# Materials Selection
# For Refineries & Associated Facilities

***R A WHITE***

**Materials and Corrosion Group Manager**
**Materials Quality Services Department**
**Bechtel Corporation**

***E.F. EHAUKE***

**Consultant**
**Corrosion and Materials**
**Concord. California**

# Materials Selection for Refineries and Associated Facilities

*R.A. WHITE*

Materials and Corrosion Group Manager
Materials Quality Services Department
Bechtel Corporation

*E.F. EHMKE*

Consultant
Corrosion and Materials
Concord, California

## PREFACE

During the last 25 years, much has been learned about construction materials for petroleum facilities. Unfortunately, the information is scattered throughout various technical articles in open literature, technical committee minutes, and engineering office files. This book brings together this information for the first time in one document and also represents a summary of the authors' engineering experience during the last 30 years.

The first part of Chapter One contains some introductory material on refinery processes for those unfamiliar with them. The remainder of the book deals with key factors to be considered in selecting construction materials and equipment used in the various processes and associated facilities.

Four appendixes are included. Appendix A contains standard materials selection used by many refiners and contractors in petroleum processing equipment. Appendix B contains a *rules of thumb* overview of refinery materials of construction. Appendix C contains background information on hydrogen diffusion through vessel walls, and Appendix D contains a standard specification for steel line pipe.

This book is, by necessity, condensed, and information on materials performance is continually being generated. Because the technology is dynamic, not static, and materials performance is affected by so many variables, it is of paramount importance that comprehensive research be done before any materials selection decision is made. Therefore, the reader is urged to consult the source articles listed in the bibliographies at the end of each chapter in this book. The reader should also consult any other sources that might contribute to the making of a thoroughly informed decision on materials selection.

The information for this book was originally gathered for a six hour seminar on refinery construction materials for engineers unfamiliar with the subject. It has been expanded into a 20 hour course available through Bechtel Corporation.

Numerous colleagues contributed valuable suggestions that were incorporated into the book, for which the authors are extremely grateful. The authors would particularly like to thank Y. Chung, P.B. Lindsay, H.T. Richardson, and H.R. Siewert, as well as the 30 Ecopetrol engineers who took the first 20 hour course.

This acknowledgment would be incomplete without including the secretaries and word processors, Sydney Anton, Glee Foster, Roberta Morgan, and Nancy Jastremski, who transformed the handwritten manuscript into finished copy despite one author's handwriting.

Finally, R.A. White is eternally indebted to his wife Barbara for her constant support.

San Francisco, California
Concord, California

R.A. White
E.F. Ehmke

# *TABLE OF CONTENTS*

## *LIST OF FIGURES*

### CHAPTER ONE

### CHAPTER TWO

## CHAPTER THREE

## CHAPTER FOUR

## CHAPTER FIVE

## *LIST OF TABLES*

### CHAPTER ONE

### CHAPTER THREE

### CHAPTER FIVE

Chapter
# ONE

# Petroleum Refining Process Corrosion, Crude Fractionation Units, and Utilities

## *OVERVIEW*

### Refinery Processes

The common refinery processes are as follows:

Distillation: Crude, vacuum, and downstream conversion unit distillation that separates molecules by their boiling points.

Hydrotreating: A catalytic reaction of distillate fractions with hydrogen at elevated pressures that is primarily used to desulfurize the feed. The products are hydrogen sulfide and hydrocarbon; organic nitrogen compounds react to form ammonia and hydrocarbon, while some hydrogen cyanide may be made from heavier fractions.

Catalytic Reforming: A catalytic reaction of heavy naphtha(1) used to produce high-octane gasoline. The byproducts are hydrogen and light hydrocarbons; the primary reaction is dehydrogenation of naphthenes to produce aromatics. Some reshaping of paraffins to produce aromatics and some isomerization of paraffins to produce isoparaffins also occur.

Cracking: The several categories of cracking include thermal cracking, fluid catalytic cracking (FCC), and hydrocracking (a type of catalytic cracking). All cracking processes reduce the size of the molecules to produce lighter products with lower boiling points.

> Thermal Cracking: The most prevalent thermal processes are visbreaking and coking, both of which are applied to residium.(2) Visbreaking is a mild thermal cracking; coking is a severe thermal cracking.
>
> Fluid Catalytic Cracking: Distillates heavier than diesel are fed to this unit to crack them catalytically, primarily into gasoline. Also produced are light components consisting of four-carbon molecules, three-carbon molecules, two-carbon molecules, and light gas. The three- and four-carbon molecule fractions contain olefins that can be converted to gasoline by alkylation with isobutane. The two-carbon molecules and lighter gas contain hydrogen sulfide, ammonia, and some hydrogen cyanide. Fractions heavier than gasoline, called cycle oils, are also produced.
>
> Hydrocracking: Distillates heavier than diesel are catalytically cracked at high pressure in the presence of hydrogen to produce either gasoline or diesel and lighter products. Generally, the objective is to produce diesel and lighter products such as two-carbon

---

(1) Naptha is often confused with naphthene. Naphthenes are cyclic hydrocarbons; naptha is defined as hydrocarbons with boiling points from 120 to 400°F (50 to 200°C).

(2) Residium is heavy petroleum from the bottom of a fractionator that has the lighter petroleum products, such as gasoline, removed by distillation.

molecules and lighter gas, three-carbon molecules, and four-carbon molecules. The two-carbon molecules and lighter gas contain hydrogen sulfide and some ammonia. Most of the ammonia and an equivalent amount of hydrogen sulfide are removed with wash water.

Alkylation: Fractions containing light olefins (like FCC three- and four-carbon molecules) are alkylated with isobutane by using sulfuric acid or hydrofluoric acid as a catalyst to produce gasoline (alkylate).

Polymerization: Light olefins are polymerized to gasoline in a process using a solid catalyst containing phosphoric acid.

Supporting Processes: The primary support process units are as follows:

Amine Unit: Light gases are brought into contact with amine to absorb hydrogen sulfide. The amine is regenerated by removing hydrogen sulfide, which is then fed to a sulfur plant.

Sulfur Plant: Acid gas (hydrogen sulfide and carbon dioxide) is fed to a sulfur plant, where the hydrogen sulfide is converted to elemental sulfur by partial oxidation with air.

Sour Water Stripper: Sour water is fed to a stripper to remove ammonia and hydrogen sulfide. The wet ammonia/hydrogen sulfide overhead is fed to the sulfur plant. In cases where there is an appreciable amount of ammonia, a two-stage stripper is used to produce separate hydrogen sulfide and ammonia products.

Hydrogen Plant: Natural gas (or refinery gas) and steam react catalytically to form carbon dioxide and hydrogen. The carbon dioxide is removed by absorption, and the hydrogen is used in hydrotreaters and the hydrocracker.

Figure 1.1 is a simplified block flow diagram of a refinery processing a high-sulfur crude to obtain a large number of products. The crude is fractionated in an atmospheric distillation unit at ~50 psia (345 kPa) at temperatures up to ~700°F (370°C). Naphtha and lighter components are produced at the top of the column (overhead products). The kerosene, diesel, and light gas-oil that are produced in the middle of the column are removed from the side of the column (sidecut products). The overhead is condensed; water is separated from the naphtha; the naphtha is fed to a stabilizer and gasoline splitter to produce butane and lighter components, light gasoline, and heavy naphtha. The bottom product from the atmospheric column is fed to a vacuum distillation unit to recover additional light gas-oil and heavy gas-oil as distillate products. The vacuum unit operates at ~1.45 psia (10.0 kPa) and at temperatures up to ~775°F (415°C). The boiling ranges of the products are generally as follows:

- light ends: butane and lighter;
- light gasoline: $C_5$ to 180°F (82°C);
- heavy naphtha: 180 to 350°F (82 to 177°C);
- kerosene: 350 to 500°F (177 to 260°C);
- diesel: 500 to 650°F (260 to 343°C);
- light gas-oil (atmospheric column): 650 to 700°F (343 to 370°C);
- light gas-oil (vacuum column): 700 to 850°F (370 to 455°C);
- heavy gas-oil: 850 to 1,050°F (455 to 565°C); and
- residium: 1,050°F (565°C) plus.

Butane and lighter gases from the atmospheric crude distillation unit, naphtha hydrotreater, catalytic reformer, and hydrocracker are fed to a gas plant to recover propane and butane. The remaining light gas and other refinery light gases are fed to an amine unit in which hydrogen sulfide is removed by absorption and recovered by regenerating the amine. Hydrogen sulfide from the amine unit is fed to a sulfur plant.

Light gasoline from the splitter may require sweetening (conversion of mercaptan to disulfides) before being sent to the gasoline pool. Heavy naphtha is hydrotreated to remove sulfur (and nitrogen) and is then fed to the catalytic reformer to produce high-octane gasoline.

To remove sulfur, the kerosene and diesel sidecuts are fed to hydrotreaters or hydrodesulfurizers (HDSs). Light gas-oil is fed to a hydrocracker to convert it to diesel and lighter products. The HDS units and hydrocracker consume hydrogen supplied by the catalytic reformer and a hydrogen manufacturing plant.

Heavy gas-oil is fed to an FCC unit, where the primary product is gasoline. The light olefin containing the three- and four-carbon molecule cut is fed to an alkylation plant.

Vacuum residium can be a fuel oil product after FCC cycle oil is added to reduce its viscosity. To feed the light cycle oil to the hydrocracker, the vacuum residium can be fed to a visbreaker for viscosity reduction. Alternatively, the vacuum residium may be fed to a coker for conversion to light products and coke.

