risk-limiting measures are often not cost effective for such low-stress situations. If capital cost is a concern, the ten percent rule may justify avoiding expenses such as those of hardness controls, PWHT and normalizing.

There are at least four exceptions where risk-limiting measures may be justified in low-stress situations:

1. For new equipment subject to local laws that mandate conformance to an engineering code in which such measures are required
2. In cases where through-thickness cracks, even though stable, would release a lethal, flammable or corrosive substance in a site of potential harm
3. For thin-ligament pressure-containing components where leaks could develop quickly and would require unscheduled maintenance (e.g., tube-to-tubesheet welds)

4. In new equipment or piping where subsequent inspection and/or repairs after long-term service would be excessively expensive (e.g., where congestion may make it very difficult to mobilize equipment or where such activities would lead to unacceptably long plant shutdowns)

In the event that the risk of stress corrosion cracking is too high for carbon or low-alloy steels, consider selecting a material immune to stress corrosion cracking. For example, use carbon steel clad with Type 304L SS in severe amine services.

What follows is a brief summary of some of the common crack-inducing agents, conditions and materials that are known to cause stress corrosion cracking.

2. Crack-Inducing Agents

A distinction should be made between an *active* crack-inducing agent and one that, while present, causes no harm. Most crack-inducing agents require the presence of an electrolyte in order to be active. For example, H_2S is not regarded as a crack-inducing agent for carbon steel if it is not accompanied by liquid water or some other electrolyte.

There are a few crack-inducing agents that do not require the presence of an electrolyte addition. An example is attack of copper alloys by ammonia. Accordingly, the template should include the information necessary to determine if a crack-inducing agent is active or can become active.

Amines

Amines can cause alkaline stress corrosion cracking in carbon steels. This is a form of anodic stress corrosion cracking. It has become standard practice to postweld heat treat all welds in carbon steel components if the amine concentration exceeds two wt. percent, regardless of the service temperature. An exception is equipment and piping in uncontaminated (i.e., fresh) amine service, in which stress corrosion cracking does not occur. Various forms of hydrogen-related cracking can occur in carbon steels exposed to amines rich in H_2S . Refer to the section "Wet Sour Service" (p. 196) for a discussion of such cracking.

Some users differentiate among amines, requiring postweld heat treatment for some but not for others. In other cases, users cite a service temperature threshold above which postweld heat treatment will be required for some amines but not for others. Until extensive and firm experience-based industry guidelines are established, the best policy is to require postweld heat treatment for carbon steel welds in all amine services unless user experience indicates otherwise. Note that API Publication No. 945 "Avoiding Environmental Cracking in Amine

Units" [19] does not cite a pressure threshold below which postweld heat treatment is not recommended.

Ammonia

Anhydrous liquified ammonia can cause stress corrosion cracking of carbon steel unless at least 0.1 wt. percent water is present. Transportation regulations ensure that most "anhydrous" ammonia contains sufficient water to prevent this problem. Postweld heat treatment of carbon steel welds is recommended.

Aqueous ammonia can cause stress corrosion cracking in copper and copper alloys. Such ammonia is usually unintentionally present, often being a degradation product of filming amines used for corrosion inhibition, from amines used in the gas sweetening plant or from water treatment chemicals such as hydrazine. Such alloys should not be used if they could be accidentally exposed to ammonia.

Carbonates and Bicarbonates

Combinations of carbonates and bicarbonates, present at concentrations exceeding 1 wt. percent (either individually or combined) can cause alkaline stress corrosion cracking in carbon steel. See Figures 3-9 and 3-10 for an example of this problem. Mitigation alternatives include the use of cathodic

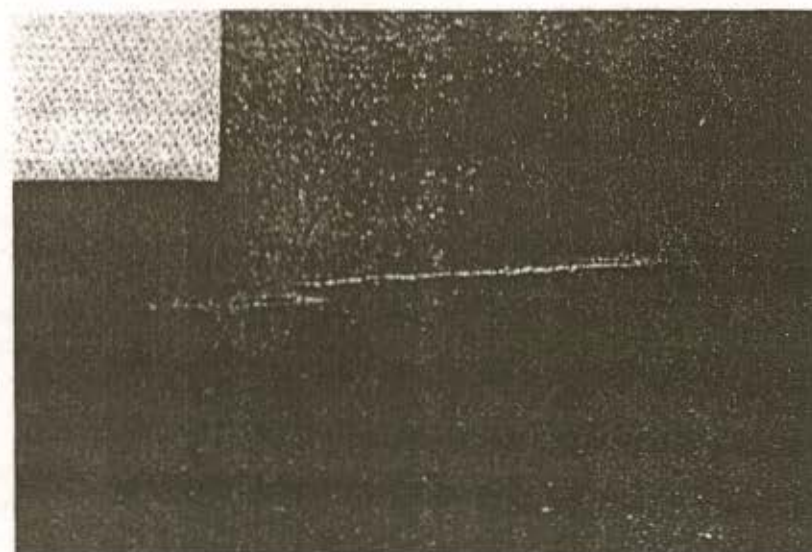


Figure 3-9 External stress corrosion cracking in a carbon steel pipeline, caused by exposure to soil containing carbonates and bicarbonates.

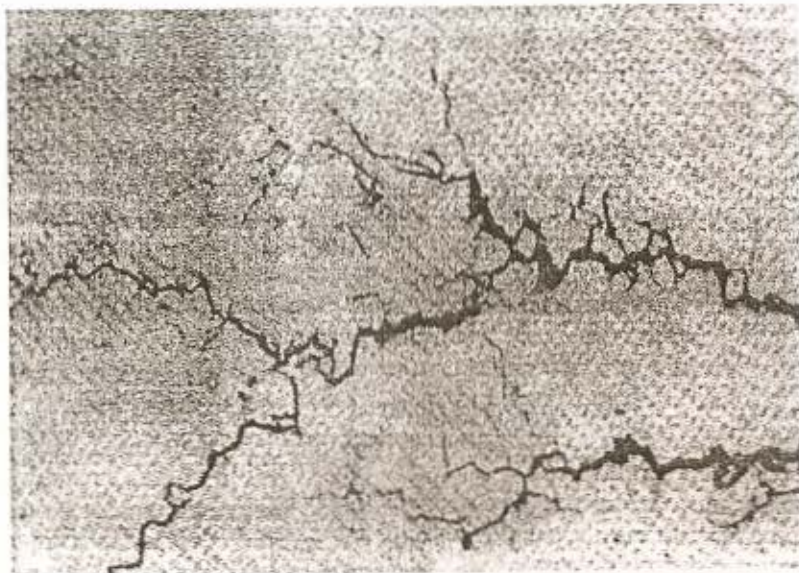


Figure 3-10 Microstructural view of the cracking shown in Figure 3-9.

protection, non-metallics (for low-pressure applications) and upgrades to either duplex or austenitic stainless steels. Coatings alone are usually not recommended for protection from alkaline stress corrosion cracking. Postweld heat treatment is normally required.

This type of stress corrosion cracking can be inhibited, as is shown by the successful use of inhibited hot carbonates in some proprietary CO₂ removal systems in which carbon steel is the recommended material of construction. Carbonate/bicarbonate cracking has occurred externally in some hot buried carbon steel pipelines. Such cracking is relatively uncommon and is usually associated with disbanded coatings. Cracking in pipelines occurs most often in the parent metal, so postweld heat treatment is not an effective mitigation measure.

Caustics

Virtually all caustics can cause stress corrosion cracking of carbon steel and low-alloy steels, in stainless steels and even in nickel-based alloys under severe conditions. However, carbon steel is the recommended material of construction for moderate temperatures and concentrations. Threshold concentrations and temperatures are indicated in the NACE caustic soda service curve [14] shown in Appendix 3. Note that these thresholds are not valid for heavily cold-worked

carbon steel applications such as tubes rolled into tubesheets. Postweld heat treatment is recommended for carbon steel weldments in services above the NACE threshold. An exception may be considered for low-pressure systems where the combined stress in tension is less than the ten percent rule. Valve trim is usually 12 Cr stainless steel.

Upset conditions are probably the main cause of caustic stress corrosion cracking in modern plants. In particular, upsets such as high-temperature episodes in otherwise cool caustic systems are the usual cause of such cracking. There have been reports of caustic stress corrosion cracking in systems that have been steamed out without prior water washing or flushing. Cracking has also been observed in carbon steel systems because of caustic carryover during upsets. Such cracking usually occurs because the system has not been stress relieved or postweld heat treated. Systems in which such upsets can occur should be stress relieved/postweld heat treated, if constructed of carbon steel, or should be made of appropriate alloys.

Caustics are usually contaminated with chlorides. Although caustic solutions tend to inhibit chloride stress corrosion cracking in austenitic stainless steels, such cracking can occur. Since there are other reasonably competitive materials choices, selection of austenitic stainless steels for caustic service is usually avoided. In any case, austenitic stainless steels should not be used in caustic services at temperatures exceeding 250°F (120°C), the threshold temperature for caustic stress corrosion cracking of such alloys.

Where carbon steel cannot be used, Alloy 400 is usually recommended. For severe caustic services, or where product purity is a concern, commercially pure nickel (Alloy 200) or plastic-lined carbon steel is often specified. There are a number of paint coatings, polymers and reinforced plastics that are resistant to about 200°F (93°C). There are a few polymers such as polypropylene and rubbers (e.g., neoprene) that are useful up to about 250°F (120°C).

Chlorides

Austenitic stainless steels are well known for their susceptibility to failure by chloride stress corrosion cracking (CSCC). See Figure 3-11 for an example of this phenomenon. Research metallurgists have found that they can cause CSCC in austenitic stainless steels under almost any set of circumstances, as long as they are permitted to use an extreme value of one or more of the critical variables. The practical limits of this cracking are described below.

- *Temperature.* CSCC is virtually unknown for neutral pH solutions at temperatures below 140°F (60°C).
- *Chloride concentration.* "Safe" chloride concentrations as a function of temperature are given in Appendix 8. In evaluating the risks for CSCC, consider concentration mechanisms such as evaporation, which can

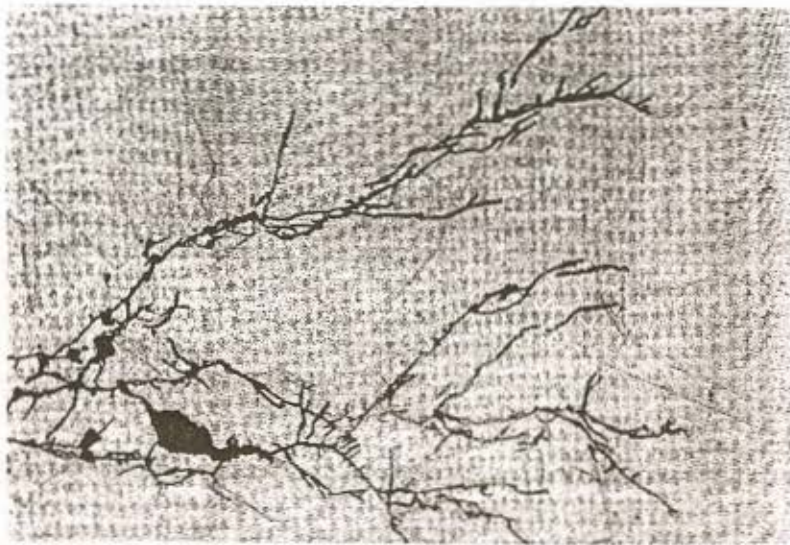


Figure 3-11 Chloride stress corrosion cracking of Type 304 stainless steel. (Courtesy of Mr. C. P. Dillon, C. P. Dillon & Assoc.)

increase low concentrations to dangerous levels. For this reason, vapor-liquid interfaces and crevices such as socket welds are to be avoided. Note also that extreme values of other variables such as pH or stress can cause an otherwise safe concentration to initiate C SCC.

- **Stress.** C SCC requires the exposed surface to be in tension. Such stresses are usually due to the residual tensile stress caused by welding or by cold work such as U-bending heat exchanger tubes. Solution annealing is effective in reducing such stresses but usually causes warping. Postweld heat treatment is sometimes used to reduce welding-induced residual stresses in austenitic stainless steels. Some users employ stress relief heat treatment to control the effects of cold work, for example, U-bends in heat exchanger tubes. Sometimes shot peening is used to ensure that exposed surfaces are in compression.

Recall from the discussion of sensitization in Part 2 of this chapter, that postweld heat treatment and/or stress relief heat treatment of stainless steels can cause severe sensitization. Use of stabilized grades that have been previously stabilization annealed is usually required if postweld heat treatments or stress relief is a fabrication requirement.

- **Oxygen.** Under normal circumstances, dissolved oxygen must be present at a concentration of at least 100 ppbw in order for C SCC propagation to proceed. Refer to Appendix 8 for guidelines.

C SCC of austenitic stainless steels can usually be avoided by controlling one or more of the above variables. However, a good design can be made susceptible by upsets or oversights such as low pH episodes, high-temperature excursions, inadvertent crevices or vapor-liquid interfaces. Accordingly, C SCC resistant alloys should be specified where C SCC is anticipated. Examples of such alloys include the higher nickel types such as Alloy 400 and Alloy 825, or duplex stainless steel alloys such as Alloy 2205 (22Cr-5.5Ni-3Mo-N; UNS S31803). The latter alloy has a C SCC threshold of about 350°F (175°C) in neutral saline waters. In some vessel and piping applications, clad construction is used. Carbon or low-alloy steel is used for pressure containment, with a resistant alloy inner cladding or weld overlay for protection from C SCC.

In focusing on the process side, do not forget that austenitic stainless steels may be subject to external C SCC. Such steels may be exposed to wet chlorides in atmospheric marine environments or to chlorides deposited externally by wind, dust or water. The risk of external C SCC may be complicated by the necessity for external insulation. Insulation prevents normal cleansing by rainwater. It may also be a source of chlorides, may concentrate chlorides during wet-dry cycles and may act to keep the external surfaces wet. Given the potentially catastrophic nature of an externally induced C SCC rupture, the evaluation of its risk should be regarded as a safety issue. There are several mitigation measures for external C SCC:

- In some cases an external paint coating may be adequate. (Normally, one does not depend on a paint coating for protection from environmental cracking. However, in this instance, one often does not have many economical choices.) Epoxy coatings are normally used for metal temperatures up to about 250°F (120°C), with modified silicone-based coatings used for higher metal temperatures.
- Clad construction (carbon steel overlaid or clad with stainless steel) may be specified for vessels, heat exchangers and piping.
- Alloys immune to C SCC may be specified.
- Peening is occasionally used to prevent chloride stress corrosion cracking. The method is not without risk, as operating stresses, pipe movement, etc. may nullify the benefits of peening.

Cyanides

Cyanides act as a cathodic poison. By themselves, they pose no threat of SCC. However, in combination with wet hydrogen sulfide, they can cause accelerated

sulfide stress corrosion cracking of carbon and low-alloy steels, if present at a concentration greater than about 20 ppmw. Postweld heat treatment is recommended for carbon and low-alloy steel welds exposed to combinations of cyanides and wet H_2S .

In addition to acting as a cathodic poison, cyanides can accelerate metal loss due to wet hydrogen sulfide corrosion. Normally, sulfide films are relatively stable. Their formation usually reduces the rate of metal loss due to corrosion. However, cyanides can convert iron sulfide scale deposits into soluble iron salt complexes. The underlying carbon steel then becomes susceptible to rapid corrosion.

Hydrogen Sulfide

Hydrogen sulfide can cause sulfide stress corrosion cracking (SSCC), hydrogen induced cracking (HIC) and stress oriented hydrogen induced cracking (SOHIC). SSCC is a form of hydrogen stress cracking, known to occur in many steels and alloys. HIC occurs in "dirty" steels. Stress is not required for such cracking. SOHIC is a stress-assisted form of HIC. When observed, it is usually seen in or near the heat affected zones of restrained welds, where growth of the cracks is probably assisted by residual stresses.

All of the above forms of hydrogen cracking begin with wet hydrogen sulfide corrosion, which supplies hydrogen as a corrosion product when the sulfide ion combines with iron to form iron sulfide. The sulfide ion is a cathodic poison, encouraging two phenomena.

1. Nascent hydrogen tends to dissolve into the metal rather than combining with another hydrogen atom to form hydrogen gas.
2. Normally, this type of corrosion is rapidly slowed by the formation of a polarizing layer of H_2 at the anode. However, the sulfide ion prevents such polarization. Thus, corrosion continues, with the generation of a large amount of nascent hydrogen, until the corrosion process is brought to a halt by the formation of a thick film of dense iron sulfide.

Sulfide Stress Corrosion Cracking (SSCC)

Sulfide stress corrosion cracking is a form of hydrogen stress cracking. It is relatively uncommon in carbon steel. Conventional welding processes usually do not produce the excessively hard weld or heat affected zones in which this type of cracking occurs.

Sulfide stress corrosion cracking can develop in areas of excessive metal hardness. For carbon steels, hardnesses in excess of Rockwell C22 are usually required. See Figure 3-12 for an example of this type of cracking. These cracks typically initiate at the internal toe of a weld and propagate along an excessively hard heat affected zone until they form a through-thickness crack. Such cracks



Figure 3-12 An example of sulfide stress corrosion cracking in carbon steel. (Courtesy of Dr. R. D. Kane, CLI International, Inc.)

can be very long, up to several feet, before they become unstable. They have caused several sudden ruptures in vessels, piping and pipelines. Some of these failures may have been assisted by hydrogen embrittlement.

The low- to medium-strength carbon steels are most resistant to SSCC. Piping and vessel carbon steels are usually kept at specified minimum tensile strengths of 70 ksi (480 MPa) or less. Experience has shown that the risk of SSCC increases for tensile strengths up to about 90 ksi (620 MPa). Higher-strength steels are very susceptible to SSCC.

It is essential to control weld hardness. NACE RP0472 [7] places a limit of 200 BHN on carbon steel weld metal hardness. Weld procedure qualification testing requires the heat affected zone hardnesses not to exceed 248 VHN. NACE MR0175 contains detailed recommendations on hardness and fabrication limitations for many of the metals and alloys encountered in plant design.

For the low- to medium-strength carbon steels used in chemical process and hydrocarbon plants, it is actually difficult to generate weld metal or heat affected zone hardnesses sufficient to cause SSCC. When seen, cracking caused by excessive hardness is usually due to one of the following.

- Dilution effects in a dissimilar metal weld.

- A weld joint, without adequate preheat, that combines two pieces of greatly different section thicknesses. Tube-to-tubesheet welds and low-heat-input single-pass welds such as tray ring attachments are examples.
- Cold working that increases the residual stress of the area that subsequently cracks.
- Use of a microalloyed steel, in which welding creates hard spots in the heat affected zone.

As was discussed in Chapter 2, microalloyed carbon steels have a tendency to produce excessively hard weld heat affected zones. It has been shown that such heat affected zones are often difficult to temper (i.e., soften) by postweld heat treatment. Microalloyed carbon steels should not be used in welded construction subject to SSCC unless the welding procedures are carefully qualified to show that they produce heat affected zones of acceptable hardness. Weld procedure qualification tests should include microhardness surveys across the heat affected zone in order to show that the procedure does not produce localized "hard spots." NACE RP0472 [7] and NACE MR0175 [8] are useful in specifying the requirements for controlling heat affected zone hardnesses.

Preheat and proper welding procedures are the appropriate measures for controlling hardnesses associated with welding ordinary carbon steels, since the hardness of their weldments is usually not a problem. Postweld heat treatment is usually not necessary unless other crack-inducing agents (such as amines) or other cathodic poisons (such as cyanide) are also present. In such cases, reduction of residual stress is usually necessary to reduce the susceptibility to stress cracking. For such severe SSCC services, postweld heat treatment is recommended.

Hydrogen Induced Cracking (HIC)

While HIC is technically not a form of stress corrosion cracking, it is related. One of its variants, stress oriented hydrogen induced cracking, is caused partly by residual stresses adjacent to the heat affected zone in thick section welds.

Hydrogen induced cracking occurs primarily in plate and plate products made of "dirty" steels. Such steel plates contain excessive amounts of non-metallic inclusions (primarily manganese sulfides), flattened by the rolling process. The resulting flattened inclusions are parallel to the plate surface, although they are usually staggered in location with respect to the thickness of the plate. The flattened inclusions are ordinarily less than one mm in length, but may be much smaller in clean steels and much larger in very dirty steels. Hydrogen induced cracking rarely occurs in product forms other than plate or plate products.

The tendency of a steel to undergo HIC is aggravated by a banded ferrite-pearlite microstructure (see Figure 3-13 for an example of banding). Banding is a relatively common microstructure in carbon steel plate rolled from ingots. As



Figure 3-13 A banded ferrite-pearlite microstructure in carbon steel plate. (Courtesy of Dr. E. V. Bravenec, Anderson & Assoc.)

the ingot solidifies in its mold, it has a tendency to segregate into zones or regions of slightly different compositions. These zones, of differing hardnesses, separate into finely divided layers of ferrite and pearlite when hot rolled. Steel made from continuously cast steels (steels that are poured through a chilled mold and solidify as an elongated slab) are typically less segregated. When hot rolled, these steels produce plate with minimal banding. The ASTM specifications used for purchasing conventional carbon steel plate do not address banding. Consequently, banding can be controlled only by specifying that the parent metal steel be continuously cast. This requirement is rarely specified by users.

"Control rolled" plate is rolled at comparatively low-temperatures (1300 to 1650°F (705 to 900°C)). It can be particularly susceptible to HIC. At these rolling temperatures, the manganese sulfide inclusions are appreciably softer than the steel and easily flatten to form the crack initiation sites characteristic of HIC.

Hydrogen-induced cracking is essentially a crack initiation mechanism. As wet hydrogen sulfide corrodes the surface of the steel, corrosion-induced nascent hydrogen diffuses into the steel. Non-metallic inclusions serve as catalyst sites for the recombination of the diffusing hydrogen into hydrogen gas (H_2). As the gas accumulates adjacent to the inclusions, pressure builds up, causing the



Figure 3-14 Hydrogen induced cracking in carbon steel plate. (Courtesy of Mr. M. S. Al-Omairy and Dr. E. M. Moore, Jr.)

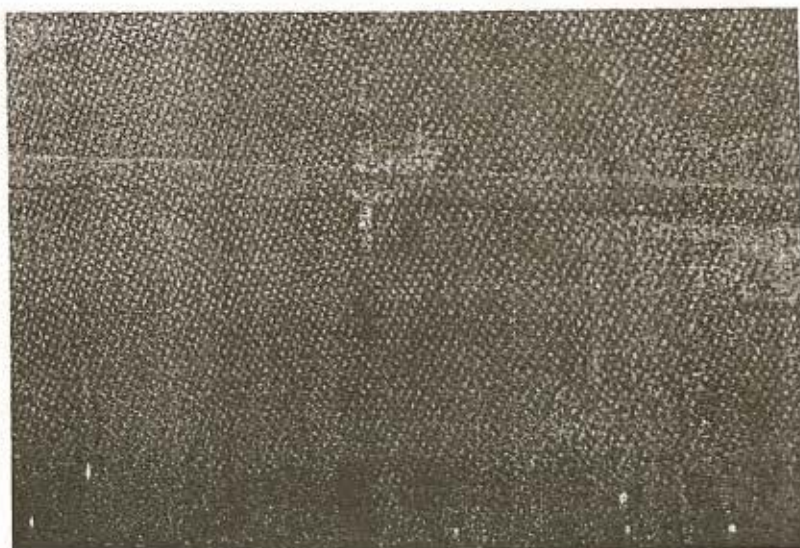


Figure 3-15 Hydrogen surface blisters in steel pipe, caused by H₂S service.

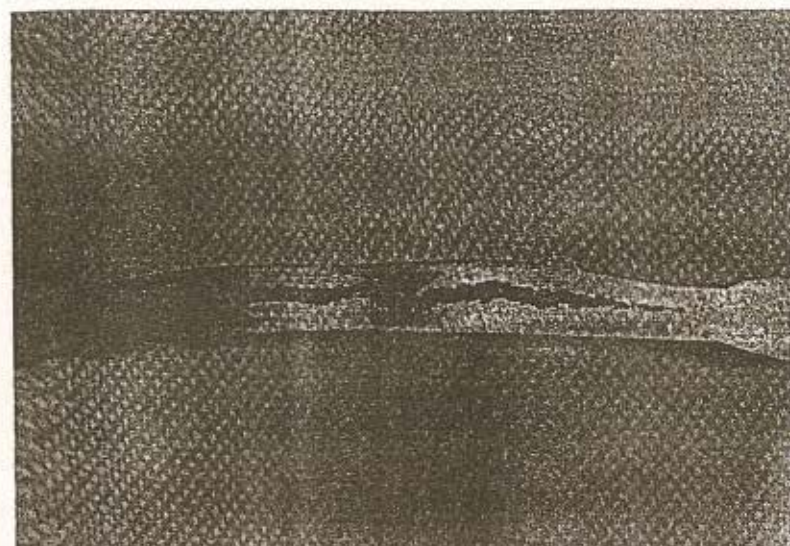


Figure 3-16 Splitting and bulging in carbon steel plate, caused by the growth of an embedded blister. (Courtesy of Mr. M. S. Al-Omairy and Dr. E. M. Moore, Jr.)

inclusion-matrix interface to split. This separation initiates an HIC crack (Figure 3-14). If the initiation site is near a free surface, the HIC crack results in a blister (Figure 3-15). If the plate contains multiple initiation sites that are internally embedded and the plate is relatively thin (less than about 1/2" (12.5 mm)), a split can develop parallel to the surfaces of the steel plate. The effect is often viewed as a very large blister. (See Figure 3-16 for an example of an embedded blister.) If the plate is relatively thick, staggered internal HIC cracks can link up, via cross-tearing (sometimes called *stepwise cracking*). In extreme cases, stepwise cracking can cause through-thickness cracks. (See Figure 3-17 for an example of stepwise cracking.)

Hydrogen induced cracking occurs in the temperature range of 32 to about 130°F (0 to 55°C). Above 130°F (55°C), HIC damage proceeds slowly, if at all. Note, however, that HIC damage can occur during cooldown in systems that normally operate at temperatures above 130°F (55°C). Depending on whether the system can be kept from cracking by purging, lowering the H₂S partial pressure, etc., such cooldowns should be regarded as crack-inducing upset conditions, which should be noted on the materials selection template.

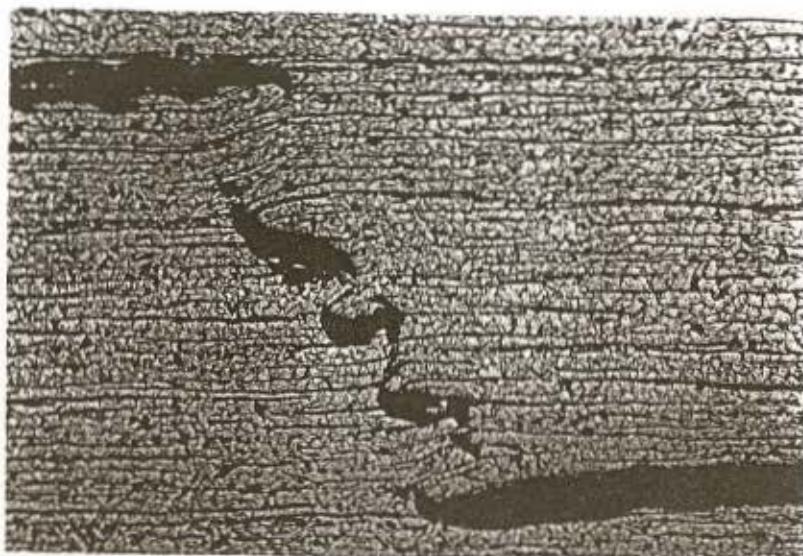


Figure 3-17 Hydrogen induced cracking that has developed into stepwise cracking. (Courtesy of Mr. M. S. Al-Omairi and Dr. E. M. Moore, Jr.)

Conventional carbon steel fabrication utilizes carbon steel plate chemistries and welding procedures that produce relatively soft welds and heat affected zones. Under these circumstances, HIC is much more likely to occur than sulfide stress corrosion cracking. Older plants in wet sour service, built before the common availability of clean steels, usually show evidence of HIC activity. Cracking ranges from gross indications such as blisters or stepwise cracks emerging at a surface to the characteristic ultrasonic inspection signals from cracked multiple staggered inclusions, at various depths in the plate.

HIC initiation is not significantly influenced by either hardness or heat treatments such as normalizing or postweld heat treatment. Propagation of cracks initiated by HIC can be inhibited by the increased fracture toughness that results from such heat treatments. HIC is minimized in plate and plate products by specifying a clean steel and a requirement for inclusion shape control. For a discussion of HIC resistant carbon steel, refer to the section "Wet Sour Service" (p. 196); also see Appendix 7. Forgings, castings and seamless pipe are considered to be essentially immune to HIC, since they normally do not contain the flattened non-metallic inclusions necessary to generate HIC cracks.

Plate made from continuous cast strand can be particularly susceptible to HIC if measures are not specified to ensure a clean steel. This unusual

susceptibility is due to the segregation of tramp elements such as sulfur to the center line of the strand during continuous casting. Since this fact is widely known by plate and pipe manufacturers, who routinely take appropriate countermeasures, problems are rare. However, care should be exercised when dealing with manufacturers of plate or welded pipe who are not experienced in HIC control.

Stress Oriented Hydrogen Induced Cracking (SOHIC)

SOHIC forms through-thickness cracks by linking up stacked small internal cracks. It usually occurs in heat affected zones associated with the residual stresses of welds. (See Figure 3-18 for an example of this type of cracking.) Thick, restrained welds such as those of heavy nozzles are reported as being especially susceptible. The mechanism involves two components:

1. HIC cracks form in a stacked manner, that is, they are stacked vertically. This forms a crack plane which is perpendicular to the surfaces of the plate. The component cracks are usually very short but closely spaced.
2. A through-thickness crack forms by shearing the ligaments between the stacked HIC cracks.

The development of the through-thickness linkage (and perhaps the initiation of the stacked cracks) seem to be driven by the strong residual stress fields of adjacent welds. Consequently, postweld heat treatment and normalizing are usually recommended, as well as clean steel resistant to hydrogen induced cracking.

Cross-tearing (also called *stepwise cracking*) of HIC cracks has been seen with some frequency in pipelines but is not as common in vessels, heat exchangers or tanks. Conversely, SOHIC has been seen in vessels and heat exchangers but is not as common in pipelines (although both experience and research have shown that the common pipeline steels are susceptible to SOHIC). Explanation of these observations probably involves differences in design factors, maximum code-allowable stresses, steel making and environment.

Mercury

Liquid metallic mercury causes rapid intergranular cracking in copper alloys and both intergranular cracking and pitting corrosion in aluminum alloys. The cracking mechanism is called *liquid metal embrittlement*. The result is virtually indistinguishable from intergranular stress corrosion cracking.

Cryogenic natural gas systems can pose a special hazard. Large amounts of such gases are processed in liquified natural gas (LNG) plants and in plants that take feed from LNG. The problem is mercury in the feedstock. Even low concentrations of mercury in the feedstock gas, over a long period of time, can generate concentrated pockets of mercury. Such pockets have caused serious

cracking problems in aluminum "cold boxes" during shutdowns, when the mercury liquifies as the cold box warms up.

Zinc

Zinc can cause liquid metal embrittlement in both iron and aluminum alloys. Galvanized carbon steel is not recommended for services in which the temperature exceeds 390°F (200°C). Intergranular penetration of the steel substrate by zinc, from the galvanized surface, has been reported for the temperature range 390 to 570°F (200 to 300°C). In addition, peeling of the galvanized layer has been observed at temperatures exceeding 390°F (200°C).

Some users prefer not to have galvanized products adjacent to stainless steel piping, vessels and/or equipment. Under certain circumstances (usually involving a plant fire), zinc can rapidly destroy the pressure integrity of an austenitic stainless steel. At least one major plant disaster is thought to have resulted from the phenomenon.

A report based on laboratory testing sheds some light on the problem of liquid metal attack by zinc on stainless steel [27]. Zinc melts at 787°F (420°C). At temperatures hotter than 1380°F (750°C), molten zinc will rapidly attack the grain boundaries of austenitic stainless steel, at rates on the order of inches per second.

This type of failure is very rare because:

- The zinc must first melt, *and*
- The molten zinc must be heated to at least 1380°F (750°C), without vaporizing or oxidizing, then come into contact with a hot austenitic stainless steel surface, *or*
- The molten zinc must come into contact with an austenitic stainless steel surface heated to a temperature of at least 1380°F (750°C).

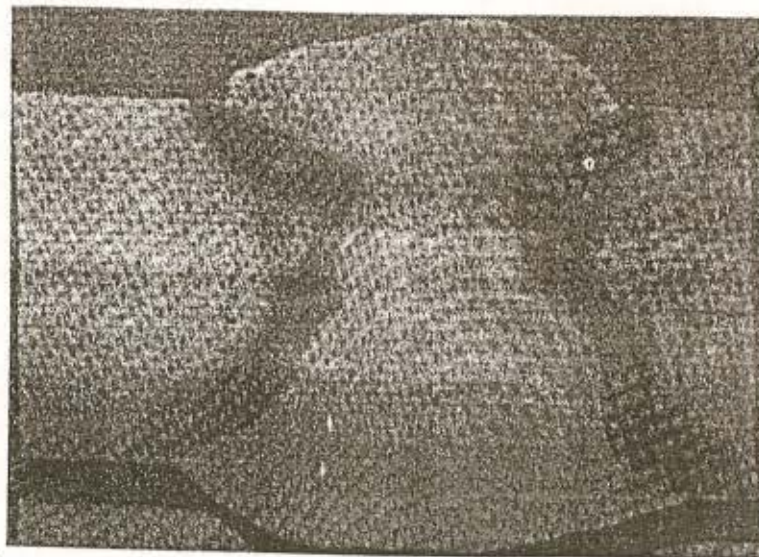
The following situations are suspected of causing failures:

- Welding or cutting stainless steel components that have been coated with a zinc-rich product such as inorganic zinc paint. Usually, such contamination is inadvertent (e.g., by overspray).
- Welding a galvanized steel part to an austenitic stainless steel component without first thoroughly removing the galvanizing adjacent to the weld preparation.
- Secondary failures in which molten zinc drips onto stainless steel components during a plant fire. Some users are sensitive to this aspect of the problem and require materials selection and piping and structural configurations that avoid this situation.

Higher alloys such as Alloy 20 Cb-3 (20Cr-35Ni-2.5Mo-Cb; UNS N08020) and Alloy C-276 (15Cr-54Ni-16Mo; UNS N10276) do not appear to be as



(a)



(b)

Figure 3-18 Stress oriented hydrogen induced cracking in carbon steel. [(a) Courtesy of Dr. R. D. Kane, CLI International, Inc.; (b) courtesy of Dr. R. D. Kane, CLI International, Inc.]

susceptible as the conventional austenitic stainless steels. However, laboratory tests show that such alloys are structurally attacked by liquid zinc at high-temperatures. Accordingly, these materials should not be contaminated with zinc.

Zinc contamination of stainless steels can occur during construction or maintenance. The following mitigation measures are recommended:

- Avoid painting or overspraying stainless steel with zinc-containing products. Prior to cutting or welding zinc-contaminated stainless steel, the contaminant must be thoroughly removed.
- Never permit galvanized components to be welded to stainless steel unless the zinc coating has been adequately cut back.
- See that stainless steel components in danger of colliding with galvanized structurals are covered or padded, for example, when hoisting stainless steel or high-alloy heater tubes or coils into a heater that is surrounded by galvanized structural steel.
- Make sure that any markers used for marking or writing on stainless steel components do not contain more than a few parts per million zinc. Many users also place the same limit on lead, cadmium and tin, which can also cause liquid metal embrittlement problems.

D. WET SOUR SERVICE

Wet sour services are common in the hydrocarbon producing and processing industries. The major concern for such services is the various forms of hydrogen cracking produced by wet hydrogen sulfide corrosion. NACE MR0175 is useful in defining what is meant by a wet sour service and what can be done to minimize the risk of cracking.

It should be noted that the use of NACE MR0175 for "downstream" applications is the subject of some controversy. Many downstream users, including some refineries and gas plants, regard MR0175 as not applicable to their operations. Yet, hydrogen cracking mechanisms do not respect the artificial division between "upstream" (hydrocarbon production) and downstream (hydrocarbon processing) operations. In fact, in many downstream facilities, the hydrogen cracking environment is more severe than in many upstream operations. A strong case can be made that if MR0175 is applicable to upstream facilities, it is even more applicable to downstream facilities. Thus, until a downstream equivalent of MR0175 is developed, the document provides useful guidance on fabrication practices designed to minimize the risk of hydrogen cracking in all facilities exposed to this type of environmental cracking.

For a wet gas system, NACE MR0175 [8] specifies all of the following for wet sour service:

- Liquid water is present
- The total pressure is at least 65 psia (0.45 MPa)
- The hydrogen sulfide partial pressure in the vapor exceeds 0.05 psia (0.34 kPa)

NACE MR0175 does not define a threshold for sour water. A widely accepted definition is that sour water is a wet sour service if it contains at least 50 ppmw dissolved H_2S . To be consistent with MR0175, sour water should be regarded as a wet sour service only if its maximum pressure is at least 65 psia (0.45 MPa).

While the 0.05 psia (0.34 kPa) H_2S partial pressure threshold has been found useful for the majority of applications involving wet sour service, it should be noted that cracking can occur at lower partial pressures. Such cracking usually occurs in systems with unusually low pH, or with materials having hardness exceeding HRC 30.

The 65 psia (0.45 MPa) total pressure threshold cited in the definitions of wet sour service has nothing to do with the initiation of sulfide stress corrosion cracks. The 65 psia (0.45 MPa) threshold essentially addresses the ten percent rule. In practice, these low-pressure systems have such low stresses that they do not propagate a brittle, catastrophic crack. Excessively hard steels can suffer sulfide stress corrosion crack propagation at pressures less than 65 psia (0.45 MPa) if the hydrogen sulfide partial pressure is high enough and the surface is water-wetted. Indeed, residual stresses alone are sometimes sufficient to propagate sulfide stress corrosion cracks. In practice, however, such crack propagation is not catastrophic. Leak-before-break governs. Thus, such low-pressure systems are considered "safe," and mitigation measures such as hardness controls may be unnecessary. Exceptions should be made for thin-ligament components such as tube-to-tubesheet welds or for facilities in which leakages are unacceptable. Other corrosion control measures may be considered, but rarely are. Wet hydrogen sulfide corrosion is usually not a serious problem unless the system contains oxygen, cyanides or ammonia.

Even transient wet sour service can quickly crack an excessively hard weld or heat affected zone. Hardnesses in excess of about HRC 45 can crack in minutes. Consequently, relevant upset conditions including startup and shutdown, presulfiding, catalyst regeneration, etc., should be included in wet sour service evaluations. Note that most "dry" sour overhead services become wet sour upon shutdown. If upset conditions can produce a wet sour service, the upset condition should be regarded as governing for the purposes of materials selection. The materials selection template should contain a note to the effect that the upset condition is governing.

A number of other services such as hydrofluoric acid can generate the nascent hydrogen that causes hydrogen embrittlement, hydrogen stress cracking, hydrogen induced cracking (HIC) and/or stress oriented hydrogen induced cracking (SOHIC) in carbon steels. Such services should be treated as wet sour for the purposes of materials selection.

As discussed earlier in this chapter (p. 114), carbon and low-alloy steels in wet sour service can be exposed to the combined risk of hydrogen embrittlement and hydrogen stress cracking. The combined risk is acceptable for most applications of conventional low- to medium-strength (70 ksi (480 MPa) specified minimum tensile strength) carbon steels in simple wet sour services. Consequently, only minimal mitigation measures are justified for simple wet sour services. However, the air-hardening low-alloy steels (e.g., Cr-Mo steels) can be sensitive to the combination of hydrogen embrittlement and hydrogen stress cracking, even in simple wet sour services. Air-hardening steels exposed to such conditions should not be pressurized at temperatures less than about 250°F (120°C), the threshold for hydrogen embrittlement.

Carbon steels in severe wet sour services also have a history of various types of cracking and embrittlement problems. For materials subject to such embrittlement and/or cracking, special mitigation measures should be taken, or materials resistant to such problems should be selected. Given the potential complexity of dealing with the combined risks of hydrogen embrittlement and wet sour service, the following guidelines may be useful.

1. Low-Risk Service

Low-risk service applies to metals and alloys in wet sour services for which the maximum design pressure is less than 65 psia (0.45 MPa). No special metallurgical requirements are usually necessary except for:

- New equipment subject to local laws that mandate conformance to an engineering code in which such measures are required.
- Facilities in which leakages are unacceptable.
- Thin-ligament pressure-containing components where leaks could develop quickly and would require unscheduled maintenance. Examples include tube-to-tubesheet welds and thin-fillet welds used to attach tray support rings. Hardness controls are usually adequate in such cases. Pay particular attention to the potential hardness problems of dissimilar metal welds.
- Cases where through-thickness cracks, even though stable, would release a lethal substance. Such cases should be subject to the requirements of "simple" or even "severe" wet sour service (as defined on p. 199).
- New equipment and piping, where subsequent repairs after long-term service would be excessively expensive, for example, where congestion

would make it very difficult to mobilize equipment or where such activities would lead to unacceptably long plant shutdowns. Such cases should be regarded as "simple" or even "severe" wet sour services (as below).

Note that there are some services with maximum design pressures less than 65 psia (0.45 MPa) that are especially susceptible to hydrogen induced cracking (HIC). Examples include the overhead systems of fluid catalytic cracking units and delayed coker units. Such processes typically contain significant quantities of cyanides. These services should be regarded as "simple" services. In addition to the requirements indicated by "simple wet sour service," plate and plate products should be specified as HIC resistant.

2. Simple Wet Sour Services

Simple wet sour services contain no other crack-inducing agents or cathodic poisons and exist when the maximum design pressure is at least 65 psia (0.45 MPa). Such services require that all metals and alloys conform to the hardness, manufacturing and fabrication limitations of NACE MR0175 [8]. It is important that:

- All weld metal, heat affected zones and parent metal be hardness controlled. This requirement should be adopted even if the fabrication is postweld heat treated.
- The weldment hardnesses for carbon steels is limited in accordance with NACE RP0472 [7].

Postweld heat treatment is usually not required for carbon steel construction. Note that postweld heat treatment may be used to soften welds determined to be excessively hard or may be specified for thin-ligament weldments (such as tube-to-tubesheet welds), in which excessive hardness is probable.

Postweld heat treatment should be mandatory for air-hardening low-alloy steels such as the Cr-Mo alloys.