For convenience, the discussion of materials for these various processes is divided into five chapters. Crude units and utilities are discussed in this chapter. FCCs, fluid cokers, delayed cokers, sour water strippers, and sulfur plants are covered in Chapter Two. Desulfurizers, reformers, hydrocrackers, and flue gas are discussed in Chapter Three. Hydrogen plants, methanol plants, ammonia plants, and gas treating are discussed in Chapter Four. Underground piping, pipelines, production equipment, and tankage associated with the refinery industry are covered in Chapter Five. Discussed throughout these chapters are many common environments and equipment (e.g., sour or foul water, distillation, etc.) that appear in the various types of refinery process plants.

## General Guidelines for Materials Selection

Environments in refineries can be broken down into various categories such as hydrocarbon and sulfur, hydrocarbon plus hydrogen sulfide plus hydrogen, etc. The materials required for vessels, exchangers, etc., are listed as a function of temperature on the materials recommendation sheets in Appendix A. In general, when different environments are on opposite sides of a piece of equipment (e.g., an exchanger tube), the most severe service governs. In some cases, a material different from the materials on either side may be the proper choice. Another more general guide to materials is found in Appendix B. The various materials-related phenomena are listed as a function of temperature and then as a function of environment. Further information on petroleum refinery materials selection can be found in the bibliography listed at the end of each chapter.

Materials selection for centrifugal pumps is contained in API[3] 610, Appendixes E and F. Another source of information is API's *Guide for Inspection of Refinery Equipment*, Chapter II. In addition, both NACE Group Committee T-8 on Refining Industry Corrosion and the API Corrosion Committee publish minutes of their semiannual meetings. An index of Group Committee T-8's minutes has been produced so that information on any topic discussed can be located.

## *CRUDE UNITS*

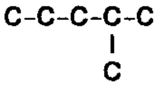
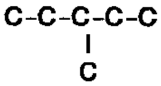
### Crude Oil

Crude oil is a mixture of hydrocarbon molecules of various weights. The arrangements (structure) of the carbon and hydrogen atoms vary significantly. The common arrangements are as follows:

| | | |
|---|---|---|
| Paraffin Series | $C_nH_{2n+2}$ | Saturated (-ane suffix); e.g., hexane |
| Olefin or ethylene | $C_nH_{2n}$ | Unsaturated (double bond; -ene suffix); e.g., ethylene |

---

[3] American Petroleum Institute, Washington, DC.

| | | |
|---|---|---|
| Naphthenes | $C_nH_{2n}$ | Saturated, ring compound; e.g., cyclohexane |
| Aromatic | $C_nH_{2n-6}$ | Benzene series |
| Diolefin | $C_nH_{2n-2}$ | Two double bonds |
| Cyclic series | $C_nH_{2n-2}$ | $C_nH_{2n-8}$, etc. — uncommon |
| Paraffin isomers |  $\mathrm{C{-}C{-}C{-}\underset{\underset{C}{\vert}}{C}{-}C}$ |  $\mathrm{C{-}C{-}\underset{\underset{C}{\vert}}{C}{-}C{-}C}$ |

A typical asphaltic crude might be composed of the following constituents:

| Constituents | Volume Percent |
|---|---|
| Heavy oil (approx. $C_{35}$) | 29 |
| Asphalt (approx. $C_{50}$) | 2 |
| Wax (approx. $C_{40}$) | 2 |
| Paint thinner (approx. $C_{10}$ – $C_{12}$) | 12 |
| Kerosine/jet fuel (approx. $C_{12}$ – $C_{16}$) | 12 |
| Gasoline ($C_7$ – $C_{11}$) | 31 |
| Miscellaneous hydrocarbon impurities | 12 |
| Salt, water, sulfur, and nitrogen compounds | Trace |

## Corrosive Constituents in Oil

The constituents in oil that cause corrosion are sulfur compounds, salt water, inorganic and organic chlorides, inorganic and organic acids, and nitrogen (which forms cyanides). The sulfur compounds found in crude oil are shown in Figure 1.2. As can be seen from the tabulation, a wide variety of sulfur compounds may be present in crude oil. A crude containing more than 0.05 $ft^3$ dissolved hydrogen sulfide per 100 gal (455 L) of oil is called sour. However, a crude containing less than 0.5 $ft^3$ of hydrogen sulfide per 100 gal (455 L) of oil is not corrosive to steel in petroleum processing equipment. The compounds shown in Figure 1.2 decompose thermally during processing into constituents such as hydrogen sulfide and mercaptans (organic sulfur compounds). In sufficient quantities (above ~0.2 wt%), the compounds are corrosive to carbon and low-alloy steels at temperatures above ~450 to 550°F (230 to 290°C) and up to 850°F (455°C). Above 850°F (455°C), corrosion rates drop if the walls coke up; otherwise, the corrosion rates continue to increase.

Assays of crude should be current. Recovering heavier oils from an oil field changes the sulfur and organic acid contents. Once steam flooding begins, the specific gravity and sulfur content of the crude increases. Fire flooding, which is used in some fields, increases the organic acid content. Since total acid numbers and weak acid numbers do not differentiate between naturally occurring naphthenic acid and some acids caused by oxidation, it becomes difficult to determine whether or not naphthenic acid corrosion will be a problem. The increase in crude-specific gravity makes the determination of the total acid number more difficult and increases the probability of error.

Organic acids (e.g., naphthenic acid) can cause severe corrosion above ~450°F (230°C) (although attack has been seen as low as 340°F [170°C] in turbulent areas) if the neutralization number exceeds 2.0 mg of potassium hydroxide per gram (mg KOH/g). The naphthenic acid content is generally determined by titration with KOH, as described in ASTM[4] D974 or D664 for *neutralization value*. This value (called the *neutralization number*) is expressed in mg of KOH required to neutralize the acid constituents present in 1 g of sample. Crudes from Venezuela and California often contain naphthenic acid. Crudes with neutralization numbers in excess of 0.5 mg KOH/g cause serious corrosion problems in the vacuum tower flash zone.

When inorganic chlorides (e.g., ammonium chloride) and organic chlorides collect (usually in the tops of columns and equipment connected to the tops of columns), mild to severe corrosion occurs. When organic nitrogen compounds in the feed exceed 0.05 wt% (500 ppm), cyanides and ammonia form. These compounds collect in the aqueous phases and cause corrosion of certain materials. The corrosion problems in the aqueous phases are discussed in the following section on overhead systems, in the Chapter Two section on characteristics of sour water, and in the Chapter Three section on coolers.

## Corrosion in Crude Units

### *Overview*

Figure 1.3 shows a simplified flow diagram and process description of a crude distillation unit. The crude is first desalted to minimize corrosion in the waters that are condensed from the gases that come off the top of the fractionator columns. As the crude is heated above 450 to 550°F (232 to 288°C) in exchangers and in the fired heater, corrosion occurs as a result of breakdown of sulfur compounds. Condensing water containing hydrogen sulfide and salts causes corrosion in the overhead system of the atmospheric column. Corrosion caused by breakdown of sulfur compounds continues in the atmospheric column; it is worst at the inlet from the fired heater as a result of turbulence from high velocities and flashing. The cycle of corrosion above 450 to 550°F (232 to 288°C) and in the condensing water in the overhead system is repeated in the other two columns as the bottom product from the preceding column is further distilled.

### *Overhead Systems*

Figure 1.3 shows a single drum overhead system. Double drum systems are also used. The difference between the two systems is the reflux temperature at the top of the tower. In the single drum system, total liquid condensation occurs in the overhead condensers. The reflux will be cool and will keep the tower top cool. It is advisable to check the hydrochloric acid dew point vs partial pressure to determine the anticipated location of corrosion. For example, tower top temperatures above 250°F (120°C) can transfer corrosion to the cold reflux. Where dew point conditions exist in the tower, it may be desirable to add ammonia to the reflux to neutralize the acid.

The initial corrosion control system used in a crude unit is a desalter. Modern desalters separate oil and water electrostatically. The internals used to accomplish electrostatic separation are normally of a proprietary design. The vessel itself is usually carbon steel. The bottom is often cement lined to protect it from salt water corrosion. The payout on a desalter is difficult to establish. Desalters are normally used when the salt content of the crude exceeds 20 lb per 1,000 barrels (ptb). When high reliability of the unit is desired, crudes with salt contents of 8 to 10 ptb are desalted. When desalting is used, the target is 1 ptb or less. Fluctuations in salt content are particularly troublesome to the downstream equipment; therefore, the desalter should be designed for the maximum anticipated salt content.

Desalting is used to remove bottoms, sludge, and water, as well as any brines in the crude that result from lack of settling in the oil field, salt water from tankers, and emulsified salt brine in the crude. Additives are used to help break the emulsion after the crude is heated to ~200°F (90°C). Wash water, preheated by the effluent water, helps dissolve the salts from the crude. Although mixing the water and crude is important, some systems are not designed to accommodate this procedure. For example, some systems are not designed for the 30 psi (207 kPa) pressure drop required across the mixing valve.

Removal of salts from the crude is important to avoid corrosion and plugging of the overhead system. Any plugging is normally caused by ammonium chloride. Salt water in crude is usually similar to ocean water. Sodium chloride, which is quite soluble in hot water, is easily removed. Magnesium chloride,

---

[4] ASTM, Philadelphia, PA.

not as easily removed as sodium chloride, hydrolyzes to hydrochloric acid. Desalting to 1 ptb can keep tower overhead condensates under 50 ppm of hydrochloric acid. A 50 ppm concentration of hydrochloric acid is quite corrosive to carbon steel. The overhead condensate should not have more hydrochloric acid than 10 ppm.