3. Severe Wet Sour Services

This category includes wet sour processes in which the maximum design pressure is at least 65 psia (0.45 MPa) and specifically includes systems known to be especially susceptible to various forms of wet H₂S cracking. Examples include:

- Wet sour light hydrocarbons such as wet sour liquid petroleum gas or natural gas liquids
- High-pressure separation systems downstream of hydrotreaters and hydrocracking units

Refer to NACE Technical Committee Report 8X194 "Materials and Fabrication Practices for New Pressure Vessels Used in Wet H₂S Refinery Service" [28] for a detailed discussion of equipment in severe wet sour service in refineries.

Other severe wet sour services include:

- Processes that include other crack-inducing agents such as amines.
- Processes that tend to increase the concentration of nascent hydrogen dissolved in the carbon steel, for example:
 - Processes that include other cathodic poisons such as cyanides in excess of 20 ppmw.
 - Processes that include salt-forming cations that permit high concentrations of aqueous sulfides. The most common such cation is ammonia, which produces highly soluble NH₄HS.
 - Processes that interfere with the stability of the iron sulfide film that usually protects carbon steel from active corrosion by wet hydrogen sulfide. Examples include chemical cleaning and erosion due to impingement or excessive stream velocities.
- Systems in cyclic service.

Severe wet sour service mitigation measures include all of the requirements that apply to simple wet sour service. In addition, the following requirements should be specified for carbon steel plate and plate products.

- *Killed carbon steel.* Carbon steel plate and plate products (e.g., welded pipe) should be made of fully killed plate made to fine grain practice (e.g., ASTM A516).
- *HIC resistance.* Carbon steel plate and plate products in severe wet sour service should be made of HIC-resistant plate.
 - Sulfur concentration should not exceed 0.002 wt. percent.
 - The steel should be treated with calcium or rare earth metal for inclusion shape control. Calcium treatment is the most common and is preferred because it is less likely to cause welding problems.
 - If purchased in heat quantities, each heat may be economically tested per NACE TM0284 [29], using the low pH solution of NACE TM0177 [30]. This requirement is normally restricted to cross-country pipelines made of welded pipe. Acceptance criterion should be that the crack length ratio (CLR) should not exceed 15 percent. Modern steel making practice can reliably produce welded pipe with CLRs of 5 percent or less.
 - For cross-country pipelines, HIC-resistant plate should be required for welded pipe intended for either simple or severe wet sour services. Note that seamless pipe, castings and forgings are exempt from HIC concerns.

• Heat treatments.

- Except for cross-country pipelines, HIC-resistant carbon steel plate should be normalized.
- Welded pipe intended for plant service should have the longitudinal weld seam normalized.
- Postweld heat treatment should be mandatory for all carbon and low-alloy steels.

Many simple or severe wet sour services, for which it can be shown that the maximum design pressure hoop stress is less than the ten percent rule, may be regarded as a low-risk service. Note, however, that blistering can still occur. Some users are upset by blistering, even though blisters usually represent an aesthetic problem rather than a threat to pressure integrity. Low-pressure systems that are especially susceptible to HIC, such as the overhead systems of fluid catalytic cracking units and/or delayed coker units, should be regarded as "simple" services. HIC-resistant plate and plate products should be specified for such services.

E. CORROSION ALLOWANCE

Corrosion allowance is normally provided for vessels and piping. Most end users require only an internal corrosion allowance. However, some companies also require an external corrosion allowance for special circumstances such as external insulation or buried piping.

For many applications, corrosion allowance is a waste of money. Experience shows that almost all corrosion damage is due to localized mechanisms such as pitting. In areas subject to localized metal loss, corrosion allowance may provide a few years of life extension. However, the vast majority of the corrosion allowance paid for is never used. Further, a net present worth analysis quickly shows that such extended life, unless taken advantage of in the first few years of equipment life, cannot pay for itself. Note that early payoff also implies early failure. Finally, the whole concept of corrosion allowance can be difficult to justify on technical grounds:

- The real yield and tensile strengths of a material are usually 10–50 percent higher than the minimum values in specifications such as those of ASTM. The section thickness of vessel pressure plate and pipe wall thickness is determined by the maximum code-allowable stress. The latter is determined by the specified minimum yield or tensile strength. Accordingly, the section thickness as determined by the engineering code often has an inherent corrosion allowance of 10–50 percent.
- The calculated section thickness is based on the maximum design pressure. The maximum design pressure is sometimes a good deal greater than the maximum operating pressure.

- ASTM specifications allow for mill under-tolerance on section thickness. For plate and plate products, under-tolerance is usually 0.010" (2.5 mm). For many pipe specifications, the under-tolerance on thickness is 12.5 percent. The common piping codes require that thickness, as determined by the maximum allowable stress and the maximum design pressure, be adjusted upwards by the mill under tolerance.
- The wall thickness selected is usually the next standard thickness (i.e., schedule) available above the calculated thickness. This provides even more inherent corrosion allowance.
- In low-pressure applications, section thickness is often determined by welding considerations. Section thicknesses less than about 0.2" (5 mm) can generate problems with lineup, distortion or burn-throughs. Section thickness may also be dictated by availability. The thickness used therefore has an inherent corrosion allowance. In many such cases, virtually the entire thickness is corrosion allowance.

Criticism of the concept of corrosion allowance notwithstanding, it must be recognized that the concept is widely accepted in industry. Indeed, in some cases corrosion allowance can be justified—usually for the moderate extension of an otherwise short expected operating life. For example, in pilot plant work, the design life of carbon steel equipment in a corrosive service may be extended by a year or two by specifying a large corrosion allowance. If such life extension is needed to complete the plant performance objectives, the cost of the corrosion allowance is usually substantially less than a material upgrade. In some services such as sheet piling in seawater, an abundant corrosion allowance may be the only cost effective alternative.

The requirement for corrosion allowance is spelled out in many user design standards and purchasing specifications. In the absence of user or process licensor guidance, the following guidelines are offered:

1. Design Life

The corrosion allowance for vessels, heat exchangers and tanks should provide for 20 years of corrosion. For piping, 10 years of corrosion allowance should be required, based on the easier replaceability of piping.

2. Vessels, Heat Exchangers and Tanks

A minimum of $\frac{1}{8}$ " (3 mm) corrosion allowance should be provided for carbon steel and low-alloy vessels, heat exchangers and tanks, unless the service is deemed non-corrosive.

For high alloys, some users require a nominal corrosion allowance of about $\frac{1}{16}$ " (1.5 mm). In the absence of a user requirement, zero corrosion allowance may be specified for high alloys. These recommendations apply to alloy plate, the clad layer of clad plate and the overlay of overlaid plate.

In some cases, service requirements encourage different corrosion allowances for different parts of the same vessel, heat exchanger or tank. For example, the lower course and bottom of a crude oil storage tank may have $\frac{1}{8}$ " (3 mm) corrosion allowance, for water corrosion. The upper courses, which are not exposed to water corrosion, may have only $\frac{1}{16}$ " (1.5 mm) or even zero corrosion allowance.

The alloy layer of clad or overlaid plate will normally be specified to be a minimum of 0.125" (3 mm) thick. For heat exchangers, greater thickness or special designs may be required to prevent, or compensate for, damage during bundle insertion and removal. If overlaying, consider whether a two-layer overlay should be required, to accommodate weld dilution in the first layer.

3. Piping

The following corrosion allowances are usually adequate for carbon steel piping:

	Corrosivity			
	Non-corrosive	Mild	Moderate	Severe
Corrosion allowance	0" (0 mm)	$\frac{1}{16}$ " (1.5 mm)	$\frac{1}{8}$ " (3 mm)	$\frac{1}{4}$ " (6.4 mm)
Examples	Air, nitrogen, dry hydrocarbons	Treated cooling water, steam, wet hydrocarbons	Wet sour gas, sour water, utility water, lean amines, caustics	Aerated water, rich amines, ambient temperature wet CO ₂ , hot sulfur or sulfide (>500°F (260°C)), wet salts, corrosive deadlegs, hot steam (>1000°F (>540°C))

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CORROSION TESTING

A. INTRODUCTION

Corrosion testing is a broad discipline that includes topics such as corrosion monitoring, investigating the nature of threshold conditions, evaluating materials durability and understanding corrosion mechanisms. While all of these activities produce information that can affect materials selection, it is corrosion testing for materials durability that is of primary interest to personnel responsible for materials selection.

In this chapter, the primary emphasis is on the factors that affect the design of corrosion testing programs developed for the purpose of evaluating materials. The objectives are (1) to explain what corrosion-testing programs can accomplish and (2) to provide guidance that will be useful in developing such programs. The user can then turn to the literature [1, 2] and/or to specialists in the area of testing for assistance in developing appropriate programs. When corrosion testing is necessary, reference to these sources is strongly recommended.

Corrosion testing is not widely practiced when designing plants for mature technologies such as most hydrocarbon and chemical process plants. However, even mature technologies are being constantly upgraded. Occasionally, upgrades result in unexpected corrosion problems. For example, over the years, it has become necessary to use titanium for the condenser tubing in many sour water stripper overhead systems, primarily due to the increasing presence of dissolved acid salts. When corrosion testing is necessary for these plants, the test program is normally relatively straightforward, since the test objective(s) are well defined by the problem itself. Corrosion testing for these types of problems may start with some laboratory testing, but usually the most favored materials under consideration are tested in an operating plant. Pilot plant testing is desirable for screening tests, if such a facility is available.

For technologies that are new or for "improved" technologies, corrosion testing may be a significant activity. Test objectives may vary from being well defined because of previous testing or operating experience to ill defined for a prototype process. The objectives usually involve evaluating the durability of materials, but may also include the effects, if any, of materials of construction on the process itself. An example of the latter objective is product contamination by the material of construction.

Unlike refineries and most petrochemical plants, where companies often have similar equipment, many industrial chemical units are one-of-a-kind. This often means that there is no operating history to use as the basis for selecting materials. Also, it may be only a few years before technology advances make the process obsolete. A third consideration is that the equipment may be called on to make more than one product. Sometimes this multi-product use is part of the original design but sometimes it is the result of changing conditions and/or technology. These factors tend to create conflicting objectives between selecting (1) materials that will give long, reliable service and (2) materials of lesser reliability but also of lower cost. There is no uniquely correct answer as to what strategy to use. However, whatever strategy is chosen, it is always important that the tests conducted provide reliable results so that materials selection choices are made on the basis of accurate and meaningful data.

There are two key elements in a corrosion testing program designed to provide data suitable for selecting materials of construction. The testing program must be designed to accommodate both of the following:

- *Test variables:* the effects of temperature, pressure, pH, etc.
- *Test methods:* specimen immersion, electrochemical methods, types of specimens, etc.

In the following sections, these elements will be discussed in detail.

B. IMPORTANT VARIABLES

The variables affecting corrosion depend, to some extent, on whether the process is a batch or continuous operation.

1. Continuous Processes

In a continuous process, the variables are often regarded as relatively constant, since the usual goal is to maintain a constant process environment. However, even continuous operations are subject to upset conditions such as startup and shutdown and to differences between start-of-run and end-of-run.

In many cases, continuous processes are easier to characterize because, when the process is operating under control, the environment in any part of the process is fairly constant. Care must be taken to ensure that the effects of process startups, shutdowns and other upsets are considered, since the most damaging conditions may occur during these times.

Another characteristic of continuous processes is that each unit supplies raw materials to the following unit. Thus, if any piece of process equipment or piping fails, the entire process must be shut down until the equipment can be repaired. This adds a premium for reliability of continuous process equipment and piping, and to an ability to predict the remaining life of equipment components.

2. Batch Processes

In batch processes, the piping and equipment see continual changes in process conditions throughout the batch cycle. This often results in requiring the materials of construction to resist a broad range of operating environments. In common with continuous processes, the corrosivity of a batch process can be affected by upset conditions such as startup and shutdown and differences between start-of-run and end-of-run.

One approach to testing materials for a batch process is to expose samples of the candidate materials of construction in a number of batch cycles in a plant, pilot plant or research laboratory. However, when this option is not available, the problem of creating meaningful test environments is difficult and the results are subject to considerable error. A good understanding of the process chemistry and the behavior of candidate materials in various chemical environments is very helpful in improving the validity of these tests.

Industrial chemical processes include both batch and continuous operations, and some can include a combination of the two. As discussed above, each operational mode presents its own set of requirements for the tests needed to characterize materials requirements.

In Chapter 3, it became apparent that there are many variables that can affect the corrosivity of a system. These variables are also important in testing for materials durability.

3. Temperature

Plastics, coatings, linings, elastomers and the like have rather severe temperature limits and can be used successfully only within these limits. Table 2-4 (p. 61) lists the maximum operating temperature for a number of plastics and coatings. A word of caution is in order about the temperatures listed in this table. These

temperatures are for non-corrosive applications. The maximum temperature for a specific application may be much different. For example, the maximum temperature for vinyl ester-reinforced thermosetting resin construction, for air service, is 355°F (180°C) and for steam it is 220°F (104°C). For deionized water, the maximum recommended temperature is 180°F (82°C) and for dichloroethane it is only 80°F (27°C). To be safe, the person selecting a plastic for chemical service must obtain data on the behavior of that material in the specific environment. The literature [3] and manufacturer's data are often very useful in determining maximum service temperatures or in helping to define the temperature range to use in a corrosion testing program.

For many corrosive environments, the rate of corrosion of metals and alloys increases with increasing temperature. However, there are exceptions, such as the corrosion of carbon steel by wet CO₂, discussed in Chapter 3. Another notable exception is the corrosion of carbon steel by water in an open system, discussed in the following section.

Some forms of corrosion, such as stress corrosion cracking, crevice corrosion and pitting can be especially sensitive to temperature. In some cases, threshold temperatures exist, below which the risk of such corrosion is insignificant. Temperature changes may also affect the polarity of galvanic couples. An example is the iron-zinc couple (e.g., galvanized steel). In some domestic waters, iron may become anodic to zinc at temperatures over 180°F (82°C).

The effects of heat transfer on corrosion rate depends on the system. If corrosion is under activation control, the presence of heat transfer might not have much effect. On the other hand, if corrosion is controlled by diffusion (e.g., oxygen), then heat transfer may greatly change the corrosion rate. There are three possible causes.

1. A temperature difference between the wall and bulk solution may affect the solubility and diffusion coefficient of the diffusing species.
2. Boiling at the surface can increase turbulence or increase diffusion.
3. Heat transfer in the absence of fluid flow, as in a stagnant tank, can cause natural convection currents that enhance mass transfer.

4. Pressure

In most cases pressure does not have a large influence on corrosion behavior. A significant exception is when the concentration of a corrodent is determined by its vapor pressure (e.g., wet CO₂). A classic example is the difference in corrosion behavior of carbon steel in water in open and closed vessels (see Figure 4-1). Dissolved oxygen is a major source of corrosion of steel by water. As the temperature increases, the corrosion rate increases until about 175°F (80°C). In this temperature range the water vapor pressure increases rapidly,

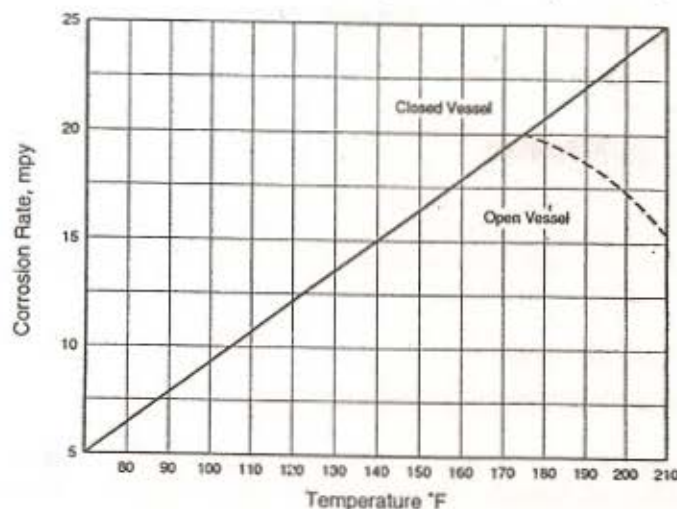


Figure 4-1 Retaining dissolved oxygen in a closed system boosts the corrosion rate. (©Copyright ASTM. Reprinted with permission [1, p. 345].)

thereby reducing the oxygen partial pressure. This results in essentially zero oxygen in the open system at the boiling point. However, if the system is closed, the oxygen cannot escape and the corrosion rate continues to increase as the temperature rises. This is why it is so important to remove dissolved oxygen from boiler feed water.

5. pH

In strong acids and bases, pH is a valid measure of total acidity or alkalinity, because of the total ionization of the electrolyte. For weaker acids and alkalis, which are less completely ionized, total acidity (or alkalinity) is a better indication of corrosivity than is pH. With these acids (or alkalis), the un-ionized material serves as a reservoir of potential protons available for corrosion. Corrosion data are more reliable than either pH or total acidity (or alkalinity) for indicating corrosivity in complex process mixtures. Nevertheless, pH and total acidity (or alkalinity) are useful indicators of potential corrosion behavior and should be identified whenever possible.

Carbon steel is a good example of a material being sensitive to pH. In the pH range of 4.5 to 9, the corrosion rate is governed by dissolved oxygen. Below pH 4.5, the corrosion rate is controlled by hydrogen evolution. Above about pH 9, the rate is suppressed by an insoluble film of ferric hydroxide. At very high

pH levels, especially at elevated temperatures, steel becomes susceptible to stress corrosion cracking.

6. Velocity

The influence of fluid flow rate on corrosion depends on the alloy, the fluid chemistry, the physical properties of the fluid and the geometry of the equipment/piping system, and can depend on the corrosion mechanism. In some cases, the dependence is fairly direct. For example, the rate of corrosion of carbon steel in water in the near-neutral pH range is governed by dissolved oxygen acting as a cathodic depolarizer. The overall rate of reaction is governed by the rate of mass transfer of dissolved oxygen from the bulk fluid to the surface. The rate of mass transfer is, in turn, governed by either the diffusion rate of the dissolved oxygen or by factors such as turbulence.

The presence of fluid flow can sometimes be beneficial in preventing or decreasing localized attack, such as pitting and crevice corrosion. For example, oxide-stabilized alloys, such as Types 304 and 316 stainless steel and many nickel-chromium alloys, will pit in stagnant seawater more readily than in flowing seawater. When water is stagnant, the mass transfer rate of oxygen is insufficient to maintain a completely passive surface and pitting can result. Low flow velocities of seawater also contribute to the formation of deposits and marine growth such as mollusks and barnacles, both of which promote crevice corrosion attack.

Under other circumstances, fluid flow may cause erosion of the surface through the mechanical force of the fluid itself. When solids are present in the liquid, they can accelerate wear or solid particle erosion. In either case, the rate of attack can be accelerated by the combined effects of erosion and corrosion. Erosion corrosion results when the passive films that form on alloys are removed and the underlying metal is attacked. Erosion corrosion rates can be very rapid.

7. Process Chemistry

The composition of the process stream is usually the most important of the variables affecting corrosivity. A sound understanding of the process is required in order to select the proper environments for corrosion tests in a continuous process. In some equipment such as distillation towers, there is a continuous change in process conditions through the unit. It is not always practical to conduct tests at all of these conditions, yet the raw material or product streams may not represent the most severe conditions. The use of a good process simulation model with good physical property data can go a long way in helping to identify the range of conditions present and therefore in helping to select the best test conditions.

The presence of small quantities of chemicals as contaminants is frequently overlooked in designing tests for selecting materials for industrial chemical applications. Often, such contaminants are chemicals that are present unintentionally, and usually they have no effect on corrosion behavior and can be safely ignored. However, sometimes this is not the case. Consider, for example, the effect of a few drops of water in an otherwise all-organic environment. This water may have no effect on the process, but it can completely change the corrosion environment.

- Whereas carbon steel might have been satisfactory if water were not present, stainless steel may be required to avoid contaminating the process with the corrosion products of iron. If the organic chemicals include a halogenated compound, higher alloys or a lining (e.g., glass) may be required to avoid pitting, crevice corrosion and/or stress corrosion cracking.
- If the vapor phase contains a crack-inducing agent such as hydrogen sulfide, local damage from sulfide stress cracking, stress oriented hydrogen induced cracking and hydrogen induced cracking may occur.

In another example, a small quantity of a contaminating compound resulted in equipment failure at a chemical plant that used a fiber-reinforced plastic (FRP) tank for a process stream that was essentially dilute hydrochloric acid. This is a service where the FRP tank would normally be completely satisfactory. However, this process stream contained a small quantity of benzene. Over time, the benzene dissolved into the plastic resin, softening it to the point that the tank suddenly failed, sending a wave of HCl into a nearby control room. Fortunately, no one was hurt, but the process was down until the tank was replaced.

Perhaps the most common chemical contaminant is the chloride ion. Chloride ions accelerate the corrosion of iron in acidic solutions. The most notable effects of the chloride ion are pitting and crevice corrosion of oxide-stabilized alloys and stress corrosion cracking of austenitic stainless steels and related alloys. Most pitting and crevice corrosion is associated with chlorides. Bromides and hypochlorites can be similarly harmful. Fluorides and iodides have comparatively little pitting tendencies.

Crevice corrosion may occur under deposits, under gaskets or any other place where the opening is wide enough to permit liquid entry but narrow enough to create a stagnant zone. While halides are not necessary for crevice corrosion to occur, their presence promotes the formation of more acidic conditions in the crevice and much more rapid corrosion.

Oxidizing metal ions with chlorides are aggressive pitting agents. Even the most corrosion-resistant alloys can be pitted by cupric chloride and ferric chloride. By comparison, chlorides of non-oxidizing metal ions such as sodium chloride and calcium chloride cause pitting to a much lesser degree.

Chloride stress corrosion cracking is a constant concern when austenitic stainless steels are used at elevated temperatures. There is no true threshold of chloride concentration or temperature below which stress corrosion will not occur. However, experience has provided some guidelines where stainless steel can be used with confidence. The example of chlorides in cooling water was discussed earlier. Equipment designed to reduce opportunities for chlorides to concentrate is helpful. It is also desirable to reduce the presence of deposits that provide an opportunity for chloride concentration.

Trace amounts of oxygen can also be a major cause of accelerated corrosion and can contribute to stress corrosion cracking, as discussed in Chapter 3.

C. TEST METHODS

1. Real-Time Versus Accelerated Tests

Both real-time and accelerated test methods are used to evaluate the susceptibility of materials to corrosion and other degradation damage. The advantage of real-time test data is that they are predictive of the behavior of materials of construction, to the extent that the test environment and test specimen duplicate the anticipated operating conditions.

- Many real-time corrosion tests provide data on weight loss per unit time. Most testing is based on coupon exposures, in laboratory or process streams.
- Other real-time coupon tests are used to produce data on the efficacy of chemical cleaning programs, inhibitors, etc.
- Many of the electrochemical tests performed in the laboratory are real-time tests, providing data on phenomena such as passivation, galvanic corrosion and the threshold temperatures for pitting and crevice corrosion in oxide-stabilized alloys.
- Some real-time coupon tests provide data requiring long-term exposure. Examples include creep tests, paint panel tests (both immersion and atmospheric) and tests for sensitization and embrittlement.

Accelerated test methods are usually employed to provide data on failure mechanisms such as stress corrosion cracking, disbonding of cladding or overlays due to exposure to hydrogen gas, deterioration of paint coatings, etc. Accelerated testing uses severe test conditions to produce data that are indicative of the resistance of the test material to the test medium. To produce a sufficiently severe environment, one or more of the test variables is made deliberately far more severe than will be seen in actual service. Examples include tests for hydrogen induced cracking (HIC) resistance, salt spray tests for materials exposed to marine environments and autoclave tests for various types of disbonding.

In some cases, accelerated test data can be used to judge the probability of success of a material in a particular service. This ability is usually based on being able to relate operating history to accelerated test data [4]. However, in most cases, accelerated testing is not predictive of what is to be expected in service. The tests are primarily intended to rank the resistance of materials to the test medium. In practice, even the best ranked material may fail in actual service. In other cases, the poorest ranked material may prove to be suitable for the intended service. Unless one has access to historical operating data that relate accelerated test data to operating success, it is best to use accelerated test data only for ranking materials.

Occasionally, one hears the argument that accelerated testing is too severe, that it does not realistically represent long-term operating conditions. It must be kept in mind that the purpose of the accelerated test is to produce failure data, in a short time, for failure phenomena that usually take a long term of service to develop. Reducing the severity of accelerated tests would simply produce a longer list of materials showing resistance to the test medium, without improving the ability to rank materials.

2. Metals and Alloys

Corrosion test methods for metals and alloys can be grouped into two categories: electrochemical and non-electrochemical. Among the electrochemical techniques that have been used successfully for corrosion prediction are potentiodynamic polarization scans, electrochemical impedance, corrosion current monitoring, controlled potential tests for cathodic and anodic protection, and the rotating cylinder electrode for studies of velocity effects [1; in particular, refer to Chapters 7 and 9]. Though not literally a test, potential-pH (Pourbaix) diagrams [5] have been used as road maps to help understand the results of other tests.

The non-electrochemical techniques primarily involve coupon testing in a test fluid, in either the laboratory or the plant. The test program should include, as applicable:

- Vapor phase coupons and partially submerged coupons in addition to normal immersion testing
- Weld metal, heat affected zone and deliberately sensitized specimens
- Appropriate coupons if fabrication or construction will include cold work, stress relief and/or postweld heat treatment
- Creviced samples, usually made with artificial crevices created with a serrated washer
- Test samples exposed to the corrodent on one side and heated or cooled on the other side in order to evaluate heat transfer effects
- Stressed samples to evaluate stress corrosion cracking tendencies

3. Plastics and Elastomers

Test Environment

When the process fluid is a mixture or solution with more than one component, which is most often the case, it is likely that each of the components will react with the polymeric material differently. Therefore, it is critical that the volume of test fluid be sufficiently large for all of the components to react with the polymeric material being tested and that the test fluid be refreshed frequently. The ideal situation is to conduct the test in an actual process stream so that even the chemicals present in trace quantities are continually refreshed.

When a process stream is not available, laboratory tests are necessary. In this case it is important that:

- The test fluid represents the service conditions as closely as possible.
- All organic chemicals contained in the process stream are present, even if in trace quantities.
- Any inorganic acids that can act as catalysts be indicated if they are present in the process stream.
- The test fluid be changed frequently to ensure that components consumed by the reaction with the polymeric material are replaced. When trace quantities of organic compounds are present, this requirement is especially important.
- When liquid and vapor exposure will occur in service, test samples are present in both the liquid and vapor phases of the test fluid.

Test Samples

The nature of the test sample depends on the application. If the polymeric material is to be used as a structural shape, a sheet sample is usually used. On the other hand, if the polymeric material is to be used as a lining, a coated sample might be considered. This is particularly appropriate if permeation that could lead to disbonding of the coating is a concern. At this time, there is no universally accepted test sample size, shape or form. Sheet samples are most frequently used, since they are the least expensive and are the easiest to work with.

Standard Tests

Current test methods for chemical resistance include the following ASTM procedures. There are a number of other tests for polymeric materials that are used to evaluate properties other than chemical resistance; these are not included in this list.

- ASTM C 581: "Standard Practice for Determining Chemical Resistance of Thermosetting Resins Used in Glass-Fiber Reinforced Structures Intended for Liquid Service."

- ASTM D 570: "Standard Test Method for Water Absorption of Plastics."
- ASTM D 3681: "Standard Test Method for Chemical Resistance of Reinforced Thermosetting Resin Pipe in a Deflected Condition."
- ASTM D 471: "Standard Test Method for Rubber Property—Effect of Liquids."
- ASTM D 4398: "Standard Test Method for Determining the Chemical Resistance of Fiberglass-Reinforced Thermosetting Resins by One-Side Panel Exposure."

A test method based on a test described by Fisher and Carpenter in 1981 [6] has been proposed by Niesse [7]. This method is being evaluated by NACE Technical Committee T-3L-19, "Chemical resistance of Polymeric Materials by Periodic Evaluation." The test involves periodic evaluation of samples exposed in a test fluid. The initial test periods are typically short and increase in duration as the test progresses. This procedure permits more effective monitoring of changes in properties over time, since the initial changes are often rapid and become slower with time.

Test observations may include changes in weight, hardness, color, dimensions and appearance. Of these, weight is the primary measurement since it is easy to obtain accurate values without damaging the specimen. Typically, a plot of weight change vs. time is prepared. This reveals rate-of-change information and can be used to make reliable predictions of polymer performance. This test has been used for thermoplastics, thermosets and elastomers.

An important feature of this test is the requirement of drying the samples at the end of the immersion test. One should also record the weight change vs. time curve for this process. This drying or desorption portion of the test is carried out at the same temperature as the immersion portion. If the sample's final weight after drying is similar to the original weight, this is an indication that there may not have been permanent damage to the sample material. A large weight loss is an indication of leaching of a component from the sample, while a large weight gain is an indication of possible damage by absorption or other chemical reactions.

This test has a number of advantages over traditional test methods. The sequential observations allow determination of the rate of property change, which helps in predicting long-term behavior. Initial observations can quickly identify those materials that would perform poorly. This makes the selection process more efficient by early elimination of poor performers. Drying (desorption) data can reveal leaching, a condition of concern. The testing can be done in process fluids and, in some cases, in an operating process. The samples can be subjected to mechanical property tests at the end of the test sequence.

This test method does have some disadvantages. More testing effort is required. Because the samples are removed from the fluid and re-exposed, there

is more handling required than with conventional tests. This extra handling may be of special concern if the test fluids are toxic or otherwise hazardous. Also, the process of removing samples, handling them and reinserting them into the process may affect the results. This is especially critical with elastomers, for which the results may be biased by excessive pressure when drying the samples for weight observations. Obviously, this is of concern only if some of the absorbed fluid can be squeezed out of the sample. Differences in the size or thickness of samples may affect comparison of results. For example, a thin sample would saturate earlier than a thicker sample. Finally, criteria for acceptable performance of different materials in this test have not been established. The guidelines developed in other tests do provide a basis for evaluating the results. These will be discussed later in this section.

The concerns about handling and reinserting samples into the test environment can be overcome by starting with enough samples of each material to be tested, so that a new sample is examined at each time interval. This greatly increases the number of samples involved but is otherwise an acceptable alternative.

Criteria

The acceptance criteria for selecting a polymeric material depend on the application. There is almost always some absorption of the process fluid into the polymeric material. With elastomers, and to a lesser extent with other polymeric materials, permeation may occur. Permeation is caused by diffusion of one or more of the components of the process fluid through the wall of the polymeric material. In many cases, this is not harmful but it can result in disbonding of linings or loss of product. The following criteria are typical for many applications but do not fit all cases.

Weight changes of 5 to 10 percent are often acceptable. Volume increase (swelling) usually occurs with weight increases. There is no exact limit to the amount of swelling that can be tolerated. For many elastomer applications, a volume increase of greater than 10 percent can be accepted. Large changes in hardness are a cause for concern, since this may be an indication of chemical attack. Again, specific limits will depend on the application. A 10-point change in hardness is often cited as a reasonable limit. Visual changes in surface texture or color are indications of attack, as is a change in color of the test fluid. These visual changes can be cause for rejection, especially if they are noted early in the test program.

D. DESIGNING A CORROSION TESTING PROGRAM

The selected test program must adequately simulate the limiting conditions of the process. However, not all tests must closely simulate process conditions. One

strategy is to start the test program by sorting the promising from the less promising materials with simple tests such as immersion corrosion tests in environments that crudely simulate the process conditions. There is the problem that this approach could exclude a material that would in fact be satisfactory in the process, because the test environment did not properly simulate the process conditions. However, unless one already has good estimate of the type of materials that are candidates, some sort of sorting process is necessary before detailed testing is conducted. Otherwise, the test program would be too cumbersome to manage.

Once the list of candidate materials has been reduced to a manageable number, testing can begin. The first objective in the test program is to understand how each material behaves within the expected range of process conditions. The specific testing program for a process must be based on the requirements of that process, and each program will be different. A typical program might include immersion and electrochemical tests in process fluids. The process fluids required for testing are either simulated or obtained from operating units. The program might also include tests for sensitivity to velocity and for susceptibility to crevice corrosion, pitting and stress corrosion cracking.

If plastics, elastomers, coatings, linings, etc., are being considered, it is necessary to conduct the tests long enough for degradation to be measured.

1. Existing Processes

Plant and laboratory tests each have a place for exploring materials for a new unit of an existing process.

Plant tests can be used to explore the behavior of new materials under current operating conditions far better than can laboratory tests. When possible, plant testing is favored, since laboratory test simulations are always imperfect. Also, in most situations, plant tests can be conducted with more materials at a far lower cost than is possible with laboratory tests. One drawback to in-plant testing is that it may be necessary to time the start and end of the test with scheduled equipment outages, which may postpone the data collection. An advantage of laboratory testing is that it permits exploring the effects of process changes on corrosion behavior without putting plant equipment at risk.

Some of the more sophisticated corrosion tests are suitable for use in a laboratory setting only. These tests can give more information about a material's tendencies toward localized corrosion, velocity-influenced corrosion and the like, than can conventional plant tests.

When localized corrosion is a concern, a combination of plant and laboratory tests is probably the best choice. The following is an example of how complementary laboratory and plant tests were used to solve a complex chemical plant corrosion problem. The problem was to determine how to treat a waste

stream from an entire chemical plant so that it could be handled in carbon steel equipment. One characteristic of waste streams is that their compositions vary widely over time. Therefore, a single sample from the stream might not be representative of the most corrosive conditions to be experienced. The fluid for laboratory testing was prepared from "typical" compositions of the various plant streams that are combined to create the waste product. This fluid was used in the laboratory to evaluate the effects of a proprietary sulfite-containing inhibitor, pH, and fluid velocity. Testing involved using a combination of electrochemical impedance and rotating cylinder electrode techniques. Plant tests included corrosion coupons and electrical resistance probes. The laboratory tests indicated that the combination of inhibitor and pH control at pH 9 provided adequate protection to carbon steel. It also suggested that pH control was critical, with the corrosion rate increasing by an order of magnitude at pH 7. The plant test results supported the laboratory data but showed that extended exposure to pH 9 fluid resulted in a steel surface that withstood short excursions to pH 7 without rapid corrosion.

2. New Processes

With a new process, there is no history of materials performance and no existing operating unit available for plant testing. Therefore, even if a pilot plant exists, laboratory testing is usually required to determine the relative performance of materials under the expected operating conditions. The exact conditions each unit will be exposed to may not be known. However, modern process simulation models can provide fairly accurate estimates of the actual operating conditions. Simulating these conditions in the laboratory may be quite another matter. From a practical standpoint, test media are usually restricted to raw materials, reaction products and various cuts from distillation processes. In some cases, one can test intermediate reaction products, but often these compounds are not stable. For more information on designing a test program for a new chemical process, see reference [8], which includes a list of corrosion testing standards by ASTM and other organizations.

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5

THE PROCESS OF MATERIALS SELECTION

In this chapter, a materials selection process is described, in which the materials selection template and its Notes addendum form the centerpiece. The process proceeds in three steps. In the first step, information about basic metallurgy, corrosion and degradation phenomena are collected and used to design templates and Notes addenda tailored to the specific needs of a plant. In the second step, materials of construction are selected. In the third step, the materials selection diagram is used to check for materials selection consistency and to document any special measures used for corrosion or degradation control.

A. DESIGNING A TEMPLATE

1. Introduction

A template should be as simple as possible. Creating an unnecessarily elaborate template is costly and will slow the process of materials selection. It is better to decide what information is necessary, then format the template to highlight the required information. After the template has been developed, it is good practice to ask that all requested information be provided, even if the answer is "Trace Amount," "Not Applicable," "per Code," etc.

Before designing a template, one should first identify any special requirements that will affect materials selection. Examples of such special requirements include unusual design life, product contamination concerns and

use of operating conditions rather than design conditions for materials selection. It is helpful to include such requirements in the Notes section of the template addendum.

To help decide what information should be requested in a template, review the discussions in Chapter 1 regarding template information. The threshold information necessary for developing the Notes section of the template addendum is available in Chapters 2 through 4, or from previous experience, plant or pilot plant testing, process licensors, the published literature or material manufacturers.

2. Customizing a Template

For small or uncomplicated jobs, using a simple template may be preferable to designing a customized template. For example, it is not worthwhile to develop a customized template for a job or project involving replacing or revamping a couple of vessels or a small piping system, or for a unit involving only a few, if any, corrosives. For such jobs, it is often adequate to use a rubber stamp template with a process flow diagram, to quickly create a materials selection diagram. This approach is illustrated in Example #1, at the end of the chapter (p. 235).

For jobs involving complex combinations of corrosives, crack-inducing agents, upset conditions and/or design conditions, a detailed template is usually required. Detailed templates, suitable for a refinery, are shown in Examples #2 and #3 at the end of the chapter (pp. 236 and 238). The template shown in Example #2 would be useful for a small job, while the spreadsheet template shown in Example #3 would be useful for larger jobs.

Many jobs will benefit from a job-specific customized template. The customized template should request information only about corrosives, crack-inducing agents and upset conditions known to be characteristic of the job. Example #4 (p. 240) is a template customized for an ammonia plant. Example #5 (p. 241) is a template that could be customized for a chemical plant that operates batch processes.

B. MATERIALS SELECTION STEPS

There are probably as many ways of using a material selection template to select materials as there are people charged with doing the job. What follows is one logical and efficient approach, using first a template, then the materials selection diagram for a consistency check.

As noted in Chapter 1, this book uses design conditions for materials selection. This practice has been adopted in the following discussions. In the

event that the reader uses operating conditions as the basis for materials selection, please substitute "operating" for "design," as appropriate.

The recommended procedure for selecting a material of construction is a two-stage, relatively straightforward process. In the first stage, a template is used to select a material of construction. The minimum design temperature is used to choose a material of adequate toughness. Then, the maximum design temperature is used to modify the selection, if necessary, to obtain satisfactory resistance to corrosion or to thermal degradation.

If an upgrade is necessary, one must iterate to ensure that the upgrade material has adequate toughness at the minimum design temperature. In many cases in which an upgrade becomes necessary, the upgrade candidates may actually consist of one or more families of materials such as high alloys or non-metallics. In such cases, it is necessary to evaluate alternatives before proceeding. The criteria used to evaluate alternatives will depend to a large extent on job or project objectives and constraints. Minimal cost, minimal maintenance, short schedule, extended design life and consequences of a leak or rupture are typical job objectives or constraints.

A checklist is then used to determine if special requirements such as postweld heat treatment, hardness controls, external coating, etc., are necessary. The final step is to ensure that the template is properly filled out and that the template contains all necessary special notes.

In the second stage, the materials selection information on the various templates is entered on a simplified process flow diagram (PFD), creating a materials selection diagram (MSD). The MSD is then reviewed for consistency. A checklist is used to determine if factors such as excessive pressure drop must be addressed.

C. MATERIALS SELECTION CRITERIA

While the normal criteria for materials selection address design life, there are other instances when other criteria govern. It is helpful to indicate these exceptions on the MSD and to provide notes to explain each exception. These notes should refer to items in the Notes section of the template addendum. Examples include product contamination and reliability.

1. Product Contamination

Many food, drug, polymer and fine chemical manufacturing processes are sensitive to corrosion-induced contamination. Such contamination may include flaking of scales such as mill scale. While carbon steels may have acceptably low corrosion rates, they often cannot be used because of concerns about iron

contamination. If product contamination is a materials selection criterion, indicate the areas of concern on the MSD.

A closely related consideration is corrosion debris in processes that are not otherwise sensitive to such debris. In some processes, downstream catalysts can be damaged by reactions with corrosion debris. Excessive debris can affect flow or heat transfer efficiencies or cause mechanical problems. The production of excessive corrosion debris depends primarily on the amount of surface area exposed to the process. Accordingly, components such as packed beds and the heat transfer surfaces of heat exchangers are the primary sources of such corrosion products. Even though the corrosion rate of the exposed material may be acceptably low from the standpoint of design life, the extensive exposed surface area is capable of rapidly generating a very large volume of corrosion products.

2. Reliability

Some systems are expected to have unusual reliability. An example is fire water systems, which must be capable of fast response and operation under severe conditions, including hydraulic surges and fire exposure. The latter is often cited as the reason for not using plastic or fiberglass piping in corrosive fire water systems. In other cases, reliability may not be very important, permitting the choice of less expensive materials of construction, for example, drain valves in low-pressure service.

Some users have design standards and materials selection limitations that may override materials selected in accordance with a template. Recall that some users forbid the use of galvanized steel where a plant fire could cause liquid zinc to drip onto austenitic stainless steel hydrocarbon piping, vessels or equipment. The recommendations of process licensors usually override selections made in accordance with a template. Normally, such recommendations are more conservative than those made in accordance with the template. Nevertheless, process licensor recommendations are subject to review for compliance with design life and safety requirements.

In selecting a material, it is often helpful to keep in mind what might be called the "common sense" of materials selection.

- Ease of maintenance, replacement and/or repairability of components should be evaluated. For example, consider a design that calls for 100 percent spares (e.g., one pump running, one on standby). In this case, ease of maintenance or replacement may permit the use of less expensive, or even nonrepairable, materials such as cast iron pump internals. In some cases, repairability may influence selection, such as the use of cast steel, which is repairable by welding, instead of cast iron.

- Plant experience is particularly useful in choosing appropriate materials of construction for processes for which there is no broad base of experience. Plant experience is also useful for selecting materials for water services. In some cases, plant experience may indicate that a lower grade of material is adequate in a service for which the available nomographs and corrosion charts indicate otherwise, for example, some high-temperature sulfur services in chemical and hydrocarbon plants.

For pilot plants or for plants utilizing new processes, materials selection may require a testing program. Refer to Chapter 4, "Corrosion Testing," for a discussion of this topic.

D. MATERIALS SELECTION PROCEDURE: EXCEPTIONS

The procedure used for materials selection is, for the most part, independent of the component. The primary exceptions are piping, pumps and fabricated equipment.

1. Piping

Materials selected for piping in mild to moderately corrosive services are sometimes less conservative than those for vessels, heat exchangers, tanks and pumps in the same services. In this case, piping materials may be chosen on the basis of a shorter design life. This is usually justified because piping is easier to inspect, both on line and off line. Also, piping is usually easier to replace and does not have the problem of long lead time often associated with fabricated equipment, vessels, etc.

2. Pumps

API Standard 610 "Centrifugal Pumps for General Refinery Service" [1] is a widely used guide for selecting materials for pumps. This standard provides guidance on materials selection for pumps in various hydrocarbon, chemical process and utility services. ASME B73.1M, "Specification for Horizontal End Suction Centrifugal Pumps for Chemical Processes," [2] and ASME B73.2M, "Specification for Vertical In-Line Centrifugal Pumps for Chemical Processes," [3] are normally used to specify pumps in chemical process plants. Neither of the latter specifications provides guidance on materials selection. However, some manufacturers of such pumps provide materials selection literature.