One way to reduce the amount of magnesium chloride is to use a caustic injection after the desalter. The injection amount is guided by the amount of salt in the overhead condensate. Spent caustic washes can be used if they do not contain contaminants that cause increased corrosion or plugging. For example, a spent alkylation plant caustic would add sulfur dioxide, which can react with hydrogen sulfide to cause sulfur plugging. The following steps are required to avoid problems with a caustic injection system:

- use an injection quill designed to avoid caustic embrittlement at the injection point;
- put the crude on the tube side of preheat exchangers. This will prevent the caustic from concentrating in pockets around baffles and floating heads; and
- avoid overfeeding. Overfeeding caustic, mixing poorly, or using a caustic that is too strong causes furnace tube coking and caustic embrittlement.

Caustic injection is used to convert magnesium chloride to sodium chloride, since sodium chloride does not readily hydrolize to hydrochloric acid. Reducing hydrochloric acid is helpful in both the atmospheric tower and the vacuum tower overheads. However, one drawback should be pointed out: when magnesium chloride hydrolizes, both hydrochloric acid and magnesium hydroxide are formed. Magnesium hydroxide is stable and insoluble. It will end up in the coke from a coker or in the total dissolved solids in fuel oil. Sodium chloride in heavy oils can be cracked in cokers, FCCs, hydrocrackers, and hydrodesulfurizers and can lead to ammonium chloride plugging problems in coker fractionators, reformer depropanizers, etc. However, plugging is only a problem if the quantity of chloride is large.

With a single drum system, the top of the tower is subjected to water condensation that contains hydrogen chloride, ammonia, and hydrogen sulfide. Corrosion rates can be severe if the chloride content is high. For this reason, Monel(5) 400 is often used as a tower lining and as a tray material. Monel 400 is resistant to these waters below 250°F (121°C); however, corrosion will occur if the ammonia exceeds 3 wt%, or if the pH becomes too high. Monel 400 valve trays are not acceptable because the valves wipe the protective scale from the contact surface causing severe corrosion. This occurrence has not been reported on cage-type valve trays or sieve trays.

Corrosion protection in a single drum system is achieved by neutralizing the water condensate to a pH value of 6 to 6.5 and by using an inhibitor. Neutralizers used are ammonia and neutralizing amines. There are pros and cons associated with each neutralizer. Control of pH with ammonia is difficult because of the strong effect that hydrogen chloride or ammonia have on condensate pH if too little or too much ammonia is used. Neutralizing amines buffer the water so that pH control is easier over a wide range of amine concentrations. Neutralizing amines are soluble in both water and hydrocarbon. If the amine chloride concentration in hydrocarbon is high, the amine chloride will return to the fractionator and cause chloride corrosion.

Both neutralizers are injected in the fractionator overhead line in order to be present when the dew point of hydrochloric acid in solution is reached. It is important to use a quill to inject neutralizers or inhibitors because drip injection can cause dissolution of the protective scale on the inside of the pipe, which can result in corrosion and erosion in that area. Often, however, neutralization is not accomplished, and severe corrosion from hydrochloric acid still occurs at the dew point. The pH is controlled at the overhead receiver water draw because dew point pH measurement is not feasible. One method of controlling the dew point pH is to recycle water from the drum to the overhead line. This water buffers the condensate at the hydrochloric acid dew point and also provides water in which the ammonia can dissolve.

A double drum system operates with a high tower top temperature that is above the dew point of the water-hydrogen chloride solution. A heat exchange with crude or another stream condenses only hydrocarbon in the first drum. This hydrocarbon, usually called heavy naphtha, is a hot reflux that controls

---

(5) Trade name.

the tower top temperature. There should be no water draw from the first drum. The vapors from the first drum travel through condensers to cool them to the temperature required for gas and gasoline separation [~100°F (38°C)]. Corrosion can occur in these condensers; therefore, the same corrosion controls used in a single drum system can be implemented in a double drum system.

Materials used in the overhead condensers vary with the source of the cooling water, the amount of chloride, and the success of inhibitors, pH control, wash water, etc. For refineries with brackish or salt water cooling, the use of titanium tubes is economical since carbon steel cannot be used. Titanium is cost competitive with stainless steels (SS's), Monel 400, brasses, and copper-nickel alloys. If ammonium chloride forms and plugs the hot areas, pitting of copper base alloys can occur. This has been reported for both air coolers and water coolers. Brasses such as admiralty brass have been used successfully where waterside velocities are controlled to under 8 ft/s (2.4 m/s), and ammonia content is not high enough to corrode or crack the brass (pH below 7.2). Copper-nickel alloys are much more resistant to ammonia but will corrode if the hydrogen sulfide content is high. Duplex alloys such as UNS S31500 and UNS S31803 as well as ferritic alloy UNS S44400 have experienced under-deposit corrosion in overhead systems. Conversely, austenitic alloy UNS N08904 has worked well. Carbon steel is used only where there is very careful cooling water control.

Figures 1.4 through 1.10 apply to carbon steel overhead systems. Figure 1.4 can be used to calculate the amount of ammonia that must be added to an overhead system to obtain a desired pH when the total sulfur ($H_2S$ + $HS^-$) in solution or the partial pressure of hydrogen sulfide is known. For comparison, the pH of a pure hydrogen sulfide-water system is shown as a function of hydrogen sulfide partial pressure in Figure 1.9. The chloride concentration at 32 to 250°F (0 to 120°C) can be estimated from Figure 1.10 if the hydrogen chloride and water vapor partial pressures are known. Once the overhead pH has been estimated or measured under pressure, the corrosion rate can be estimated from Figure 1.6. Figure 1.7 shows how the corrosion rate on carbon steel increases as the temperature decreases. The increase in solubility of corrosive gases with decreasing temperatures more than offsets the slowing of corrosion processes as a result of the temperature decrease. Figure 1.8 shows that the corrosion rate appears to drop with decreasing pH below 5.25 before the corrosion rate again increases with a decrease in pH, as indicated in Figure 1.6.

Figure 1.5 is a good example of how metal loss is reduced by desalting to remove chloride. However, using the two corrosion rates shown can be misleading. Fouling is very important to heat transfer, unit throughput, and bundle life. For example, after desalting, a 3.2 mpy (0.08 mm/y) corrosion rate predicts that a 0.083 in. (2.1 mm) wall tube will last 25 y. However, experience reveals that the scale formed is about seven times the volume of metal loss, and the bundle would be completely plugged in 4 y, assuming 3/16 in. (4.76 mm) ligaments on the tubesheet. Square pitch bundles can be cleaned, but triangular pitch bundles must be retubed because they cannot be cleaned once they are plugged. The 9.3 mpy (0.24 mm/y) corrosion rate (before desalting) predicts a 9 y life. However, the bundle would be completely plugged with scale in 1 to 4 y. In both cases, an inhibitor must be used to reduce the corrosion rate and keep the tubes clean.

### *Corrosion of Equipment and Piping*

After the crude passes through the desalter, it goes into the crude heater. Here, the sulfur compounds are partially decomposed thermally. As mentioned previously, when the sulfur exceeds ~0.2 wt%, corrosion of carbon steel becomes excessive. Therefore, the corrosion rate data of carbon steel vs wt% sulfur [or volume percent (vol%) hydrogen sulfide] for 650 and 750°F (343 and 400°C) in Figure 1.11 are inconsistent with long-term experience.

The higher the chromium content in the alloy, the more resistant the alloy is to sulfidation. This is illustrated in the corrosion rate vs temperature data in Figure 1.12. The corrosion rates in Figures 1.11 and 1.12 are from an API survey. The survey results reflect the experience of refiners who have had problems (refiners with problems have the most data); therefore, these rates are higher than average by as much as a factor of two. This is because furnace tube data (where high velocities are encountered) are included, and these data contribute to higher-than-average rates.

In general, furnace tubes and piping are made of 5Cr-½Mo steel for sulfur-bearing crudes when the temperature exceeds ~550 F (290°C) and 9Cr–1Mo when the temperature exceeds ~750°F (400°C). The temperature at which excessive corrosion of carbon steel occurs is a function of the characteristics of the sulfur compounds in the crude. This temperature can be estimated by measuring the amount of hydrogen vacuum system will corrode if chlorides are present. This corrosion is reduced if corrosion in the atmospheric tower overhead is reduced by desalting, caustic injection, or both.

Naphthenic acid corrosion is quite severe in vacuum and visbreaker towers. Crudes with total acid numbers over 2.0 mg KOH/g have corroded type 316 SS in the inlet areas. At times, type 317 (UNS S31700) SS, 904L (UNS N08904), or other corrosion resistant alloys are needed. Matching weld filler metal must be used. In one case, a type 310 (UNS S31000) SS weld filler metal was used on type 316 SS lining. While the strip lining was not attacked, the weld dissolved in one year.

Heat exchangers are treated in a manner similar to columns (i.e., 12Cr clad shells and channels and 5Cr-½Mo tubes are usually used above 550°F [288°C]). When selecting materials for exchangers, one must take into account crevices, changes in direction, and actual tube metal temperatures (since the tubes are exposed to fluids of different temperatures).

The wear parts of pumps and valves are usually highly alloyed because of the close tolerances required. Valves are usually 12Cr trimmed (seat and stem) for all temperatures. Pump impellers (and often pump cases as well) are 12Cr for temperatures above 550°F (288°C).

## *UTILITIES*

### Cooling Water

For materials selection, cooling water is normally categorized as either freshwater or salt water. Freshwater may come from lakes, rivers, or wells. Well water often contains bacteria that accelerate the corrosion of carbon steel (and cast iron) and the pitting of many alloys, including SS's. The corrosion rate of carbon steel in both freshwater and salt water is a function of the oxygen content (in the neutral pH range) and temperature. The corrosion rate of carbon steel doubles approximately every 60°F (16°C) in a closed system. The oxygen content decreases in an open system; therefore, the increased carbon steel corrosion rate resulting from the increase in temperature is partially offset by the decreased oxygen solubility.

### Corrosion in Freshwater

A cooling water system can be categorized further as either a once-through system (in which the water is not treated or concentrated by evaporation) or a circulating water system that uses a cooling tower. A circulating water system is treated by pH adjustment to prevent scaling and by inhibitors to prevent corrosion. Biocides such as chlorine or ozone are added to control both corrosion-inducing and fouling-causing bacteria. The presence of iron or manganese (greater than ~5 ppm) in the water indicates corrosive bacteria may be present. When corrosive bacteria are present, chlorination or other biocide treatment is imperative. Raising the pH to 10.5 (minimum) or boiling the water for 15 min. are effective methods of preventing microbiologically influenced corrosion.

Some circulating water systems are maintained in a closed loop called a tempered water system. Since the water does not travel through a cooling tower, oxygen, which could cause corrosion, does not enter the system. Still, biocide treatment may be necessary since many corrosion-causing bacteria are anaerobic.

In an uninhibited (usually once-through) freshwater system, the corrosiveness will diminish if a calcium carbonate scale (calcareous deposit) precipitates uniformly on the metal surface. Conversely, heat transfer is reduced by the formation of a calcareous deposit. Most cooling water systems are designed to minimize scaling and corrosion. There are several indexes for determining whether or not a calcareous deposit will form and reduce corrosion. The most common index is Langelier's Saturation Index. To calculate the Langelier Index, a water analysis containing the following information is needed:

- temperature;
- total dissolved solids in ppm or mg/L;

vacuum system will corrode if chlorides are present. This corrosion is reduced if corrosion in the atmospheric tower overhead is reduced by desalting, caustic injection, or both.

Naphthenic acid corrosion is quite severe in vacuum and visbreaker towers. Crudes with total acid numbers over 2.0 mg KOH/g have corroded type 316 SS in the inlet areas. At times, type 317 (UNS S31700) SS, 904L (UNS N08904), or other corrosion resistant alloys are needed. Matching weld filler metal must be used. In one case, a type 310 (UNS S31000) SS weld filler metal was used on type 316 SS lining. While the strip lining was not attacked, the weld dissolved in one year.

Heat exchangers are treated in a manner similar to columns (i.e., 12Cr clad shells and channels and 5Cr-½Mo tubes are usually used above 550°F [288°C]). When selecting materials for exchangers, one must take into account crevices, changes in direction, and actual tube metal temperatures (since the tubes are exposed to fluids of different temperatures).

The wear parts of pumps and valves are usually highly alloyed because of the close tolerances required. Valves are usually 12Cr trimmed (seat and stem) for all temperatures. Pump impellers (and often pump cases as well) are 12Cr for temperatures above 550°F (288°C).

## *UTILITIES*

### Cooling Water

For materials selection, cooling water is normally categorized as either freshwater or salt water. Freshwater may come from lakes, rivers, or wells. Well water often contains bacteria that accelerate the corrosion of carbon steel (and cast iron) and the pitting of many alloys, including SS's. The corrosion rate of carbon steel in both freshwater and salt water is a function of the oxygen content (in the neutral pH range) and temperature. The corrosion rate of carbon steel doubles approximately every 60°F (16°C) in a closed system. The oxygen content decreases in an open system; therefore, the increased carbon steel corrosion rate resulting from the increase in temperature is partially offset by the decreased oxygen solubility.

### Corrosion in Freshwater

A cooling water system can be categorized further as either a once-through system (in which the water is not treated or concentrated by evaporation) or a circulating water system that uses a cooling tower. A circulating water system is treated by pH adjustment to prevent scaling and by inhibitors to prevent corrosion. Biocides such as chlorine or ozone are added to control both corrosion-inducing and fouling-causing bacteria. The presence of iron or manganese (greater than ~5 ppm) in the water indicates corrosive bacteria may be present. When corrosive bacteria are present, chlorination or other biocide treatment is imperative. Raising the pH to 10.5 (minimum) or boiling the water for 15 min. are effective methods of preventing microbiologically influenced corrosion.

Some circulating water systems are maintained in a closed loop called a tempered water system. Since the water does not travel through a cooling tower, oxygen, which could cause corrosion, does not enter the system. Still, biocide treatment may be necessary since many corrosion-causing bacteria are anaerobic.

In an uninhibited (usually once-through) freshwater system, the corrosiveness will diminish if a calcium carbonate scale (calcareous deposit) precipitates uniformly on the metal surface. Conversely, heat transfer is reduced by the formation of a calcareous deposit. Most cooling water systems are designed to minimize scaling and corrosion. There are several indexes for determining whether or not a calcareous deposit will form and reduce corrosion. The most common index is Langelier's Saturation Index. To calculate the Langelier Index, a water analysis containing the following information is needed:

- temperature;
- total dissolved solids in ppm or mg/L;

- calcium (as $CaCO_3$)(8) in ppm or mg/L;
- total alkalinity (as $CaCO_3$) in ppm or mg/L; and
- pH.

The total alkalinity, also called the methyl orange alkalinity, is the sum of the hydroxide, carbonate, and bicarbonate ions. When alkalinity is specified without further definition, the methyl orange alkalinity is inferred from it. For water below pH 8.5, the total alkalinity can be considered equal to the bicarbonate ions without affecting the accuracy of the calculation. The phenolphthalein alkalinity is the hydroxide ion plus one-half of the carbonate ion. If the pH is greater than the pHs,(9) scale will form, and the corrosion rate will decrease (Langelier Index positive). If the pH is less than the pHs, the water tends to be corrosive (Langelier Index negative). As mentioned previously, most cooling systems are designed so that the water chemistry keeps both scaling and corrosion at a minimum (i.e., Langelier Index zero). Figure 1.17 is a chart that can be used in place of calculations to arrive at a Langelier Index value. The index should be used with caution, as recent studies indicate a poor correlation between the Langelier Index and the corrosiveness of waters.

The corrosion rates of carbon steel and cast iron in freshwater are not uniform. In selecting a corrosion allowance, one must account for both the uniform and pitting corrosion rates. Pitting rates can range from one to five times the uniform rate. In freshwater, the total penetration rate (uniform and pitting) is on the order of 10 mpy (0.25 mm/y) for carbon steel and cast iron at room temperature. Since most waters are treated to prevent scaling by adjusting the pH to equal the pHs (saturation index equal to zero), a 10 mpy (0.25 mm/y) average penetration rate is often used as a design basis for fully oxygenated water systems.

The use of a constant rate of corrosion for design purposes is a conservatism that most materials engineers use. Actually, in most aqueous environments, the corrosion rate decreases with time unless erosion removes the protective film. The decrease in corrosion rate with time can be estimated by the following equation:

$$V = k_1 t^{-k_2} \tag{1.1}$$

where: V = the average corrosion rate in $g/m^2 \times d$
t = time in hours
$k_1$ = 0.5
$k_2$ = 0.5

For example, the equation predicts that the corrosion rate after 20 y is one-half the rate after 5 y.

The average corrosion rate of cast iron is only slightly lower (about 20%) than that of carbon steel. The reasons for this are as follows: (1) cast iron is produced in much thicker sections than carbon steel so that it has a large corrosion allowance built into the wall. Since the corrosion rate decreases with time, double the corrosion allowance will last much longer than twice as long. (2) More significantly, cast iron appears to corrode at lower rates than carbon steel because of graphitic corrosion. Graphitic corrosion is preferential corrosion of the iron that leaves the graphite network in place. With the graphite network in place, the pipe can be corroded completely (i.e., iron oxide plus graphite) yet appear to be intact. However, graphitically corroded cast iron has no strength.

As mentioned previously, oxygen controls the corrosion rate in the neutral pH range. If the oxygen is less than 1 ppm, the penetration rate in carbon steel or cast iron will be less than 1 mpy (0.025 mm/y) at room temperature, provided no corrosive bacteria are present. If corrosion-inducing bacteria are present, treatment with a biocide such as chlorine is imperative. In theory, because freshwater can be treated, carbon steel exchanger tubes can be used. However, control of water treating equipment is sufficiently difficult and

---

(8) Also called calcium hardness. Total hardness is the sum of the calcium and magnesium hardness (as $CaCO_3$).

(9) Calculated pH of calcium carbonate saturation.

expensive that, in practice, copper alloy tubes are commonly used. Carbon steel can be used for pipes because sufficient corrosion allowance can be added to compensate for moderate corrosion.

Since carbon steel and, in most cases, cast iron are not suitable for aerated water service, either organic coating or more corrosion resistant material is required. Organic coating usually requires repair in 5 to 10 y. In addition, organic coating requires flanged connections. Galvanized zinc coating, though effective in preventing atmospheric corrosion, extends the life of carbon steel only 1 to 3 y in water service.

Copper base alloys generally exhibit penetration (general corrosion plus pitting) rates on the order of 1 mpy (0.025 mm/y) in freshwater in the neutral pH range around room temperature. Therefore, the life of copper base alloys depends on factors such as erosion, dealloying, underdeposit pitting, and whether or not aggressive species are present (e.g., the pH from ammonia should not exceed 7.2 for admiralty brass, and sulfide should not exceed 0.007 mg/L for copper-nickel alloys).