In processes expected to be mildly to moderately corrosive, it is not unusual to choose a pump metallurgy more conservative than the mating piping. This practice takes into account that high velocities and turbulence may accelerate corrosion rates.

When selecting materials for pumps, first determine if the pump will be operating continuously or intermittently and whether or not it will be spared. Less expensive materials can sometimes be specified for pumps that will be spared, because they can be withdrawn from service for repairs. Pumps expected to operate after being stagnant for long periods of time may require either upgraded materials or special layup procedures that control corrosion.

3. Fabricated Equipment

Fabricated equipment such as blowers, turbines, lube oil skids, etc. is usually ordered as "Manufacturer's Standard" for the intended service. Other "standard equipment," such as valves and pumps, is also usually supplied with "off-the-shelf" materials of construction. Most often, any deviations in materials proposed by the fabricator or supplier will exceed the minimum material of construction selected in accordance with the template. However, the proposed materials should be reviewed for compliance with template requirements, including any special fabrication specifications such as NACE MR0175 [4] and safety and design life requirements.

In reviewing a proposed materials list, it is normal to make sure that the proposed materials will be suitable for the corrosive and crack-inducing agents present in the process. However, do not forget to check for suitability for low- and/or high-temperature service, including excursions, if applicable.

Some pieces of equipment such as separators, distillation towers and heat exchangers can be characterized by two or more sets of process conditions. In such cases, it is useful to use more than one template for the piece of equipment.

- For shell and tube heat exchangers, use one template for the shell side and another for the tube side.
- For separators and distillation towers, use one template for the overhead section and another for the bottoms section. For distillation towers with multiple feeds and/or draws, multiple templates are usually necessary.

E. MATERIALS SELECTION PROCEDURE

The first step in the normal procedure of materials selection is to consider the effect of the design temperatures.

1. Low-Temperature Toughness

Consider the minimum design temperature. Be sure that the upset conditions listed in the template have been considered in establishing the minimum design

temperature. Use Figure A1-1 and Table A1-1 (pp. 297 and 298, respectively) to help select the preliminary minimum acceptable material. Keep in mind the minimum code requirements for Charpy impact testing. As the template information is subsequently reviewed for the effects of corrosion, crack-inducing agents, embrittlement, etc., make sure that any changes made will retain compliance with the low-temperature requirements.

There is no good rule of thumb to use in determining "low-temperature" service for vessels, heat exchangers, etc., since the impact testing rules of ASME Section VIII, for both Divisions 1 and 2, [5] are complicated. If there is any indication that "low-temperature" service may require impact testing, probably the most effective procedure is to make notes on the template and the MSD to that effect. This will help to alert design engineers, via equipment data sheets, that low-temperature requirements will have to be addressed.

The piping Code, ASME B31.3 [6], specifies low-temperature toughness requirements that are more inflexible than those of the conventional vessel codes (ASME Section VIII, Div. 1 and 2 [5]). The latter codes are a good deal more complex and flexible than is the piping code. This can lead to odd combinations of materials selected for a plant that is exposed to low-temperature operation. For example, in a gas plant subject to autorefrigeration, ASME Section VIII, Div. 1 carbon steel vessels may be permitted at temperatures as low as -150°F (-100°C), without impact testing. The associated piping, chosen to conform to the impact testing requirements of the piping code, will probably be specified to be an austenitic stainless steel.

2. High-Temperature Degradation

The preliminary material of construction should be checked against the maximum design temperature for the risk of thermally induced degradation:

- Is it susceptible to thermally induced embrittlement or thermal degradation which could cause failure during high-temperature service? Examples: creep embrittlement and spheroidization or graphitization.
- Will sustained operation at the maximum design temperature cause the material to be brittle at lower operating temperatures? Example: sigma phase embrittlement of stainless steels.
- Will sustained operation at the maximum design temperature cause the material to be susceptible to corrosion at lower temperatures? Example: polythionic acid attack of stainless steels.

Upgrade the material as necessary, making sure that the upgraded material has adequate toughness at the minimum design temperature. The suitability of the upgraded material for the anticipated corrosion/degradation environment

will be evaluated later. If sustained operation at the maximum design will cause the material to be brittle at lower operating temperatures, the design engineer should be advised to prepare appropriate operating instructions.

At this point, one should ensure that the candidate material of construction is adequate for the anticipated external environment. For example, external chloride stress corrosion cracking, induced by a marine atmosphere, may be a concern.

3. Grouping Process Regions

When different sections of the process stream are exposed to essentially the same environment, it is possible to save some time by grouping them together for the purpose of materials selection. It is expected that piping and equipment items in each of these sections should have similar materials requirements, when allowances are made for the specific requirements of each type of equipment. Care should be taken to ensure that common materials selection criteria are uniform with respect to upset and transient conditions. In the following example, which is for a refinery, the process stream templates are divided into four types of commodities:

- *Hydrogen and hydrogen mixtures:* either pure hydrogen gas or commodities that are mixtures of hydrogen gas with other components, such as hydrocarbons.
- *Hydrocarbons:* commodities that are hydrocarbons or mixtures of hydrocarbons with other materials such as water, hydrogen, or steam.
- *Non-corrosive gases:* commodities such as nitrogen and dry plant air at ambient temperature.
- *Other services:* commodities such as amines, cooling water, fire water and chemicals such as sulfur, caustics, acids, and oxidants.

4. Corrosion

The maximum design temperature should be used as follows for assuring corrosion resistance.

Hydrogen and Hydrogen Mixtures

Check all hydrogen services, including any mixtures of hydrogen with other commodities, against the Nelson curves [7] (see Appendix 4). Establish the minimum acceptable material, using the maximum design temperature or the maximum operating pressure plus a design margin (usually 25 or 50°F (14 or 28°C)). The material selected will be the minimum acceptable material for pressure containment. The hydrogen partial pressure, needed for using the

Nelson curves, should be based on the maximum anticipated hydrogen mole fraction in the vapor phase.

Hydrocarbons

Consider all streams containing either sulfur and/or hydrogen sulfide. If the maximum temperature exceeds 500°F (260°C), use either the McConomy [8] (see Appendix 5) or Couper-Gorman [9] (see Appendix 6) curves to select the minimum acceptable material. When using the Couper-Gorman curves, remember to choose the curve (either naphtha or gas oil diluent) most similar to the process stream hydrocarbon.

In the event that an 18Cr-8Ni SS is indicated, select a stabilized grade (e.g., Type 321 SS) if the design temperature exceeds 800°F (425°C).

If naphthenic acid attack is probable, Type 316 SS or Type 317 SS (L grade if it is to be welded) or Type 316Ti (for plate and plate products) should be selected. In the Notes section of the template, ensure that the Mo content of the Type 316 grades is not less than 2.5 wt. percent. Also, include a note to ensure that:

- For Types 316 and 316L, the design includes provision to exclude air and/or liquid water during shutdown or
- The operating manual includes instructions regarding a neutralizing wash during the front end of a shutdown. Refer to NACE RP0170, "Protection of Austenitic Stainless Steel from Polythionic Acid Stress Corrosion Cracking During Shutdown of Refinery Equipment," [10].

If hydrogen is involved in the process, the material selected for resistance to sulfur must also meet the minimum requirements for hydrogen service, in accordance with the Nelson curves. In many cases, combined hydrogen-sulfur or hydrogen-hydrogen sulfide service will require cladding or overlays, to provide combined corrosion/hydrogen resistance at an affordable cost.

Review the remainder of the hydrocarbon services. Carbon steel will be selected in most cases, with the major exception being for services with maximum design temperatures exceeding 800°F (425°C).

For low-pressure applications such as decoking, it is not unusual to use carbon steel up to 1000°F (540°C) despite its tendency to graphitize at temperatures exceeding 800°F (425°C). Recall that killed carbon steel has a larger maximum code-allowable stress at temperatures above 900°F (480°C) and that silicon-killed carbon steels are preferred for temperatures above 800°F (425°C).

In some low-pressure services with intermittent excursions to temperatures exceeding 1000°F (540°C), carbon steel is chosen, usually with the expectation of early replacement.

For higher pressure applications, the minimum acceptable material is 1¼Cr-½Mo. For temperatures in excess of about 1050°F (565°C), a higher chromium alloy is required.

Recall the beneficial effects of external insulation and jacketing and internal refractory lining in using steel and alloys above their oxidation threshold temperatures.

Non-Corrosive Gases

Carbon steel is the normal material of construction for non-corrosive gases.

Other Services

- **Chemicals.** Refer to Chapter 3, "Failure Modes," for guidance on materials selection for the commonly encountered chemicals. For other chemicals, refer to the available literature and:
 - **Proprietary technologies:** follow the guidance of the process licensor. Such guidance should always be subject to review for compliance with safety and design life requirements.
 - **Plant experience:** in some cases, the user will specify materials based on plant experience or pilot plant testing.
- **Water services.** There is extensive literature available on various water services. Whenever possible, it is best to start with plant history, utilizing the same or similar water chemistries. Note that for maximum design temperatures up to about 200°F (93°C), paint coatings may be useful in the control of corrosion in immersion service.

If corrosion concerns require a material upgrade, make sure that the upgraded material has adequate toughness at the minimum design temperature. If the upgrade involves evaluating one or more families of materials, make sure that the job or project objectives and constraints are considered. As mentioned previously, these considerations may include minimal cost, minimal maintenance, short schedule, extended design life, or consequences of a leak or rupture. Complete the evaluation and choose a candidate material before proceeding.

5. Upset Conditions

Finally, check the template for upset conditions, to make sure that all relevant upset conditions have been evaluated.

6. Review

Several items of concern should then be reviewed, as follows:

- Review all material selections for high-temperature services in order to avoid oxidation, scaling or spalling problems for temperatures greater than 1000°F (540°C). Figure A1-1 (p. 297) in Appendix 1 is useful for

evaluating such problems. This figure is also useful for evaluating various forms of thermally induced embrittlement for temperatures exceeding 700°F (370°C).

- For carbon steel in hydrogen stress cracking services, determine if heavy section/sharp thickness gradients such as thick nozzles will be required. These gradients may indicate a need for HIC-resistant plate and postweld heat treatment to prevent SOHIC. Determine where HIC-resistant plate is to be used for vessels, heat exchangers and/or piping. Determine if normalizing and postweld heat treatment should be specified.
- Review all carbon steel templates for which postweld heat treatment was indicated. Consider the maximum operating pressure. If it is less than 65 psia (0.45 MPa) or if the combined stress in tension is less than that indicated by the ten percent rule, postweld heat treatment may be unnecessary.

Corrosion allowance is probably unnecessary for pressures less than 65 psia (0.45 MPa), particularly for piping.

- Consider recommending the use of "L" grades if non-stabilized austenitic stainless steels have been recommended and they require welding as part of the fabrication process. This will minimize potential problems caused by sensitization; in addition, the "L" grades are easier to weld.
- For fired heaters, make sure that the fire-side tube metal temperature was considered in materials selection. In the absence of better information, assume that the fire-side tube metal temperature is 100°F (38°C) higher than the process temperature. If necessary, make a note on the template to ensure that creep is accommodated during design of heater tubes, in accordance with API 530 [11]. Recall that process stream temperatures, not tube metal temperatures, are used for heater evaluation per the McConomy curves.
- For all heat exchangers, evaluate the effect of leaks that permit mixing of the non-process side with the process side. In some processes, leaks will require an immediate shutdown. In such cases, an upgrade in materials may be justified. In addition, evaluate the potential effects of a loss of flow on both the non-process and process sides. If such events are regarded as likely, an upgrade in materials may be required.

For shell-and-tube heat exchangers, make sure that the front- and backside metallurgies and corrosion allowances of the tubesheet(s) are consistent with the channel and shell processes, respectively.

- Compile the appropriate corrosion notes in the Notes section of the template:
 - Where galvanic couples or alloy crevices are exposed to electrolytic corrosion, consider the need to provide cathodic protection, for example, at tube-to-tubesheet joints in heat exchangers.

- For austenitic stainless steels exposed to chloride-bearing external environments, consider the need to require external coatings to prevent stress corrosion cracking or heat affected zone pitting, as necessary.
- Where an alternate process may provide better or more economical service, indicate the alternative, for example, steam tracing to keep water from condensing in a carbon steel line containing CO₂, versus using austenitic stainless steel as the material of construction. Such notes should be discussed with process engineers or designers during subsequent review(s) of the materials selection diagram.
- For processes in which hydrogen stress cracking may occur, consider such concerns as weld joints having significantly mismatched component thicknesses. Joints such as tray attachment welds and tube-to-tubesheet welds could have excessive weld metal and HAZ hardnesses.
- Indicate special corrosion-based requirements such as:
 - Hardness limits in accordance with NACE MR0175 [4] and NACE RP0472 [12] for hydrogen stress cracking services.
 - Paint/coating requirements for insulated piping and equipment or buried piping.
 - Paint/coating and cathodic protection for submerged or buried structures or piping.
 - Coatings/cathodic protection for the internal surfaces of tanks or vessels in corrosive service.
- Complete the final steps in the materials selection process:
 - For each template, make sure that the metallurgy, valve trim, postweld heat treatment and corrosion allowance requirements are filled in. Recall that the specification of valve trim is usually required only for piping.
 - Use the Notes section on the template to indicate special requirements such as inspection categories, positive material identification, special flange-face machined finishes, etc.
 - Specify postweld heat treatment in the template only if required by the process, for example, for carbon steel in amine service. If postweld heat treatment is not required for process reasons, indicate "per Code."

F. MATERIALS SELECTION DIAGRAM

Obtain a simplified process flow diagram (PFD). It need not contain detailed process data; however, all piping and equipment for which templates have been

generated, should be indicated on the simplified PFD, using the same stream numbers and equipment designations utilized on the respective templates. It is helpful if the simplified PFD shows design temperatures and pressures for all piping and equipment. It is also helpful if the simplified PFD incorporates the templates or includes them as attachments.

Enter the preliminary material selections on the simplified PFD, along with corrosion allowances. Use arrows with legends, color codes or some other method to identify the material/corrosion allowance for each pipe run and piece of equipment. Refer to Examples 16 through 19 (pp. 259–262) in the Supplement for an illustration of a materials selection diagram and how it is generated. This generates the materials selection diagram. The MSD is useful for several activities, including the following:

- Compare the metallurgies and corrosion allowances of the incoming and outgoing lines for each piece of equipment versus the equipment metallurgy and its corrosion allowance. This is done as a consistency check. Highlight any inconsistencies for later resolution.
- If materials selection depends on corrosion control by chemical treatment or wash water injection, indicate the position of the injection points and the type of chemical to be injected. Examples include corrosion inhibitors, scale inhibitors, biocides, and pH control chemicals. Also indicate the location of proposed corrosion monitoring and sampling sites.
- If degradation processes such as high temperature embrittlement or autotrefrigeration will affect operating procedures such as pressurization during startup, indicate such limitations as general notes to the MSD.
- Check for large pressure drops such as can occur at control valves.
 - Determine if pressure drops will induce corrosive flashing. Flash spools (usually about 10' long, of a corrosion resistant alloy) should be specified downstream of the affected control valve.
 - When the pressure drop is directly into a vessel, a corrosion-resistant alloy impingement plate (sometimes called a splash plate) may be necessary.
- Indicate convenient specification breaks. Specification breaks are points where the materials of construction change from one type to another.
- Indicate the need for check valves, to protect upstream piping and equipment from damage by corrosive reverse flows. Note that, in most cases, an upgrade of the upstream piping is less expensive than a corrosion-resistant alloy check valve.

If review of the MSD causes any changes in the templates, make sure that the changes are documented.

G. CONCLUSIONS

The procedure we have discussed should not be viewed as a "cookbook" process. Heavy reliance on prior plant experience should always be part of the process of materials selection. Common sense should always play a role in evaluating various candidate materials. This means that time must be taken to determine the leeway provided by ease of maintenance, repairability and sparing. In some cases, these considerations may require upgrading of the materials or fabrication procedures (e.g. postweld heat treatment). In other cases, it may make sense to recommend changes in the design conditions or in the process itself, in order to specify a lower-cost or more reliable material. Finally, unusual project conditions, such as an anticipated short design life or concern about product contamination, will often lead to non-conventional material selections.

Sometimes the user will want to pursue a more conservative course and will demand a more expensive material or material processing that exceeds the minimum requirements, for example, postweld heat treatment when it is not otherwise required by the construction code and is not justified by the process. Once the user understands the reasons for the recommended material or material processing, the issue becomes a management decision.

Occasionally, the user will demand the use of a material that will not meet the minimum requirements. In this situation, safety and design life requirements as well as potential consequences should be reviewed and the results documented to the user.

Finally, new materials and materials technologies are continually coming into the market. In some cases, conditions will encourage their use on a prototype basis. However, experience with prototype technologies strongly suggests that it is best to let someone else be the first to try them out. Correcting mistakes is difficult and costly. The best approach is always to take the time to do it right the *first* time.

Example #1: Simplified Template

Operating Temperature (Minimum/Maximum): _____

Operating Pressure (Minimum/Maximum): _____

Commodity: _____ Phases: _____ Liquid Water (Y/N): _____

Corrodents: _____

Crack-Inducing Agents: _____

Metallurgy: _____

PWHT (Y/N): _____ Valve Trim: _____ Corrosion Allowance: _____

Notes: _____

Example #2: General Template for a Refinery

Stream or Equipment Number: _____

Design Temperature (Minimum/Maximum): _____

Design Pressure (Minimum/Maximum): _____

Commodity: _____ Phases: _____ Liquid Water (Y/N): _____

Corrodents: ¹ _____Crack-Inducing Agents: ² _____

Upset Conditions: _____

Liquid Water (Y/N): _____

Corrodents: ¹ _____Crack-inducing Agents: ² _____

Autorefrigeration (Y/N): _____

If Yes, indicate minimum temperature: _____

Other: _____

Wet Sour Service (Y/N): _____

If Yes, indicate severity: _____

Metallurgy: _____

PWHT (Y/N): _____ Valve Trim: _____ Corrosion Allowance: _____

Notes: _____

¹Corrodents. Indicate:

- Concentrations of acidic components (only if liquid water or other electrolyte is present):
 - Inorganic or organic acids: in wt. percent (indicate Total Acid Number if naphthenic acid is present).
 - Acid gases such as H₂S, NO₂, SO₂ and CO₂: in mole percent if in vapor and wt. percent if dissolved in water.
 - Acid salts such as ammonium bisulfide or ammonium chloride, if present at greater than 2 wt. percent: in wt. percent.
 - Anticipated pH.

- Oxidants such as oxygen and chlorine: in wt. percent.
- Other corrodents suspected of being significant, such as dissolved oxygen content in water or microbiological agents.
- Total sulfur:
 - As wt. percent sulfur, only if T > 500°F (260°C) and the hydrogen partial pressure is less than 50 psia (0.34 MPa).
 - As mole percent H₂S, only if T > 500°F (260°C) and the hydrogen partial pressure 50 psia (0.34 MPa) or greater.

²Crack-inducing agents (list only if liquid water or other electrolyte is present (except for H₂)); indicate concentration of the following agents, if present above their threshold concentrations):

- Amines: present at greater than 2 wt. percent: in wt. percent.
- Carbonates and bicarbonates when the concentration of either or both (combined) exceeds 1 wt. percent: in wt. percent.
- Hydrogen, when partial pressure is 100 psia (0.69 MPa) or greater: in either mole percent or partial pressure in psia (MPa or kPa).
- Chlorides, in any concentration: in ppmw.
- Cyanides, if present at greater than 20 ppmw: in ppmw.
- NaOH, in any concentration if T > 115°F (46°C): in wt. percent.
- Hydrogen sulfide:
 - Gas phase, if the partial pressure of H₂S exceeds 0.05 psia (0.34 kPa): in either mole percent or partial pressure in psia (MPa or kPa).
 - Sour water, if the concentration of H₂S dissolved in water is at least 50 ppmw: in ppmw.
- Other known crack-inducing agents (e.g., HF).

Example #3: General Template for a Refinery

			Stream number		
Stream Description	Units	Reference	1	2	Etc.
Commodity					
Phase: Liq/Vap/Solids	L/V/S				
Design Temperature Min/Max	°F				
Design Pressure Min/Max	psig				
Operating Temp Normal/Min/Max	°F				
Operating Pressure Normal/Min/Max	psig				
Fluid Velocity	ft/sec				
Free Water Yes/No		Note 5			
Crack-Inducing Agents		Note 4			
Chloride	ppmw	Note 4			
Cyanide	ppmw	Note 4			
Hydrogen (partial pressure)	psia	Note 4			
Hydrogen Sulfide	Note 4	Note 4			
Amine	wt. %	Note 4			
NaOH or Other Caustics	wt. %	Note 4			
Other		Note 4			
Corrodents		Note 3			
Sulfur	Notes 1&2	Notes 1&2			
Acids	wt. %				
Acid Gases	mole %				
Acid Salts	wt %				
pH					
Other		Note 3			
Upset Conditions		Note 6			
Wet Sour Service	yes/no				
- If Yes, Simple or Severe					
Metallurgy		Note 7			
Corrosion Allowance	inch				
Valve Trim					
Notes					

Notes for Example #3 Template

¹Indicate in wt. percent, only if T > 500°F and the hydrogen partial pressure is less than 50 psia (0.34 MPa).

²Indicate in mole percent, only if T > 500°F and the hydrogen partial pressure is at least 50 psia (0.34 MPa).

³Corrodents. Indicate:

- Mole percent of acidic corrodents such as inorganic or organic acids and acid gases such as H₂S, NO₂, SO₂ and CO₂. Indicate Total Acid Number if naphthenic acid is present.
- Wt. percent of acid salts, if present at greater than 2 wt. percent such as ammonium bisulfide or ammonium chloride.
- Wt. percent of oxidants such as oxygen and chlorine.
- Other corrodents suspected of being significant such as dissolved oxygen content in water or microbiological agents.

⁴Crack-inducing agents (list only if liquid water or other electrolyte is present (except for H₂)); indicate concentration of the following agents, if present above their threshold concentrations):

- Hydrogen, if partial pressure exceeds 100 psia: in either mole percent or partial pressure in psia.
- Amines, if present at greater than 2 wt. percent: in wt. percent.
- Carbonates and bicarbonates, when the concentration either or both (combined) exceeds 1 wt. percent: in wt. percent.
- Chlorides, in any concentration: in ppmw.
- Cyanides, if present at greater than 20 ppmw: in ppmw.
- NaOH, in any concentration, if T > 115°F: in wt. percent.
- Hydrogen sulfide:
 - Gas phase, if the partial pressure of H₂S exceeds 0.05 psia: in either mole percent or partial pressure in psia.
 - Sour water, if the concentration of H₂S dissolved in water is at least 50 ppmw: in ppmw.
- Other known crack-inducing agents (e.g., HF).

⁵Include indication of liquid water, for normal operation.

⁶For upset conditions, indicate autorefrigeration, liquid water, wet sour service, carryover of crack-inducing agents or corrodents, etc. Consider startups, shutdowns, regeneration, presulfiding, loss of flow, etc.

⁷Provide metallurgy in generic form (e.g., CS, 18Cr-8Ni SS, 3Cr-1Mo, etc.).

Example #4: Ammonia Plant Template

Stream or Equipment Number: _____

Design Temperature (Minimum/Maximum): _____

Design Pressure (Minimum/Maximum): _____

Commodity: _____ Phases: _____ Liquid Water (Y/N): _____

Corrodents¹: _____Crack-Inducing Agents²: _____

Upset Conditions: _____

Liquid Water (Y/N): _____

Corrodents¹: _____Crack-Inducing Agents²: _____

Autorefrigeration (Y/N): _____

If Yes, indicate minimum temperature: _____

Other: _____

Metallurgy: _____

PWHT (Y/N): _____ Valve Trim: _____ Corrosion Allowance: _____

Notes: _____

¹ Corrodents (only if liquid water or other electrolyte is present).

- Indicate wt. percent for any acids.
- Indicate partial pressure for wet CO₂.
- Be alert to the danger of metal dusting in hot, high-alloy streams with CO/CO₂ ratios greater than 0.5.

² Crack-inducing agents (list only if liquid water (or other electrolyte) is present (except for NH₃ and H₂); indicate concentration of the following agents, if present above their threshold concentrations).

- Anhydrous ammonia: water content in wt. percent. 0.1 wt. percent water is required to inhibit stress corrosion cracking in carbon steel. Note that inhibition will be ineffective in vapor spaces.
- Hydrogen, if the partial pressure is 100 psia or greater.
- In lines and equipment in the CO₂ recovery unit: in wt. percent caustic or wt. percent amines.
- Chlorides, any concentration: in ppmw.

Stream or Equipment Number: _____

Step:^a _____

Mechanical Design Conditions:

	Operating		Design	
	Low	High	Low	High
Temperature:	_____	_____	_____	_____
Pressure:	_____	_____	_____	_____

Process Chemistry:

- Chemicals Present:^b _____
- Phases Present: _____
- Corrodents Present:^c _____
- Crack-Inducing Agents Present:^d _____

Upset Conditions:^e _____

Material of Construction: _____

PWHT: _____ Corrosion Allowance: _____ Valve Trim: _____

Notes: _____

^a For batch processes, a template must be prepared for each step in the process. Indicate the step for which the template is intended.^b 1. List all chemicals present. Include contaminants and impurities as well as the major constituents.

2. Indicate if the process fluid is an electrolyte. If not, are other electrolytes present?

^c Indicate which chemicals are known corrodents.^d Indicate which chemicals are known crack-inducing agents.^e Describe the nature and duration of possible anticipated upset conditions. Consider whether the upset conditions are for start-of-run, end-of-run or both, or whether they will occur during the run. For each upset condition, indicate the presence of corrodents, crack-inducing agents or electrolytes introduced because of upset conditions. For autorefrigeration, indicate the anticipated minimum temperature.

REFERENCES

1. *Centrifugal Pumps for General Refinery Service*, API Standard 610, API, Washington, D.C. (latest edition).
2. *Specification for Horizontal End Suction Centrifugal Pumps for Chemical Processes*, ASME B73.1M, American Society of Mechanical Engineers, New York (latest edition).
3. *Specification for Vertical In-Line Centrifugal Pumps for Chemical Processes*, ASME B73.2M, American Society of Mechanical Engineers, New York (latest edition).
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SUPPLEMENT

Examples

The following examples are offered to illustrate how the materials selection process works. Recall that the process is aimed at specifying the minimum cost material that will meet all of the requirements of the template.

A. HYDROCARBON PROCESSES

The first ten examples involve hydrocarbon processes. The template shown in Example No. 2 in Chapter 5 (p. 236) will be used to illustrate how to use templates for hydrocarbon processes. It is worthwhile to review this template example in Chapter 5, including the notes to the template.

Example #1

Process Data

This piping run is in sour wash water service. It contains no other crack-inducing agents and has no upset conditions. These data, as well as design data, are listed in Template #1 (p. 265).

Materials Selection

While the H_2S concentration exceeds the threshold for sour water service, the maximum design pressure is less than the 65 psia threshold set by NACE MR0175. Thus, this is a low-risk service. Carbon steel is the recommended material of construction, with 12 Cr valve trim. The service is moderately corrosive, so the recommended corrosion allowance is $\frac{1}{8}$ ".

Question: What would change if the maximum design pressure were 75 psig?

Answer: Refer to Template #1a (p. 266).

- Wet Sour Service: Yes (Simple Wet Sour Service)
- Notes: NACE MR0175/RP0472

Example #2

Process Data

This is a horizontal gas/oil separator vessel. The commodity is sour crude oil along with associated gas. The gas phase contains 3 mole percent each of CO_2 and H_2S . The oil phase contains emulsified water, which is about 25 percent salt. The system contains no other corrodents or crack-inducing agents. Shutdown, when water can condense from the vapor phase, is an upset condition. These data along with the design pressures and temperatures are indicated in Template #2 (p. 267).

Materials Selection

During operation, the system is essentially noncorrosive because of:

- The water being tied up in an emulsion, with the oil phase an effective corrosion inhibitor. Accordingly, Template #2 does not show water as a separate phase during normal operation.
- The hydrogen sulfide quickly developing a protective sulfide film on exposed carbon steel.

However, during shutdown, water will condense from the vapor phase, creating a simple wet sour service. Therefore, the indicated material of construction is killed carbon steel. The service is moderately corrosive, so the recommended corrosion allowance is $\frac{1}{8}$ ". NACE MR0175 and RP0472 apply.

Example #3

Process Data

This line is in rich diethanolamine (DEA) service, having absorbed H_2S . It contains no other crack-inducing agents and has no upset conditions. These

data, as well as the design pressures and temperatures, are listed in Template #3 (p. 268).

Materials Selection

This line is in severe wet sour service. It contains an additional cracking agent which alone would require postweld heat treatment. The recommended material of construction is carbon steel. In accordance with MR0175, the material must be either hot rolled or otherwise heat treated. Normalizing is the conventional heat treatment. Postweld heat treatment is required. NACE MR0175 and RP0472 should be required. If the pipe to be used is made from welded plate, the plate should be resistant to hydrogen induced cracking (HIC). Recall that velocities should be limited to 6 ft/sec (2 m/s) for carbon steel in rich amine services. Rich amine is normally considered to be a corrosive service, with a recommended corrosion allowance of $\frac{1}{4}$ ". If inhibitors are used, consider recommending a corrosion allowance of $\frac{1}{8}$ ".

The recommended valve trim is Type 316 SS, because of the amine service.

Question: What changes would occur for a maximum design pressure of 15 psig?

Answer: Refer to Template #3a (p. 269).

This line would be classified as a low-risk service. NACE MR0175/RP0472 would no longer apply. However, because this is an amine service, i.e., a crack-inducing service, considerations other than wet sour service may govern.

The pressure stresses are very likely too low to permit crack propagation, although crack initiation could still occur. This should result in a leak-before-break condition. If the combined stress in tension can be shown to be less than ten percent of the specified minimum tensile strength, hardness controls (NACE MR0175/RP0472), mill heat treatment, postweld heat treatment and hydrogen induced cracking resistance should not be required. If capital cost is a major criterion, the following changes should be discussed:

- Wet Sour Service: No (Low-Risk Service)
- Metallurgy: Carbon Steel
- Postweld Heat Treatment: per Code. Note that API Publication No. 945, "Avoiding Environmental Cracking in Amine Units," does not cite a pressure threshold below which postweld heat treatment is unnecessary.

Example #4

Process Data

This is a liquid petroleum gas line. It contains neither corrodents nor crack-inducing agents. It normally operates at 105°F (40°C) and is to be uninsulated. It

can autorefrigerate to -65°F (-54°C). These data and the design data are listed in Template #4 (p. 270).

Materials Selection

Carbon steel is the preferred material of construction, if it can be qualified by impact testing. The ASME B31.3 piping Code requires impact testing for carbon steels intended for services colder than -50°F (-46°C). However, such pipe would be special order, since standard ASTM grades of carbon steel pipe are not supplied with mill testing at temperatures colder than -50°F (-46°C). Unless a long lead time is available, this option is probably not practical.

Using Table A1-1 (pp. 298–300), the conventional choice would be 3½ Ni (see ASTM A333 Gr 3), which is mill impact tested at -150°F (-101°C). Type 304 SS is an alternative material, although more expensive, if schedule problems develop with the 3½ Ni material.

No corrosion allowance is necessary, as there are no process corrodents and there is no concern about corrosion under insulation. Occasional autorefrigeration episodes will not affect either internal or external corrosion. The recommended valve trim is Type 316 SS because of the low temperature toughness requirement. Type 304 SS, which is cheaper, would work as well but is usually not as readily available.

Question: What would change if this were a vessel rather than a piping run?

Answer: Refer to Template #4a.

If this were an ASTM Section VIII, Div. 1 vessel, carbon steel might be exempt from impact testing. The rules of this Code are a good deal more flexible than those of the piping Code. If impact testing were to be required, suitable plate materials are readily available (see Table A1-1 for recommendations).

Example #5

Process Data

This is a furnace inlet line containing approximately 95 mole percent hydrogen and 5 mole percent hydrocarbon. It contains no corrodents and no crack-inducing agents other than hydrogen. It has no upset conditions. These data as well as the design pressures and temperatures are listed in Template #5 (p. 272).

Materials Selection

This line is not subject to hydrogen damage, according to the Nelson curves (see Appendix 4) because the hydrogen partial pressure is too low. However, since the maximum design temperature exceeds the threshold for the spheroidization and graphitization of carbon steel, 1¼Cr-½Mo is the recommended material of

construction. 12Cr valve trim is recommended. No corrosion allowance is necessary, since no corrodents are present. With no risk of damage from the hydrogen gas, and in the absence of other crack-inducing agents, the process does not require postweld heat treatment.

In view of the relatively low pressure in this service, carbon steel is a low-cost candidate material. It will slowly deteriorate due to spheroidization and graphitization, but it will not creep, since the applied stresses can be kept below the stress rupture value. In this leak-before-break situation, carbon steel would probably be a safe choice. Extensive plant experience indicates virtually indefinite service life under such circumstances. This option should be presented to the user for consideration.

Question: What changes would occur if the maximum design temperature were 1050°F (565°C)?

Answer: Refer to Template #5a (p. 273).

Carbon steel would not be a candidate, as the maximum design temperature exceeds the oxidation threshold. While external insulation may mitigate such oxidation, the service life could be quite short due to spheroidization and/or graphitization. 1¼Cr-½Mo has adequate oxidation resistance [see Table A1-2 (p. 301) in Appendix 1] and is resistant to spheroidization and graphitization.

Question: What changes would occur if the maximum design pressure was 500 psig?

Answer: Refer to Template #5b (p. 274).

- Metallurgy: Carbon steel would no longer be a candidate, as it would be ruled out by the Nelson curves (see Appendix 4). 1¼Cr-½Mo is permitted by the Nelson curves.
- Postweld Heat Treatment: Yes (for all Cr-Mo alloys in hydrogen service).
- Notes: NACE MR0175; weld metal: 225 BHN, maximum, due to hydrogen service.

Example #6

Process Data

This pump suction line conveys hot sulfur-containing liquid hydrocarbons. It has no other corrodents or crack-inducing agents. It has no upset conditions. These data and the design pressures and temperatures are indicated on Template #6 (p. 275).

Materials Selection

The McConomy curves (see Appendix 5) indicate that 5Cr-½Mo is required. The indicated corrosion rate is about 8 mpy. For 10-year life, a corrosion allowance of

$\frac{1}{8}$ " is appropriate. The recommended valve trim is 12 Cr. In the absence of crack-inducing agents, the process does not require postweld heat treatment.

Note the low maximum design pressure. The thickness of the line is essentially all corrosion allowance. It is doubtful that a formal corrosion allowance would begin to contribute to the life of the line until probably after 20 years of service. Even carbon steel in this service would last a minimum of 5 years without any formal corrosion allowance.

Example #7

Process Data

This is a reactor feed line containing hydrocarbon gas, hydrogen (82 mole percent) and a small amount of hydrogen sulfide (0.82 mole percent). It has no other crack-inducing agents. The only upset condition is shutdown, when liquid water can condense in the presence of H_2S . These data and the design pressures and temperatures are listed in Template #7 (p. 276).

Materials Selection

Although the Nelson curves (see Appendix 4) would permit 2½Cr-1Mo, the Couper-Gorman curves indicate corrosion rates too high for carbon and low-alloy steels. Refer to Appendix 6 for use of the Couper-Gorman curves; for this example, use the naphtha curves. Therefore, an 18Cr-8Ni stainless steel is required. Given the risk of polythionic acid attack, a stabilized grade (either Type 321 or Type 347 SS) is recommended. Valve trim is recommended in the same materials.

This is a simple wet sour service. Because the service is wet sour, NACE MR0175 applies. Purging this line prior to shutdown will avoid exposure to wet sour conditions.

In general, postweld heat treatment is not a process requirement for stainless steels. Components that have been substantially cold worked should be subsequently solution annealed.

Corrosion allowance: the estimated corrosion rate is about 1.5 mpy. The smallest practical corrosion allowance is $\frac{1}{16}$ ", far more than is necessary. Since piping usually has a large inherent corrosion allowance, it is reasonable to recommend zero corrosion allowance. See the discussion of piping corrosion allowance in Chapter 3 (p. 201).

Question: What changes would occur if naphthenic acid were present?

Answer: Refer to Template #7a (p. 277).

Either Type 316 or Type 317 SS would be recommended. The notes section of the template should indicate that Type 316 SS must contain at least 2.5 wt. percent

molybdenum. The notes must also indicate that polythionic acid attack will have to be prevented by operating controls per NACE RP0170.

Example #8

Process Data

This vessel is a hydrotreater reactor. Feed is a hot, light hydrocarbon mixed liquid-vapor plus hydrogen gas (76 mole percent in the vapor phase). The feed is sour, with 2.85 mole percent H_2S in the vapor phase. The process stream contains no other crack-inducing agents or corrosives. Shutdown is an upset condition, as liquid water can condense in the presence of hydrogen sulfide. These data as well as the design pressures and temperatures are listed in Template #8 (p. 278).

Materials Selection

The Nelson curves (see Appendix 4) indicate that the minimum material required for the pressure shell is 1¼Cr-½Mo. Creep embrittlement should not occur, since the maximum design temperature (800°F (425°C)) is less than the creep embrittlement threshold temperature. Hydrogen service indicates weld metal hardness controls and postweld heat treatment. Postweld heat treatment is recommended for all Cr-Mo steels in hydrogen service.

The exposure of the 1¼Cr-½Mo material to high-pressure, high-temperature hydrogen could lead to hydrogen embrittlement. It is conventional in such cases to ensure that the operating manual states that the vessel will not be pressurized at temperatures less than about 250°F (120°C). Above this temperature, hydrogen embrittlement is not a concern.

The Couper-Gorman curves indicate that an 18Cr-8Ni stainless steel will be required for corrosion protection. Refer to Appendix 6 and note that the naphtha curves must be used for this example. Because of the risk of polythionic acid attack during shutdowns, the stainless steel should be either a Type 321 SS cladding or a Type 347 SS overlay. No corrosion allowance is necessary.

Shutdown represents a simple wet sour service. However, this does not require anything additional, since NACE MR0175 hardness controls have already been specified because of the hydrogen service.

Question: What changes would occur if the maximum design temperature were 900°F (480°C)?

Answer: Refer to Template #8a (p. 279).

Although still permitted by the Nelson curves, 1¼Cr-½Mo would no longer be a good choice, since it would be susceptible to creep embrittlement. We don't know how to minimize or delay this form of degradation. 2½Cr-1Mo would be a

better choice, since we know how to deal with its embrittlement mechanism, that is, temper embrittlement.

Example #9

Process Data

This is a reactor feed exchanger. As previously discussed, heat exchangers serve two processes, the shell side and the tube side. Use a separate template for each process. Refer to Templates #9a (P. 280) and #9b (P. 281) for this example.

Shell Side

The shell-side process is a mixture of sour heavy gas oil and hydrogen (82 mole percent in the vapor phase). Shutdown is an upset condition, as liquid water can condense in the presence of hydrogen sulfide. The process contains no other crack-inducing agents or corrodents. These data as well as the design pressures and temperatures are listed in Template #9a (p. 280).

Tube Side

The tube-side process is a sour mixture of hydrocarbon liquids and hydrogen gas. Shutdown is an upset condition, again because liquid water can condense in the presence of hydrogen sulfide. The tube-side process contains no other crack-inducing agents or corrodents. The tube-side process conditions and design pressures and temperatures are listed in the tube-side Template, #9b (p. 281).

Materials Selection

Shell Side

The Nelson curves (see Appendix 4) indicate the use of $1\frac{1}{4}\text{Cr}-\frac{1}{2}\text{Mo}$ steel. The Couper-Gorman curves indicate a corrosion rate of about 30 mpy. Refer to Appendix 6 and note that the gas oil curves are to be used for this example. This rate is too corrosive for vessel walls. An 18-8 stainless steel barrier layer is indicated. Because of the risk of polythionic acid attack, Type 321 SS cladding or Type 347 SS overlay is recommended. Since this is a Cr-Mo alloy in hydrogen service, postweld heat treatment and weld metal hardness controls are recommended. Note that even though the maximum design temperature would permit a Type 304L SS overlay, the required postweld heat treatment would sensitize this material.

The shell-side process is a simple wet sour service, since the system will be water-wet only during a shutdown, when water can condense. Compliance with NACE MR0175 should be required. Hydrogen induced cracking resistance should not be necessary, since the substrate steel is protected by cladding. During shut-

down, the system will not be subject to the additional effects of hot, high-pressure hydrogen gas.

Tube Side

The Nelson curves indicate the use of $1\frac{1}{4}\text{Cr}-\frac{1}{2}\text{Mo}$ or better. The Couper-Gorman curves (see Appendix 6) for this material indicate a corrosion rate on the order of 50 mpy (use the gas oil curves for this example). This suggests using an 18-8 stainless steel, to withstand sulfur corrosion. Given the risk of polythionic acid attack, a stabilized grade should be specified. Either Type 321 or Type 347 SS is suitable. Cr-Mo alloys in hydrogen service are subject to both postweld heat treatment and hardness controls. Note that this is a simple wet sour service requiring compliance with NACE MR0175.

- Tubes: Either Type 321 or Type 347 SS.
- Tubesheet: $1\frac{1}{4}\text{Cr}-\frac{1}{2}\text{Mo}$ cannot withstand the severe sulfur corrosion environments on either the tube side or the shell side of the tubesheet. These surfaces should be either clad with Type 321 SS or overlaid with Type 347 SS. No corrosion allowance is necessary for either side of the tubesheet, because of the protection provided by the SS overlay or cladding. Note that it is sometimes more economical to purchase a solid stainless steel tubesheet.
- Channel: The channel should be specified to be the same as the tube side of the tubesheet, i.e., $1\frac{1}{4}\text{Cr}-\frac{1}{2}\text{Mo}$. It should be either clad with Type 321 SS or overlaid with Type 347 SS. No corrosion allowance is required because of the SS cladding or overlay. Postweld heat treatment and weld metal hardness control should be required.

Example #10

Process Data

This is a low-pressure "syngas" transfer line. The source of the syngas is a coal gasification process that produces fuel gas with a large amount of impurities, including H_2S (2.5 mole percent), CO_2 (15 mole percent), CO and variable quantities of chlorides. The gas is saturated with water vapor. Shutdown is an upset condition, since liquid water will form from the vapor phase. Liquid water will probably form during normal operation as well, even in a well-insulated line, if the gas stream is truly saturated. These data as well as the design pressures and temperatures are listed in Template #10 (p. 282).

Materials Selection

The ratio of H_2S to CO_2 is high enough that CO_2 corrosion is not a concern. The wet H_2S conditions during shutdown indicate a simple wet sour service. Carbon steel is

the recommended material of construction. NACE MR0175 and RP0472 apply. A corrosion allowance of $1/8$ " should be adequate. Valve trim should be 12 Cr.

Question: What would change if the H_2S concentration were negligible?

Answer: Refer to Template #10a (p. 283).

Without sufficient H_2S to provide a protective iron sulfide scale, carbon steel would be subject to CO_2 corrosion. Using the de Waard-Milliams nomograph in Appendix 2, the estimated corrosion rate for carbon steel is about 5 mm/yr (200 mpy). However, CO_2 corrosion in this system would be expected to occur under condensing conditions. The maximum rate would be expected to be about 20 mpy (0.5 mm/yr) for non-turbulent, non-impingement service. Carbon steel, with a corrosion allowance of $1/4$ ", is the recommended material of construction for a design life of 10 years. Valve trim should be 12 Cr. A note should be made to the effect that velocities should be kept to less than 60 ft/sec (20 m/s) and that long-radius elbows should be used to avoid impingement.

Question: What would change if the syngas contained an appreciable quantity (> 20 ppmw) of cyanides?

Answer: Refer to Template #10b (p. 284).

This line would be in severe wet sour service. It contains a cathodic poison that will accelerate the various forms of hydrogen induced cracking damage. The recommended material of construction is carbon steel. MR0175 requires the carbon steel to be either hot rolled or to have a mill heat treatment. Normalizing is the conventional heat treatment. Postweld heat treatment is required. NACE MR0175 and RP0472 should be required. If the pipe to be used is made from welded plate, the plate should be resistant to HIC.

The cyanides will tend to destabilize the sulfide film, making it less protective. The additional measures used for CO_2 corrosion resistance, velocity limitation and long-radius elbows, should be required (see Template #10a, p. 284).

B. PETROCHEMICAL PROCESSES

The next five examples are for petrochemical processes. The generalized template shown in Example No. 1 in Chapter 5 (p. 235) will be used to illustrate the use of templates for petrochemical processes.

Example #11

Process Data

This vessel is an monoethanolamine (MEA) absorber tower, stripping CO_2 from a flue gas stream. Corrosion control for this vessel depends on contact of inhibited

MEA on all surfaces exposed to gaseous CO_2 . The only upset condition is loss of inhibitor, during which CO_2 corrosion will probably occur. The above data as well as the design pressures and temperatures are listed in Template #11 (p. 285). Materials selection should include the pressure-retaining components and internals, including the packing rings.

Materials Selection

Killed carbon steel is the normal recommended material of construction for amine services with design temperatures not exceeding 300°F (150°C). Since MEA is a crack-inducing agent for alkaline stress corrosion cracking, postweld heat treatment is recommended for carbon steels. This is consistent with the recommendations of API 945. Normalizing is also usually recommended for carbon steels in an alkaline stress corrosion cracking environment. Accordingly, the following would be the normal recommendations:

- Metallurgy: killed carbon steel
- Pressure retaining components to be normalized
- Postweld heat treatment required

However, the maximum design pressure should be too low for crack propagation (i.e., leak-before-break). If the combined stress in tension is less than ten percent of the specified minimum tensile strength, normalizing and postweld heat treatment should not be necessary. The following minimum requirements should be recommended to the user, if capital cost is a major project criterion:

- Metallurgy: killed carbon steel
- Postweld Heat Treatment: per Code. Note that API Publication No. 945, "Avoiding Environmental Cracking in Amine Units," does not cite a pressure threshold below which postweld heat treatment is unnecessary.

In either case, the recommended corrosion allowance is $1/8$ ". This value should be adequate if the inhibitor program is effective. Recall that velocities should be limited to 6 ft/sec (2 m/s) for rich amine services.

Two special concerns require consideration:

- Experience has shown that the vapor spaces at the bottom of the absorber may not be effectively inhibited by wet MEA. Accordingly, consider either adding a sparger or cladding or overlaying the affected areas with a corrosion resistant alloy. Type 405 or Type 410 (Type 410S if welded) stainless steel would be adequate. Solid stainless steel may be an economical alternative for internals.

Type 304L SS should be considered. The low design pressure indicates that the required shell thickness may be economical for stainless steel construction. If this material is used, both inhibitors and the sparger can be avoided.

- The packing rings will have a huge total exposed surface area. At even very low corrosion rates, they can generate excessive amounts of corrosion products, which may cause fouling and plugging problems downstream of the vessel. The rings should be made of a corrosive resistant alloy such as Type 304 SS or a suitable non-metallic material such as polypropylene.

Note the -50°F (-46°C) minimum design temperature. Impact testing may be required for pressure-retaining components.

Example #12

Process Data

This example involves a neutralization sump. This unit functions as a vented, below-ground, temporary storage tank, used to collect and neutralize acidic and caustic waste streams. The waste streams are usually heavily contaminated with chlorides and other inorganic materials that are water soluble. The waste streams will not be permitted to contain significant organic contaminants.

The tank is used only periodically; on the average, once per week for a few hours at a time. Depending on the waste stream, the initial pH can be either acidic or caustic. It is neutralized with either 98 percent sulfuric acid or 20 percent caustic soda. These and other data are shown in Template #12 (p. 286).

Materials Selection

None of the common materials of construction will withstand the wide range of contaminants and pH swings typical of this service. Consequently, it is common practice to use either carbon steel or concrete to provide for pressure stresses and structural integrity, with a liner chosen for its resistance to hot, dilute solutions of sulfuric acid and caustic soda. Neoprene appears to be a good liner candidate [1]. The concentrations of acid and caustic, as well as operating temperatures, may have to be restricted in order to select a material with adequate resistance. Consult with lining suppliers for specific limits.

Example #13

Process Data

This example involves the high-temperature shift converter in an ammonia plant. The feed to this vessel is a gas composed of hydrogen, nitrogen, carbon monoxide, carbon dioxide and steam. The catalyst in the vessel promotes the conversion of carbon monoxide to carbon dioxide. Shutdown is an upset condition, since liquid water will condense, permitting corrosion by wet carbon dioxide. Refer to Template #13 (p. 287) for pertinent data.

Materials Selection

Carbon dioxide is the only process component regarded as a corrodent. Since there is no liquid water in the process stream during normal operation, no electrolytic corrosion is anticipated. However, liquid water will form during shutdowns. The wet CO_2 corrosion rates will be variable as the vessel cools during the shutdown. The de Waard-Milliams corrosion rate (refer to Appendix 2), for a condensing system, will be as high as 50 mpy (1.3 mm/yr) at 155°F (68°C). However, this rate must be prorated over the operating life of the vessel. When prorated, the corrosion rate is negligible. Nevertheless, it is conventional to specify a nominal corrosion allowance; $1/16"$ should be adequate.

The hydrogen partial pressure exceeds 100 psia, so this is a hydrogen service. The Nelson curves (see Appendix 4) indicate that the minimum acceptable material is $1\frac{1}{2}\text{Cr}-\frac{1}{2}\text{Mo}$. Recall that postweld heat treatment should be required of all Cr-Mo steels in hydrogen service. Hardness controls should also be required. $1\frac{1}{2}\text{Cr}-\frac{1}{2}\text{Mo}$ should not be subject to creep embrittlement in this service. The relatively low minimum design temperature may require impact tested material.

Example #14

Process Data

This line conveys superheated ammonia in a plastics plant. The service involves no upset conditions. Alloy 800 has been used in the past but has proved to be susceptible to rapid nitriding. An alternative material is desirable. Refer to Template #14 (p. 288) for relevant data.

Materials Selection

Anhydrous liquid ammonia is known to be a crack-inducing agent for carbon steel. However, this service involves high-temperature, high-pressure ammonia gas. Ammonia gas is not regarded as a crack-inducing agent for carbon steel.

Ignoring nitriding for the moment, $1\frac{1}{2}\text{Cr}-\frac{1}{2}\text{Mo}$ would be the minimum material for this service, since the maximum design temperature exceeds that normally permitted for carbon steel. At the maximum temperatures shown in the template, this material may be susceptible to creep embrittlement. $2\frac{1}{2}\text{Cr}-1\text{Mo}$ would be preferable. Since these materials would be even more susceptible to nitriding than nickel alloys, they would have to be protected by a material resistant to nitriding. Aluminum is known to be essentially immiscible with nitrogen.

A low-Cr-Mo steel internally lined with vapor-deposited aluminum would appear to be a better and cheaper alternative. The fabrication welds could be a problem, since the aluminum coating must be cut back to make a good weld. To solve this problem, a short spool piece of a suitable nickel alloy should be welded

to the Cr-Mo pipe prior to the vapor deposition process. Any subsequent welds would then have much improved nitriding resistance.

There are a number of nickel-based alloys much more resistant to nitriding than is Alloy 800. Manufacturers of nickel alloys should be consulted for alternative materials.

Example #15

Process Data

This example involves an acetic acid heat exchanger, having high purity acid on the tube side and cooling water on the shell side. The cooling water is regarded as being clean and is chemically treated to be benign to carbon steel. However, it contains a relatively large concentration of chlorides. The exchanger is expected to experience no significant upsets. Refer to Template #15 (pp. 289-290) for relevant data.

Materials Selection

Type 316L stainless steel is the conventional material of construction for pure acetic acid, for temperatures up to the boiling point of the acid. If we accept the template data as stated, carbon steel is the recommended material of construction for the shell side. Type 316 SS (316L if welded) is the recommended material for the tubes, with carbon steel, overlaid or clad with Type 316L SS, recommended for the tubesheet and channel.

This example illustrates one of the pitfalls of materials selection. It would appear that a relevant upset condition may have been overlooked: loss of flow on the shell side (cooling water). If this were to happen, the recommended tube-side metallurgy could become susceptible to chloride stress corrosion cracking. A cautionary note has been added to the template to address this concern. Alternatively, one could investigate this potential upset and ignore it if it is shown to be of no concern.

C. CHEMICAL PROCESSES

In this section five examples of chemical processes are discussed. The first four examples involve a dilution system that uses sulfuric acid to adjust the pH of cooling tower water. This is a continuous process and Figure S-1 is used to generate the required templates. These examples are also used to generate a materials selection diagram.

The last example involves a batch process. Figure S-2 is used to generate the template for this example.

Stream or Equipment Number: _____

Mechanical Design Conditions:

	Operating		Design	
	Low	High	Low	High
Temperature:	_____	_____	_____	_____
Pressure:	_____	_____	_____	_____

Process Chemistry:

- Chemicals Present:^a _____
- Phases Present: _____
- Corrodents Present:^b _____
- Crack-Inducing Agents Present:^c _____

Upset Conditions:^d _____

Material of Construction: _____

PWHT: _____ Corrosion Allowance: _____ Valve Trim: _____

Notes: _____

^a 1. List all chemicals present. Include contaminants and impurities as well as the major constituents.

2. Indicate if the process fluid is an electrolyte. If not, are other electrolytes present?

^b Indicate which chemicals are known corrodents.

^c Indicate which chemicals are known crack-inducing agents.

^d Describe the nature and duration of possible anticipated upset conditions. For each upset condition, indicate the presence of corrodents, crack-inducing agents or electrolytes introduced because of upset conditions. For autorefrigeration, indicate the anticipated minimum temperature.

Figure S-1 Template to be used for continuous chemical processes.

Stream or Equipment Number: _____

Step:^a _____

Mechanical Design Conditions:

	Operating		Design	
	Low	High	Low	High
Temperature:	_____	_____	_____	_____
Pressure:	_____	_____	_____	_____

Process Chemistry:

- Chemicals Present:^b _____
- Phases Present: _____
- Corrodents Present:^c _____
- Crack-Inducing Agents Present:^d _____

Upset Conditions:^e _____

Material of Construction: _____

PWHT: _____ Corrosion Allowance: _____ Valve Trim: _____

Notes: _____

^a For batch processes, a template must be prepared for each step in the process. Indicate the step for which the template is intended.

^b 1. List all chemicals present. Include contaminants and impurities as well as the major constituents.

2. Indicate if the process fluid is an electrolyte. If not, are other electrolytes present?

^c Indicate which chemicals are known corrodents.

^d Indicate which chemicals are known crack-inducing agents.

^e Describe the nature and duration of possible anticipated upset conditions. Consider whether the upset conditions are for start-of-run, end-of-run or both, or whether they will occur during the run. For each upset condition, indicate the presence of corrodents, crack-inducing agents or electrolytes introduced because of upset conditions. For auto-refrigeration, indicate the anticipated minimum temperature.

Figure S-2 Template to be used for batch chemical processes.

EXAMPLES #16, 17, 18 and 19

Figure S-3 is a process flow diagram for a sulfuric acid dilution system. Concentrated acid (93 or 98 percent) is pumped from a storage tank (101) to a mixing pipe (5) where it is mixed with process water to produce dilute sulfuric acid (< 10 percent). Components in this system include the following:

- Storage tank for concentrated sulfuric acid (101)
- Transfer line to and from the strong acid pump (1)
- Strong acid pump (P1)
- Feed water lines (2), (3) and (4)
- Feed water pump (P2)
- Acid dilution pipe (5)
- Dilute acid pipe (6) (this line has essentially the same process conditions as (5))

Templates are developed for the sulfuric acid storage tank (101), the acid transfer line (1), the strong acid pump (P1) and the acid dilution pipe (5) and the dilute acid pipe (6). Templates will not be necessary for the feed water pump (P2) and the feed water lines (2), (3) and (4), since such feed water is assumed to be moderately corrosive. Carbon steel piping with 12 Cr valve trim and a corrosion allowance of 1/8" is the normal selection for such water services. The P2 pump is typically selected to be (1) cast iron with cast iron or carbon steel internals, (2) carbon steel with either cast iron or carbon steel internals or (3) 12 Cr with 12 Cr internals. The latter selection is usually made only if experience indicates that such metallurgy is necessary.

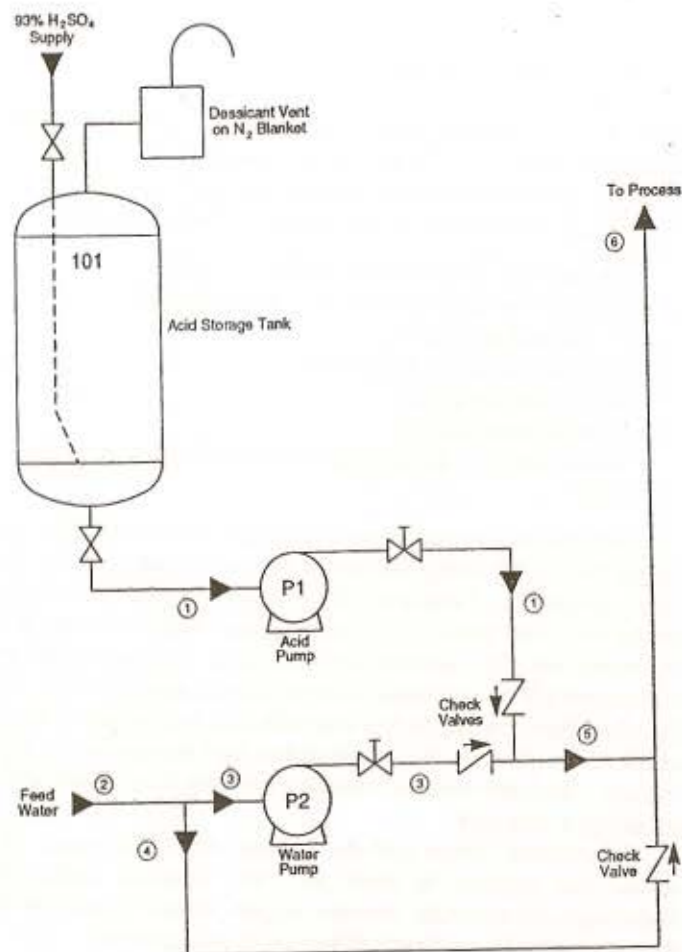
Concentrated sulfuric acid has a strong affinity for water. If the system is drained and exposed to moist air, very corrosive weak acid will form. Accordingly, the materials selection diagram should include the following note, since it is applicable to all parts of the acid-handling system.

All piping and equipment must be protected from direct exposure to air. The acid handling portion of the dilution system must be drained under nitrogen purge. The nitrogen purge must be maintained until the system has been thoroughly washed.

EXAMPLE #16: Sulfuric Acid Storage Tank (101)

Process Data

The tank contains concentrated sulfuric acid (93 to 98 percent), commercial grade. The tank is blanketed with nitrogen, so it will contain non-aerated acid. Since the acid already contains some contaminants and it will be used only to adjust the pH of cooling water tower, acid contamination is not a concern. No significant upset conditions are anticipated. Refer to Template #16 (p. 291) for relevant data.



Stream No.	①	②	③	④	⑤	⑥
H ₂ SO ₄ %	93	0	0	0	5.5	1.2
H ₂ O %	7	100	100	100	94.5	98.8
Flow Rate GPM	1.6*	250	50	200	52	252
Temp. °F	70	70	70	70	120**	74

* Acid flow rate is a function of the alkalinity of the cooling tower water. This flow rate is for water of high alkalinity.

** Temperature after full mixing. Local temperature where acid meets the water may be at the boiling point.

Figure S-3 Simplified process flow diagram for a sulfuric acid dilution system.

Materials Selection

Carbon steel is the preferred material of construction for concentrated sulfuric acid storage tanks. However, as discussed in Chapter 3, velocities must not be allowed to exceed 3 ft/sec (0.9 m/s). For this reason the tank should have top entry nozzles. The inlet tubes should be located near the center of the tank and should be oriented straight down to avoid turbulence and acid splashing against the tank side walls. The discharge nozzles should be made of Type 316 SS to resist erosion corrosion. Refer to reference [2] for design details.

EXAMPLE #17: Acid Transfer Line (1)

Process Data

This line takes feed from the sulfuric acid storage tank, so it has the same process chemistry and operating temperatures and pressures. The only additional upset condition would be reverse flow from the acid dilution line. A check valve has been provided to address this potential problem. Refer to Template #17 (p. 292) for relevant data.

Materials Selection

As discussed in Chapter 3, carbon steel is sometimes used for piping concentrated sulfuric acid. However, Type 316 SS is becoming the standard metallic material of construction for this service (Type 316L SS for welded construction). Type 316L SS would be preferred if the upset conditions included occasional transient exposure to dilute sulfuric acid. For small-diameter piping systems (8" diameter and less), plastic lined carbon steel may be useful. Polyvinylidene fluoride (PVDF) is often recommended for this service. Both Alloy C-276 (15Cr-54Ni-16Mo, UNS N10276) and Alloy 20 Cb-3 (20Cr-35Ni-2.5Mo, Cb stabilized (UNS N08020)) are used for valve bodies, or valve body weld overlays, and trim. No corrosion allowance should be necessary.

This line should enter the acid dilution line from the bottom, since the higher-gravity concentrated acid will tend to prevent back-flow from the acid-mixing line.

EXAMPLE #18: Strong Acid Pump (P1)

Process Data

The process and operating conditions for this pump are the same as those of the acid transfer line. Refer to Template #18 (p. 293) for relevant data.

Materials Selection

As discussed in Chapter 3, recommended materials of construction for pumps in this service include 14 percent silicon cast iron or the cast version of Alloy 20 Cb-3.

Materials Selection

Since contamination of either the acid or the solvent is not permitted, the reactor must be constructed of materials that are resistant to 93 to 98 wt. percent H_2SO_4 . Candidate materials include austenitic stainless steels, nickel-based high alloys and glass-lined carbon steel. The final choice will be based on the installed cost. In general, glass-lined carbon steel, off-the-shelf, will be least costly for the reactor size needed. For larger reactors, alloy construction would probably be less expensive, since glass-lined equipment is not readily available in larger sizes.

Pumps, valves and piping for the batch system would be similar to those indicated in Examples #17–18. Carbon steel should not be allowed for the acid storage tank, since it would generate unacceptable iron contamination. Carbon steel lined with a resistant polymer such as PVDF should probably be selected for acid storage.

MATERIALS SELECTION TEMPLATE: EXAMPLE #1

Stream or Equipment Number: Sour Wash Water Line

Design Temperature (Minimum/Maximum): 32/210°F

Design Pressure (Minimum/Maximum): —/45 psig

Commodity: Sour Water Phases: Liquid Liquid Water (Y/N): Yes

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: NA

Corrodents: H_2S (2.3 wt. %)

Crack-Inducing Agents: H_2S (2.3 wt. %)

Upset Conditions: None

- Liquid Water (Y/N):
- Corrodents:
- Crack-Inducing Agents:
- Autorefrigeration (Y/N):
- Other:

Wet Sour Service (Y/N): No (Low-Risk Service)

Metallurgy: CS

PWHT: Per Code

Valve Trim: 12 Cr

Corrosion Allowance: $\frac{1}{8}$ "

Notes: None

MATERIALS SELECTION TEMPLATE: EXAMPLE #1a

Stream or Equipment Number: Sour Wash Water Line

Design Temperature (Minimum/Maximum): 32/210°F

Design Pressure (Minimum/Maximum): —/75 psig

Commodity: Sour Water Phases: Liquid Liquid Water (Y/N): Yes

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: NA

Corrodents: H₂S (2.3 wt. %)

Crack-Inducing Agents: H₂S (2.3 wt. %)

Upset Conditions: None

- Liquid Water (Y/N):
- Corrodents:
- Crack-Inducing Agents:
- Autorefrigeration (Y/N):
- Other:

Wet Sour Service (Y/N): Yes

If Yes, indicate severity: Simple Wet Sour Service

Metallurgy: CS

PWHT: Per Code

Valve Trim: 12 Cr

Corrosion Allowance: 1/8"

Notes: NACE MR0175/RP0472

MATERIALS SELECTION TEMPLATE: EXAMPLE #2

Stream or Equipment Number: Gas/Oil Separator

Design Temperature (Minimum/Maximum): -20/250°F

Design Pressure (Minimum/Maximum): 0/125 psig

Commodity: Sour Crude Phases: Liq. + Vap. Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: NA

Corrodents: CO₂ (3 mole %) + H₂S (3 mole %)

Crack-Inducing Agents: H₂S (3 mole %)

Upset Conditions: Shutdown

- Liquid Water (Y/N): Yes
- Corrodents: CO₂ (4.2 psia) + H₂S (4.2 psia)
- Crack-Inducing Agents: H₂S (4.2 psia)
- Autorefrigeration (Y/N): No
- If Yes, indicate minimum temperature:
- Other:

Wet Sour Service (Y/N): Yes

If Yes, indicate severity: Simple Wet Sour Service

Metallurgy: KCS

PWHT (Y/N): per Code

Valve Trim: NA Corrosion Allowance: 1/8"

Notes: NACE MR0175/RP0472

MATERIALS SELECTION TEMPLATE: EXAMPLE #3

Stream or Equipment Number: Rich DEA Line

Design Temperature (Minimum/Maximum): 32/210°F

Design Pressure (Minimum/Maximum): —/1600 psig

Commodity: DEA + H₂S Phases: Liquid Liquid Water (Y/N): Yes

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: NA

Corrodents: H₂S (3 wt. %) + DEA (23 wt. %)

Crack-Inducing Agents: H₂S (3 wt. %) + DEA (23 wt. %)

Upset Conditions: None

- Liquid Water (Y/N):
- Corrodents:
- Crack-Inducing Agents:
- Autorefrigeration (Y/N):
- Other:

Wet Sour Service (Y/N): Yes

If Yes, indicate severity: Severe Wet Sour Service

Metallurgy: CS

PWHT: Yes Valve Trim: Tp 316 SS Corrosion Allowance: 1/4"

Notes: NACE MR0175/RP0472. If welded pipe, require HIC-resistant plate and normalize the weld. CA may be 1/8" if inhibitors are used. Limit the velocity to 6 ft/sec (3 m/s).

MATERIALS SELECTION TEMPLATE: EXAMPLE #3a

Stream or Equipment Number: Rich DEA Line

Design Temperature (Minimum/Maximum): 32/210°F

Design Pressure (Minimum/Maximum): —/15 psig

Commodity: DEA + H₂S Phases: Liquid Liquid Water (Y/N): Yes

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: NA

Corrodents: H₂S (3 wt. %) + DEA (23 wt. %)

Crack-Inducing Agents: H₂S (3 wt. %) + DEA (23 wt. %)

Upset Conditions: None

- Liquid Water (Y/N):
- Corrodents:
- Crack-Inducing Agents:
- Autorefrigeration (Y/N):
- Other:

Wet Sour Service (Y/N): No (Low-Risk Service)

Metallurgy: CS

PWHT: per Code Valve Trim: Tp 316 SS Corrosion Allowance: 1/4"

Notes: CA may be 1/8" if inhibitors are used. API 945 recommends PWHT. Limit the velocity to 6 ft/sec.

MATERIALS SELECTION TEMPLATE: EXAMPLE #4

Stream or Equipment Number: LPG Line

Design Temperature (Minimum/Maximum): 32/155°F

Design Pressure (Minimum/Maximum): 100/230 psig

Commodity: LPG Phases: Liquid Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: NA

Corrodents: None

Crack-Inducing Agents: None

Upset Conditions: Autorefrigeration

- Liquid Water (Y/N): None
- Corrodents: None
- Crack-Inducing Agents: None
- Autorefrigeration (Y/N): Yes
- If Yes, indicate minimum temperature: -65°F
- Other:

Wet Sour Service (Y/N): No

If Yes, indicate severity:

Metallurgy: Impact tested carbon steel (may be a risky choice). 3½ Ni or 18-8 SS are acceptable alternatives.

PWHT (Y/N): per Code Valve Trim: Tp 316 SS Corrosion Allowance: 0"

Notes: Normally operates at 105°F; no insulation required.

MATERIALS SELECTION TEMPLATE: EXAMPLE #4a

Stream or Equipment Number: LPG Vessel

Design Temperature (Minimum/Maximum): 32/155°F

Design Pressure (Minimum/Maximum): 100/230 psig

Commodity: LPG Phases: Liquid Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: NA

Corrodents: None

Crack-Inducing Agents: None

Upset Conditions: Autorefrigeration

- Liquid Water (Y/N): None
- Corrodents: None
- Crack-Inducing Agents: None
- Autorefrigeration (Y/N): Yes
- If Yes, indicate minimum temperature: -65°F
- Other:

Wet Sour Service (Y/N): No

If Yes, indicate severity:

Metallurgy: Carbon steel will probably be a good choice; see the Code toughness rules. Alternatives: 3½ Ni or 18-8 SS.

PWHT (Y/N): per Code Valve Trim: NA Corrosion Allowance: None

Notes: None

MATERIALS SELECTION TEMPLATE: EXAMPLE #5

Stream or Equipment Number: Furnace Inlet Line

Design Temperature (Minimum/Maximum): -20/1000°F

Design Pressure (Minimum/Maximum): -/85 psig

Commodity: HC + H₂ Phases: Vapor Liquid Water (Y/N): No

High-Temperature Total Sulfur: None

High-Temperature Hydrogen Sulfide: None

Corrodents: None

Crack-Inducing Agents: H₂ (95 mole %)

Upset Conditions: None

- Liquid Water (Y/N):
- Corrodents:
- Crack-Inducing Agents: H₂ (95 psia)
- Autorefrigeration (Y/N):
- If Yes, indicate minimum temperature:
- Other:

Wet Sour Service (Y/N): No

If Yes, indicate severity:

Metallurgy: 1¼Cr-½Mo

PWHT (Y/N): per Code Valve Trim: 12 Cr Corrosion Allowance: None

Notes: CS is permissible if "early replacement" is acceptable. Note that 1¼Cr-½Mo may be susceptible to creep embrittlement in this service.

MATERIALS SELECTION TEMPLATE: EXAMPLE #5a

Stream or Equipment Number: Furnace Inlet Line

Design Temperature (Minimum/Maximum): -20/1050°F

Design Pressure (Minimum/Maximum): -/85 psig

Commodity: HC + H₂ Phases: Vapor Liquid Water (Y/N): No

High-Temperature Total Sulfur: None

High-Temperature Hydrogen Sulfide: None

Corrodents: None

Crack-Inducing Agents: H₂ (95 mole %)

Upset Conditions: None

- Liquid Water (Y/N):
- Corrodents:
- Crack-Inducing Agents: H₂ (95 psia)
- Autorefrigeration (Y/N):
- If Yes, indicate minimum temperature:
- Other:

Wet Sour Service (Y/N): No

If Yes, indicate severity:

Metallurgy: 1¼Cr-½Mo

PWHT (Y/N): per Code Valve Trim: 12 Cr Corrosion Allowance: None

Notes: Note that 1¼Cr-½Mo may be susceptible to creep embrittlement in this service.

MATERIALS SELECTION TEMPLATE: EXAMPLE #5b

Stream or Equipment Number: Furnace Inlet Line

Design Temperature (Minimum/Maximum): -20/1000°F

Design Pressure (Minimum/Maximum): -/500 psig

Commodity: HC + H₂ Phases: Vapor Liquid Water (Y/N): No

High-Temperature Total Sulfur: None

High-Temperature Hydrogen Sulfide: None

Corrodents: None

Crack-Inducing Agents: H₂ (95 mole %)

Upset Conditions: None

- Liquid Water (Y/N):
- Corrodents:
- Crack-Inducing Agents: H₂ (490 psia)
- Autorefrigeration (Y/N):
- If Yes, indicate minimum temperature:
- Other:

Wet Sour Service (Y/N): No

If Yes, indicate severity:

Metallurgy: 1¼Cr-½Mo

PWHT (Y/N): per Code Valve Trim: 12 Cr Corrosion Allowance: None

Notes: NACE MR0175; weld metal: 225 BHN, maximum. Note that 1¼Cr-½Mo may be susceptible to creep embrittlement in this service.

MATERIALS SELECTION TEMPLATE: EXAMPLE #6

Stream or Equipment Number: Pump Suction Line

Design Temperature (Minimum/Maximum): 32/620°F

Design Pressure (Minimum/Maximum): -/75 psig

Commodity: HC Phases: Liquid Liquid Water (Y/N): No

High-Temperature Total Sulfur: 1.5 wt. %

High-Temperature Hydrogen Sulfide: NA

Corrodents: High-temperature sulfur (1.5 wt. %)

Crack-Inducing Agents: None

Upset Conditions: None

- Liquid Water (Y/N):
- Corrodents:
- Crack-Inducing Agents:
- Autorefrigeration (Y/N):
- If Yes, indicate minimum temperature:
- Other:

Wet Sour Service (Y/N): No

If Yes, indicate severity:

Metallurgy: 5Cr-½Mo

PWHT (Y/N): per Code Valve Trim: 12 Cr Corrosion Allowance: 1/8"

Notes: Carbon steel is acceptable on an "early replacement" basis; note the low design pressure (and probably much lower operating pressure).

MATERIALS SELECTION TEMPLATE: EXAMPLE #7

Stream or Equipment Number: Reactor Feed Line

Design Temperature (Minimum/Maximum): 32/800°F

Design Pressure (Minimum/Maximum): —/1870 psig

Commodity: Sour HC + H₂ Phases: Vapor Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: 0.82 mole %

Corrodents: High-temperature H₂S (0.82 mole %)Crack-Inducing Agents: H₂S (0.82 mole %) + H₂ (82 mole %)

Upset Conditions: Shutdown

- Liquid Water (Y/N): Yes
- Corrodents: H₂S (15 psia)
- Crack-Inducing Agents: H₂S (15 psia) + H₂ (1545 psia)
- Autorefrigeration (Y/N): No
- If Yes, indicate minimum temperature:
- Other: None

Wet Sour Service (Y/N): Yes

If Yes, indicate severity: Simple Wet Sour Service

Metallurgy: Tp 321 or 347 SS

PWHT (Y/N): per Code Valve Trim: Tp 321 or 347 SS

Corrosion Allowance: None

Notes: NACE MR0175

MATERIALS SELECTION TEMPLATE: EXAMPLE #7a

Stream or Equipment Number: Reactor Feed Line

Design Temperature (Minimum/Maximum): 32/800°F

Design Pressure (Minimum/Maximum): —/1870 psig

Commodity: Sour HC + H₂ Phases: Vapor Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: 0.82 mole %

Corrodents: High-temperature H₂S (0.82 mole %) + naphthenic acidCrack-Inducing Agents: H₂S (0.82 mole %) + H₂ (82 mole %)

Upset Conditions: Shutdown

- Liquid Water (Y/N): Yes
- Corrodents: H₂S (15 psia)
- Crack-Inducing Agents: H₂S (15 psia) + H₂ (1545 psia)
- Autorefrigeration (Y/N): No
- If Yes, indicate minimum temperature:
- Other: None

Wet Sour Service (Y/N): Yes

If Yes, indicate severity: Simple Wet Sour Service

Metallurgy: Tp 316Ti, Tp 316 or 317 SS

PWHT (Y/N): per Code Valve Trim: Tp 316 or 317 SS

Corrosion Allowance: None

Notes: NACE MR0175. Tp 316Ti is available in plate only. Tp 316 SS must have at least 2.5 wt. percent Mo; check the mill certificate(s). Operating instructions must cover prevention of polythionic acid attack by neutralizing washes per NACE RP0170.

MATERIALS SELECTION TEMPLATE: EXAMPLE #8

Stream or Equipment Number: Hydrotreater Reactor

Design Temperature (Minimum/Maximum): 32/800°F

Design Pressure (Minimum/Maximum): —/1560 psig

Commodity: Sour HC + H₂ Phases: Liq. + Vap. Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: 2.85 mole %

Corrodents: High-temperature H₂S (2.85 mole % H₂S)

Crack-Inducing Agents: H₂S (2.85 mole %) + H₂ (76 mole %)

Upset Conditions: Shutdown

- Liquid Water (Y/N): Yes
- Corrodents: H₂S (45 psia)
- Crack-Inducing Agents: H₂S (45 psia) + H₂ (1200 psia)
- Autorefrigeration (Y/N): No
- If Yes, indicate minimum temperature:
- Other: None

Wet Sour Service (Y/N): Yes

 If Yes, indicate severity: Simple Wet Sour Service

Metallurgy: 1¼Cr-½Mo with 18-8 SS overlay

PWHT (Y/N): Yes Valve Trim: NA Corrosion Allowance: None

Notes: NACE MR0175. Specify the overlay to be Tp 347 weld overlay or Tp 321 cladding. The base metal should not be susceptible to creep embrittlement, since the maximum design temperature is colder than 850°F. The vessel should not be pressurized at temperatures colder than 250°F.

MATERIALS SELECTION TEMPLATE: EXAMPLE #8a

Stream or Equipment Number: Hydrotreater Reactor

Design Temperature (Minimum/Maximum): 32/900°F

Design Pressure (Minimum/Maximum): —/1560 psig

Commodity: Sour HC + H₂ Phases: Liq. + Vap. Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: 2.85 mole %

Corrodents: High-temperature H₂S (2.85 mole % H₂S)

Crack-Inducing Agents: H₂S (2.85 mole %) + H₂ (76 mole %)

Upset Conditions: Shutdown

- Liquid Water (Y/N): Yes
- Corrodents: H₂S (45 psia)
- Crack-Inducing Agents: H₂S (45 psia) + H₂ (1200 psia)
- Autorefrigeration (Y/N): No
- If Yes, indicate minimum temperature:
- Other: None

Wet Sour Service (Y/N): Yes

 If Yes, indicate severity: Simple Wet Sour Service

Metallurgy: 2¼Cr-1Mo with 18-8 SS overlay

PWHT (Y/N): Yes Valve Trim: NA Corrosion Allowance: None

Notes: NACE MR0175. Overlay to be Tp 347 weld overlay or Tp 321 cladding. The vessel should not be pressurized at temperatures colder than 250°F.

MATERIALS SELECTION TEMPLATE: EXAMPLE #9a (Shell side)

Stream or Equipment Number: Reactor Feed Exchanger

Design Temperature (Minimum/Maximum): 32/650°F

Design Pressure (Minimum/Maximum): —/1870 psig

Commodity: Sour HGO + H₂ Phases: Liq. + Vap. Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: 0.82 mole %

Corrodents: High-temperature H₂S (0.82 mole %)Crack-Inducing Agents: H₂S (0.82 mole %) + H₂ (82 mole %)

Upset Conditions: Shutdown

- Liquid Water (Y/N): Yes
- Corrodents: H₂S (15 psia)
- Crack-Inducing Agents: H₂S (15 psia) + H₂ (1545 psia)
- Autorefrigeration (Y/N): No
- If Yes, indicate minimum temperature:
- Other: None

Wet Sour Service (Y/N): Yes

If Yes, indicate severity: Simple Wet Sour Service

Metallurgy: 1¼Cr-½Mo with 18-8 SS overlay

PWHT (Y/N): Yes Valve Trim: NA Corrosion Allowance: None

Notes: NACE MR0175; weld metal: 225 BHN, maximum. Specify the overlay to be Tp 347 weld overlay or Tp 321 cladding.

MATERIALS SELECTION TEMPLATE: EXAMPLE #9b (Tube side)

Stream or Equipment Number: Reactor Feed Exchanger

Design Temperature (Minimum/Maximum): 32/675°F

Design Pressure (Minimum/Maximum): —/1560 psig

Commodity: Sour HGO + H₂ Phases: Liq. + Vap. Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: 2.85 mole %

Corrodents: High-temperature H₂S (2.85 mole %)Crack-Inducing Agents: H₂S (2.85 mole %) + H₂ (76 mole %)

Upset Conditions: Shutdown

- Liquid Water (Y/N): Yes
- Corrodents: H₂S (45 psia)
- Crack-Inducing Agents: H₂S (45 psia) + H₂ (1200 psia)
- Autorefrigeration (Y/N): No
- If Yes, indicate minimum temperature:
- Other: None

Wet Sour Service (Y/N): Yes

If Yes, indicate severity: Simple Wet Sour Service

Metallurgy

- Tubes: Tp 321 SS.
- Tubesheet: 1¼Cr-½Mo, with Tp 321 cladding or Tp 347 overlay on both sides.
- Channel: 1¼Cr-½Mo, with Tp 321 cladding or Tp 347 overlay.

PWHT (Y/N): Yes Valve Trim: NA Corrosion Allowance: None

Notes: NACE MR0175; weld metal: 225 BHN, maximum.

MATERIALS SELECTION TEMPLATE: EXAMPLE #10

Stream or Equipment Number: Syngas Transfer Line

Design Temperature (Minimum/Maximum): 32/150°F

Design Pressure (Minimum/Maximum): —/75 psig

Commodity: HC + acid gases Phases: Vapor Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: NA

Corrodents: H₂S (2.5 mole %) + CO₂ (15 mole %)Crack-Inducing Agents: H₂S (2.5 mole %) + chlorides

Upset Conditions: Shutdown

- Liquid Water (Y/N): Yes
- Corrodents: H₂S (2.25 psia) + CO₂ (13.5 psia)
- Crack-Inducing Agents: H₂S (2.25 psia) + chlorides
- Autorefrigeration (Y/N): No
- If Yes, indicate minimum temperature:
- Other: None

Wet Sour Service (Y/N): Yes

If Yes, indicate severity: Simple Wet Sour Service

Metallurgy: CS

PWHT (Y/N): per Code Valve Trim: 12 Cr Corrosion Allowance: 1/8"

Notes: NACE MR0175/RP0472

MATERIALS SELECTION TEMPLATE: EXAMPLE #10a

Stream or Equipment Number: Syngas Transfer Line

Design Temperature (Minimum/Maximum): 32/150°F

Design Pressure (Minimum/Maximum): —/75 psig

Commodity: HC + acid gases Phases: Vapor Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: NA

Corrodents: H₂S (trace only) + CO₂ (15 mole %)

Crack-Inducing Agents: chlorides

Upset Conditions: Shutdown

- Liquid Water (Y/N): Yes
- Corrodents: H₂S (trace only) + CO₂ (13.5 psia)
- Crack-Inducing Agents: chlorides
- Autorefrigeration (Y/N): No
- If Yes, indicate minimum temperature:
- Other: None

Wet Sour Service (Y/N): No

If Yes, indicate severity:

Metallurgy: CS

PWHT (Y/N): per Code Valve Trim: 12 Cr Corrosion Allowance: 1/4"

Notes: Keep velocities to less than 60 ft/sec (20 m/s); use long-radius elbows.

MATERIALS SELECTION TEMPLATE: EXAMPLE #10b

Stream or Equipment Number: Syngas Transfer Line

Design Temperature (Minimum/Maximum): 32/150°F

Design Pressure (Minimum/Maximum): —/75 psig

Commodity: HC + acid gases Phases: Vapor Liquid Water (Y/N): No

High-Temperature Total Sulfur: NA

High-Temperature Hydrogen Sulfide: NA

Corrodents: H₂S (2.5 mole %) + CO₂ (15 mole %)Crack-Inducing Agents: H₂S (2.5 mole %) + chlorides

Upset Conditions: Shutdown

- Liquid Water (Y/N): Yes
- Corrodents: H₂S (2.25 psia) + CO₂ (13.5 psia)
- Crack-Inducing Agents: H₂S (2.25 psia) + chlorides
- Autorefrigeration (Y/N): No
- Other: Cyanides present at greater than 20 ppmw.

Wet Sour Service (Y/N): Yes

If Yes, indicate severity: Severe Wet Sour Service

Metallurgy: CS

PWHT (Y/N): Yes Valve Trim: 12 Cr Corrosion Allowance: 1/8"

Notes: NACE MR0175/RP0472. If welded pipe, require HIC-resistant plate and normalize the weld. Keep velocities to less than 60 ft/sec (20 m/s); use long-radius elbows.

MATERIALS SELECTION TEMPLATE: EXAMPLE #11

Stream or Equipment Number: MEA Absorber Tower

Design Temperature (Minimum/Maximum): —50/160°F

Operating Temperature (Minimum/Maximum): —40/125°F

Design Pressure (Minimum/Maximum): —/20 psig

Operating Pressure (Minimum/Maximum): —/5 psig

Commodity: MEA + CO₂ + Inhib. Phases: L + V Liquid Water (Y/N): YesCorrodents: CO₂ (3 mole % in vapor) + MEA (30 wt. %) + 8 mole % O₂

Crack-Inducing Agents: MEA (30 wt. %)

Upset Conditions: Loss of inhibitor

Metallurgy: KCS; use normalized plate.

PWHT (Y/N): Yes Valve Trim: NA Corrosion Allowance: 1/8"

Notes: Use a sparger to keep the vapor space metal surfaces wet with inhibitor; alternatively, use Tp 405 or 410 (410S if welded) SS as cladding or weld overlay for vapor space components. Solid stainless steel may be an economical alternative for internals. Use Tp 410 SS or a nonmetallic material (e.g., polypropylene) for packing rings. Limit the velocity to 6 ft/sec (2 m/s).

Consider construction of solid Type 304L SS, with deletion of inhibitors and the sparger.

Note that the operating pressure is probably too low for crack propagation; leak-before-break will occur. If the combined stress in tension is less than ten percent of the specified minimum tensile strength, normalizing and PWHT should not be necessary. These recommendations should be discussed if capital cost is a major criterion.