The erosion resistance of copper alloy condenser tubes can be related directly to velocity. The velocity limits for common copper base alloys are shown in Figure 1.18. The velocity limit is roughly proportional to the strength of the alloy (i.e., copper is the weakest material and displays the poorest erosion resistance); copper-30% nickel is one of the strongest alloys and displays the best erosion resistance.

The extent of dealloying or preferential attack of the less noble phase (i.e., zinc in brasses, aluminum in aluminum-bronze, and nickel in copper-nickel alloys) depends on the specific conditions. For example, loss of the zinc-rich phase in brasses is favored by a high-dissolved salt content, a high free carbon dioxide content, pH values toward the extreme ends of the scale, and elevated temperatures. Dealloying of zinc brasses can occur when the zinc content exceeds 15%. The dealloying takes two forms — plug-type and layer-type. Plug-type attack is favored by high temperatures and high-salt contents in the neutral-to-alkaline pH range. Layer or uniform dezincification is favored by low-salt contents and waters in the acid pH range. The addition of small amounts of arsenic, antimony, or phosphorus to brass with up to 30% maximum zinc tends to inhibit loss of the zinc-rich phase. The dealloying inhibitors are ineffective for brasses with greater than 30% zinc.

CDA(10) alloys 443, 444, and 445 (admiralty brass) are 30% zinc alloys inhibited with arsenic, antimony, and phosphorus respectively. Recent work indicates that a viable mechanism does not appear to exist for the role of arsenic as a dealloying suppressant; however, the CDA 443 alloy remains the most popular of the three.

Dealloying of aluminum-bronze (when the structure is two-phase, i.e., greater than 8% aluminum) and copper-nickel alloys is also favored by severe conditions such as high temperatures, low velocities, and high-salt contents. Dealloying of aluminum-bronze can be a problem in castings with aluminum contents in excess of 8.0%, and the problem can be severe when the aluminum content exceeds 9.1%, particularly in crevices. Two approaches are used to minimize this problem in susceptible alloys. In the United States, a temper anneal consisting of heating to 1,250°F (677°C) and holding 6 h, followed by rapid cooling, is commonly used for casting products and after welding. There is evidence that these heat treatments are inadequate for severe conditions such as crevices found in socket welds, gaskets, and backing rings. In Europe, nickel additions are used when the aluminum content exceeds 8.0%. The aluminum in these nickel-aluminum-bronzes is limited to 8.5% plus half the nickel content.

Austenitic SS's are also used in freshwater. However, because of cost their use is limited mainly to applications in which copper-zinc alloys are unsuitable, as in tubes in which the process side is incompatible with copper base alloys. To avoid pitting, type 304 (UNS S30400) SS is normally limited to services in which the chloride ion concentration is at a maximum of 100 ppm, and type 316 SS is limited to services in which the chloride ion is a maximum of 500 ppm. The relative pitting and crevice corrosion resistance of SS alloys can be approximated by the following equation:

$$\text{PRE} = \%\text{Cr} + 3.3\%\text{Mo} + 16\%\text{N} \tag{1.2}$$

The higher the PRE, the more resistant the material.

---

(10) Copper Development Association, Greenwich, CT.

Theoretically, pitting will not occur (regardless of the chloride ion concentration) if the temperature in degrees Celsius is limited to 5°C plus 7 times the molybdenum content. Thus, for a 2% molybdenum alloy (e.g., type 316 SS), the limit would be as follows:

$$5 + 7(2) = 19°C \tag{1.3}$$

The temperature should be limited to 140°F (60°C) in the neutral pH range to avoid stress corrosion cracking (SCC). Above 140°F (60°C), in the absence of concentration mechanisms such as local boiling or crevices, the time to failure is a function of chloride ion concentration and temperature (Figure 1.19). When austenitic SS's are required, low carbon or stabilized grades should be used for which welding or prolonged heating in the sensitizing range of 800 to 1,500°F (425 to 815°C) is involved in order to avoid intergranular corrosion.

## Corrosion in Salt Waters

Salt waters are commonly limited to once-through systems because it is usually not economical to treat salt water to minimize scale and corrosion. The corrosion of metals in salt water is similar to that of metals in freshwater (dealloying, pitting, etc., occur), except that the penetration rates in salt water are higher. For example, carbon steel has an average penetration rate of ~25 mpy (0.64 mm/y) in fully oxygenated seawater vs an average penetration rate of ~10 mpy (0.25 mm/y) in freshwater. The only practical means of reducing corrosion to the point at which bare carbon steel can be used are deaeration and the addition of an oxygen scavenger to ensure that oxygen is less than 20 ppb. The penetration rate of carbon steel in deaerated salt water is ~3 mpy (0.076 mm/y) at pH 6.5 or greater. The corrosion rate increases rapidly as the pH is reduced below 6.5 (Figure 1.20). The pH of deaerated seawater must be held in a narrow range since scaling begins to be a problem when the pH exceeds 7. The corrosion rate of carbon steel in seawater increases rapidly if the velocity of treated seawater exceeds 15 ft/s (4.57 m/s).

Although admiralty brass has been used for exchanger tubes in seawater, copper-nickel and aluminum-bronze alloys perform somewhat better. The cost of titanium tubes can often be justified when life expectancy is taken into account. Copper-nickel alloys, particularly CDA alloy 706 (90% Cu, 10% Ni), are very susceptible to sulfide attack. If the sulfides exceed 0.007 mg/L in the cooling water, severe corrosion of the copper-nickel alloys can be expected. Where the salt water in petroleum streams contains sulfides, admiralty brass and, to a lesser extent, aluminum-bronze perform better than the copper-nickel alloys. Aluminum-bronze has performed satisfactorily in waters containing up to 25 to 30 ppm hydrogen sulfide. It is not satisfactory at high concentrations (e.g., an 8% aluminum-bronze specimen disintegrated in a visbreaker reflux line). Titanium is resistant to sulfides but is subject to embrittlement from hydriding, particularly in the presence of hydrogen, if the temperature exceeds 160°F (70°C). In addition, corrosion from salt plugs has occurred when the velocity in titanium tubes was below 3 ft/s (0.9 m/s).

Theoretically, austenitic SS's can be used in salt water if the velocity exceeds 3 ft/s (0.9 m/s). Experience has shown that stagnant conditions will always occur in a salt water system resulting in rapid pitting (average penetration rates are on the order of 70 mpy [1.78 mm/y]). For this reason, the use of austenitic SS's in seawater is usually limited to thick pump parts. The new super SS's that are high in molybdenum and resistant to seawater attack are being used more frequently in cases in which seawater attacks from both sides. Some super SS's are fully austenitic and some are ferritic, while others are a mixture of austenite and ferrite (duplex SS's). Currently, most of the super SS's are best known by their supplier designations (e.g., Sandvik SAF 2205(11) [2% Mo], and Allegheny Ludlum AL-6XN(12) [6% Mo]). Some common ASTM designations for 2205 are A789 and A790 (UNS S31803). Common ASTM designations for AL-6XN are B675, 676, and B688 (UNS N08367). In general, the duplex SS's such as SAF 2205 are

---

(11) Trade name.

(12) Trade name.

limited to less than about 100°F (38°C) in seawater. Therefore, the six molybdenum SS's are usually used for the warm seawater applications or where high reliability is imperative. The ratio of austenite to ferrite in duplex SS's should be 50 to 50 ±10% for maximum corrosion resistance. The amount of sigma phase that can form in wrought duplex SS can be estimated as follows:

$$\text{sigma} = \%\text{Cr} + 3\left(\frac{\%\text{Mo} + \%\text{Si}}{\%\text{Ni} + 30\%\text{C} + 26\%\text{N}}\right) \tag{1.4}$$

## Corrosion Inhibition

Corrosion can be prevented by adding inhibitors as well as by using resistant alloys. As previously mentioned, adding oxygen scavengers such as sodium sulfite is an effective method of inhibiting corrosion. Oxygen scavengers change the environment and are therefore not truly inhibitors. In general, inhibitors form a film on the surface that changes (polarizes) the electrochemical potential so that the corrosion current is greatly reduced. Inhibitors are basically either cathodic or anodic.

Cathodic inhibitors reduce corrosion by rapidly polarizing the cathode. Examples of cathodic inhibitors are filming amines, magnesium salts, and calcium salts. In waters containing carbon dioxide, calcium carbonate precipitates (as discussed above) to form a protective film.

Anodic inhibitors reduce corrosion by polarizing the anodes rapidly. If insufficient anodic inhibitors are used, severe localized pitting will occur in the unprotected areas. Examples of anodic inhibitors are phosphates, silicates, nitrates, and chromates.

Chromates compose one of the most effective classes of inhibitors, but their use is now limited to closed systems because chromium is highly toxic to aquatic life. As little as 0.05 ppm hexavalent chromium can be lethal to some types of aquatic life.

For an inhibitor to be effective, it must form a film on the surface of the metal to be protected. Therefore, inhibitors are usually ineffective in high velocity and turbulent areas. When velocities exceed 15 ft/s (4.5 m/s), the inhibitor supplier should be consulted to ensure that the specific inhibitor will be effective.

Another factor influencing the effectiveness of inhibitors is the anion concentration. At concentrations on the order of 10,000 ppm, some anions (e.g., sulfate) interfere with the inhibitor film formation. Again, the supplier of the specific inhibitor should be consulted.