MATERIALS SELECTION TEMPLATE: EXAMPLE #12

Stream or Equipment Number: Neutralizing Sump

Design Temperature (Minimum/Maximum): 32/225°F

Operating Temperature (Minimum/Maximum): 50/212°F

Design Pressure (Minimum/Maximum): —/10 psig

Operating Pressure (Minimum/Maximum): —/5 psig

Commodity: Waste waters Phases: Liquid Liquid Water (Y/N): Yes

Corrodents: NaOH and H₂SO₄; 1 < pH < 12

Crack-Inducing Agents: NaOH, carbonates, bicarbonates, chlorides, etc.

Upset Conditions: None

Metallurgy: CS, internally lined (with external coating and cathodic protection)

PWHT (Y/N): per Code Valve Trim: NA Corrosion Allowance: None

Notes: Internally lined concrete is an acceptable alternative. Neoprene may be suitable as an internal lining. Acid and/or caustic concentrations in the sump may have to be limited during operation. Consult with lining suppliers for specific limits.

MATERIALS SELECTION TEMPLATE: EXAMPLE #13

Stream or Equipment Number: High-temperature Shift Converter

Design Temperature (Minimum/Maximum): -35/840°F

Operating Temperature (Minimum/Maximum): -25/815°F

Design Pressure (Minimum/Maximum): —/525 psig

Operating Pressure (Minimum/Maximum): —/475 psig

Commodity: Reformer gas Phases: Vapor Liquid Water (Y/N): No

Corrodents: NA (no liquid water). CO₂ (8 mole %, 43 psia) corrosion is likely if liquid water forms.

Crack-Inducing Agents: H₂ (23 mole %); partial pressure is 124 psia

Upset Conditions: Shutdown (liquid water condenses)

Metallurgy: 1½Cr-½Mo (impact tested?)

PWHT (Y/N): Yes Valve Trim: NA Corrosion Allowance: 1/16"

Notes: NACE MR0175; weld metal: 225 BHN, maximum, due to hydrogen service.

MATERIALS SELECTION TEMPLATE: EXAMPLE #14

Stream or Equipment Number: Superheated Ammonia Line

Design Temperature (Minimum/Maximum): 0/950°F

Operating Temperature (Minimum/Maximum): 10/900°F

Design Pressure (Minimum/Maximum): —/3575 psig

Operating Pressure (Minimum/Maximum): —/3500 psig

Commodity: Ammonia Phases: Gas Liquid Water (Y/N): No

Corrodents: None

Crack-Inducing Agents: None

Upset Conditions: None

Metallurgy: 2¼Cr-1Mo, internally coated with vapor-deposited aluminum

PWHT (Y/N): per Code Valve Trim: Ni alloy Corrosion Allowance: None

Notes: There are a number of nickel-based alloys much more resistant to nitriding than Alloy 800. Manufacturers of nickel alloys should be consulted for alternative materials.

MATERIALS SELECTION TEMPLATE: EXAMPLE #15 (Shell side)

Stream or Equipment Number: Acetic Acid Heat Exchanger

Design Temperature (Minimum/Maximum): 32/140°F

Operating Temperature (Minimum/Maximum): 45/120°F

Design Pressure (Minimum/Maximum): —/175 psig

Operating Pressure (Minimum/Maximum): —/125 psig

Commodity: Clean cooling water Phases: Liquid Liquid Water (Y/N): Yes

Corrodents: None

Crack-Inducing Agents: Chlorides (300 ppm)

Upset Conditions: Possible loss of shell-side flow

Metallurgy: KCS

PWHT (Y/N): per Code Valve Trim: NA Corrosion Allowance: 1/8"

Notes: None

MATERIALS SELECTION TEMPLATE: EXAMPLE #15 (Tube side)

Stream or Equipment Number: Acetic Acid Heat Exchanger

Design Temperature (Minimum/Maximum): 75/180°F

Operating Temperature (Minimum/Maximum): 60/160°F

Design Pressure (Minimum/Maximum): -/200 psig

Operating Pressure (Minimum/Maximum): -/150 psig

Commodity: Acetic acid Phases: Liquid Liquid Water (Y/N): No

Corrodents: None

Crack-Inducing Agents: None

Upset Conditions: None

Metallurgy:

- Tubes: Tp 316 SS (316L if welded)
- Tubesheet: KCS, overlayed or clad with 1/8" Tp 316L SS on the tube side
- Channel: KCS, overlayed or clad with 1/8" Tp 316L SS

PWHT (Y/N): per Code Valve Trim: NA Corrosion Allowance: None

Notes: In the event of loss of flow on the shell side, the cooling water becomes susceptible to heating to temperatures exceeding 140°F (60°C), above which chloride stress corrosion cracking of the tubes becomes possible. If such loss of cooling water flow is to be regarded as a potential upset condition, either the tube-side metallurgy must be upgraded or operating guidelines, to shut off tube-side flow during the upset, must be adopted.

MATERIALS SELECTION TEMPLATE: EXAMPLE #16

Stream or Equipment Number: Sulfuric Acid Storage Tank (101)

Mechanical Design Conditions:

	Operating		Design	
	Low	High	Low	High
Temperature:	32°F	104°F	-20°F	120°F
Pressure:	Atm.	Atm.	0 psig	15 psig

Process Chemistry:

- Chemicals Present: 93 to 98 wt. percent H₂SO₄, commercial grade
- Phases Present: liquid + vapor; liquid is an electrolyte
- Corrodents Present: 93 to 98 wt. percent H₂SO₄
- Crack-Inducing Agents Present: none for carbon steel

Upset Conditions: The most likely upset condition is introduction of water vapor through the vent, causing dilution of the acid. This will not significantly change the operating conditions. A plugged vent could result in a vacuum during tank drainage. This should be prevented via proper operation and maintenance and is not regarded as a governing condition. Higher than indicated design temperatures are possible in desert and tropical locations. This can be mitigated by painting the tank white or providing it with shade.

Material of Construction: Carbon Steel

PWHT: per Code Corrosion Allowance: 1/8" Valve Trim: NA

Notes: None

MATERIALS SELECTION TEMPLATE: EXAMPLE #17

Stream or Equipment Number: Acid Transfer Line (1)

Mechanical Design Conditions:

	Operating		Design	
	Low	High	Low	High
Temperature:	32°F	104°F	-20°F	120°F
Pressure:	Atm.	Atm.	0 psig	15 psig

Process Chemistry:

- **Chemicals Present:** 93 to 98 wt. percent H_2SO_4 , commercial grade
- **Phases Present:** liquid; liquid is an electrolyte
- **Corrodents Present:** 93 to 98 wt. percent H_2SO_4
- **Crack-Inducing Agents Present:** none for the materials of construction under consideration

Upset Conditions: Except for vacuum exposure, possible upsets are similar to those of Template #16. To address an additional risk, the check valve on upstream of the acid dilution line is designed to prevent a potentially damaging reverse flow.

Material of Construction: Type 316L for welded construction; also consider carbon steel lined with PVDF.

PWHT: per Code **Corrosion Allowance:** Zero

Valve and Valve Trim: Alloy C-276 or Alloy 20 Cb-3 for control valves; Type 316L SS for shutoff valves.

Notes: Consider plastic-lined carbon steel valves.

MATERIALS SELECTION TEMPLATE: EXAMPLE #18

Stream or Equipment Number: Strong Acid Pump (P1)

Mechanical Design Conditions:

	Operating		Design	
	Low	High	Low	High
Temperature:	32°F	104°F	-20°F	120°F
Pressure:	Atm.	Atm.	0 psig	15 psig

Process Chemistry:

- **Chemicals Present:** 93 to 98 wt. percent H_2SO_4 , commercial grade
- **Phases Present:** liquid; liquid is an electrolyte
- **Corrodents Present:** 93 to 98 wt. percent H_2SO_4
- **Crack-Inducing Agents Present:** none for the materials of construction under consideration

Upset Conditions: See description for Template #17.

Material of Construction: Gr CN-7M per ASTM A351, 743 or 744

PWHT: per Code **Corrosion Allowance:** Zero

Valve and Valve Trim: NA

Notes: Alternative materials include lined carbon steel (glass or polymer linings are available) and proprietary materials such as Lewmet¹ 55 (32Cr-33Ni-6Co-4Mo-3Cu).

¹Registered Trademark of Charles S. Lewis & Company, Inc.

MATERIALS SELECTION TEMPLATE: EXAMPLE #19

Stream or Equipment Number: Acid Dilution Line (5)

Mechanical Design Conditions:

	Operating		Design	
	Low	High	Low	High
Temperature:	32°F	104°F	-20°F	120°F
Pressure:	Atm.	Atm.	0 psig	15 psig

Process Chemistry:

- **Chemicals Present:** 93 to 98 wt. percent H_2SO_4 , commercial grade; dilution to less than 10 percent acid is possible
- **Phases Present:** liquid + vapor; liquid is an electrolyte
- **Corrodents Present:** H_2SO_4 , from < 10 percent up to 98 percent
- **Crack-Inducing Agents Present:** none for the materials of construction under consideration

Upset Conditions: Temperatures in excess of 212°F (100°C) must be avoided via operating controls. Materials selection to include concerns about high pressures that can occur because of local violent boiling.

Material of Construction: Plastic-lined carbon steel (PTFE or PVDF).

PWHT: No (would ruin plastic lining)

Corrosion Allowance: Zero

Valve and Valve Trim: Same as pipe

Notes: None

MATERIALS SELECTION TEMPLATE: EXAMPLE #20

Stream or Equipment Number: Batch Reactor

Step: Drying pentane

Mechanical Design Conditions:

	Operating		Design	
	Low	High	Low	High
Temperature:	Amb.	Amb.	70°F	100°F
Pressure:	Atm.	Atm.	0 psig	15 psig

Process Chemistry:

- **Chemicals Present:** pentane, water and 93 to 98 % H_2SO_4
- **Phases Present:** liquid + vapor; liquid is electrolytic
- **Corrodents Present:** 93 to 98 % H_2SO_4
- **Crack-inducing Agents Present:** none for the materials being considered

Upset Conditions: If the pentane is very wet, the temperature in the reactor at the start of the run may rise above the design temperature. Accordingly, operational controls must be provided to avoid excessive start-of-run temperatures.

Material of Construction: Glass-lined carbon steel

PWHT: per Code Corrosion Allowance: Zero Valve Trim: NA

Notes: Consider austenitic stainless steel for large vessels. Provide operational controls to avoid excessive start-of-run temperatures.

REFERENCES

1. Philip A. Schweitzer, *Corrosion Resistance Tables*, Marcel Dekker, New York, 1991.
2. *Design, Fabrication, and Inspection of Tanks for the Storage of Concentrated Sulfuric Acid and Oleum at Ambient Temperatures*, NACE RP0294, NACE International, Houston (latest edition).



APPENDIX 1

Materials of Construction as a Function of Temperature

This appendix should be used to help select materials suitable for the temperature range indicated by the design conditions. Other considerations, such as suitable corrosion resistance, are addressed elsewhere.

Figure A1-1 displays the typical temperature ranges that may be used for the basic materials of construction. Note that the indicated temperature ranges and the thresholds for high-temperature damage phenomena (e.g., embrittlements) can vary because of specific alloy chemistry, fabrication practices such as cold work, etc. Thus, this figure should be used only as a preliminary guide. Once candidate materials have been chosen, their suitability for high temperature service should be confirmed. The upper temperatures indicated in Figure A1-1 are the highest temperatures for which allowable stresses are provided by the ASME pressure vessel and piping codes.

Table A1-1 shows the useful lower limits for common materials of construction intended for low temperature service. In both Figure A1-1 and Table A1-1, the indicated lower limits should be regarded as guidelines. In some cases, such as carbon and low-alloy steels, the lower limits may be influenced by factors such as section thickness and heat treatment.

Figure A1-1 and Table A1-1 should be used to ensure that the desired material of construction is a candidate for the intended range of design temperatures. If it appears that the material may be a marginal choice, the user may need to consult with vendors or alloy specialists to establish suitability.

Table A1-2 shows typical upper temperature limits for avoiding oxidation and scaling of the basic materials of construction. Note that these limits may be

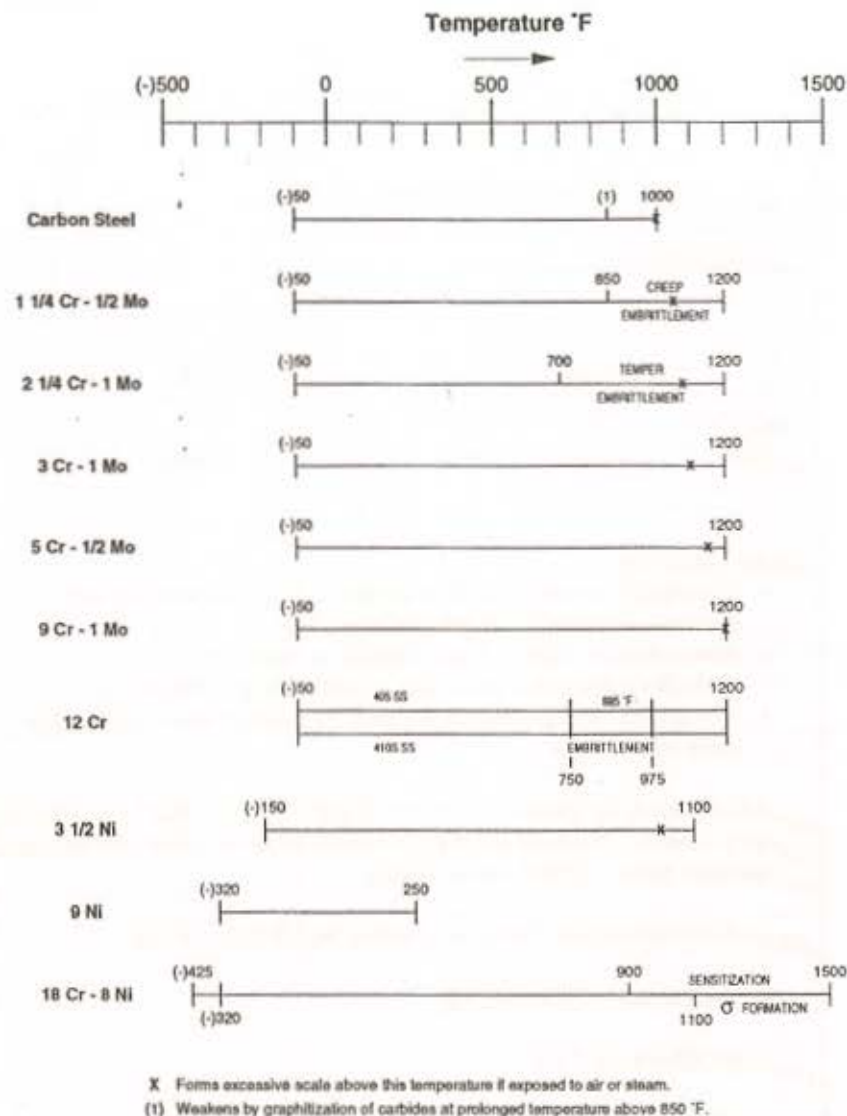


Figure A1-1 Materials selection as a function of temperature. (The upper value of the temperature range represents the limit for which code-allowable stresses are available.)

Table A1-1 Materials for low temperatures

Component	Minimum Design Metal Temperature, °F	
	-50 to -21	-150 to -51
Plate and Pipe Fabricated from Plate	A516 ^{2,3}	A203 Gr D&E 2" max to -150°F ² or A203 Gr A&B 2" max to -100°F ² or A537 to -75°F ^{2,3}
Tube	<0.098" thick: A179 or A214. ≥0.098" thick: A334 Gr 1 or 6	A334 Gr 3 to -150°F or Gr 7 to -100°F
Pipe	A333 Gr 1 or Gr 6	A333 Gr 3
Welding Fittings	A420 Gr WPL6 or WPL6W	A420 Gr WPL3 or WPL3W
Forgings, Including ANSI Flanges, Fittings, Valves, Non-standard Pressure Vessel and Equipment Components ⁴	A350 Gr LF2 or A765 Gr II	A350 Gr LF3 or A765 Gr III
Castings, Including ANSI Fittings and Valves, Non-standard Pressure Vessel Components, Pumps and Compressors	A352 Gr LCB	A352 Gr LC3 ⁶
Structural Steel Shapes and Members ⁷	< ½" thick: A36. ≥ ½": A36 - S2 or A633	9Ni or 18Cr-8Ni
Plate Clips, Lugs, Skirts, Saddles, Legs, etc. ⁷	Same as pressure shell material	
Bolts/Nuts	A193 Gr B7M/A194 Gr 7 ^{8,9}	A320 Gr L7/A194 Gr 7M

Table A1-1 (Continued)

Component	Minimum Design Metal Temperature, °F	
	-32 to -151	-425 to -321
Plate and Pipe Fabricated from Plate	A240 ¹⁰ or A353 or A553 Tp I, 2" max., to -320°F or A553 Tp II or A645 to -275°F or B209 Alloy 5083/5456	A240 ¹⁰ or B209 Alloy 5083/5456
Tube	A249 or A213 ¹⁰ or A334 Gr 8 to -320°F or B209 Alloy 5083/5456	A249 or A213 ¹⁰ or B234 Alloy 6061
Pipe	A358 or A312 ¹⁰ or A333 Gr 8 or B209 Alloy 5083/5456	A358 or A312 ¹⁰ or B241 Alloy 6061
Welding Fittings	A420 Gr WPL8	A403 ¹⁰ or B361 Alloy 6061
Forgings, Including ANSI Flanges, Fittings, Valves, Non-standard Pressure Vessel and Equipment Components ⁴	A182 ¹⁰ or A522 or B247 Alloy 6061	A182 ¹⁰ or B247 Alloy 6061
Castings, Including ANSI Fittings and Valves, Non-standard Pressure Vessel Components, Pumps and Compressors	A352 Gr LC9 ⁶	A351 Grade to Match Wrought Chemistry ⁶

Table A1-1 (Continued)

Component	Minimum Design Metal Temperature, °F	
	-320 to -151	-425 to -321
Structural Steel Shapes and Members ²	9Ni or 1Cr-8Ni	A666 Tp304, 304L, 316, and 316L
Plate Clips, Lugs, Skirts, Saddles, Legs, etc. ⁷	Same as pressure shell material	
Bolts/Nuts	A320 Gr B8, Cl 2/A194 Gr 8	A320 Gr B8, Cl 1/A194 Gr 8A

¹ 3½ Ni steels have an intermittent history of welding problems. Austenitic stainless steels are a better choice.

² Unless exempted by paragraph UCS-66 of ASME Section VIII, Div. 1, this material must be impact tested at the minimum design metal temperature and meet the requirements of paragraph UG-84.

³ Materials designated in curve D of ASME Section VIII, Div. 1, Fig. UCS-66 are alternatives.

⁴ API 605 flanges are included.

⁵ The thicknesses indicated are at the weld ends of the forgings.

⁶ Cast austenitic stainless steels for ASME Section VIII, Division 1 and 2 applications shall be impact tested per the appropriate code. For ASME B31.3 and other applications, impact testing shall comply with paragraph 323.3 of ASME B31.3.

⁷ The maximum thickness of a structural shape welded directly to a pressure-containing component shall be ¾" (19 mm). When heavier thicknesses are required or if plate or pipe materials are used, the material for the part shall be selected from the table.

⁸ A193 Gr B7 bolting, with A194 Gr 7 nuts, may be used for temperatures down to -40°F (-40°C).

⁹ See ASME B31.3, Appendix A Tables, note 42:

- A194 Gr 1 & 2 nuts: -20 to 900°F (-29 to 482°C).
- A194 Gr 2H & 2HM nuts: -50 to 1100°F (-46 to 593°C).

¹⁰ Types/Grades 304, 304L, 316, 316L and 347 are acceptable for temperatures of -425°F (-254°C) and warmer. Other types and grades, including Type 321, are acceptable for temperatures of -320°F (-196°C) and warmer (see Table UHA-23 of ASME Section VIII, Div. 1). The low-carbon and stabilized grades are preferred for welded construction.

Table A1-2 Oxidation threshold temperatures for commonly used materials of construction

MATERIAL	MAXIMUM PROLONGED TEMPERATURE IN AIR OR STEAM WITHOUT EXCESSIVE SCALING
Carbon Steel	1000°F (538°C)
1¼Cr-1½Mo	1050°F (566°C)
2¼Cr-1Mo	1075°F (579°C)
3Cr-1Mo	1100°F (593°C)
5Cr-½Mo	1150°F (621°C)
9Cr-1Mo	1200°F (649°C)
3½Ni	1000°F (538°C)
9 Ni	1000°F (538°C)
12 Cr	1500°F (816°C)
Stainless Steels (18Cr-8Ni types)	1650°F (899°C)
Type 309 and Type 310 SS ¹	2000°F (1093°C)

¹ See Note 7 on p. 362.

exceeded in atmospheres that are reducing or when insulation or refractory protects the metal from an oxidizing environment.

Table A1-3 is useful for selecting bolting materials as a function of the design temperature range. The indicated limits are consistent with code recommendations. However, the user should always check specific code limitations, as these may vary somewhat among the codes.

Table A1-4 contains detailed information on the lower and upper temperature limits for the commonly used ASME Section VIII and ASME B31.3 materials. This table also includes the ASTM specifications available for the various product forms that may be required. Since code information changes periodically, the user must always refer to the most current code for confirmation. Specifications in Table A1-4 that are indicated in italics do not have Code maximum allowable stresses.

Table A1-3 Temperature ranges for common bolting materials¹

TEMPERATURE RANGE	MATERIAL	BOLTS	NUTS
-20 to 1100°F (-29 to 593°C)	Cr-Mo-V	A193 Gr B16	A194 Gr 7
-40 to 1000°F (-40 to 538°C)	414X	A193 Gr B7	A194 Gr 7
-50 to 1000°F (-46 to 538°C)	414X	A193 Gr B7M	A194 Gr 7
-150 to 700°F (-101 to 371°C)	414X	A320 Gr L7	A194 Gr 7M
-425 to 1500°F (-254 to 816°C)	Tp 304 SS	A193 Gr B8, C11	A194 Gr B8
-325 to 1000°F (-198 to 538°C)	Tp 304 SS	A320 Gr B8, C12	A194 Gr 8
-425 to 1500°F (-254 to 816°C)	Tp 304 SS	A320 Gr B8, C11	A194 Gr 8A

¹See also A453 for selecting high-strength, high-alloy bolts for high-temperature service and the following ASTM specifications for selecting a variety of bolting materials for use in general service:

- A307 "Carbon Steel Bolts and Studs, 60,000 psi Tensile Strength"
- A325 "High Strength Bolts for Structural Steel Joints"
- A354 "Quenched and Tempered Alloy Steel Alloy Bolts, Studs and Other Externally Threaded Fasteners"
- A449 "Quenched and Tempered Steel Bolts and Stud"
- A574 "Alloy Steel Socket-Head Cap Screws"

Table A1-4 ASTM specifications for common materials of construction

Material	Table	Page
Section 1: Carbon and Low-Alloy Steels		
Cast Iron	A1-4.1	305
Carbon Steel	A1-4.2	306
1½Cr-½Mo	A1-4.3	308
2½Cr-1Mo	A1-4.4	309
3Cr-1Mo	A1-4.5	310
5Cr-½Mo	A1-4.6	311
9Cr-1Mo	A1-4.7	312
3½Ni	A1-4.8	313
9 Ni	A1-4.9	314
Section 2: Stainless Steels		
12 Cr	A1-4.10	315
Type 304	A1-4.11	316
Type 304L	A1-4.12	317
Type 304H	A1-4.13	318
Type 309	A1-4.14	319
Type 310	A1-4.15	320
Type 316	A1-4.16	321
Type 316L	A1-4.17	322
Type 316H	A1-4.18	323
Types 316Ti and 316Cb	A1-4.19	324
Type 321	A1-4.20	325
Type 321H	A1-4.21	326
Type 347	A1-4.22	327
Type 347H	A1-4.23	328
Type 348	A1-4.24	329
Type 348H	A1-4.25	330
Duplex Stainless Steels	A1-4.26	331
Section 3: Super Austenitic Stainless Steels		
Alloy 254 SMO	A1-4.27	332
Alloy 20-Mod	A1-4.28	333
Alloy AL-6XN	A1-4.29	334
Alloy 904L	A1-4.30	335

Table A1-4 (Continued)

Material	Table	Page
Section 4: Nickel Alloys		
Alloy 200	A1-4.31	336
Alloy 201	A1-4.32	337
Alloy 400	A1-4.33	338
Alloy X	A1-4.34	339
Alloy C-22	A1-4.35	340
Alloy G-30	A1-4.36	341
Alloy C-4	A1-4.37	342
Alloy 600	A1-4.38	343
Alloy 625	A1-4.39	344
Alloy G-3	A1-4.40	345
Alloy 20 Cb-3	A1-4.41	346
Alloy 800	A1-4.42	347
Alloy 825	A1-4.43	348
Alloy C-276	A1-4.44	349
Alloy B-2	A1-4.45	350
Section 5: Copper Alloys		
Inhib. Admiralty Brass	A1-4.46	351
Naval Brass	A1-4.47	352
Aluminum Bronze	A1-4.48	353
Ni-Al Bronze	A1-4.49	354
90/10 Cu/Ni	A1-4.50	355
70/30 Cu/Ni	A1-4.51	356
Section 6: Miscellaneous Alloys		
Aluminum	A1-4.52	357
Ni-Resist	A1-4.53	358
Tantalum	A1-4.54	359
Titanium	A1-4.55	360
Zirconium	A1-4.56	361

Table A1-4.1 ASTM specifications for common materials of construction

Material: Cast Iron (General Note 4, p. 362)

Oxidation Scaling Threshold: 1000°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-450 to 650°F ¹	No listings.	-20 to 650°F ¹

Product forms for which code-allowable stresses are availableCastings: VIII, Div. 1: A47², A278³, A667⁴ & A748⁴.B31.3: A47², A48³, A126³, A197², A278³ & A395⁵.
A220⁶, A532⁷, A536⁵, A861⁸ & A874⁹.Compatible There are no Code or ASTM listings for cast iron bolts. See Table
Bolting: A1-3 (p. 302).*Note:* Specifications that are indicated in italics do not have Code maximum allowable stresses.¹ Upper temperature allowable may depend on the specification.² Malleable cast iron.³ Gray cast iron.⁴ Dual-layer gray and white cast iron.⁵ Ductile cast iron.⁶ Pearlitic malleable iron.⁷ White cast iron.⁸ High-silicon cast iron.⁹ Ferritic ductile iron.

Table A1-4.2 ASTM specifications for common materials of construction

Material: Carbon Steel (General Notes 1-4, p. 362)

Oxidation Scaling Threshold: 1000°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-50 to 1000°F	-50 to 700°F	-50 to 1100°F

Product forms for which code-allowable stresses are available

Plate:	A36; A283; A285; A299; A455; A515 ¹ ; A516 ² ; A537 ³ ; A562; A570; A612; A662; A724; A737; A738.
Pipe:	A53 Gr A & B; A106; API 5L; A134; A135; A139; A333 ⁴ Gr 1 & 6; A369; A381; A524; A587; A671; A672; A691.
Tubing:	For $t < 0.098"$, suitable to -50°F: A178, A179, A192, A210, A214, A226, A556 and A557. For $t \geq 0.098"$, suitable to -50°F: A334 ⁴ Gr 1 & 6. For general use: A178, A179, A192, A210, A214, A226, A556 and A557.
Fittings:	A234 Gr WPB; A420 ⁴ Gr WPL6 & WPL6W.
Forgings:	A105 ⁵ ; A181 ⁵ ; A266 ⁶ ; A350 ^{4,5} Gr LF2; A372 ⁶ ; A508 ^{6,7} ; A541 ⁶ ; A727; A765 ^{4,6} .
Bars:	A36; A675; A695
Castings:	A216 Gr WCB; A352 ⁴ Gr LCB.
Compatible	A193 Gr B7 (with A194 Gr B7 nuts): to -40°F;
Bolting:	A193 Gr B7M (with A194 Gr B7M nuts): to -50°F.

*See the appropriate code for the allowable temperature ranges for bolting.*¹ Preferred for sustained temperatures above 800°F.² Preferred for sustained temperatures less than 800°F.³ Preferred for low-temperature services too severe for A516 (see Table A1.15 of ASTM A20).⁴ Mill qualified to -50°F.⁵ Intended for piping.⁶ Intended for pressure vessels.⁷ Mill qualified at 70°F, 40°F, 0°F or -20°F, depending on grade.**Table A1-4.2** (Continued)

While not having code-listed maximum allowable stresses, the following specifications are available for the indicated product forms.

Plate: A299; A414; A562¹; A812.**Pipe:** A660; A691.**Fittings:** A758; A858.**Forgings:** A707^{2,3}; A727⁴; A836¹; API 605⁴.**Castings:** A487.

Compatible See A307, A325 and A675 for carbon steel bolting materials suitable for general construction in accordance with ASME B31.3. A193 Gr B7 and Gr B7M are usually preferred for pressure-retaining applications.

¹ Intended for glass-lined piping and vessels.² Intended for pipelines.³ Mill qualified at -20°F, -50°F or -100°F, depending on grade.⁴ Intended for piping.

Table A1-4.3 ASTM specifications for common materials of construction

Material: 1 1/4Cr-1/2Mo Steel (General Notes 2 & 4, p. 362)

Oxidation Scaling Threshold: 1050°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-50 to 1200°F	-50 to 900°F	-20 to 1200°F

Product forms for which code-allowable stresses are available

Plate:	A387 Gr 11; A426 Gr CP11.
Pipe:	A335 Gr P11; A369 Gr FP11; A691 Gr 1 1/4Cr.
Tubing:	A199 Gr T11; A213 Gr T11. <i>A200 Gr T11; A250 Gr T11.</i>
Fittings:	A182 Gr F11, Cl 1 & 2; A234 Gr WP11.
Forgings:	A182 ¹ Gr F11, Cl 1 & 2; A336 ² Gr F11, Cl 1 & 2. <i>A541² Gr 11 Cl 4.</i>
Bars:	A739 Gr B11.
Castings:	A217 Gr WC6.
Compatible	A193 Gr B16: to -20°F;
Bolting:	A193 Gr B7: to -40°F; A193 Gr B7M: to -50°F.

See also A508 Gr 4n & Gr 5; *A540 Gr B21 & Gr B22.**See the appropriate code for the allowable temperature ranges for bolting.*¹ Intended for piping.² Intended for pressure vessels.

Table A1-4.4 ASTM specifications for common materials of construction

Material: 2 1/4Cr-1Mo Steel (General Notes 2 & 4, p. 362)

Oxidation Scaling Threshold: 1075°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-50 to 1200°F	-50 to 900°F	-20 to 1200°F

Product forms for which code-allowable stresses are available

Plate:	A387 Gr 22 & 22L. <i>A542 Tp A & B.</i>
Pipe:	A335 Gr P22; A369 Gr FP22; A426 Gr CP22; A691 Gr 2 1/4Cr.
Tubing:	A199 Gr T22; A213 Gr T22. <i>A200 Gr T22; A250 Gr T22.</i>
Fittings:	A182 Gr F22 Cl 1 & 3; A234 Gr WP22 Cl 1.
Forgings:	A182 ¹ Gr F22 Cl 1 & 3; A336 ² Gr F22 Cl 1 & 3. <i>A508² Gr 22 Cl 3; A541² Gr 22 Cl 3.</i>
Bars:	A739 Gr B22.
Castings:	A217 Gr WC9; A487 Gr 8, Cl A.
Compatible	
Bolting:	No Code or ASTM listings. See Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.¹ Intended for piping.² Intended for pressure vessels.

Table A1-4.5 ASTM specifications for common materials of construction**Material:** 3Cr-1Mo Steel (General Notes 2 & 4, p. 362)**Oxidation Scaling Threshold:** 1100°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-50 to 1200°F	-50 to 850°F	-20 to 1200°F

Product forms for which code-allowable stresses are available

- Plate:** A387 Gr 21 & 21L; A542 Tp C, Cl 4A; A832.
- Pipe:** A335 Gr P21; A369 Gr FP21; A426 Gr CP21; A691 Gr 3Cr.
- Tubing:** A199 Gr T21; A213 Gr T21. *A200 Gr T21.*
- Fittings:** A182 Gr F21 & F3V.
- Forgings:** A182¹ Gr F21 & F3V; A336² Gr F21 Cl 1 & 3 and F3V; A508² Gr 3V; A541² Gr 3V.
- Bars:** No Code or ASTM listings; use a forging specification.
- Castings:** No Code or ASTM listings.

Compatible**Bolting:** No Code or ASTM listings. See Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ Intended for piping.² Intended for pressure vessels.**Table A1-4.6** ASTM specifications for common materials of construction**Material:** 5Cr-½Mo (General Notes 2 & 4, p. 362)**Oxidation Scaling Threshold:** 1150°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-50 to 1200°F	-50 to 850°F	-20 to 1200°F

Product forms for which code-allowable stresses are available

- Plate:** A387 Gr 5 Cl 1 & 2.
- Pipe:** A335 Gr P5, P5b & P5c; A369 Gr FP5; A426 Gr CP5; A691 Gr 5Cr.
- Tubing:** A199 Gr T5; A213 Gr T5, T5b & T5c. *A200 Gr T5.*
- Fittings:** A182 Gr F5 & F5a; A234 Gr WP5.
- Forgings:** A182¹ Gr F5 & F5a; A336² Gr F5 & F5A. *A473 Tp 501.*
- Bars:** No Code or ASTM listings; use a forging specification.
- Castings:** A217 Gr C5.

Compatible**Bolting:** A193 Gr B5: to -20°F. See A194 Gr 3 for compatible nuts.

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ Intended for piping.² Intended for pressure vessels.

Table A1-4.7 ASTM specifications for common materials of construction**Material:** 9Cr-1Mo (General Notes 2 & 4, p. 362)**Oxidation Scaling Threshold:** 1200°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-50 to 1200°F	-50 to 700°F	-20 to 1200°F

Product forms for which code-allowable stresses are available**Plate:** A387 Gr 9, Cl 1 & Gr 91, Cl 2.**Pipe:** A335 Gr P9 & P91; A369 Gr FP9 & FP91; A426 Tp CP9.
*A691 Gr 9CR.***Tubing:** A199 Gr T9; A213 Gr T9 & T91. *A200 Gr T9 & T91.***Fittings:** A182 Gr F9 & F91; A234 Gr WP9. *A234 Gr WP91.***Forgings:** A182¹ Gr F9 & F91; A336² Gr F9 & F91. *A473 Tp 501B.***Bars:** No Code or ASTM listings; use a forging specification.**Castings:** A217 Gr C12.**Compatible****Bolting:** No Code or ASTM listings. See Table A1-3 (p. 302).*Note:* Specifications that are indicated in italics do not have Code maximum allowable stresses.¹ Intended for piping.² Intended for pressure vessels.**Table A1-4.8** ASTM specifications for common materials of construction**Material:** 3½ Ni Steel (General Note 2, p. 362; Note 1 of Table A1-1, p. 298)**Oxidation Scaling Threshold:** 1000°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-150 to 1000°F ¹	-150 to 300°F ¹	-150 to 1100°F ¹

Product forms for which code-allowable stresses are available**Plate:** A203 Gr D, E, & F.**Pipe:** A333² Gr 3.**Tubing:** A334² Gr 3.**Fittings:** A420² Gr WPL3 & WPL3W.**Forgings:** A350^{2,3} Gr LF3; A765^{2,4} Gr III. *A707^{5,6} Gr L7.***Bars:** No Code or ASTM listings; use a forging specification.**Castings:** A352² Gr LC3.**Compatible****Bolting:** No Code or ASTM listings. See Table A1-3 (p. 302).*Note:* Specifications that are indicated in italics do not have Code maximum allowable stresses.¹ The upper allowable temperature may depend on the product form.² Mill qualified to -150°F³ Intended for piping.⁴ Intended for pressure vessels.⁵ Mill qualified to -100°F.⁶ Intended for pipelines.

Table A1-4.9 ASTM specifications for common materials of construction

Material: 9% Ni Steel (General Note 2, p. 362)

Oxidation Scaling Threshold: 1000°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 250°F	-320 to 250°F	-320 to 200°F

Product forms for which code-allowable stresses are availablePlate: A353¹; A553¹ Tp I.Pipe: A333¹ Gr 8.Tubing: A334¹ Gr 8.Fittings: A420¹ Gr WPL8 & WPL8W.Forgings: A522¹ Gr I.

Bars: No Code or ASTM listings; use a forging specification.

Castings: No Code listings. Consider A352 Gr LC9¹.

Compatible

Bolting: No Code or ASTM listings. See Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ Mill qualified to -320°F.

Table A1-4.10 ASTM specifications for common materials of construction

Material: 12 Cr Stainless Steel (General Note 2, p. 362)

Tp 405: (UNS S40500)

Tp 410: (UNS S41000)

Tp 410S: (UNS S41008)

UNS S41500¹

Oxidation Scaling Threshold: 1500°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-20 to 1200°F ²	-20 to 800°F	-20 to 1200°F ²

Product forms for which code-allowable stresses are availablePlate: A240³ Tp 405, Tp 410 & Tp 410S.*A176 Tp 405, Tp 410 & Tp 410S.*Pipe: No Code listings. Consider A731 *UNS S41500¹*.Tubing: A268 Tp 405 & Tp 410. *A268 UNS S41500¹*.Fittings: A182 Gr F6a. *A815 Gr 410 & UNS S41500¹*.Forgings: A182⁴ Gr F6a; A336⁵ Gr F6. *A473 Tp 405, Tp 410 & Tp 410S.*

Bars: A479 Tp 405 & Tp 410.

Castings: A217 Gr CA-15; A487 Gr CA-6NM (preferred).

*A352 Gr CA-6NM⁶; A743 Gr CA-6NM.*Compatible A193 Gr B6⁷; A437 Gr B4C.Bolting: *A437 Gr B4B & Gr B4D, F593 Tp 410; F594 TP 410.*

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ Plate version of CA-6NM.

² The upper allowable temperature may depend on the alloy composition and the product form.

³ See A263 for clad plate.

⁴ Intended for piping.

⁵ Intended for pressure vessels.

⁶ Mill qualified at -100°F.

⁷ Equivalent to Tp 410 SS.

Table A1-4.11 ASTM specifications for common materials of construction

Material: Type 304 Stainless Steel (General Note 2, p. 362)
UNS S30400 (18Cr-8Ni)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-425 to 1500°F	-425 to 800°F	-425 to 1500°F

Product forms for which code-allowable stresses are available

Plate: A240¹ Tp 304. *A666 Tp 304.*

Pipe: A312 Tp 304; A358 Tp 304; A376 Tp 304; A409 Tp 304; A430 Gr FP304. *A688 Tp 304; A813 Tp 304; A814 Tp 304; A851 Tp 304.*

Tubing: A213 Tp 304; A249 Tp 304; A269 Tp 304; A688 Tp 304. *A271 Tp 304; A632 Tp 304; A851 Tp 304.*

Fittings: A182 Gr F304; A403 Gr 304.

Forgings: A182² Gr F304; A336³ Gr F304. *A473 Tp 304.*

Bars: A479 Tp 304. *A666 Tp 304.*

Castings: A351⁴ Gr CF-8. *A743 Gr CF-8; A744 Gr CF-8.*

Compatible

Bolting: A193 or A320, Gr B8; to -425°F. *F593 Tp 304; F594 Tp 304.*

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² Intended for piping.

³ Intended for pressure vessels.

⁴ The lower temperature limit, without impact testing, may be -20°F.

Table A1-4.12 ASTM specifications for common materials of construction

Material: Type 304L Stainless Steel (General Note 2, p. 362)
UNS S30403 (18Cr-8Ni, low carbon)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-425 to 800°F	-425 to 800°F	-425 to 1500°F

Product forms for which code-allowable stresses are available

Plate: A240¹ Tp 304L. *A666 Tp 304L.*

Pipe: A312 Tp 304L; A358 Tp 304L. *A409 Tp 304L; A688 Tp 304L; A778 Tp 304L; A813 Tp 304L; A814 Tp 304L; A851 Tp 304L.*

Tubing: A213 Tp 304L; A249 Tp 304L; A269 Tp 304L; A688 Tp 304L. *A632 Tp 304L; A851 Tp 304L.*

Fittings: A182 Gr F304L; A403 Gr 304L. *A774 Tp 304L.*

Forgings: A182² Gr F304L; A336³ Gr F304L. *A473 Tp 304L.*

Bars: A479 Tp 304L. *A276 Tp 304L; A314 Tp 304L; A666 Tp 304L.*

Castings: A351⁴ Gr CF-3. *A743 Gr CF-3; A744 Gr CF-3.*

Compatible There are no Code or ASTM listings for Tp 304L bolts.

Bolting: Machine from bar stock if compatibility is necessary; otherwise, use A193 or A320 Gr B8 & B8C; to -425°F.

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² Intended for piping.

³ Intended for pressure vessels.

⁴ The lower temperature limit, without impact testing, may be -20°F.

Table A1-4.13 ASTM specifications for common materials of construction

Material: Type 304H Stainless Steel (General Note 2, p. 362)
UNS S30409 (18Cr-8Ni, high carbon)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 1500°F	-325 to 800°F	-325 to 1500°F

Product forms for which code-allowable stresses are available

Plate:	A240 Tp 304H. ¹
Pipe:	A312 Tp 304H; A376 Tp 304H; A430 Gr FP304H; A452 Tp 304H. A358 Tp 304H; A813 Tp 304H; A814 Tp 304H.
Tubing:	A213 Tp 304H; A249 Tp 304H. <i>A271 Tp 304H.</i>
Fittings:	A182 Gr F304H; A403 Gr 304H.
Forgings:	A182 ² Gr F304H; A336 ³ Gr F304H.
Bars:	A479 Tp 304H.
Castings:	A351 ⁴ Gr CF-10.
Compatible	There are no Code or ASTM listings for Tp 304H bolts.
Bolting:	Machine from bar stock if compatibility is necessary; otherwise, use A193 or A320 Gr B8 & B8C: to -425°F.

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ No listing for ASME Section VIII, Div. 2 or ASME B31.3.

² Intended for piping.

³ Intended for pressure vessels.

⁴ The lower temperature limit, without impact testing, may be -20°F.

Table A1-4.14 ASTM specifications for common materials of construction

Material: Type 309 Stainless Steel (General Note 2, p. 362)

Tp 309: UNS S30900 (23Cr-12Ni)

Tp 309S: UNS S30908 (23Cr-12Ni, low carbon)

Tp 309H: UNS S30909 (23Cr-12Ni, high carbon)

Tp 309Cb: UNS S30940 (23Cr-12Ni, Cb stabilized)

Tp 309HCB: UNS S30941 (23Cr-12Ni, high carbon, Cb stabilized)

Oxidation Scaling Threshold: 2000°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 1500°F	-325 to 800°F	-325 to 1500°F

Tp 309 SS containing carbon in excess of 0.1 wt. percent is not permitted in ASME Section VIII, Div. 1 at temperatures less than -50°F, or in Div. 2 at temperatures less than -20°F, without impact testing.

Product forms for which code-allowable stresses are available

Plate:	A167 Tp 309; A240 ¹ Tp 309S, 309H & 309Cb. <i>A240 Tp 309HCB.</i>
Pipe:	A312 Tp 309, 309S, 309H & 309Cb; A358 Tp 309S; A813 Tp 309S & 309Cb; A814 Tp 309S & 309Cb. <i>A312 Tp 309HCB; A358 Tp 309Cb; A409 Tp 309S & 309Cb.</i>
Tubing:	A213 Tp 309S & 309Cb; A249 Tp 309S, 309H & 309Cb. <i>A249 Tp 309HCB.</i>
Fittings:	A403 Gr 309.
Forgings:	No Code listings. <i>A473 Tp 309 & 309S.</i>
Bars:	A479 Tp 309S, 309H & 309Cb.
Castings:	A351 ² Gr CH-8 ³ , Gr CH-10 ⁴ & Gr CH-20 ⁵ .
Compatible	There are no Code or ASTM listings for Tp 309 bolts.
Bolting:	Machine from bar stock or see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² The lower limit, without impact testing, is -20°F.

³ The CH-8 material is compatible with Tp 309S.

⁴ The CH-10 material is compatible with Tp 309H.

⁵ The CH-20 material is compatible with Tp 309.

Table A1-4.15 ASTM specifications for common materials of construction

Material: Type 310 Stainless Steel (General Note 2, p. 362)
 Type 310: UNS S31000 (25Cr-20Ni)
 Type 310S: UNS S31008 (25Cr-20Ni, low carbon)
 Type 310H: UNS S31009 (25Cr-20Ni, high carbon)
 Type 310Cb: UNS S31040 (25Cr-20Ni, Cb stabilized)
 Type 310HCB: UNS S31041 (25Cr-20Ni, high carbon, Cb stabilized)

Oxidation Scaling Threshold: 2000°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 1500°F	-325 to 800°F	-325 to 1500°F

Tp 310 SS containing carbon in excess of 0.1 wt. percent is not permitted in ASME Section VIII, Div. 1 at temperatures less than -50°F, or in Div. 2 at temperatures less than -20°F, without impact testing.

Product forms for which code-allowable stresses are available

Plate: A167 Tp 310; A240¹ Tp 310S, 310H & 310Cb. *A240 Tp 310HCB.*
Pipe: A312 Tp 310, 310S, 310H & 310Cb; A358 Tp 310S; A813 Tp 310S & 310Cb; A814 Tp 310S & 310Cb. *A312 Tp 310HCB; A358 Tp 310Cb; A409 Tp 310S & 310Cb.*
Tubing: A213 Tp 310S, 310H & 310Cb; A249 Tp 310S, 310H & 310Cb. *A249 Tp 310HCB; A632 Tp 310.*
Fittings: A182 Gr F310; A403 Gr 310.
Forgings: A182² Gr F310; A336³ Gr F310. *A473 Tp 310 & 310S.*
Bars: A479 Tp 310S, 310H & 310Cb.
Castings: A351⁴ Gr CK-20.

Compatible There are no Code or ASTM listings for Tp 310 bolts.

Bolting: Machine from bar stock or see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² Intended for piping.

³ Intended for pressure vessels.

⁴ The lower temperature limit, without impact testing, may be -20°F.

Table A1-4.16 ASTM specifications for common materials of construction

Material: Type 316 Stainless Steel (General Note 2, p. 362)
 UNS S31600 (16Cr-12Ni-2Mo)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-425 to 1500°F	-425 to 800°F	-425 to 1500°F

Product forms for which code-allowable stresses are available

Plate: A240¹ Tp 316. *A666 Tp 316.*
Pipe: A312 Tp 316; A358 Tp 316; A376 Tp 316; A409 Tp 316; A430 Gr FP316. *A688 Tp 316; A813 Tp 316; A814 Tp 316.*
Tubing: A213 Tp 316; A249 Tp 316; A269 Tp 316; A688 Tp 316. *A271 Tp 316; A632 Tp 316.*
Fittings: A182 Gr F316; A403 Gr 316.
Forgings: A182² Gr F316; A336³ Gr F316. *A473 Tp 316.*
Bars: A479 Tp 316. *A276 Tp 316; A314 Tp 316; A666 Tp 316.*
Castings: A351⁴ Gr CF-8M. *A743 Gr CF-8M; A744 Gr CF-8M.*
Compatible
Bolting: A193 & A320 Gr B8M: to -425°F. *F593 Tp 316; F594 Tp 316.*

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² Intended for piping.

³ Intended for pressure vessels.

⁴ The lower temperature limit, without impact testing, may be -20°F.

Table A1-4.17 ASTM specifications for common materials of construction

Material: Type 316L Stainless Steel (General Note 2, p. 362)
UNS S31603 (16Cr-12Ni-2Mo, low carbon)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-425 to 850°F	-325 to 800°F	-425 ¹ to 1500°F

Product forms for which code-allowable stresses are available

Plate: A240² Tp 316L. *A666 Tp 316L.*

Pipe: A312 Tp 316L; A358 Tp 316L. *A409 Tp 316; A778 Tp 316L; A813 Tp 316L; A814 Tp 316L.*

Tubing: A213 Tp 316L; A249 Tp 316L; A269 Tp 316L; A688 Tp 316L. *A632 Tp 316L.*

Fittings: A182 Gr F316L; A403 Gr 316L. *A774 Tp 316L.*

Forgings: A182³ Gr F316L; A336⁴ Gr 316L. *A473 Tp 316L.*

Bars: A479 Tp 316L. *A666 Tp 316L.*

Castings: A351⁵ Gr CF-3M. *A744 Gr CF-3M.*

Compatible There are no Code or ASTM listings for Tp 316L bolts.

Bolting: Machine from bar stock if compatibility is necessary; otherwise, use A193 or A320 Gr B8M: to -425°F.

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ The lower allowable temperature depends on the product form.

² See A264 for clad plate.

³ Intended for piping.

⁴ Intended for pressure vessels.

⁵ The lower temperature limit, without impact testing, may be -20°F.

Table A1-4.18 ASTM specifications for common materials of construction

Material: Type 316H Stainless Steel (General Note 2, p. 362)
UNS S31609 (16Cr-12Ni-2Mo, high carbon)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 1500°F	-325 to 800°F	-325 to 1500°F

Product forms for which code-allowable stresses are available

Plate: A240¹ Tp 316H.

Pipe: A312 Tp 316H; A376 Tp 316H; A430 Gr FP316H; A452 Tp 316H. *A358 Tp 316H; A813 Tp 316H; A814 Tp 316H.*

Tubing: A213 Tp 316H; A249 Tp 316H. *A271 Tp 316H.*

Fittings: A182 Gr F316H; A403 Gr 316H.

Forgings: A182² Gr F316H; A336³ Gr F316H.

Bars: No Code listings. *A479 Tp 316H.*

Castings: No Code listings. *A351 Gr CF-10M.*

Compatible There are no Code or ASTM listings for Tp 316H bolts.

Bolting: Machine from bar stock if compatibility is necessary; otherwise, use A193 or A320 Gr B8M: to -425°F.

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate

² Intended for piping.

³ Intended for pressure vessels.

Table A1-4.19 ASTM specifications for common materials of construction

Material: Types 316Ti and 316Cb Stainless Steel (General Note 2, p. 362)
 UNS S31635 (16Cr-12Ni-2Mo, Ti stabilized)
 UNS S31640 (16Cr-12Ni-2Mo, Cb stabilized)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 1500°F ¹	No listings.	No listings.

Product forms for which code-allowable stresses are available

Plate: A240² Tp 316Ti & Tp 316Cb.

Pipe: No Code or ASTM listings.

Tubing: No Code or ASTM listings.

Fittings: No Code or ASTM listings.

Forgings: No Code or ASTM listings.

Bars: No Code or ASTM listings.

Castings: No Code or ASTM listings.

Compatible There are no Code or ASTM listings for Types 316Ti or 316Cb

Bolting: bolts. See Table A1-3 (p. 302).

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ Code-allowable stresses are available for plate only.

² See A264 for clad plate.

Table A1-4.20 ASTM specifications for common materials of construction

Material: Type 321 Stainless Steel (General Note 2, p. 362)
 UNS S32100 (18Cr-10Ni, Ti stabilized)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-425 to 1500°F	-325 to 800°F	-325 to 1500°F

Product forms for which code-allowable stresses are available

Plate: A240¹ Tp 321.

Pipe: A312 Tp 321; A358 Tp 321; A376 Tp 321; A409 Tp 321;
 A430 Gr FP321. *A778 Tp 321; A813 Tp 321; A814 Tp 321.*

Tubing: A213 Tp 321; A249 Tp 321. *A269 Tp 321; A271 Tp 321;
 A632 Tp 321.*

Fittings: A182 Gr F321; A403 Gr 321. *A774 Tp 321.*

Forgings: A182² Gr F321; A336³ Gr F321. *A473 Tp 321.*

Bars: A479 Tp 321. *A276 Tp 321; A314 Tp 321.*

Castings: A351 Gr CF-8C. *A743 Gr CF-8C; A744 Gr CF-8C.*

Compatible

Bolting: A193 or A320 Gr B8T; to -425°F. *F593 Tp 321; F594 Tp 321.*

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² Intended for piping.

³ Intended for pressure vessels.

Table A1-4.21 ASTM specifications for common materials of construction

Material: Type 321H Stainless Steel (General Note 2, p. 362)
UNS S32109 (18Cr-10Ni, high carbon, Ti stabilized)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 1500°F	-325 to 800°F	-325 to 1500°F

Product forms for which code-allowable stresses are available

Plate: A240¹ Tp 321H.²

Pipe: A312 Tp 321H; A376 Tp 321H; A430 Gr FP321H.
A813 Tp 321H; A814 Tp 321H.

Tubing: A213 Tp 321H; A249 Tp 321H. *A271 Tp 321H.*

Fittings: A182 Gr F321H; A403 Gr 321H.

Forgings: A182³ Gr F321H. *A336⁴ Gr F321H.*

Bars: No Code listings. *A479 Tp 321H.*

Castings: No Code or ASTM listings. *Consider A351 Gr CF-8C or Gr CF-10MC; see also A743 Gr CF-8C and A744 Gr CF-8C.*

Compatible There are no Code or ASTM listings for Tp 321H bolts.

Bolting: Machine from bar stock if compatibility is necessary; otherwise, use A193 or A320 Gr B8T: to -425°F.

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² No Code listing for ASME Section VIII, Div. 1 or ASME B31.3.

³ Intended for piping.

⁴ Intended for pressure vessels.

Table A1-4.22 ASTM specifications for common materials of construction

Material: Type 347 Stainless Steel (General Note 2, p. 362)
UNS S34700 (18Cr-10Ni, Cb stabilized)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-425 to 1500°F	-425 to 800°F	-425 to 1500°F

Product forms for which code-allowable stresses are available

Plate: A240¹ Tp 347.

Pipe: A312 Tp 347; A358 Tp 347; A376 Tp 347; A409 Tp 347;
A430 Tp 347. A778 Tp 347; A813 Tp 347; A814 Tp 347.

Tubing: A213 Tp 347; A249 Tp 347. *A269 Tp 347; A271 Tp 347;
A632 Tp 347.*

Fittings: A182 Gr F347; A403 Gr 347. *A774 Tp 347.*

Forgings: A182² Gr F347; A336³ Gr F347. *A473 Tp 347.*

Bars: A479 Tp 347. *A276 Tp 347; A314 Tp 347.*

Castings: A351 Gr CF-8C. *A743 Gr CF-8C; A744 Gr CF-8C.*

Compatible A193 or A320 Gr B8C: to -425°F. *F593 Tp 347; F594 Tp 347.*

Bolting:

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² Intended for piping.

³ Intended for pressure vessels.

Table A1-4.23 ASTM specifications for common materials of construction

Material: Type 347H Stainless Steel (General Note 2, p. 362)
UNS S34709 (18Cr-10Ni, high carbon, Cb stabilized)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 1500°F	-325 to 800°F	-325 to 1500°F

Product forms for which code-allowable stresses are available

- Plate:** A240¹ Tp 347H.²
- Pipe:** A312 Tp 347H; A376 Tp 347H; A430 Gr FP347H; A452 Tp 347H.
A813 Tp 347H; A814 Tp 347H.
- Tubing:** A213 Tp 347H; A249 Tp 347H. *A271 Tp 347H.*
- Fittings:** A182 Gr F347H; A403 Gr 347H.
- Forgings:** A182³ Gr F347H; A336⁴ Gr F347H.
- Bars:** No Code listings. *A479 Tp 347H.*
- Castings:** No Code or ASTM listings. *Consider A351 Gr CF-8C or Gr CF-10MC; see also A743 Gr CF-8C and A744 Gr CF-8C.*
- Compatible:** There are no Code or ASTM listings for Tp 347H bolts.
- Bolting:** Machine from bar stock if compatibility is necessary; otherwise, use A193 or A320 Gr B8C: to -425°F.

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² No Code listing for ASME Section VIII, Div. 1 or ASME B31.3.

³ Intended for piping.

⁴ Intended for pressure vessels.

Table A1-4.24 ASTM specifications for common materials of construction

Material: Type 348 Stainless Steel (General Note 2, p. 362)
UNS S34800 (18Cr-10Ni, Cb stabilized)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 1500°F	-325 to 800°F	-325 to 1500°F

Product forms for which code-allowable stresses are available

- Plate:** A240¹ Tp 348.
- Pipe:** A312 Tp 348; A358 Tp 348; A376 Tp 348; A409 Tp 348.
A813 Tp 348; A814 Tp 348.
- Tubing:** A213 Tp 348; A249 Tp 348. *A269 Tp 348; A632 Tp 348.*
- Fittings:** A182 Gr F348; A403 Gr 348.
- Forgings:** A182² Gr F348; A336³ Gr F348. *A473 Tp 348.*
- Bars:** A479 Tp 348.
- Castings:** No Code or ASTM listings. *Consider A351 Gr CF-8C, A743 Gr CF-8C or A744 Gr CF-8C.*
- Compatible:** There are no Code or ASTM listings for Tp 348 bolts.
- Bolting:** Machine from bar stock if compatibility is necessary; otherwise, use A193 or A320 Gr B8C: to -425°F.

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² Intended for piping.

³ Intended for pressure vessels.

Table A1-4.25 ASTM specifications for common materials of construction

Material: Type 348H Stainless Steel (General Note 2, p. 362)
UNS S34809 (18Cr-10Ni, high carbon, Cb stabilized)

Oxidation Scaling Threshold: 1650°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 1500°F	-325 to 800°F	-325 to 1500°F

Product forms for which code-allowable stresses are available

Plate: No Code listings. *A240¹ Tp 348H.*

Pipe: *A312 Tp 348H. A813 Tp 348H; A814 Tp 348H.*

Tubing: *A213 Tp 348H; A249 Tp 348H.*

Fittings: *A182 Gr F348H; A403 Gr F348H.*

Forgings: *A182² Gr F348H; A336³ Gr F348H.*

Bars: No Code or ASTM listings; use a forging specification.

Castings: No Code or ASTM listings. *Consider A351 Gr CF-8C or Gr CF-10MC; see also A743 Gr CF-8C and A744 Gr CF-8C.*

Compatible There are no Code or ASTM listings for Tp 348H bolts.

Bolting: Machine from bar stock if compatibility is necessary; otherwise, use A193 or A320 Gr B8C; to -425°F.

See the appropriate code for the allowable temperature ranges for bolting.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² Intended for piping.

³ Intended for pressure vessels.

Table A1-4.26 ASTM specifications for common materials of construction

Material: Duplex Stainless Steel
Alloy 2205 (22Cr-5Ni-3Mo-N): UNS S31803
UNS S32250: 25Cr-4Ni-3Mo-2Cu

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-20 to 600°F ¹	No listings.	-60 to 600°F ²

Product forms for which code-allowable stresses are available

Plate: *A240³ (both alloys).*

Pipe: *A790 (both alloys). A928 (both alloys).*

Tubing: *A789 (both alloys).*

Fittings: *A182 (Alloy 2205). A815 (Alloy 2205).*

Forgings: *A182⁴ (Alloy 2205).*

Bars: *A479 (UNS S32550). A276 (Alloy 2205).*

Castings: *A351 Gr CD-4MCu; A743 Gr CD-4MCu; A744 Gr CD-4MCu; A890 Gr CD-4MCu & Gr 4A.*

Compatible There are no Code or ASTM listings for duplex stainless steel bolts.

Bolting: Machine from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ The upper allowable temperature for UNS S32550 is 500°F.

² This Code lists only tubing and piping.

³ See A264 for clad plate.

⁴ Intended for piping.

Table A1-4.27 ASTM specifications for common materials of construction

Material: Alloy 254 SMO (20Cr-18Ni-6Mo)
UNS S31254

Oxidation Scaling Threshold: 1800°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-320 to 750°F	No listings.	No listings.

Product forms for which code-allowable stresses are available

Plate: A240¹ UNS S31254.

Pipe: A312 UNS S31254; A358 UNS S31254. *A813 UNS S31254; A814 UNS S31254.*

Tubing: A249 UNS S31254. *A269 UNS S31254.*

Fittings: A182 Gr F44. *A403 UNS S31254.*

Forgings: A182² Gr F44.

Bars: No Code or ASTM listings; use the forging specification.

Castings: A351 Gr CK-3MCuN. *A743 Gr CK-3MCuN; A744 Gr CK-3MCuN.*

Compatible There are no Code or ASTM listings for Alloy 254 SMO bolts.

Bolting: Machine from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A264 for clad plate.

² Intended for piping.

Table A1-4.28 ASTM specifications for common materials of construction

Material: Alloy 20-Mod (22Cr-26Ni-5Mo)
UNS N08320

Oxidation Scaling Threshold: 1800°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 800°F	No listings.	-325 to 800°F

Product forms for which code-allowable stresses are available

Plate: B620.

Pipe: B619 UNS N08320; B622 UNS N08320.

Tubing: B622 UNS N08320; B626 UNS N08320.

Fittings: No Code or ASTM listings.

Forgings: No Code or ASTM listings.

Bars: B621.

Castings: No Code listings. *Consider A351 Gr CN-3MN.*

Compatible Alloy 20 Mod bolts are Code listed as bar stock. Accordingly,

Bolting: they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

Table A1-4.29 ASTM specifications for common materials of construction

Material: Alloy AL-6XN (21Cr-24Ni-6Mo)
UNS N08367

Oxidation Scaling Threshold: 1800°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 800°F	No listings.	-325 to 800°F

Product forms for which code-allowable stresses are available

Plate:	B688 UNS N08367.
Pipe:	B675 UNS N08367; B690 UNS N08367; B804 UNS N08367.
Tubing:	B676 UNS N08367; B690 UNS N08367.
Fittings:	No Code listings. <i>B366 Gr 6XN; B462 UNS N08367.</i>
Forgings:	No Code listings. <i>B366 Gr 6XN; B462 UNS N08367; B564 UNS N08367.</i>
Bars:	No Code listings. <i>B691 UNS N08367; B472 UNS N08367.</i>
Castings:	No Code or ASTM listings. <i>Consider A351 Gr CK-3MCuN.</i>
Compatible Bolting:	There are no Code or ASTM listings for Alloy AL-6XN bolts. Machine from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

Table A1-4.30 ASTM specifications for common materials of construction

Material: Alloy 904L (21Cr-25Ni-5Mo)
UNS N08904

Oxidation Scaling Threshold: 1800°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 700°F	No listings.	No listings.

Product forms for which code-allowable stresses are available

Plate:	B625 ¹ UNS N08904.
Pipe:	B673 UNS N08904; B677 UNS N08904.
Tubing:	B674 UNS N08904; B677 UNS N08904.
Fittings:	No Code or ASTM listings.
Forgings:	No Code or ASTM listings.
Bars:	B649 UNS N08904.
Castings:	No Code listings. <i>Consider A351 Gr CK-3MCuN.</i>
Compatible Bolting:	There are no Code or ASTM listings for Alloy 904L bolts. Machine from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A265 for clad plate.

Table A1-4.31 ASTM specifications for common materials of construction

Material: Alloy 200 (99Ni; commercially pure nickel)
UNS N02200

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 600°F	-325 to 600°F	-325 to 600°F

Product forms for which code-allowable stresses are available

Plate: B162¹ UNS N02200.
 Pipe: B161 UNS N02200. *B725 UNS N02200.*
 Tubing: B161 UNS N02200; B163 UNS N02200. *B730 UNS N02200.*
 Fittings: B366 UNS N02200.
 Forgings: No Code or ASTM listings.
 Bars: B160 UNS N02200.
 Castings: No Code listings. *Consider A494 Gr CZ-100.*
 Compatible Alloy 200 bolts are Code listed as bar stock. Accordingly, they
 Bolting: should be machined from bar stock if compatibility is necessary;
 otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A265 for clad plate.

Table A1-4.32 ASTM specifications for common materials of construction

Material: Alloy 201 (99 Ni; low-carbon, commercially pure nickel)
UNS N02201

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 1200°F ¹	-325 to 800°F	-325 to 1200°F ²

Product forms for which code-allowable stresses are available

Plate: B162³ UNS N02201.
 Pipe: B161 UNS N02201. *B725 UNS N02201.*
 Tubing: B161 UNS N02201; B163 UNS N02201. *B730 UNS N02201.*
 Fittings: B366 UNS N02201.
 Forgings: No Code or ASTM listings.
 Bars: B160 UNS N02201.
 Castings: No Code listings. *Consider A494 Gr CZ-100.*
 Compatible Alloy 201 bolts are Code listed as bar stock. Accordingly, they
 Bolting: should be machined from bar stock if compatibility is necessary;
 otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ The upper allowable temperature for this material depends on the product form.

² The upper allowable temperature for this material may depend on heat treatment.

³ See A265 for clad plate.

Table A1-4.33 ASTM specifications for common materials of construction

Material: Alloy 400 (67Ni-30Cu)
UNS N04400

Oxidation Scaling Threshold: 1000°F (sulfur free)

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 900°F ¹	-325 to 800°F	-325 to 900°F ¹

Product forms for which code-allowable stresses are available

Plate: B127.²

Pipe: B165. B725.

Tubing: B163 UNS N04400; B165. B730. UNS N0440.

Fittings: B366 UNS N04400.

Forgings: B564 UNS N04400.

Bars: B164 UNS N04400. Consider B164 UNS N04405 (having a higher allowable stress).

Castings: No Code listings. *Consider A494 Gr M-35-1 or M-30C.*

Compatible Bolting: Alloy 400 bolts are Code listed as bar stock. Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302). *Consider F467 & F468, UNS N04405 as well as UNS N04400, if Code maximum allowable stresses are not required.*

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ The upper allowable temperature for this material may depend on heat treatment.

² See A265 for clad plate.

Table A1-4.34 ASTM specifications for common materials of construction

Material: Alloy X (22Cr-47Ni-9Mo)
UNS N06002

Oxidation Scaling Threshold: > 2100°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 1650°F	-325 to 800°F	-325 to 1500°F

Product forms for which code-allowable stresses are available

Plate: B435 UNS N06002.

Pipe: B619 UNS N06002; B622 UNS N06002.

Tubing: B622 UNS N06002; B626 UNS N06002.

Fittings: B366 UNS N06002.

Forgings: No ASTM listings.

Bars: B572 UNS N06002.

Castings: No ASTM listings.

Compatible Bolting: Alloy X bolts are Code listed as bar stock. Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

Table A1-4.35 ASTM specifications for common materials of construction

Material: Alloy C-22 (22Cr-58Ni-13Mo-3W)
UNS N06022

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 800°F	Not listed.	-325 to 800°F

Product forms for which code-allowable stresses are available

Plate: B575¹ UNS N06022.

Pipe: B619 UNS N06022; B622 UNS N06022.

Tubing: B622 UNS N06022; B626 UNS N06022.

Fittings: B366 UNS N06022.

Forgings: No ASTM listings.

Bars: B574 N06022.

Castings: No ASTM listings.

Compatible Bolting: Alloy C-22 bolts are Code listed as bar stock. Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

¹ See A265 for clad plate.

Table A1-4.36 ASTM specifications for common materials of construction

Material: Alloy G-30 (29Cr-40Ni-15Fe-5Mo)
UNS N06030

Oxidation Scaling Threshold: > 2000°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 800°F	No listings.	No listings.

Product forms for which code-allowable stresses are available

Plate: B582¹ UNS N06030.

Pipe: B619 UNS N06030; B622 UNS N06030.

Tubing: B622 UNS N06030; B626 UNS N06030.

Fittings: B366 UNS N06030.

Forgings: No ASTM listings.

Bars: B581 UNS N06030.

Castings: No ASTM listings.

Compatible Bolting: Alloy G-30 bolts are Code listed as bar stock. Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

¹ See A265 for clad plate.

Table A1-4.37 ASTM specifications for common materials of construction

Material: Alloy C-4 (16Cr-61Ni-16Mo)
UNS N06455

Oxidation Scaling Threshold: 1900°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 800°F	-325 to 800°F	-325 to 800°F

Product forms for which code-allowable stresses are available

Plate: B575¹ UNS N06455.
Pipe: B619 UNS N06455; B622 UNS N06455.
Tubing: B622 UNS N06455; B626 UNS N06455.
Fittings: B366 UNS N06455.
Forgings: No ASTM listings.
Bars: B574 N06455.
Castings: No ASTM listings.
Compatible Bolting: Alloy C-4 bolts are Code listed as bar stock. Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

¹ See A265 for clad plate.

Table A1-4.38 ASTM specifications for common materials of construction

Material: Alloy 600 (15Cr-72Ni-8Fe)
UNS N06600

Oxidation Scaling Threshold: > 1800°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 1200°F	-325 to 800°F	-325 to 1200°F

Product forms for which code-allowable stresses are available

Plate: B168¹ UNS N06600.
Pipe: B167 UNS N06600; B517.
Tubing: B163 UNS N06600; B167 UNS N06600; B516.
Fittings: B366 UNS N06600; B564 UNS N06600.
Forgings: B564 UNS N06600.
Bars: B166 UNS N06600.
Castings: No Code listings. *Consider A494 Gr CY-40 (a high-carbon version).*
Compatible Bolting: Alloy 600 bolts are Code listed as bar stock. Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A265 for clad plate.

Table A1-4.39 ASTM specifications for common materials of construction

Material: Alloy 625 (22Cr-60Ni-9Mo, Cb stabilized)
UNS N06625

Oxidation Scaling Threshold: > 1800°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 1200°F	No listings.	-325 to 1200°F

Product forms for which code-allowable stresses are available

Plate: B443.¹

Pipe: B444; B705 UNS N06625. *B834 UNS N06625.*

Tubing: B444; B704 UNS N06625.

Fittings: B366 UNS N06625; B564 UNS N06625. *B834 UNS N06625.*

Forgings: B564 UNS N06625.

Bars: B446.

Castings: No Code listings. *Consider A494 Gr CW-6MC.*

Compatible Alloy 625 bolts are Code listed as bar stock. Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A265 for clad plate.

Table A1-4.40 ASTM specifications for common materials of construction

Material: Alloy G-3 (22Cr-47Ni-20Fe-7Mo)
UNS N06985

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 800°F	No listings.	No listings.

Product forms for which code-allowable stresses are available

Plate: B582¹ UNS N06985.

Pipe: B619 UNS N06985; B622 UNS N06985.

Tubing: B622 UNS N06985; B626 UNS N06985.

Fittings: B366 UNS N06985.

Forgings: No Code or ASTM listings.

Bars: B581 UNS N06985.

Castings: No Code or ASTM listings.

Compatible There are no ASTM listings for Alloy G-3 bolts.

Bolting: Machine from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

¹ See A265 for clad plate.

Table A1-4.41 ASTM specifications for common materials of construction

Material: Alloy 20 Cb-3 (20Cr-35Ni-2.5Mo)
UNS N08020

Oxidation Scaling Threshold: 1800°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 800°F	No listings.	-325 to 800°F

Product forms for which code-allowable stresses are available

Plate: B463¹ UNS N08020.

Pipe: B464 UNS N08020; B729 UNS N08020. *B474 UNS N08020.*

Tubing: B468 UNS N08020; B729 UNS N08020.

Fittings: B366 UNS N08020; B462 UNS N08020.

Forgings: B462 UNS N08020.

Bars: B473 UNS N08020. *B472 UNS N08020.*

Castings: No Code listings. *Consider A351² Gr CN-7M, A743² Gr CN-7M, or A744² Gr CN-7M.*

Compatible There are no ASTM listings for Alloy 20 Cb-3 bolts.

Bolting: Machine from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A265 for clad plate.

² Material should be AOD refined.

Table A1-4.42 ASTM specifications for common materials of construction

Material: Alloy 800 (21Cr-33Ni-42Fe, with Al, Ti stabilized)

Alloy 800: UNS N08800

Alloy 800H: UNS N08810

Alloy 800HT: UNS N08811

Oxidation Scaling Threshold: > 1800°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 1500°F ¹	-325 to 800°F	-325 to 1650°F ²

Product forms for which code-allowable stresses are available

Plate: B409³ UNS N08800, UNS N08810 & UNS N08811.

Pipe: B407 UNS N08800, UNS N08810 & UNS N08811;
B514 UNS N08800 & UNS N08810.

Tubing: B163 UNS N08800 & UNS N08810; B407 UNS N08800,
UNS N08810 & UNS N08811; B515 UNS N08800 &
UNS N08810. *B163 UNS N08811.*

Fittings: B366 UNS N08800; B564 UNS N08800 & UNS N08810.

Forgings: B564 UNS N08800 & UNS N08810.

Bars: B408 UNS N08800 & UNS N08810. *B408 UNS N08811.*

Castings: No Code or ASTM listings.

Compatible Alloy 800 bolts are Code listed as bar stock. Accordingly, they

Bolting: should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

¹ The upper allowable temperature for these materials may depend on alloy composition.

² This Code lists only pipe and tubing.

³ See A265 for clad plate.

Table A1-4.43 ASTM specifications for common materials of construction

Material: Alloy 825 (22Cr-42Ni-3Mo, Ti stabilized)
UNS N08825

Oxidation Scaling Threshold: 1800°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 1000°F	-325 to 800°F	No listings.

Product forms for which code-allowable stresses are available

Plate: B424¹ UNS N08825.

Pipe: B423 UNS N08825; B705 UNS N08825.

Tubing: B163 UNS N08825; B423 UNS N08825; B704 UNS N08825.

Fittings: B366 UNS N08825.

Forgings: No Code listings. *B564 UNS N08825.*

Bars: B425 UNS N08825.

Castings: No Code or ASTM listings.

Compatible Bolting: Alloy 825 bolts are Code listed as bar stock. Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A265 for clad plate.

Table A1-4.44 ASTM specifications for common materials of construction

Material: Alloy C-276 (15Cr-54Ni-16Mo)
UNS N10276

Oxidation Scaling Threshold: 1900°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 1250°F	-325 to 800°F	-325 to 1250°F

Product forms for which code-allowable stresses are available

Plate: B575¹ UNS N10276.

Pipe: B619 UNS N10276; B622 UNS N10276.

Tubing: B622 UNS N10276; B626 UNS N10276.

Fittings: B366 UNS N10276.

Forgings: No Code listings. *B564 UNS N10276.*

Bars: B574 UNS N10276.

Castings: A494 Gr CW-6M² & CW-12MW²; *however, the preferred material is Gr CW-2M, since it has better corrosion resistance.*

Compatible Bolting: Alloy C-276 bolts are Code listed as bar stock. Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302). *F467 UNS N10276; F468 UNS N10276.*

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See A265 for clad plate.

² The upper allowable temperature for this material is 1000°F.

Table A1-4.45 ASTM specifications for common materials of construction

Material: Alloy B-2 (65Ni-28Mo-Fe)
UNS N10665

Oxidation Scaling Threshold: 1000°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 800°F	-325 to 800°F	-325 to 800°F

Product forms for which code-allowable stresses are available

Plate: B333¹ UNS N10665.

Pipe: B619 UNS N10665; B622 UNS N10665.

Tubing: B622 UNS N10665; B626 UNS N10665.

Fittings: B366 UNS N10665.

Forgings: No Code or ASTM listings.

Bars: B335 UNS N10665.

Castings: A494 Gr N-12MV.²

Compatible Bolting: Alloy B-2 bolts are Code listed as bar stock. Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).

¹ See A265 for clad plate.

² The upper allowable temperature for this material is 1000°F.

Table A1-4.46 ASTM specifications for common materials of construction

Material: Inhibited Admiralty Brass (71Cu-28Zn-1Sn)
UNS C44300 (Arsenical)
UNS C44400 (Antimonial)
UNS C44500 (Phosphorized)

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 450°F	-325 to 500°F	No listings.

Product forms for which code-allowable stresses are available

Plate: B171¹ UNS C44300, UNS C44400 & UNS C44500.

Pipe: No ASTM listings.

Tubing: B111 UNS C44300, UNS C44400 & UNS C44500;
B395 UNS C44300, UNS C44400 & UNS C44500;
B543 UNS C44300, UNS C44400 & UNS C44500.
*B135 UNS C44300; B359² UNS C44300,
UNS C44400 & UNS C44500.*

Fittings: No ASTM listings.

Forgings: No ASTM listings.

Bars: No ASTM listings.

Castings: No ASTM listings.

Compatible Bolting: There are no ASTM listings for Admiralty brass bolts. Use Al-bronze or Ni-Al bronze.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See B432 for clad plate.

² Finned tubes.

Table A1-4.47 ASTM specifications for common materials of construction

Material: Naval Brass (60Cu-40Zn)
 UNS C46400
 UNS C46500 (Arsenical)
 UNS C46600 (Antimonial)
 UNS C46700 (Phosphorized)

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 400°F	-325 to 100°F	-452 to 400°F

Product forms for which code-allowable stresses are available

Plate: B171¹ UNS C46400 & UNS C46500.
Pipe: No ASTM listings.
Tubing: No ASTM listings.
Fittings: No ASTM listings.
Forgings: B283 UNS C46400. *B124 UNS C46400.*
Bars: No Code listings. *B21 UNS C46400.*
Castings: No ASTM listings.
Compatible
Bolting: B21 UNS C46400. *F467 UNS C46400; F468 UNS C46400.*

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ See B432 for clad plate.

Table A1-4.48 ASTM specifications for common materials of construction

Material: Aluminum Bronze (several compositions, including: 90Cu-5Al, 90Cu-7Al-3Fe-Sn, etc.)

Wrought Alloys		Cast Alloys
C60800, C61300, C61400, C61900, C62300 & C62400		C95200, C95300, C95400, C95410 & C95900
Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 600°F ¹	-325 to 500°F ¹	-452 to 600°F ¹

Product forms for which code-allowable stresses are available

Plate: B169 UNS C61400; B171² UNS C61400. *B169 UNS C61300; B171 UNS C61300.*
Pipe: No Code listings. *B315 UNS C61300 & UNS C61400; B608 UNS C61300 & UNS C61400.*
Tubing: B111 UNS C60800; B395 UNS C60800. *B111 UNS C61300 & UNS C61400; B315 UNS C61300 & UNS C61400.*
Fittings: No ASTM listings.
Forgings: No Code listings. *B124 UNS C61900 & UNS C62300; B150 UNS C61300, UNS C61400, UNS C61900, UNS C62300 & UNS C62400; B283 UNS C61900 & UNS C62300.*
Bars: No Code listings. *B124 UNS C61900 & UNS C62300; B150 UNS C61300, UNS C61400, UNS C61900, UNS C62300 & UNS C62400; B169 UNS C61300 & UNS C61400.*
Castings: B148 UNS C95200, UNS C95300, UNS C95400 & UNS C95410; B271 UNS C95200. *B30 UNS C95200, UNS C95300, UNS C95400 & UNS C95410 & UNS C95520; B148 UNS C95900; B505 UNS C95200, UNS C95300, UNS C95400, UNS C95410 & UNS C95900; B763 UNS C95200, UNS C95300, UNS C95400 & UNS C95410; B806 UNS C95300, UNS C95400 & UNS C95410.*
Compatible
Bolting: B150 UNS C61400, UNS C62300 & UNS C62400. *F467 UNS C61300 & UNS C61400; F468 UNS C61300 & UNS C61400.*
Also consider Ni-Al bronzes (e.g., B150 UNS C63000).

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ The upper allowable temperature depends on the composition of the material.

² See B432 for clad plate.

Table A1-4.49 ASTM specifications for common materials of construction**Material:** Nickel-Aluminum Bronze (81Cu-10Al-3Fe-5Ni)

Wrought Alloys		Cast Alloys
C63000, C63020 & C63200		C95500, C95520 & C95800
Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 700°F ¹	No listings.	-452 to 500°F ²

Product forms for which code-allowable stresses are available**Plate:** B171 UNS C63000. *B171 UNS C63200.***Pipe:** No Code listings. *B315 UNS C63020.***Tubing:** No Code listings. *B315 UNS C63020.***Fittings:** No ASTM listings.**Forgings:** No Code listings. *B124 UNS C63000 & UNS C63200; B283 UNS C63000 & UNS C63200.***Bars:** No Code listings. *B124 UNS C63000 & UNS C63020; B150 UNS C63000, UNS C63020 & UNS C63200.***Castings:** No Code listings. *B30 UNS C95800; B148 UNS C95500, UNS C95520 & UNS C95800; B505 UNS C95500, UNS C95520 & UNS C95800; B763 UNS C95500 & UNS C95800; B806 UNS C95500 & UNS C95800.***Compatible** B150 UNS C63000. *B150 UNS C63020 & UNS C63200.***Bolting:** *F467 UNS C63000; UNS F468 C63000.**Note:* Specifications that are indicated in italics do not have Code maximum allowable stresses.¹ Plate only. See B432 for clad plate.² Castings and Bolting only.**Table A1-4.50** ASTM specifications for common materials of construction**Material:** 90/10 Cu/Ni
UNS C70600

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 600°F	-325 to 450°F	-452 to 600°F

Product forms for which code-allowable stresses are available**Plate:** B171¹ UNS C70600. *B122 UNS C70600.***Pipe:** B466 UNS C70600; B467 UNS C70600. *B608 UNS C70600.***Tubing:** B111 UNS C70600; B395 UNS C70600; B466 UNS C70600; B543 UNS C70600. *B359 UNS C70600; B395 UNS C70600; B469 UNS C70600; B552 UNS C70600; B608 UNS C70600.***Fittings:** No ASTM listings.**Forgings:** No ASTM listings.**Bars:** No Code listings. *B122 UNS C70600; B151 UNS C70600.***Castings:** No Code listings. *Consider B369 UNS C96200.***Compatible** There are no ASTM listings for 90/10 Cu/Ni bolts. They should be machined from bar stock if compatibility is necessary; otherwise, use Al-bronze or Ni-Al bronze.*Note:* Specifications that are indicated in italics do not have Code maximum allowable stresses.¹ See B432 for clad plate.

Table A1-4.51 ASTM specifications for common materials of construction

Material: 70/30 Cu/Ni
UNS C71500

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-325 to 700°F ¹	-325 to 650°F	-452 to 700°F

Product forms for which code-allowable stresses are available

Plate: B171² UNS C71500. *B122 UNS C71500.*

Pipe: B466 UNS C71500; B467 UNS C71500. *B608 UNS C71500.*

Tubing: B111 UNS C71500; B395 UNS C71500; B466 UNS C71500; B543 UNS C71500. *B359 UNS C71500; B395 UNS C71500; B552 UNS C71500; B608 UNS C71500.*

Fittings: No ASTM listings.

Forgings: No ASTM listings.

Bars: No Code listings. *B122 UNS C71500; B151 UNS C71500.*

Castings: No Code listings. *Consider B369 UNS C96400.*

Compatible

Bolting: No Code listings. *F467 UNS C71500 & F468 UNS C71500.*

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ The upper allowable temperature for this material depends on heat treatment and/or product form.

² See B432 for clad plate.

Table A1-4.52 ASTM specifications for common materials of construction

Material: Aluminum

Wrought Alloys		Cast Alloys
A95083, A95456 & A96061		A03560 & A04430
Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
-452 to 400°F ¹	-452 to 300°F ¹	-452 to 400°F

Product forms for which code-allowable stresses are available

Plate: B209 UNS A95083, UNS A95456 & UNS A96061.

Pipe: B241 UNS A95083, UNS A95456 & UNS A96061; B345 UNS A95083 & UNS A96061.

Tubing: B210 UNS A95083, UNS A95456 & UNS A96061; B221 UNS A95083, UNS A95456 & UNS A96061; B234 UNS A96061; B241 UNS A95083, UNS A95456 & UNS A96061; B345 UNS A95083 & UNS A96061.

Fittings: B361 Gr WP5083 & WP6061.

Forgings: B247 UNS A95083 & UNS A96061.

Bars: B211 UNS A96061; B221 UNS A95083 & UNS A96061.

Castings: B26² UNS A03560 & UNS A04430.

Compatible Aluminum bolts are Code listed as B211 UNS A96061 bar stock.

Bolting: Accordingly, they should be machined from bar stock if compatibility is necessary; otherwise, see Table A1-3 (p. 302).
F467 UNS A96061; F468 UNS A96061.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ The upper allowable temperature depends on the composition and temper of the material.

² Listed in ASME B31.3 only.

Table A1-4.53 ASTM specifications for common materials of construction

Material: Ni-Resist (these materials are castings, having several different compositions; they typically contain 13–35 percent Ni and may contain other additions such as Si, Mn, Cu and Cr).

Oxidation Scaling Threshold: > 1500°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
No listings.	No listings.	No listings.

Product forms for which code-allowable stresses are available

Castings: *A571 Tp D-2M¹. A436²: several grades; A439: several grades.*

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ May be qualified by impact testing to -320°F.

² Tp 1 should be avoided in services requiring impact toughness.

Table A1-4.54 ASTM specifications for common materials of construction

Material: Tantalum

Oxidation Scaling Threshold: 500°F

Typical Code Temperature Ranges		
VIII, Div. 1	VIII, Div. 2	B31.3
No Code listings.	No Code listings.	No Code listings.

This material is typically used either as tubing or as a liner, with some other material serving as pressure containment.

Product forms for which code-allowable stresses are available

Plate: *B708.*

Pipe: No ASTM listings.

Tubing: *B521.*

Fittings: No ASTM listings.

Forgings: No ASTM listings.

Bars: *B365.*

Castings: No ASTM listings.