## Galvanic Corrosion

When two dissimilar metals come into contact, accelerated corrosion of the less noble metal might occur, depending on how the metals react (polarize) in the environment and on the relative areas. The most commonly used indication of galvanic corrosion is the galvanic series in seawater (shown in Figure 1.21). The more noble or corrosion resistant materials are cathodes (listed on the left) that are protected from corrosion when coupled with any material that exhibits a potential to the right. The materials to the right are anodes and will corrode. Note that SS may exhibit one of two potentials, depending on whether or not it has been activated. It is important to recognize that the galvanic series applies only to seawater and only in the temperature range indicated. Furthermore, the severity of corrosion depends on the relative areas. For example, one would expect severe attack of carbon steel when coupled to the more noble 18Cr-8Ni SS in seawater; however, this combination works well, provided that the area of carbon steel anode is much greater than 18Cr-8Ni SS. Conversely, rapid failure of the carbon steel occurs if a small area of carbon steel is coupled with a large area of 18Cr-8Ni SS cathode.

As mentioned above, the environment has a significant effect on whether or not galvanic corrosion will be a problem. For example, carbon steel will corrode rapidly if equal or larger areas of Monel 400 are coupled with it in seawater. Conversely, carbon steel is compatible with Monel 400 in concentrated caustic solutions. Even freshwater can be sufficiently different from seawater; couples incompatible in seawater work well in freshwater. For example, copper-steel and aluminum-steel couples are satisfactory for handling moderately scaling cooling water at pH 8 and 120°F (50°C), regardless of area ratio, because the rapid polarization of the cathodic metal greatly reduces the galvanic current.

Another example of the effect of polarization can be seen by coupling 18Cr-8Ni SS to CDA alloy 715 (70Cu-30Ni) in water saturated with carbon dioxide at 155°F (68°C). Alloy 715 was anodic to 18Cr-8Ni SS for 6 h after coupling. At 24 h, the 18Cr-8Ni SS was the anode. The corrosion rate of the anode was negligible in both cases.

In the absence of test data, a useful approximation is as follows: for near-equal areas in aqueous environments, the corrosion rate of the anodic member will double. As can be seen in Table 1.1, the acceleration factor varies with the area ratio.

Coupling of dissimilar metals in the atmosphere may also result in galvanic corrosion. Figure 1.22 can be used to determine the compatibility of metals when exposed to atmospheric conditions that cause corrosion (i.e., when the relative humidity exceeds ~50%).

Figure 1.22 correctly indicates that galvanized steel is compatible with the 300 series SS's if it is given one coat of primer. However, galvanized steel should *never* be welded to 300 series SS's, even if the galvanizing in the area to be welded is removed mechanically or chemically. Trace amounts of zinc will remain, and they can rapidly penetrate the grain boundaries of 300 series SS's and cause liquid metal embrittlement cracking (sometimes through the entire thickness). Conversely, very few problems have occurred when galvanized steel is welded directly to carbon and low-alloy steels, even though liquid metal embrittlement of these materials occurs under some conditions.

## Materials Selection for Cooling Water

Appendix A contains a materials selection guide for aerated freshwater systems. As indicated in Note 27 of Appendix A, in freshwater systems, admiralty brass should be limited to a maximum pH value of 7.2 from ammonia and copper-nickel alloys and should not be used in waters containing more sulfides than 0.007 mg/L. The materials selection guide is also satisfactory for seawater, although pump cases and impellers should be a suitable duplex stainless steel or nickel-aluminum-bronze (properly heat treated). Neoprene-lined water boxes should be considered. For piping, fiber-reinforced plastic (up to 150 psi [1,035 kPa] operating pressure) and neoprene-lined steel should also be considered. Titanium and high-molybdenum SS tubes should be considered where low maintenance is required or the cost can be justified by life expectancy.

## Steam and Condensate

Pure, dry steam is not corrosive to carbon steel up to ~1,000°F (540°C). Above this temperature, the oxidation rate in air and steam increases rapidly. Normally, 1¼Cr-½Mo steel is used above 850°F (455°C) to avoid graphitization. Oxidation of 1¼Cr-½Mo occurs at ~1,100°F (590°C). From 1,100 to 1,200°F (590 to 650°C), 2¼Cr-1Mo is satisfactory, although 18Cr-8Ni SS has been used above 1,100°F (590°C). The 2¼Cr-1Mo alloy is preferred in the 1,100 to 1,200°F (590 to 650°C) range because SCC of 18Cr-8Ni SS has occurred in crevices. For example, connections welded to elbows for thermowelds have failed when there has been significant solids carry-over in the steam. When austenitic SS's are used above 1,000°F (540°C), the "*H*" grades (heat treated to a coarse grain size and limited to 0.04% carbon minimum) should be specified. In addition, solution annealing should be specified after cold forming operations to avoid fine grain recrystallization or loss in creep ductility.

Problems with steam can occur in let-down valves as a result of erosion-corrosion. To prevent attack, hard facing (e.g., stellite) is commonly used when the pressure drop exceeds 150 to 200 psi (1,035 to 1,380 kPa). This limit can be raised to 500 psi (3,450 kPa) for clean, dry steam. Corrosion-erosion also occurs in wet steam. Carbon steel is unsatisfactory in wet steam when pvx, the product of the pressure (psia), velocity (ft/s), and wetness (% water) exceeds 1 x $10^5$. Resistance to wet steam is enhanced by increasing both the metal hardness and chromium content.

The effect of small amounts of copper in steel on erosion resistance is controversial. Some tests indicate a benefit, while others reveal no effect on wet steam erosion resistance. Some researchers use the equation $R = 0.61 + 2.43\ Cr + 1.64\ Cu + 0.3\ Mo$ to estimate the relative resistance of carbon steel to erosion-corrosion. Usually, either 1¼Cr-½Mo or 2¼Cr-1Mo is used for lines containing wet steam. The 2¼Cr-1Mo alloy has not exhibited attack when pvx exceeds 1 x $10^5$. The pH of the water is also a factor; increasing the pH from 8 to 9 can decrease the erosion loss by a factor from 2 to 10. To maximize erosion-corrosion resistance, the pH of boiler feedwater (BFW) should be controlled to a minimum of 9.3.

BFW can also cause erosion-corrosion in carbon steel pumps when the temperature exceeds ~250°F (120°C). Impellers of 12Cr are normally used above 250°F (120°C) in BFW pumps to avoid erosion-corrosion. Carbon steel cases have been used above 250°F (120°C), but 5Cr-½Mo or 12Cr are preferred. BFW is treated primarily to prevent corrosion from condensate rather than steam. BFW deaerators work either by combining thermal and mechanical means to drive off oxygen or chemically by adding oxygen scavengers such as hydrazine. Some of the hydrazine ($N_2H_4$) breaks down to form ammonia ($NH_3$). The ammonia, together with carbon dioxide from the decomposition of carbonates and bicarbonates, causes a corrosion problem on copper base alloys in the air removal section of surface condensers. Although published data have indicated that admiralty brass is satisfactory if the ammonia content does not exceed 10 ppm, admiralty brass tubes failed in an ammonia plant surface condenser that was designed to hold ammonia to a maximum of 10 ppm. Recently, severe corrosion fatigue cracking has been reported in a large number of deaerator vessels. Cracks are often so tight that they can be found only by fluorescent magnetic particle examination.

High solids (carbonates and bicarbonates) BFW will result in significant formation of carbon dioxide. The resulting carbon dioxide-laden condensate causes erosion-corrosion attack on carbon steel. Failure occurs by deep pitting, furrowing, or channeling. Corrosion inhibitors can be added to minimize this attack.

Solids can also be a problem if they are carried over into the condensate. Since the solids become alkaline from loss of carbon dioxide, they can readily crack austenitic SS and severely corrode aluminum. In one case, aluminum tubes designed for condensing steam failed in 48 h from solids carry-over.

Clean condensate, free of solids and gases (including oxygen), is relatively noncorrosive and can be handled in carbon steel with a minimal corrosion allowance.

## TABLE 1.1

### GENERAL GUIDE TO CORROSION RATE *ACCELERATION* FACTORS (COUPLED CORROSION RATE/UNCOUPLED CORROSION RATE) IN STATIC SEA WATER[a]

| | | | Acceleration factor[b] | | |
|---|---|---|---|---|---|
| | | | C/A area ratio | | |
| **Material corroding (A)** | **Uncoupled corrosion rate,[c] mm/year** | **Cathode member of couple (C)** | **10** | **1** | **0·1** |
| Alluminum alloys | 0·02 | More noble materials | 11 | 2 | 1 |
| Low alloy and mild steels | 0·04 | More noble materials | 12 | 2 | 1 |
| Ni–Resist | 0·03 | More noble materials | 9 | 2 | 1 |
| Copper alloys | 0·005 | Carbon<br>Monels<br>Inconel 625 | (60) | (5) | (1) |
| | | Stainless steels<br>Titanium | 15 | 2 | 1 |
| | | Copper alloys | 5 | 2 | 1 |
| Monel 400/K500 alloys | 0·02 | Carbon<br>Inconel 625 | (30) | (4) | (1) |
| | | Stainless steels<br>Titanium | 6 | 2 | 1 |
| Stainless steels | 0·001 | Inconel 625 | (6) | (2) | (1) |
| Inconel 625 | <0·001 | Titanium, carbon | .... | 1 | ... |

---

[a] D.J. Astley, J.C. Rowlands, "Modelling of Bimetallic Corrosion in Seawater Systems," *Brit. Corros. J.* 20(1985): p. 90.