Compatible

Bolting: No ASTM listings. Machine from bar stock.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

Table A1-4.55 ASTM specifications for common materials of construction**Material:** Titanium

Unalloyed:

UNS R50250: Gr 1

UNS R50400: Gr 2

UNS R50550: Gr 3

Alloyed:

UNS R52400: Gr 7 (Pd addition)

UNS R53400: Gr 12 (Mo & Ni additions)

Oxidation Scaling Threshold: 800°F (long term); 1200°F (short term)

Typical Code Temperature Ranges

VIII, Div. 1	VIII, Div. 2	B31.3
-75 to 600°F	-75 to 600°F	-75 to 600°F ¹

Product forms for which code-allowable stresses are available**Plate:** B265²: all grades.**Pipe:** B337: all grades. *B861: all grades.***Tubing:** B338: all grades.**Fittings:** No Code listings. *Consider B363 (all grades).***Forgings:** B381: all grades.**Bars:** B348: all grades.**Castings:** *B367 Gr C-2³ & Gr C-3.⁴***Compatible** No Code listings.**Bolting:** *Consider F467 & F468 UNS R50250, R50400 & R52400.*

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ This Code lists only pipe.

² Clad plate (explosion bonded) is commercially available.

³ Equivalent to UNS R50400.

⁴ Equivalent to UNS R50550.

Table A1-4.56 ASTM specifications for common materials of construction**Material:** Zirconium

Oxidation Scaling Threshold: 1000°F

Typical Code Temperature Ranges

VIII, Div. 1	VIII, Div. 2	B31.3
-452 to 700°F	No listings.	-75 to 700°F

Product forms for which code-allowable stresses are available**Plate:** B551¹ UNS R60702 & UNS R60705. *B551 UNS R60704 & UNS R60706.***Pipe:** B658 UNS R60702 & UNS R60705. *B658 UNS R60704.***Tubing:** B523 UNS R60702 & UNS R60705. *B523 UNS R60704.***Fittings:** No Code listings. *B653 UNS R60702, UNS R60704 & UNS R60705.***Forgings:** B493 UNS R60702 & UNS R60705. *B493 UNS R60704.***Bars:** B550 UNS R60702 & UNS R60705. *B351 UNS R60001, UNS R60802, UNS R60804 & UNS R60901; B550 UNS R60704.***Castings:** No Code listings. *B752.***Compatible****Bolting:** No ASTM listings. Machine from bar stock.

Note: Specifications that are indicated in italics do not have Code maximum allowable stresses.

¹ Clad plate (explosion bonded) is commercially available.

General Notes for Tables A1-2, A1-3 and A1-4

1. Carbon steels weaken by graphitization of carbides from prolonged exposure to temperatures above 800°F (427°C).
2. Refer to Table A1-1 (p. 298).
3. Above 900°F (482°C), killed steel has a higher maximum code-allowable stress.
4. Refer to the applicable Code for specific impact testing requirements, or exemptions, in establishing minimum allowable metal temperatures. The minimum temperature indicated in Table A1-1 may have to be justified by impact testing.
5. Many of the Curve D materials of Section VIII, Div. 1, Fig. UCS-66, can be impact test qualified down to -75°F (-59°C). Refer to Table A1.15 of ASTM A20.
6. The maximum thickness of a structural part welded directly to a pressure vessel should be ¾" (19 mm). For greater thicknesses, the part to be welded should be fabricated from a material equivalent to that of the vessel.
7. Type 310 SS has better spalling resistance than Type 309 SS.



APPENDIX 2

The de Waard-Milliams CO₂ Nomograph

The de Waard-Milliams nomograph is used to estimate the rate of aqueous CO₂ (i.e., carbonic acid) corrosion for carbon steel. Figure A2-1 shows a worked-out example of how to use the nomograph to estimate carbonic acid corrosion rates. However, recall that such rates are valid only for:

- Clean carbon steel surfaces, unprotected by surface deposits such as mill scale or scale produced by corrosion.
- Non-turbulent flow.
- Immersed service.
- Streams that do not include cathodic polarizers such as oxygen.

The corrosion rates estimated from Figure A2-1 may have to be adjusted for several factors not included in the nomograph.

- The corrosion rate estimate is too large for condensing systems or for systems in which protective scales form. de Waard and Lotz [1] suggest derating the nomograph rates by a multiplier of one-tenth.

The paper by de Waard and Lotz [1] also discusses the use of correction factors that can be used to adjust the estimated corrosion rates for conditions such as high temperature, high pH, high CO₂ partial pressure and scale formation.

- The corrosion rate estimate may be too low for systems subject to turbulent flow or systems that contain cathodic depolarizers such as oxygen. Turbulence and/or the presence of cathodic depolarizers can generate corrosion rates of 1000 mpy (25 mm/yr) or more.

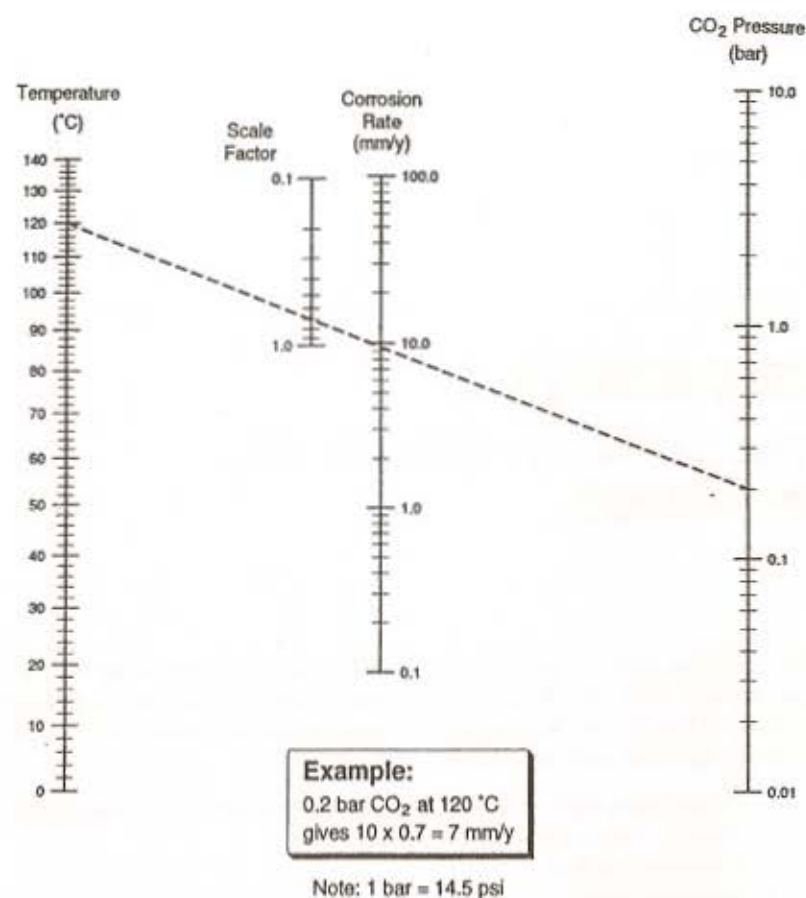
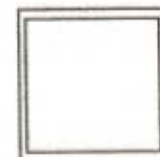


Figure A2-1 CO₂ corrosion nomograph. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

- The corrosion rates estimated for design conditions may actually be less than those for operating conditions. If materials selection is supposed to be based on design conditions, the user should check the rates for both conditions before deciding on the basis of materials selection.

REFERENCE

1. C. de Waard and U. Lotz, Prediction of CO₂ Corrosion of Carbon Steel, CORROSION/93, Paper No. 69, NACE International, Houston, 1993.



APPENDIX 3

Caustic Soda Service

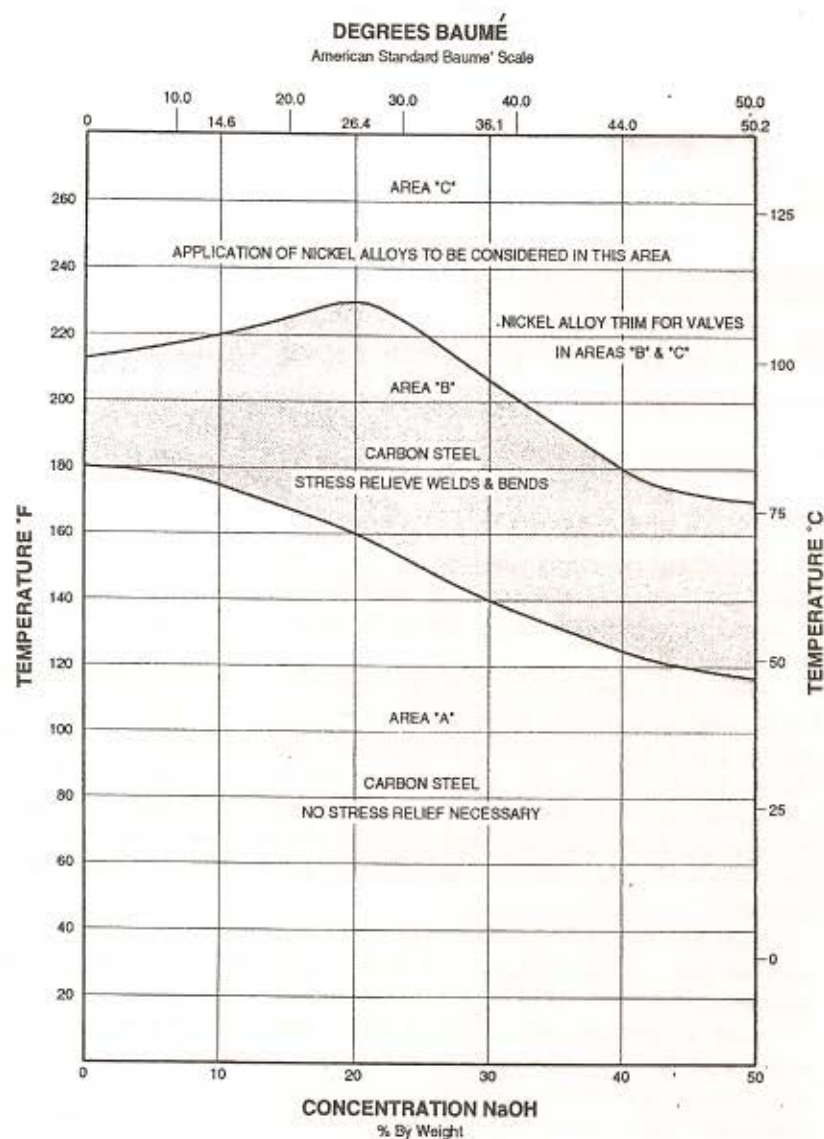
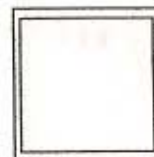


Figure A3-1 Graph for caustic soda service. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission. Refer to reference [14, p. 176] in Chapter 3.)



APPENDIX 4

The Nelson Curves

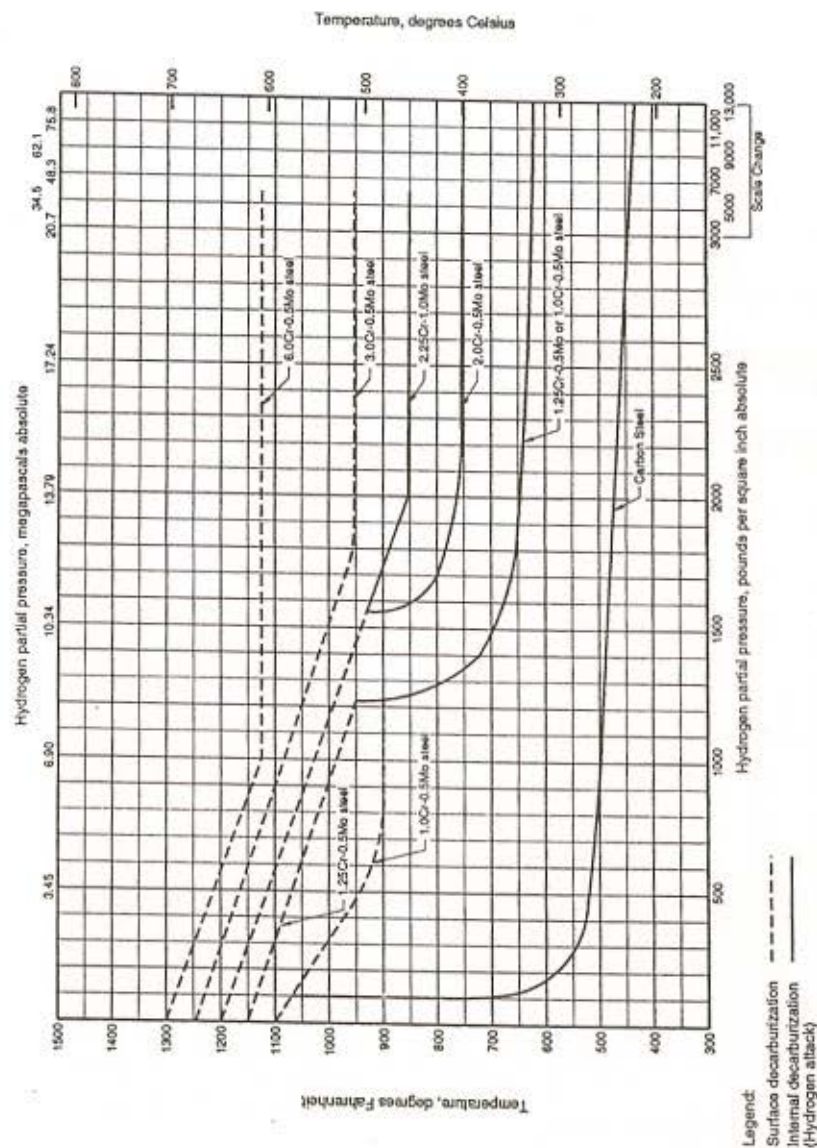


Figure A4-1 The Nelson curves. (Reprinted courtesy of the American Petroleum Institute. Refer to reference [6] in Chapter 3.)



APPENDIX 5

The McCconomy Curves

The McCconomy curves [1] apply to sour crude oils and sour crude fractions operating at temperatures in excess of 500°F (260°C). They may be used for processes containing hydrogen gas having hydrogen partial pressures of 50 psia (0.34 MPa) and less.

Figure A5-1 is used to determine a correction factor which will be used later. Use the total sulfur content, in wt. percent, to obtain the correction factor. The curve in Figure A5-1 is valid for the temperature range 550°F (290°C) to 750°F (400°C). Figure A5-2 can then be used to obtain the average corrosion rate for the materials of interest, for the maximum design temperature. Multiply the average corrosion rate by the correction factor to obtain the corrected average corrosion rate. This rate is the estimated average corrosion rate for the process stream for the material.

Note that estimates obtained from the McCconomy curves are *average* corrosion rates. While localized rates may be higher, it is conventional to use average rates to estimate the time-to-first-leak or corrosion allowances.

Many of the applications utilizing McCconomy curves for corrosion rate estimates are for low-pressure service. In such cases, many users utilize the entire wall thickness for making time-to-first-leak estimates. However, some users employ McCconomy curves only for estimating the required corrosion allowance.

Estimated corrosion rates from the McCconomy curves include considerable uncertainty. As a result, the estimates often do not agree with previous plant experience. In such cases, it is obviously better to rely on plant experience, if the operating conditions are not expected to change substantially.

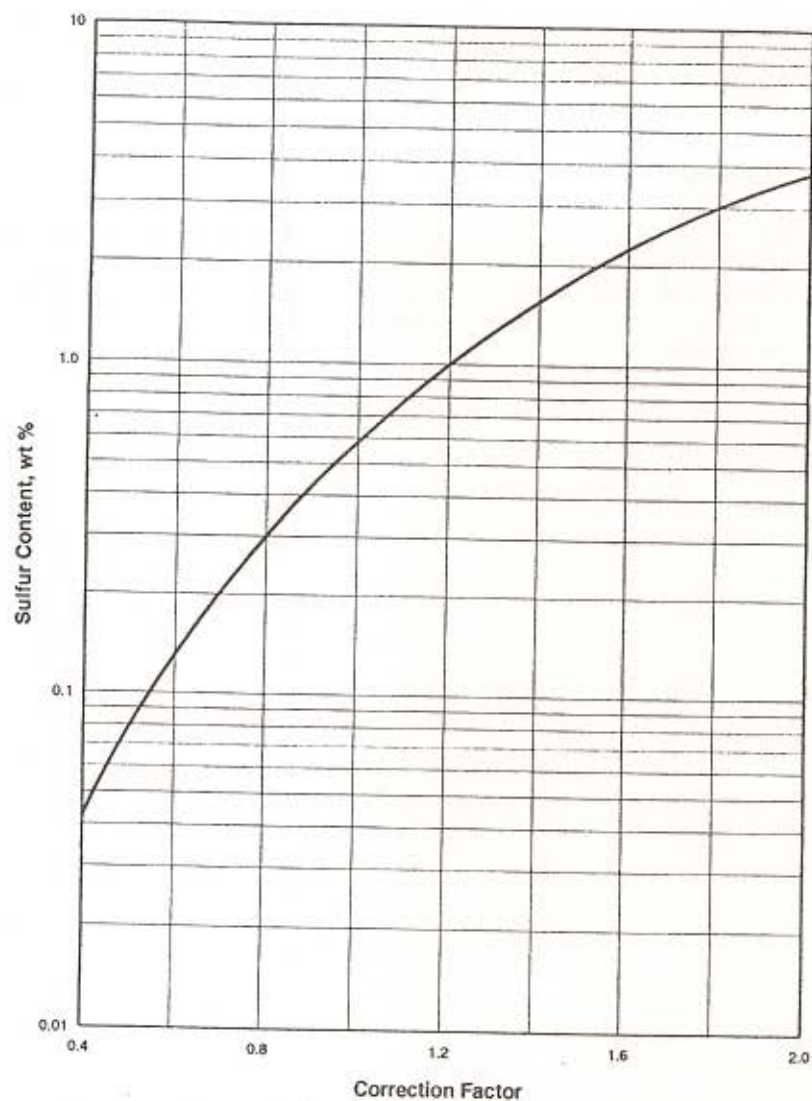


Figure A5-1 Effect of sulfur content on corrosion rates predicted by the modified McCconomy curves in 550° to 750°F (288° to 399°C) temperature range. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [2].)

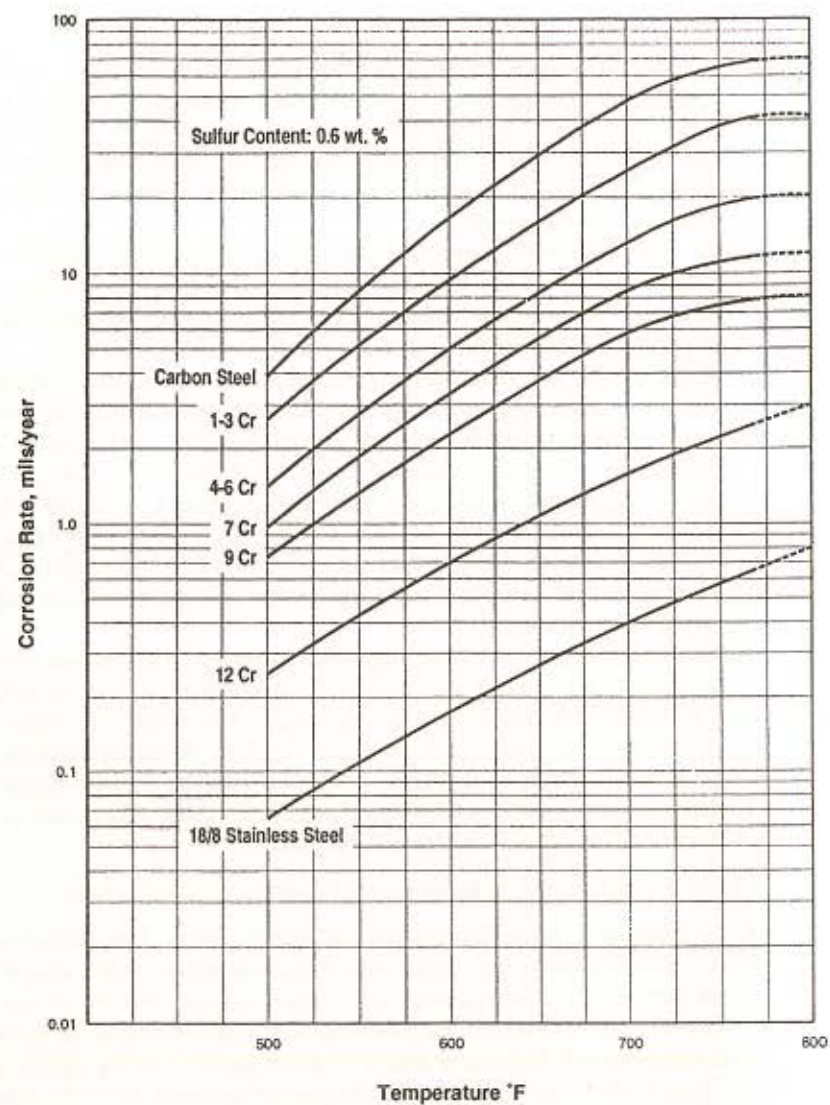


Figure A5-2 Effect of temperature on high-temperature sulfidic corrosion of various steels and stainless steels (modified McCconomy curves). (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [2].)

Experience has shown that the original McConey curves are usually conservative [2], for the following reasons:

- For most sour crude oils and their fractions, the reactive sulfur concentration is significantly less than would be indicated by the total sulfur content. For such streams, derating the curves by 50 percent for carbon steel through 12 Cr provides satisfactory agreement with published plant data. *The corrosion rate curves shown in Figure A5-2 have been derated accordingly.*

Note that some high-sulfur crudes may contain relatively small fractions of reactive sulfur. Even the 50 percent derated McConey curves may result in estimating excessive high corrosion rates. As mentioned above, it is obviously better in such cases to rely on plant experience.

- As the sour hydrocarbon stream is processed, the heavier ends concentrate the remaining sulfur bearing compounds, which indicates that they should become more corrosive. However, the heavy ends contain a greater proportion of non-corrosive sulfur species, such as thiophenes. It has been found that adjusting the sulfur concentration in the heavy ends is usually required in order to obtain realistic predicted corrosion rates. For components handling such heavy ends, the sulfur concentration in the original feed to the unit is usually used to estimate the McConey curve corrosion rate.
- The McConey curves were originally developed from data obtained from heaters used to heat sour naphtha and gas oil feed streams and from heaters used to heat sour crude oils and crude oil fractions. The temperatures represent process temperatures, not tube metal temperatures. Thus, the temperatures in Figure A5-2 also represent process temperatures, not tube metal temperatures. Accordingly, heater tubes should be handled differently from piping and equipment.

The following procedure is recommended for using the derated curves:

- As mentioned above, the original McConey curves were developed from data obtained from heaters used to heat crude oils. When used for this purpose, the derated curves predict corrosion rates that are too low. Thus, for heater tubes, use the process stream temperature and the sulfur concentration of the process stream to obtain the McConey rate from Figure A5-2. This rate should then be doubled to obtain the McConey corrosion rate.
- For piping and equipment, whether in heavy end or crude oil service, use the sulfur concentration of the feed stream to the unit to estimate the corrosion rate at the process stream temperature.

Transfer lines from heaters to fractionation towers are subject to accelerated, localized corrosion from droplets impinging on elbows and tees. This phenomenon can occur at velocities greater than 200 ft/sec (60 m/s) and can increase corrosion rates by an order of magnitude or more.

REFERENCES

1. H. F. McConey, High Temperature Sulfidic Corrosion in Hydrogen Free Environment, *API Subcommittee on Corrosion*, May 12, 1963.
2. J. Gutzeit, High Temperature Sulfidic Corrosion of Steels: *Process Industries Corrosion Theory and Practice*, edited by B. J. Moniz and W. L. Pollock, NACE International, Houston, 1986, pp. 367-372.



APPENDIX 6

The Couper-Gorman Curves

The Couper-Gorman [1] curves apply to gaseous process streams containing hydrogen sulfide, hydrogen and hydrocarbons. These curves should be used for process streams containing hydrogen gas having a partial pressure of 50 psia (0.34 MPa) or more.

For a given material, corrosion rates depend on the type of hydrocarbon. Rates are given for naphtha and gas oil. Naphtha is taken as hydrocarbons having an atmospheric boiling point below 300°F (150°C). Gas oils are those hydrocarbons having an atmospheric boiling point of 300°F (150°C) and above.

Note that estimates obtained from the Couper-Gorman curves are *average* corrosion rates. While localized rates may be higher, it is conventional to use average rates to estimate the time-to-first-leak or corrosion allowances.

Like the McConomy curves, the Couper-Gorman curves have substantial inherent "scatter." Thus, the estimated corrosion rates often do not agree with previous plant data. It is better to rely on plant data if future operating conditions are not expected to change substantially.

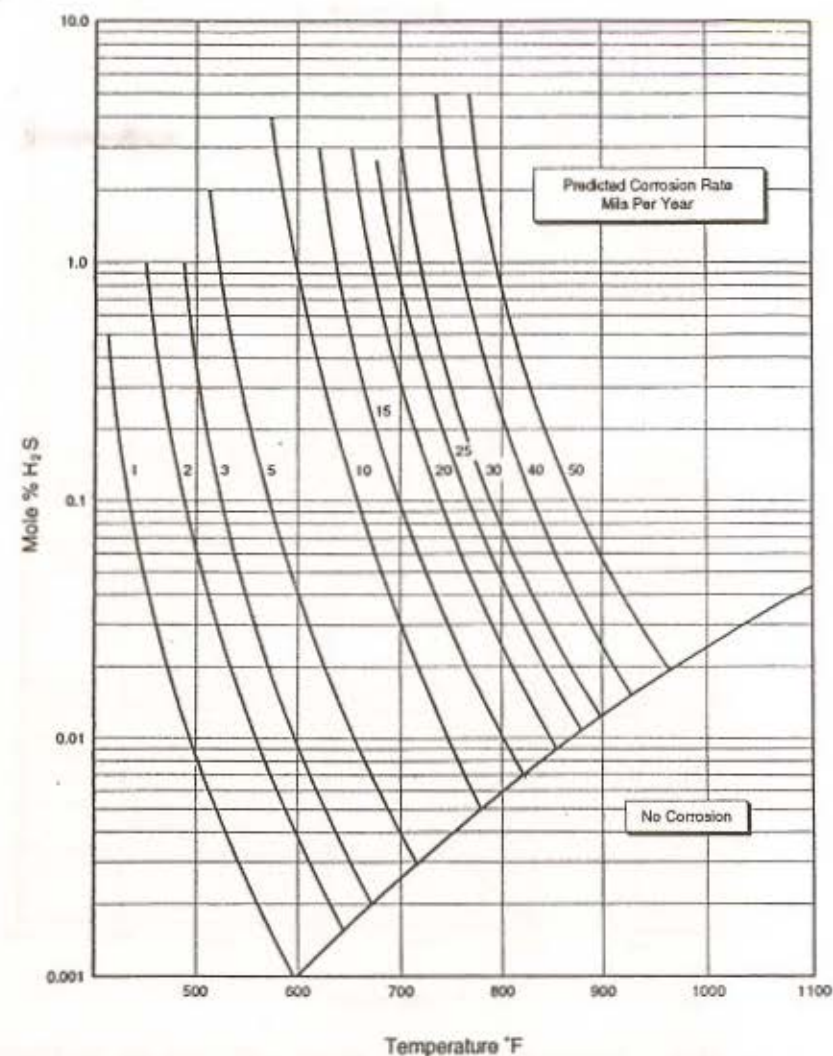


Figure A6-1 Carbon steel: naphtha diluent. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

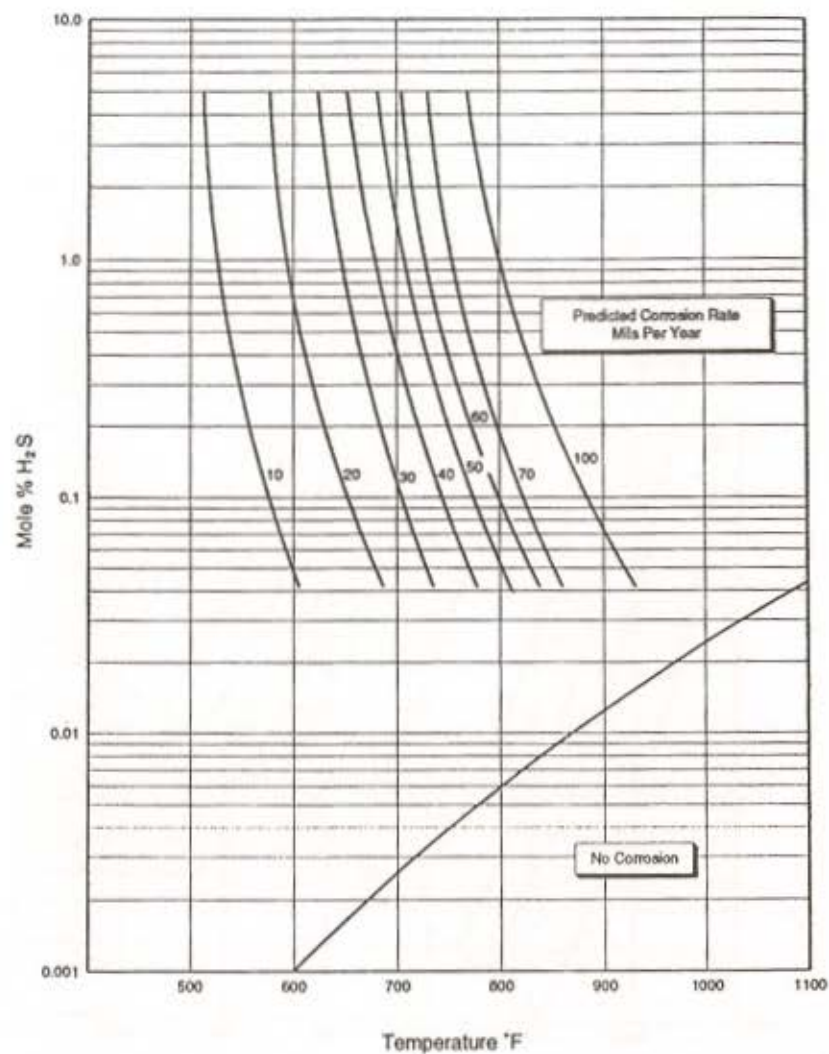


Figure A6-2 Carbon steel; gas oil diluent. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

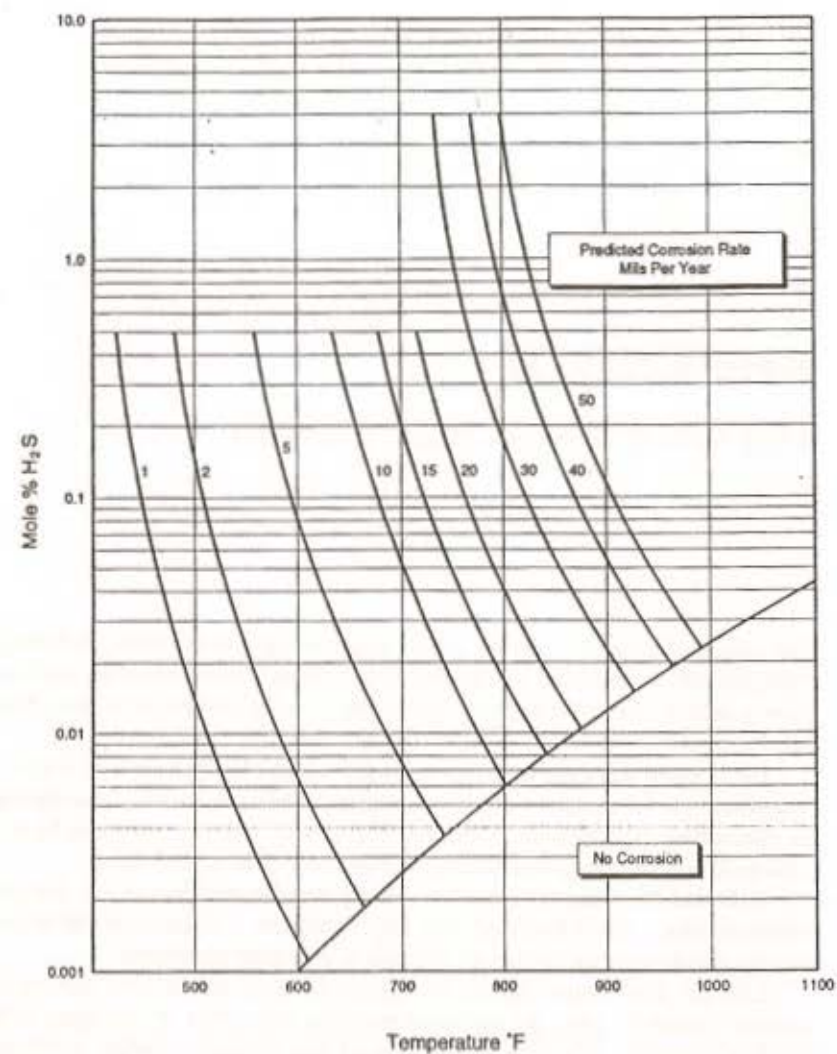


Figure A6-3 5 percent Cr steel; naphtha diluent. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

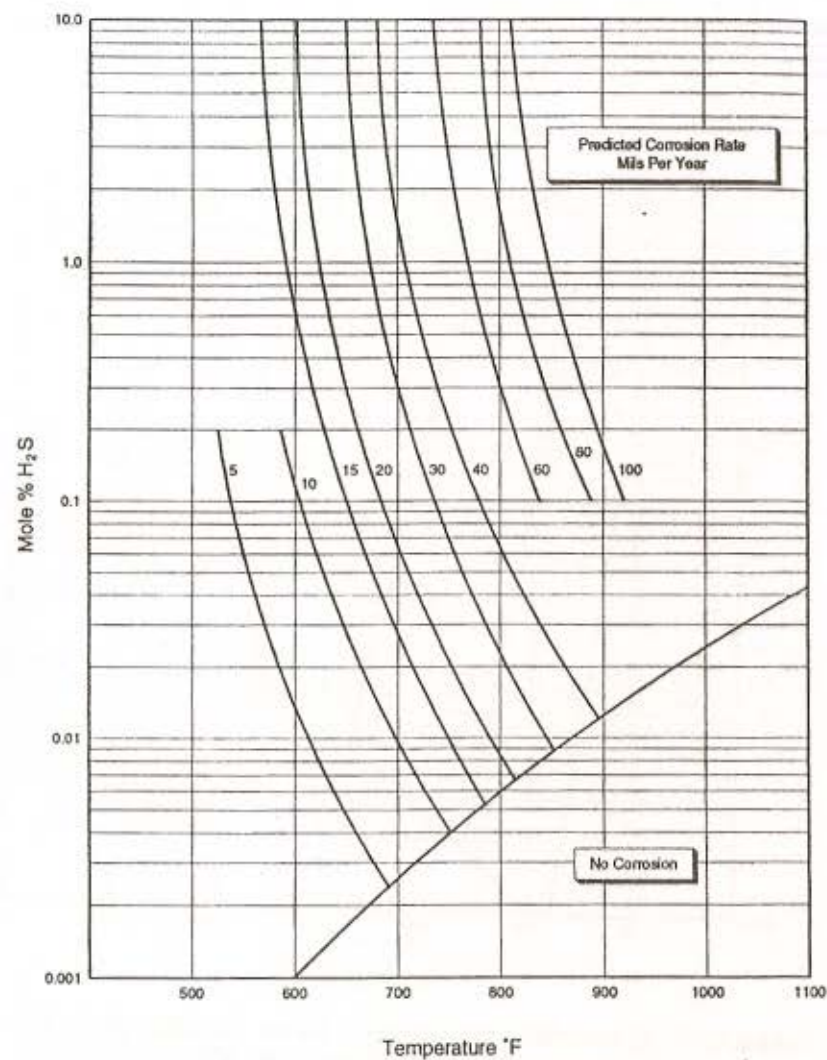


Figure A6-4 5 percent Cr steel: gas oil diluent. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

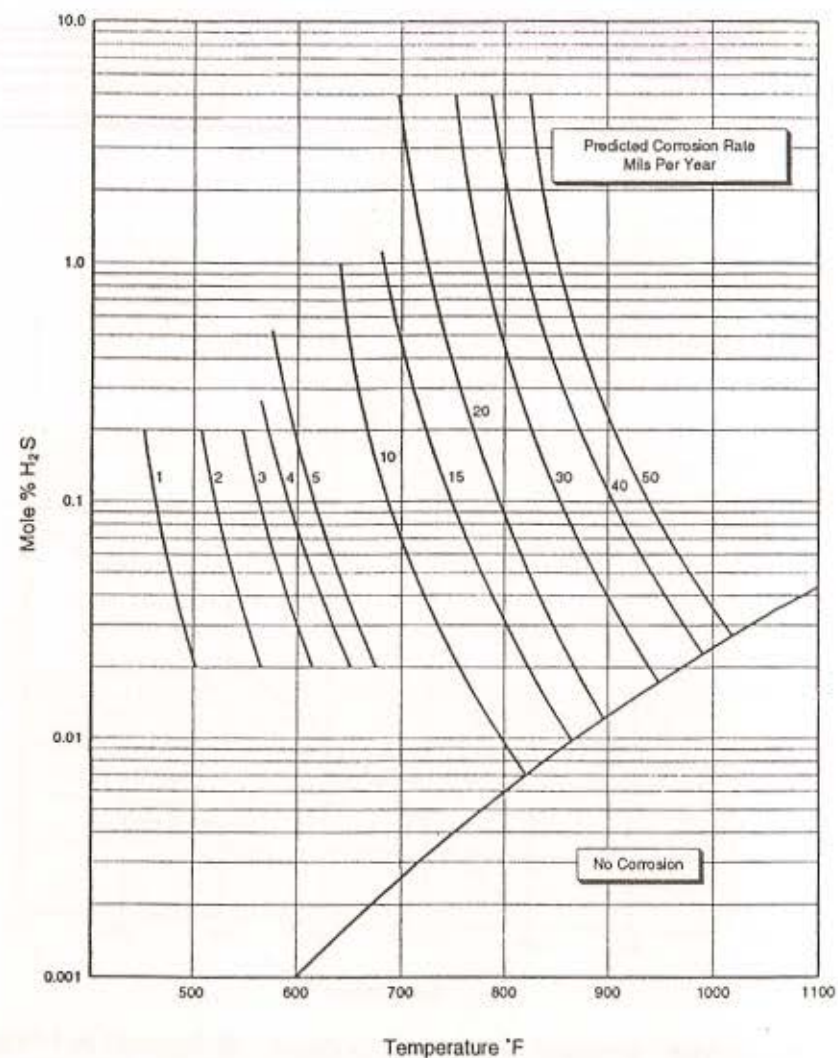


Figure A6-5 9 percent Cr steel: naphtha diluent. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

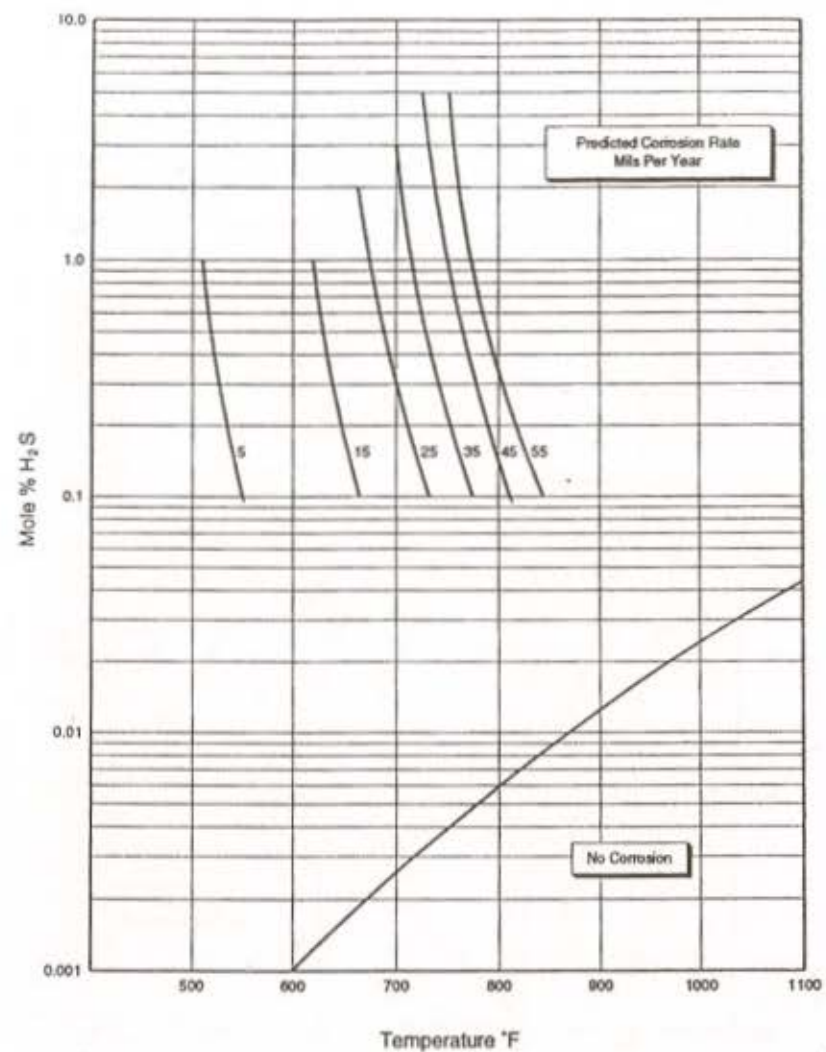


Figure A6-6 9 percent Cr steel: gas oil diluent. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