[b] Factors in parentheses have been derived on the basis of a limited amount of evidence.[18]

[c] In flowing sea water (1-2 m $s^{-1}$), factors for aluminium alloys could be about ten times higher. The corrosion rate of uncoupled aluminium alloy is the same in flowing and static sea water. Available evidence indicates that factors for materials other than aluminium alloys will be the same in flowing and in static sea water, relative to the uncoupled corrosion rates in flowing and static sea water respectively. Uncoupled corrosion rates in flowing sea water are: low alloy steels, Ni–Resist 0·10 - 0·15 mm/year, copper alloys 0·01 - 0·05 mm/year, Monels 0·002 mm/year.

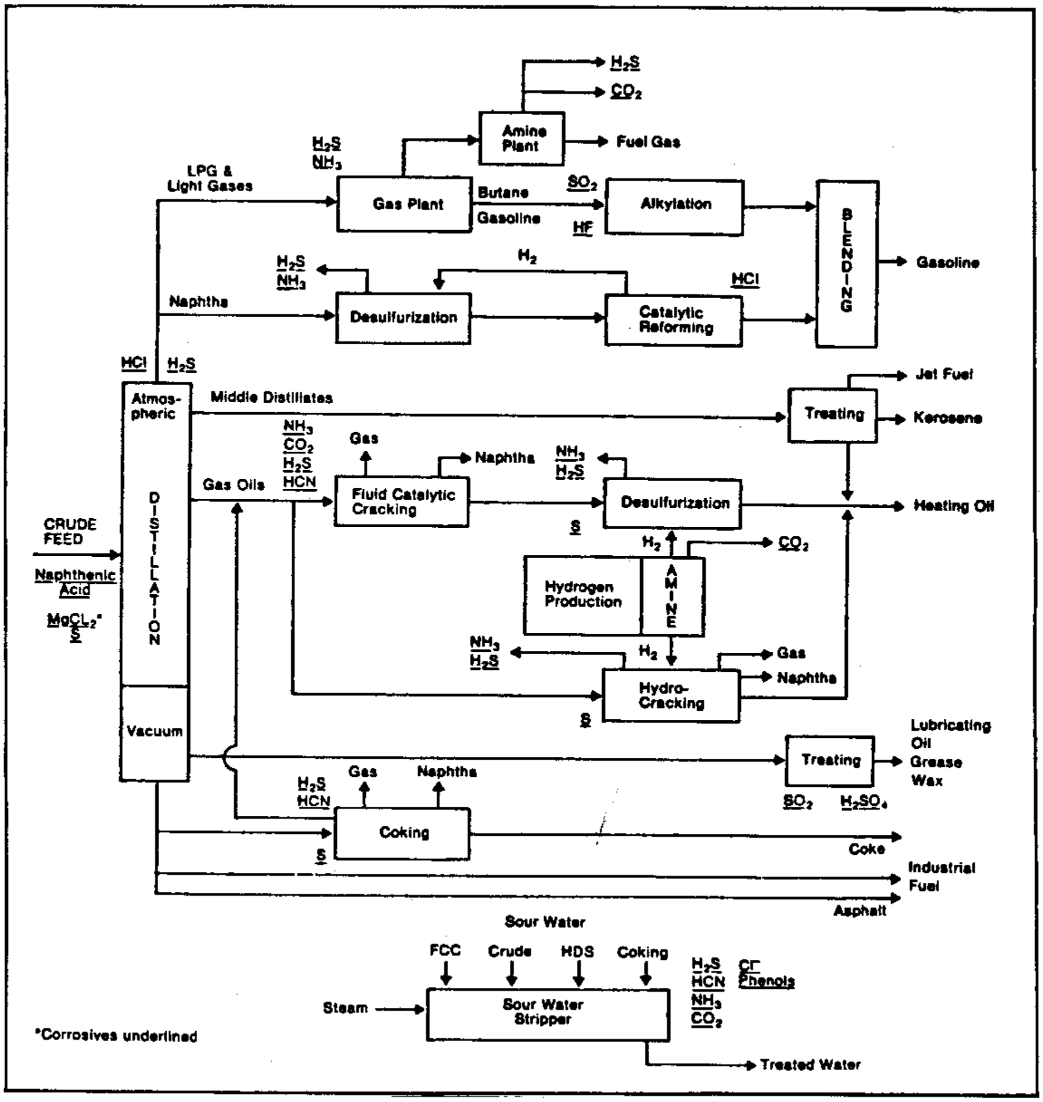


Figure 1.1 Simplified refinery process flow diagram.[1]

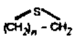
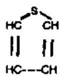
| Type | Formula | Found In<br>Crude Oil | <br>Straight-Run Products | <br>Cracked Products |
|---|---|---|---|---|
| Elemental sulfur | S | Yes | Yes | Yes |
| Hydrogen sulfide | $H_2S$ | Yes | Yes | Yes |
| Mercaptans | | | | |
| Aliphatic | RSH | Yes | Yes | Yes |
| Aromatic | RSH | Yes | Yes | Yes |
| Naphthenic | RSH | No | No | No |
| Sulfides | | | | |
| Aliphatic | R - S - R | Yes | Yes | Yes |
| Aromatic | R - S - R | No | No | No |
| Cyclic |  | Yes | Yes | Possibly |
| Disulfides | | | | |
| Aliphatic | R - S - S - H | Yes | Yes | No |
| Aromatic | R - S - S - H | ? | No | Yes |
| Thiophene and homologues |  | Yes | Yes | Yes |
| Polysulfides | R - $S_n$ - S - R | ? | Yes | Yes |

Figure 1.2 Types of sulfur compounds in crude oil and distillates.[2]

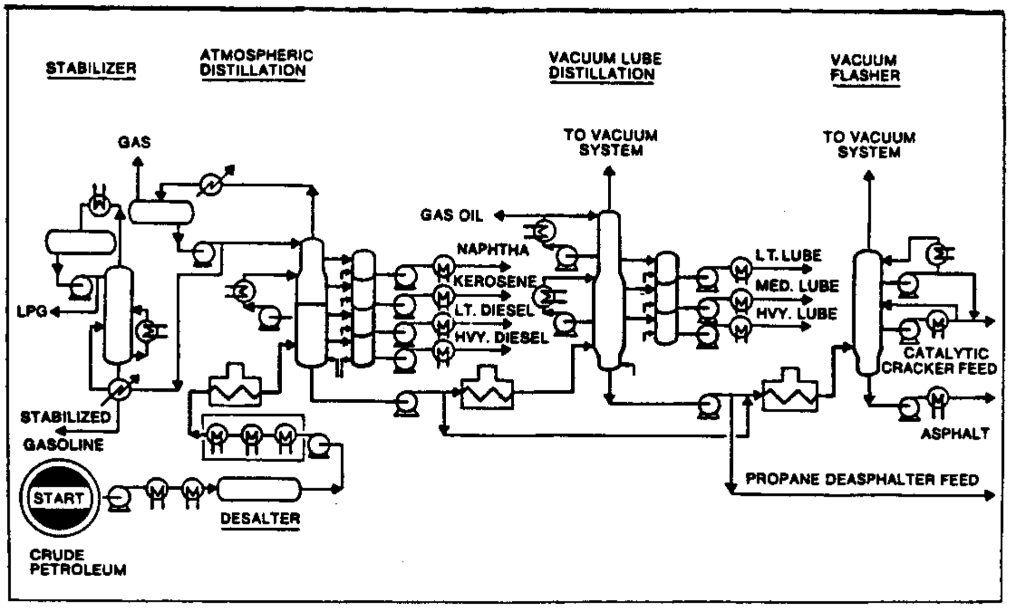


Figure 1.3 Crude distillation, three stages.[1]

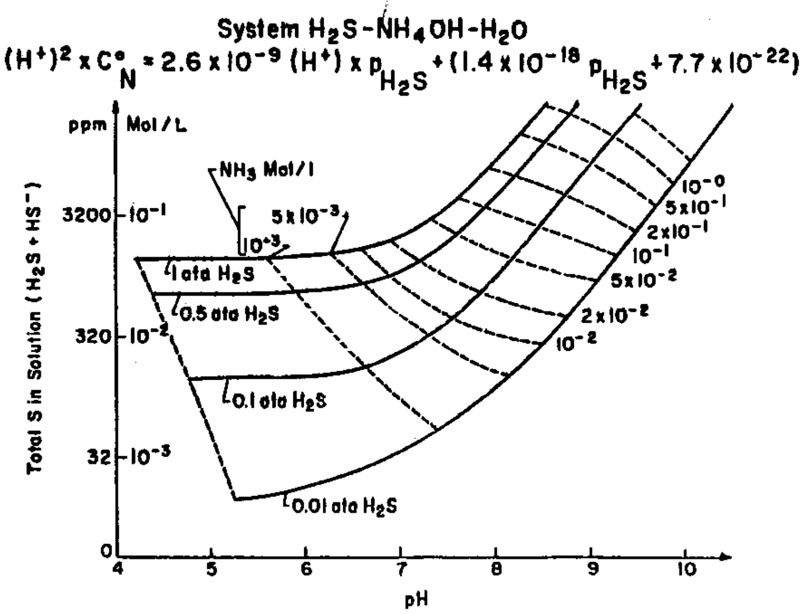


Figure 1.4 Total S in solution vs pH.[3]