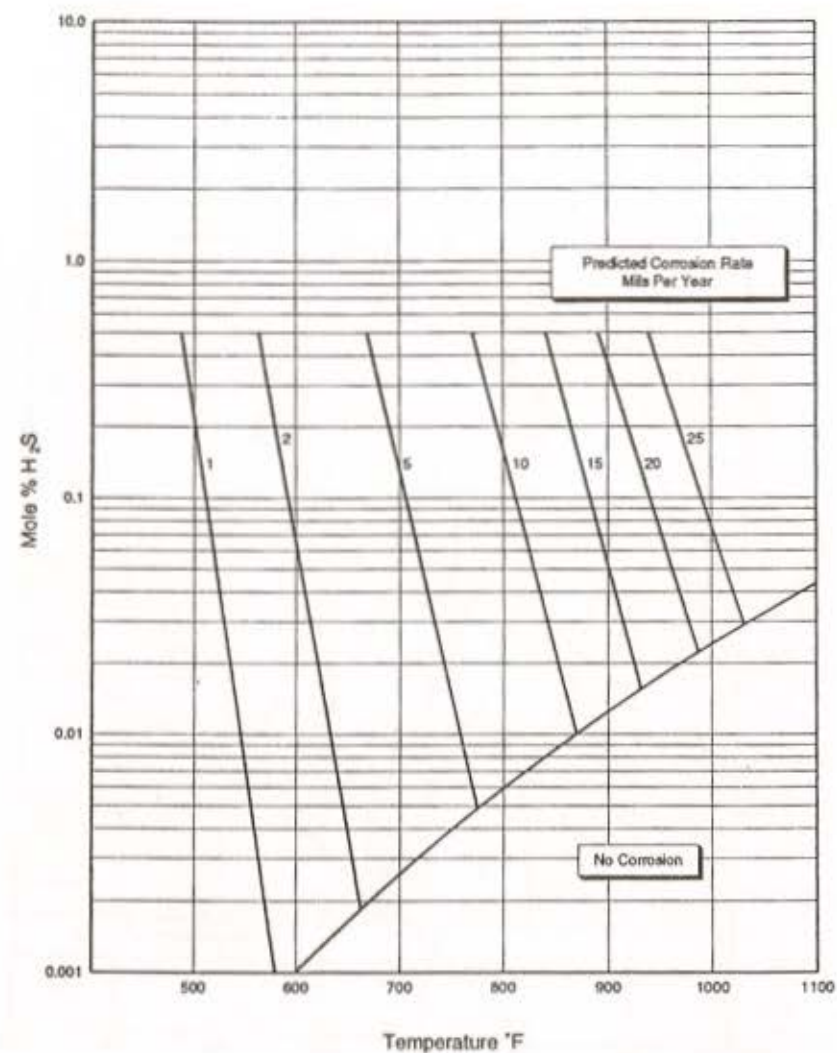


Figure A6-7 12 percent Cr steel: naphtha diluent. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

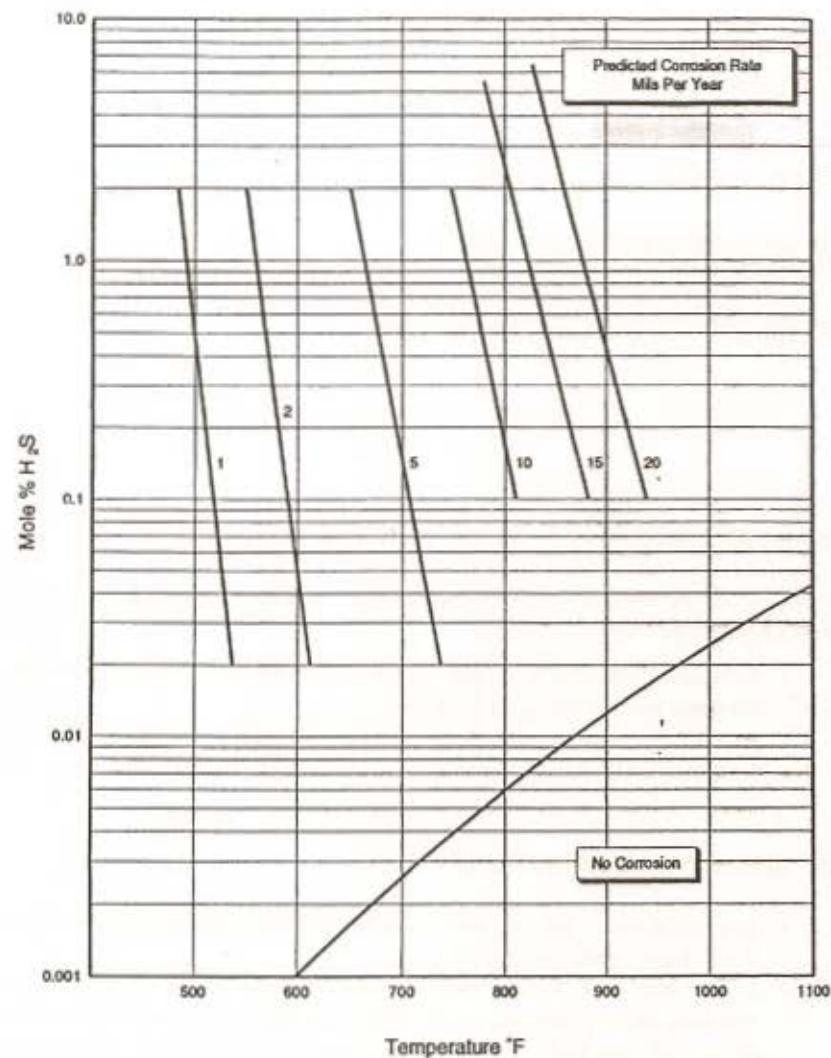


Figure A6-8 12 percent Cr steel: gas oil diluent. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

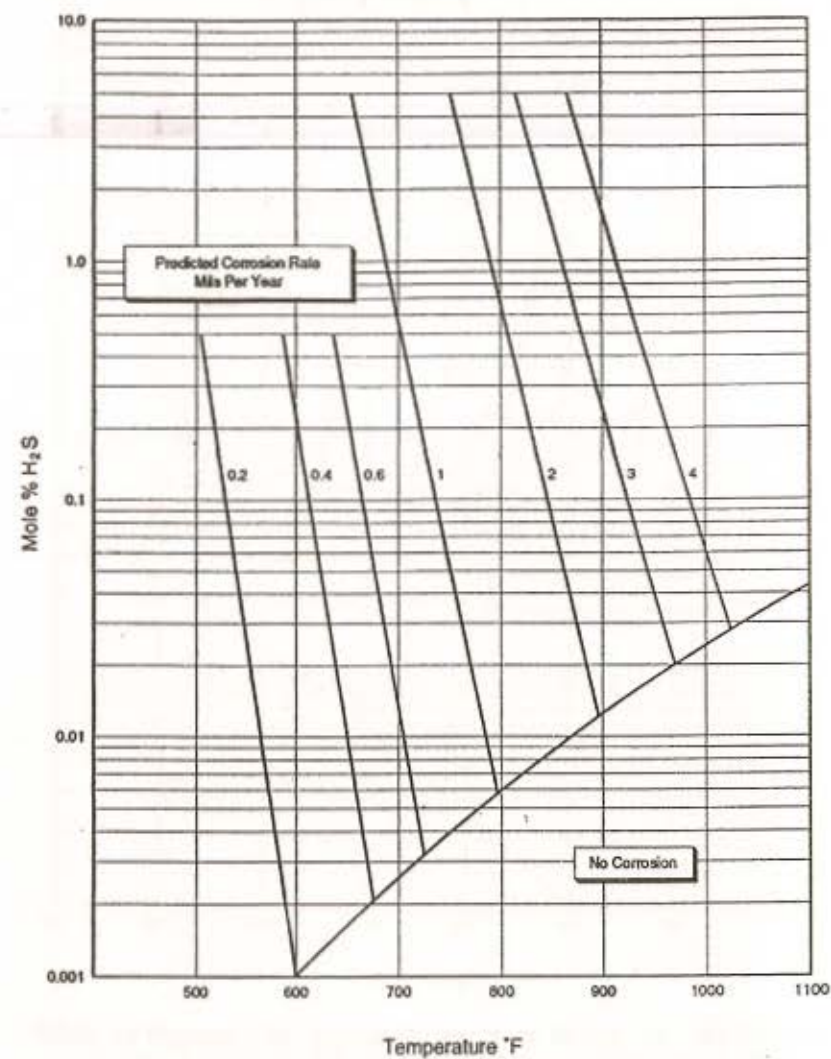


Figure A6-9 18 Cr-8 Ni steel: naphtha diluent. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

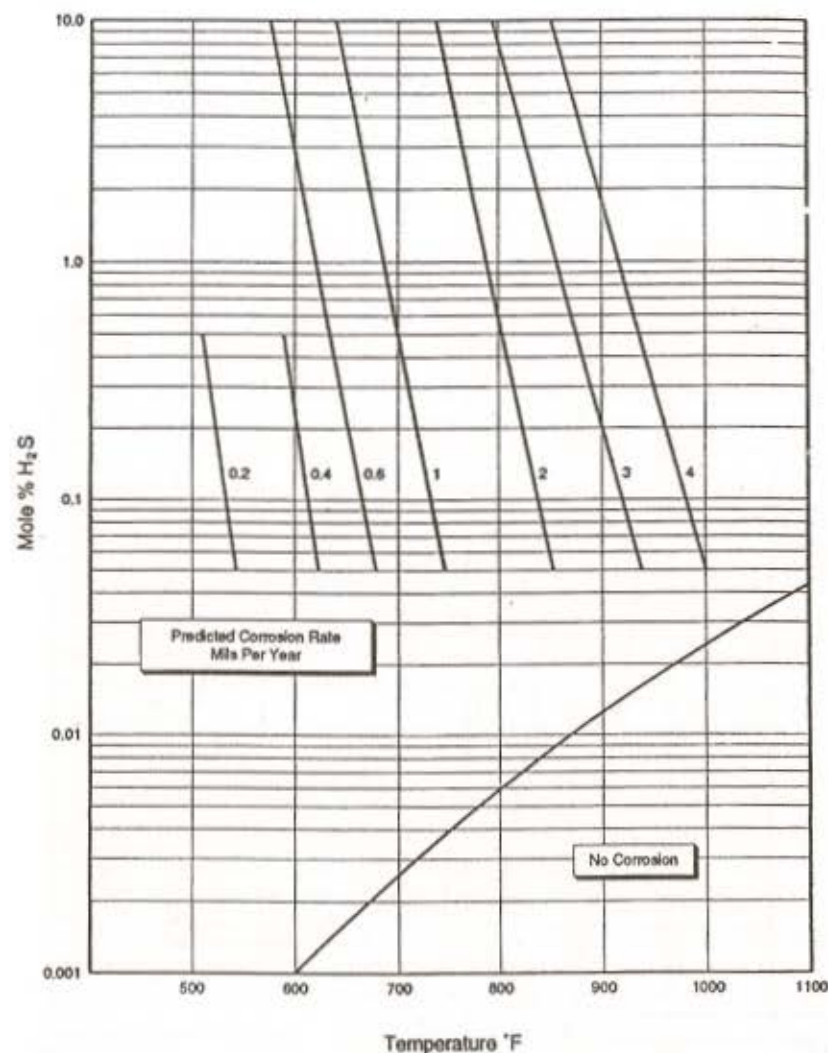
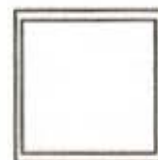


Figure A6-10 18 Cr-8 Ni steel: gas oil diluent. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission [1].)

REFERENCE

1. A. S. Couper and J. W. Gorman, Computer Correlations to Estimate High Temperature H_2S Corrosion in Refinery Streams, *Materials Protection and Performance*, Vol. 10, No. 1, pp. 31-37 (1971).



APPENDIX 7

Wet Sour Service Notes

A. ENVIRONMENT

Wet sour service refers to the following systems. In either case, the pressure is at least 65 psia (0.45 MPa).

- *Wet Gas*: liquid water is present *and* the hydrogen sulfide partial pressure in the vapor exceeds 0.05 psia (0.34 kPa).
- *Sour Water*: liquid water in which hydrogen sulfide is dissolved at a concentration of at least 50 ppmw.

B. SERVICE CLASSIFICATIONS

- *Low-Risk Service*: wet sour service for which the maximum design pressure is less than 65 psia (0.45 MPa).
- *Simple Wet Sour Service*: services containing no other crack-inducing agents or cathodic poisons and for which the maximum design pressure is at least 65 psia (0.45 MPa). Carbon steel vessels and heat exchangers which contain thick section welds (e.g., heavy nozzles) should be regarded as being in severe wet sour service.
- *Severe Wet Sour Service*: wet sour services for which the maximum design pressure is at least 65 psia (0.45 MPa) *and*
 - The service is known to be susceptible to any of the various forms of wet H_2S cracking *or*

- The service is cyclic *or*
- The process contains other crack-inducing agents (e.g., amines in excess of 2 wt. percent) or cathodic poisons (such as cyanides in excess of 20 ppmw).

C. MATERIALS CONSIDERATIONS

- *Low-Risk Service:* in most cases, no special requirements. The major exception is for low-pressure wet sour services that contain cyanide concentrations exceeding 20 ppmw.
- *Simple Wet Sour Service:* all metals and alloys should conform to the requirements of NACE MR0175 [1]. Carbon steel is also subject to the requirements of NACE RP0472 [2].
- *Severe Wet Sour Service:*
 - All metals and alloys should conform to the requirements of NACE MR0175 [1]. Carbon steel is also subject to NACE RP0472 [2].
 - All weld metal, parent metal and heat affected zones should be hardness controlled.
 - Carbon steel plate and plate products should be resistant to hydrogen-induced cracking.
 - HIC-resistant plate should be normalized. To obtain HIC-resistant plate, order to ASTM A516 specifications, with the following special requirements: (1) sulfur concentration of 0.002 wt. percent or less; (2) calcium treated for inclusion shape control.

Internals, seamless pipe, forgings and castings are exempt from HIC concerns. Carbon steel piping and equipment should be postweld heat treated, regardless of wall thickness.

REFERENCES

1. *Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment*, NACE MR0175, NACE International, Houston (latest edition).
2. *Methods and Controls to Prevent In-Service Cracking of Carbon Steel Welds in P-1 Materials in Corrosive Petroleum Refining Environments*, NACE RP0472, NACE International, Houston (latest edition).



APPENDIX 8

Guidelines on Chloride Stress Corrosion Cracking of Austenitic Stainless Steels

Figure A8-1 indicates the temperature threshold for chloride stress corrosion cracking of Types 304 and 316 stainless steels as a function of chloride content. This curve indicates the 140°F (60°C) threshold often quoted as the minimum temperature for chloride stress corrosion cracking of austenitic stainless steels in neutral saline water.

Figure A8-2 provides estimates of the time to failure of austenitic stainless steels as a function of temperature and chloride content. Failure data were measured in a variety of media. Samples were made from sheet or wire with thicknesses of $\frac{1}{16}$ " to $\frac{1}{8}$ " (1.6 to 3.2 mm). The source article advises that the user should employ a safety factor of 10 times the chloride concentration.

Figure A8-3 shows the effect of oxygen concentration on the chloride stress corrosion cracking susceptibility of a typical austenitic stainless steel.

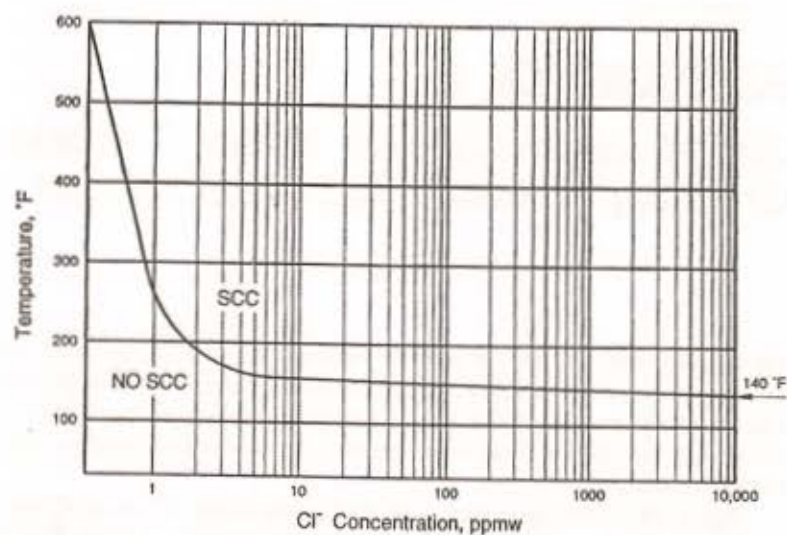


Figure A8-1 Chloride stress corrosion cracking of Type 304 and Type 316 stainless steels as a function of chloride concentration and temperature. (Reprinted with permission of MTI [1].)

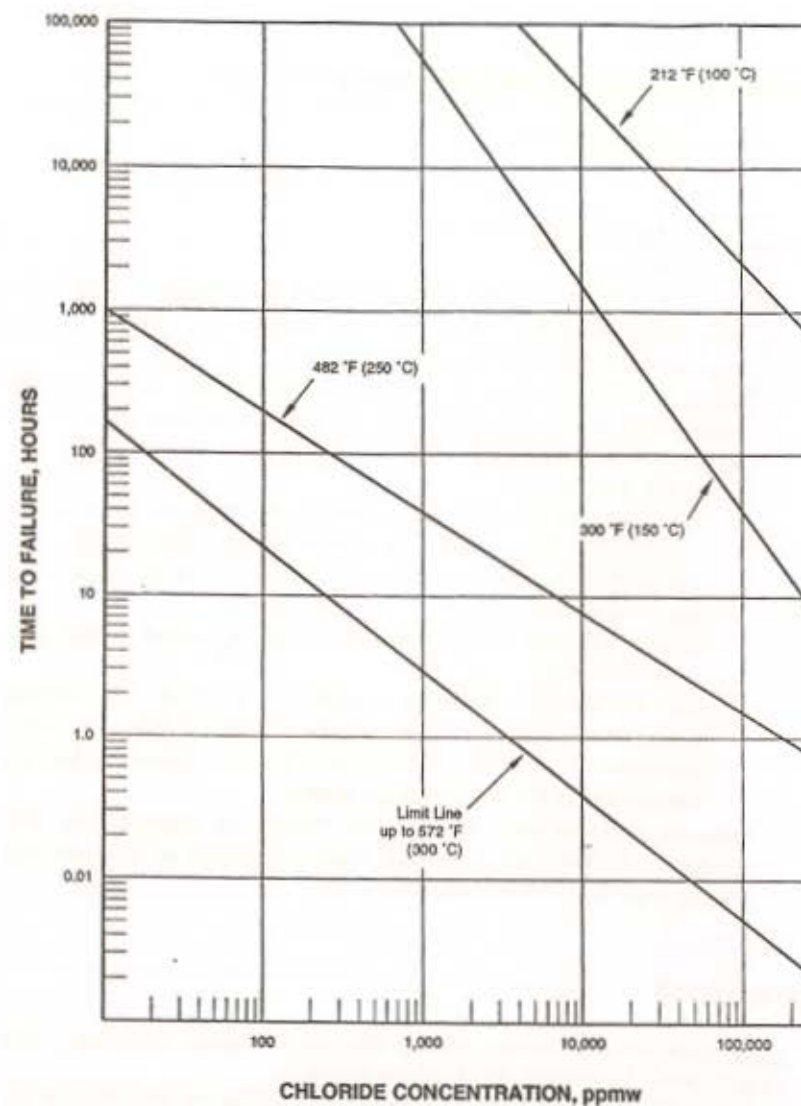


Figure A8-2 Time to failure of austenitic stainless steels due to chloride cracking. (Reprinted with permission from *Hydrocarbon Processing*, January 1975, p. 75. © Copyright 1975 by Gulf Publishing Co., all rights reserved.)

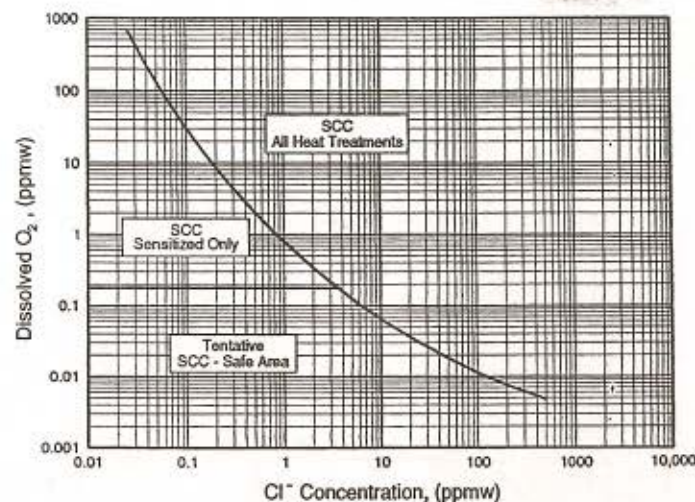


Figure A8-3 Effect of oxygen on chloride stress corrosion cracking. (Reprinted with permission of MTI [1].)

REFERENCE

1. D. R. McIntyre, Experience Survey, Stress Corrosion Cracking of Austenitic Stainless Steels in Water, *MTI Publication No. 27*, Materials Technology Institute, St. Louis, 1987.



APPENDIX 9

Use of Ryznar and Langelier Indices for Predicting the Corrosivity of Waters

A method for calculating the Langelier Saturation Index and the Ryznar Stability index has been described [1]. The calculated indices can be used to estimate the corrosivity of waters, as follows:

Langelier Saturation Index

Index Value	Corrosivity of Water
0	Neither corrosive nor scaling
>0	Scale forming
<0	Corrosive

Ryznar Stability Index

Index Value	Corrosivity of Water
4.0–5.0	Heavy scaling
5.0–6.0	Light scaling
6.0–7.0	Minor scaling or corrosion
7.0–7.5	Moderate corrosion
7.5–8.0	Severe corrosion

Of the two indices, the Ryznar index is considered to be the more quantitative.

The commonly used indicators of the potential of a water to scale or corrode are the Langelier index, L , and the Ryznar stability index, R . L is somewhat qualitative, i.e., positive values indicate scaling tendencies, and negative values corrosive tendencies. R is somewhat quantitative, i.e., decreasing values below 6 indicate increasing scaling, and increasing values above 7 indicate increasing corrosion. A stable water is neither scale-forming nor corrosive.

Both indexes relate to water pH, alkalinity, calcium hardness, total dissolved solids and temperature. Water analyses usually report constituents as calcium carbonate equivalents (CaCO_3) in grains per gallon (gpg), or parts per million by weight:

$$\text{gpg} = 0.05838 \text{ ppm}$$

$$\text{ppm} = 17.13 \text{ gpg}$$

Also, Ca expressed as CaCO_3 equivalents is 2.5 times the Ca ion concentration, and bicarbonate alkalinity expressed as CaCO_3 equivalents is 0.82 times the bicarbonate ion concentration. The nomograph solves for both indices.

EXAMPLE

Find L and R for 70°F water with

$$\text{pH} = 6.9$$

$$\text{total dissolved solids (TDS)} = 72$$

$$\text{calcium hardness as } \text{CaCO}_3 = 34 \text{ ppm}$$

$$\text{alkalinity as } \text{CaCO}_3 \text{ (methyl orange)} = 47$$

Reading at the bottom of the left-hand scale, find TDS = 72 and note the intersection of this reading with the curved 70°F line. Carry this intersection horizontally to pivot line 2; connect that point with Ca hardness = 34 on the right-hand scale; note the intersection with pivot line 3; connect that point with alkalinity = 47 on the left-hand scale; and note the intersection on pivot line 4. This intersection is then connected to pH = 6.9, and the Langelier index and Ryznar index are read as -1.8 and 10.5, respectively. This water is very corrosive.

REFERENCE

1. F. Caplan, Is Your Water Scaling or Corrosive?, *Chemical Engineering*, September 1, 1975, p. 129.

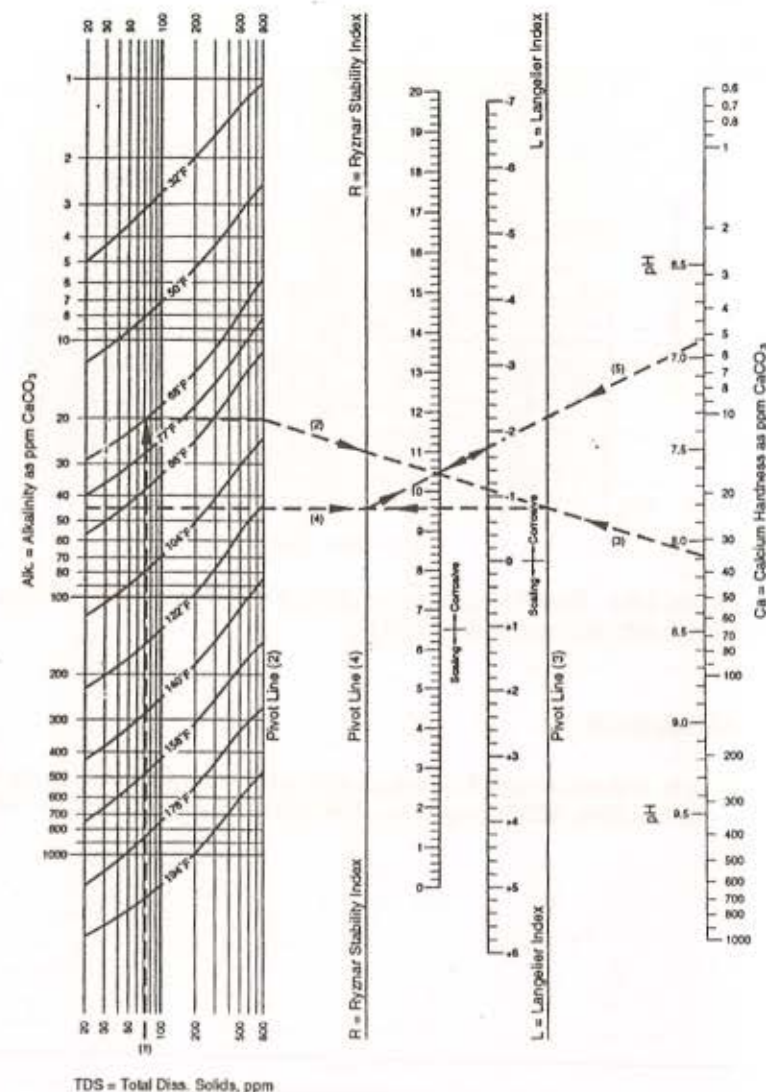
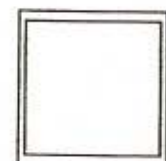


Figure A9-1 Computing the Ryznar and Langelier indices (see accompanying text). (Reprinted with permission [1].)



APPENDIX 10

The Galvanic Series in Seawater

Active or Anodic

Magnesium
Magnesium Alloys
Zinc
Galvanized Steel

Aluminum 1100
Aluminum 2024

Carbon Steel
Cast Iron

12 Cr Stainless Steels (Active)
18 Cr - 8 Ni Stainless Steels (Active)

Lead-Tin Solders
Lead
Tin

Manganese Bronze
Naval Brass

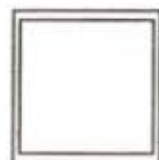
Nickel (active)
Alloy B-2

Admiralty Brass
Copper
Silicon Bronze
70/30 Cu/Ni
Silver Solder
Nickel (Passive)

12 Cr Stainless Steel (Passive)
18 Cr - 8 Ni (Passive)
Titanium

Graphite

Noble or Cathodic



APPENDIX 11

The NACE Graphs of Materials Selection for Sulfuric Acid, Hydrochloric Acid and Hydrofluoric Acid

CODE FOR SULFURIC ACID GRAPH

Materials in Shaded Zones Have Reported Corrosion Rates of <20 mpy

ZONE 1

20Cr-30Ni
66Ni-32Cu¹
62Ni-28Mo
Type 316²
Al bronze 10%¹
Copper¹
Gold
Lead
Molybdenum
Nickel cast iron
Platinum
Silver
Tantalum
Zirconium

ZONE 2

20Cr-30Ni³
66Ni-32Cu¹
62Ni-28Mo
Type 316⁵
Al bronze 10%¹
Copper¹
Gold
Lead
Molybdenum
Nickel cast iron⁴
Platinum
Silicon cast iron
Silver
Tantalum
Zirconium

ZONE 3

20Cr-30Ni³
66Ni-32Cu¹
62Ni-28Mo
Gold
Lead
Molybdenum
Platinum
Silicon iron
Tantalum
Zirconium

ZONE 4

20Cr-30Ni
62Ni-28Mo
Type 316⁷
Gold
Lead⁶
Nickel cast iron
Platinum
Silicon iron
Steel
Tantalum
Zirconium

ZONE 5

20Cr-30Ni³
2Ni-28Mo
Gold
Lead⁹
Platinum
Silicon iron
Tantalum

ZONE 6

62Ni-28Mo¹⁰
Gold
Platinum
Silicon iron
Tantalum

ZONE 7

Gold
Platinum
Silicon iron
Tantalum

ZONE 8

20Cr-30Ni
18Cr-8Ni
54Ni-15Cr-16Mo
Gold
Platinum
Steel

ZONE 9

20Cr-30Ni
18Cr-8Ni
Gold
Platinum

ZONE 10

Gold
Platinum

¹ No air
² <10 %, aerated
³ <165°F (75°C)
⁴ <20 % at 75°F (25°C)
⁵ <25 % aerated at 75°F (25°C)
⁶ >96 % concentration
⁷ >80 % concentration
⁸ <80 %, aerated
⁹ <165°F (75°C), <96 %
¹⁰ 20 to 50 mpy (0.5 to 1.25 mm/yr)

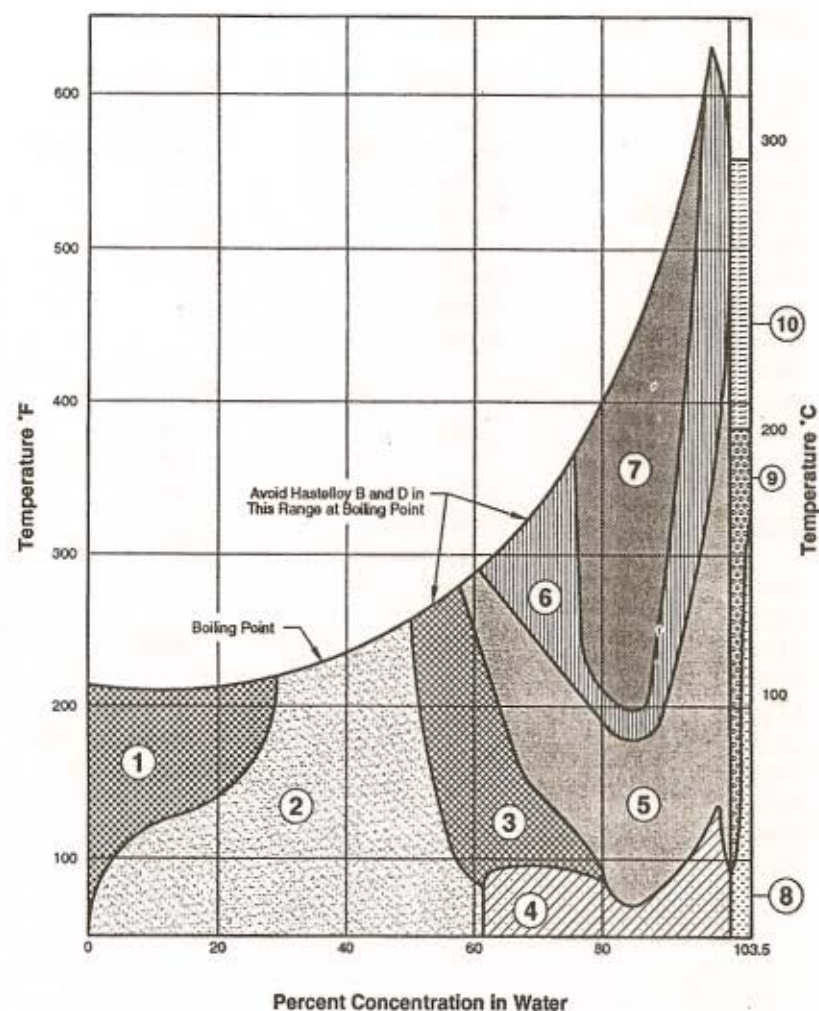


Figure A11-1 Graph for sulfuric acid service. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission. Refer to Reference [14, p. 184] in Chapter 3.)

CODE FOR HYDROCHLORIC ACID GRAPH

Materials in Shaded Zones Have Reported Corrosion Rates of <20 mpy

ZONE 1

20Cr-30Ni¹
66Ni-32Cu²
62Ni-28Mo
Copper²
Nickel²
Platinum
Silicon bronze²
Silicon cast iron³
Silver
Tantalum
Titanium⁴
Tungsten
Zirconium

ZONE 2

62Ni-32Cu
Molybdenum
Platinum
Silicon bronze²
Silicon cast iron³
Silver
Tantalum
Zirconium

ZONE 4

66Ni-32Cu^{2,6}
62Ni-28Mo⁵
Platinum
Silver
Tantalum
Tungsten
Zirconium

ZONE 3

62Ni-28Mo⁵
Molybdenum
Platinum
Silver
Tantalum
Zirconium

ZONE 5

62Ni-28Mo⁵
Platinum
Silver
Tantalum
Zirconium

¹<2% at 75°F (25°C)

²No air

³No FeCl₃

⁴<10 % at 75°F (25°C)

⁵No chlorine

⁶<0.05% concentration

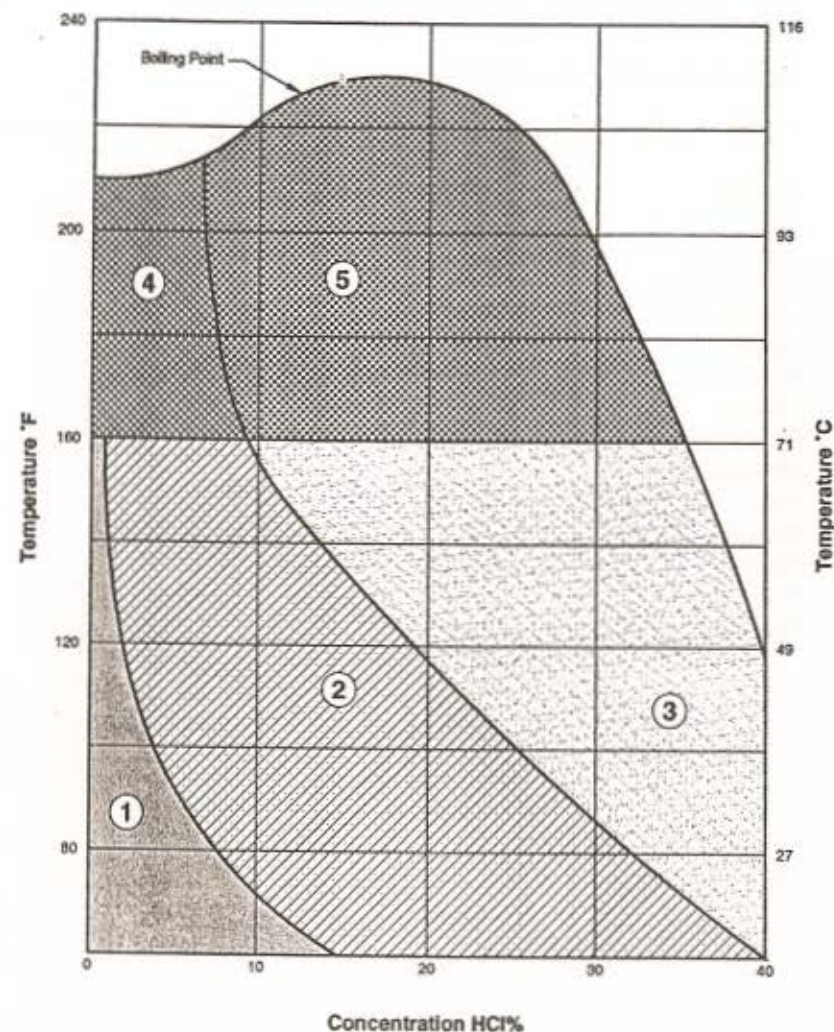


Figure A11-2 Graph for hydrochloric acid service. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission. Refer to reference [14, p. 180] in Chapter 3.)

CODE FOR HYDROFLUORIC ACID GRAPH

Materials in Shaded Zones Have Reported Corrosion Rates of <20 mpy

ZONE 1

20Cr-30Ni
25Cr-20Ni
70Cu-30Ni¹
66Ni-32Cu¹
54Ni-15Cr-16Mo
Copper¹
Gold
Lead¹
Nickel¹
Nickel cast iron
Platinum
Silver

ZONE 2

20Cr-30Ni
70Cu-30Ni¹
54Ni-15Cr-16Mo
66Ni-32Cu¹
Copper¹
Gold
Lead¹
Nickel¹
Platinum
Silver

ZONE 3

20Cr-30Ni
70Cu-30Ni¹
54Ni-15Cr-16Mo
66Ni-32Cu¹
Copper¹
Gold
Lead¹
Platinum
Silver

ZONE 4

70Cu-30Ni¹
66Ni-32Cu¹
54Ni-15Cr-16Mo
Copper¹
Gold
Lead¹
Platinum
Silver

ZONE 5

70Cu-30Ni¹
66Ni-32Cu¹
54Ni-15Cr-16Mo
Gold
Lead¹
Platinum
Silver

ZONE 6

66Ni-32Cu¹
54Ni-15Cr-16Mo
Gold
Platinum
Silver

ZONE 7

66Ni-32Cu¹
54Ni-15Cr-16Mo
Carbon steel
Gold
Platinum
Silver

No air

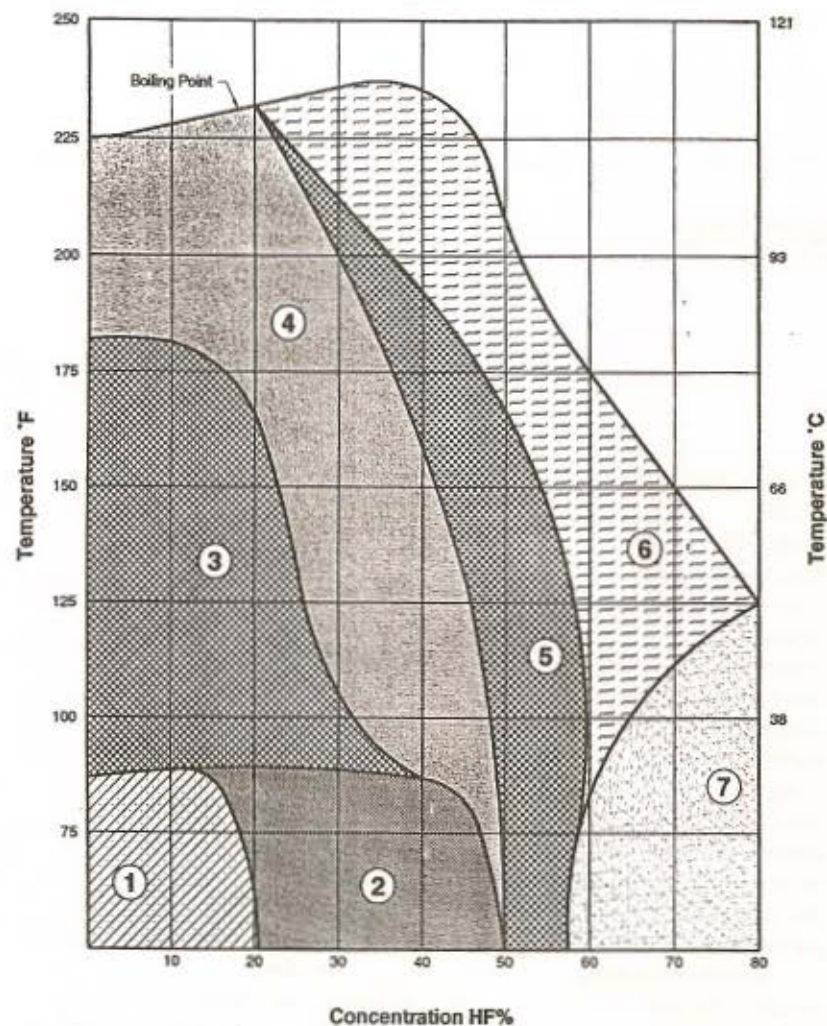


Figure A11-3 Graph for hydrofluoric acid service. (© Copyright by NACE International. All rights reserved by NACE; reprinted with permission. Refer to reference [14, p. 182] in Chapter 3.)



APPENDIX 12

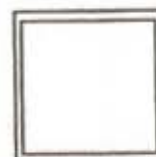
Referenced Metals and Alloys

Alloy	UNS number	Nominal Composition
Inhibited Admiralty Brass	C44300	71Cu-28Zn-1Sn
Naval Brass	C46400	60Cu-39Zn-Sn
Aluminum Bronze	C60800	95Cu-5Al
Nickel-Aluminum Bronze	C63000	81Cu-10Al-3Fe
90/10 Cu/Ni	C70600	90Cu-10Ni
70/30 Cu/Ni	C71500	70Cu-30Ni
Ni-Resist	F41000	(13 to 35)Ni-Fe
AISI 4140	G41400	1Cr-0.2Mo, C = 0.37
CA-15	J91150	13Cr
CA-6NM	J91540	13Cr-4Ni-Mo
HK-40	J94204	25Cr-20Ni
Alloy 200	N02200	99Ni
Alloy 201	N02201	99Ni, low carbon
Alloy 400	N04400	67Ni-30Cu
Alloy K500	N05500	66Ni-30Cu-3Al-Ti
Alloy X	N06002	22Cr-47Ni-18Fe-9Mo
Alloy C-22	N06022	22Cr-58Ni-13Mo-3W
Alloy G-30	N06030	29Cr-40Mo-15Fe-5Mo
Alloy C-4	N06455	16Cr-61Ni-16Mo
Alloy 600	N06600	15Cr-72Ni-8Fe

Alloy	UNS number	Nominal Composition
Alloy 625	N06625	22Cr-60Ni-9Mo-Cb
Alloy G-3	N06985	22Cr-47Ni-7Mo
Alloy 20 Cb-3	N08020	20Cr-35Ni-2.5Mo-Cb
Alloy 28	N08028	27Cr-31Ni-3.5Mo
Alloy AL-6XN	N08367	21Cr-25Ni-6.5Mo-N
Alloy 800 ¹	N08800	21Cr-33Ni-42Fe, with Ti and Al
Alloy 825	N08825	22Cr-42Ni-3Mo, Ti stabilized
Alloy 904L	N08904	21Cr-25Ni-4.5Mo
Alloy C-276	N10276	15Cr-54Ni-16Mo
Alloy B-2	N10665	65Ni-28Mo-Fe
Stellite 6 ²	R30006	60Co-29Cr-5W
Alloy 25	R30605	52Co-20Cr-10Ni-15W
17-4 PH	S17400	17Cr-4Ni-4Cu
Alloy 254 SMO	S31254	20Cr-18Ni-6Mo
Alloy 2205 (duplex SS)	S31803	22Cr-5Ni-3Mo-N
UNS S32250 (duplex SS)	S32250	25Cr-5Ni-3Mo-2Cu
Alloy 2507 (duplex SS)	S32750	25Cr-7Ni-4Mo
26-3-3	S44660	26Cr-3Ni-3Mo-Cb/Ti
25-4-4	S44635	25Cr-4Ni-4Mo
29-4	S44700	29Cr-4Mo

¹Also, Alloy 800H (UNS N08810) and Alloy 800HT (UNS N08811).

²Registered Trademark of Deloro Stellite Inc.



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