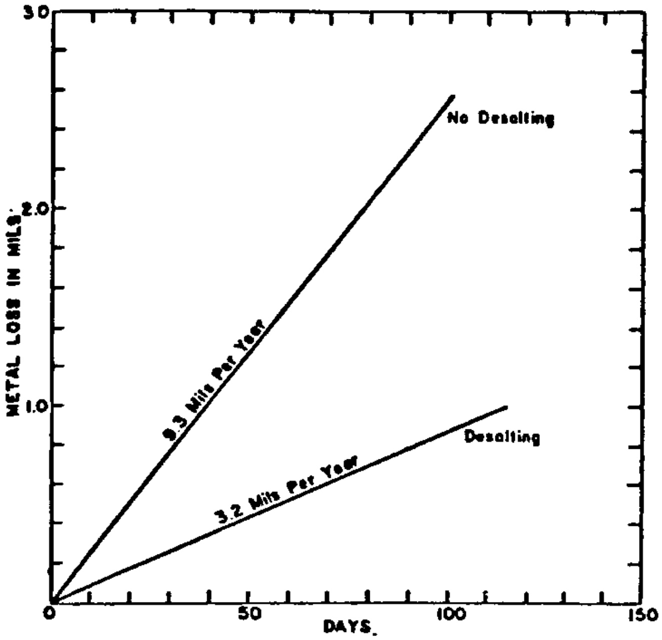


Figure 1.5 Corrosion rates of steel in a crude unit secondary tower overhead. Desalting made drastic reduction in corrosion rates.[4]

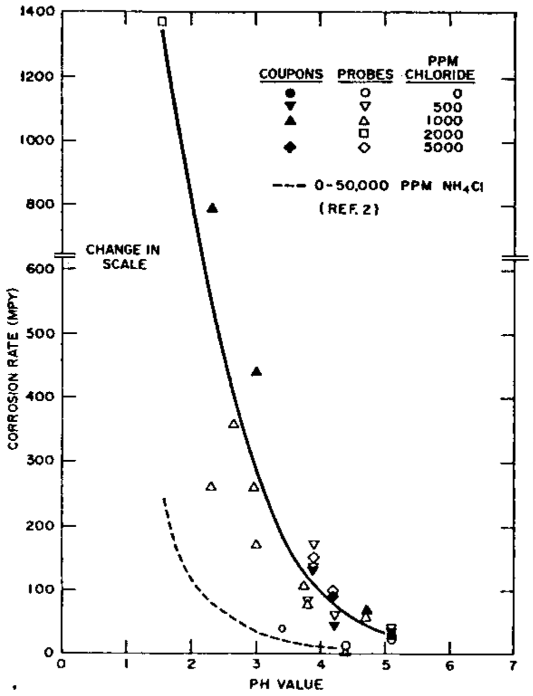


Figure 1.6 Corrosion of steel in aqueous sulfide solutions. Note the acid corrosion region because of an excess of hydrogen ions at pH values below 4.5.[5]

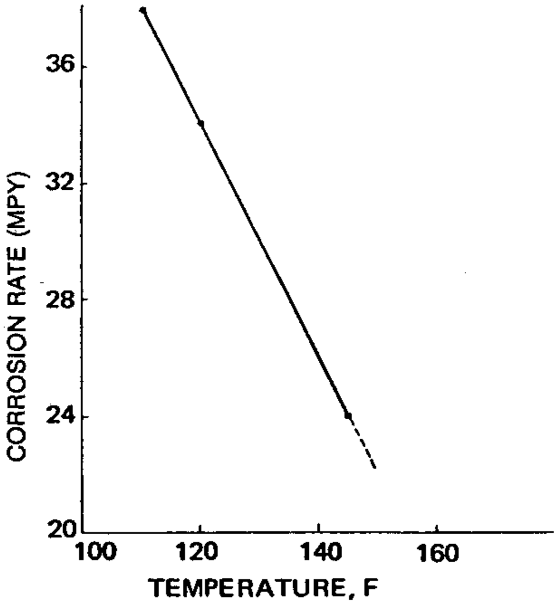


Figure 1.7 Corrosion rate of steel vs temperature of atmospheric tower sour condensate water.[3]

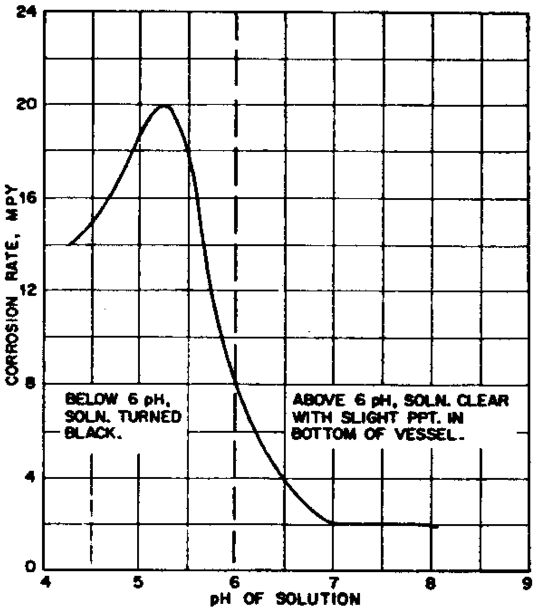


Figure 1.8 Effect of pH on corrosion rate of iron in solution of the same $H_2S$ activity.[7]

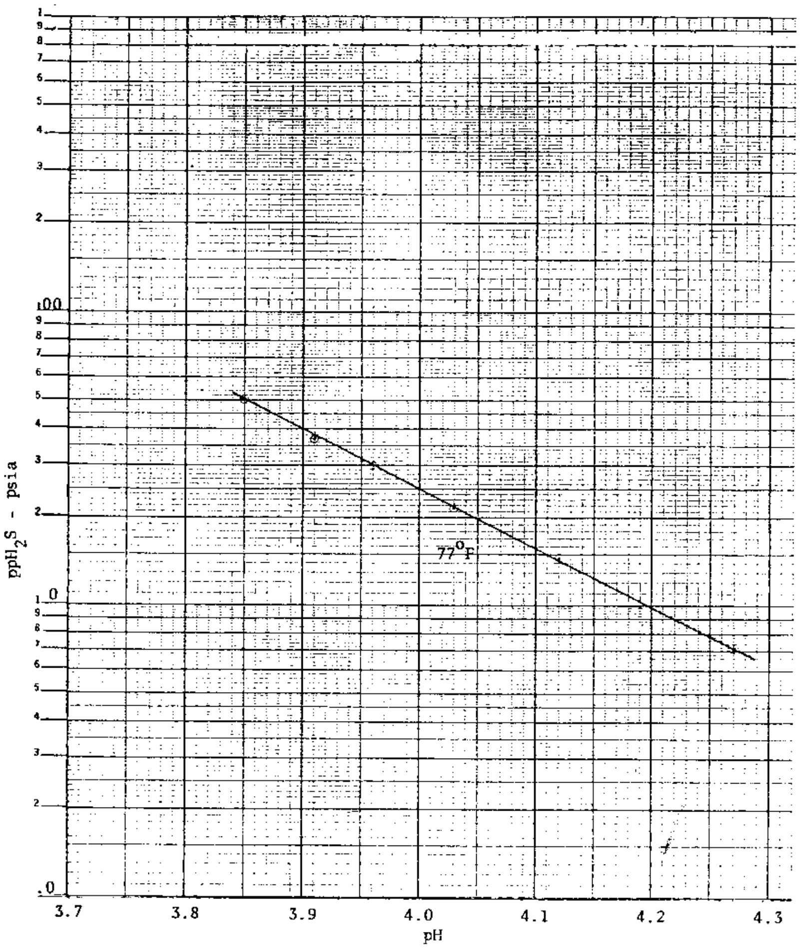


Figure 1.9 Solubility of $H_2S$ in water. Partial pressure of $H_2S$ in vapor vs pH of solution.[8]

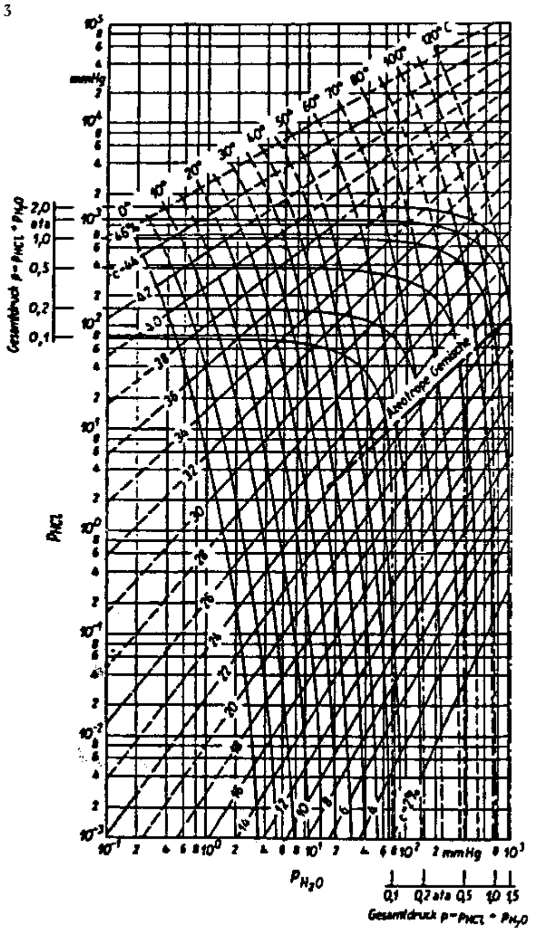


Figure 1.10 HCl and $H_2O$ partial pressures over HCl depending on temperature, total pressure, and acid concentration.[3]

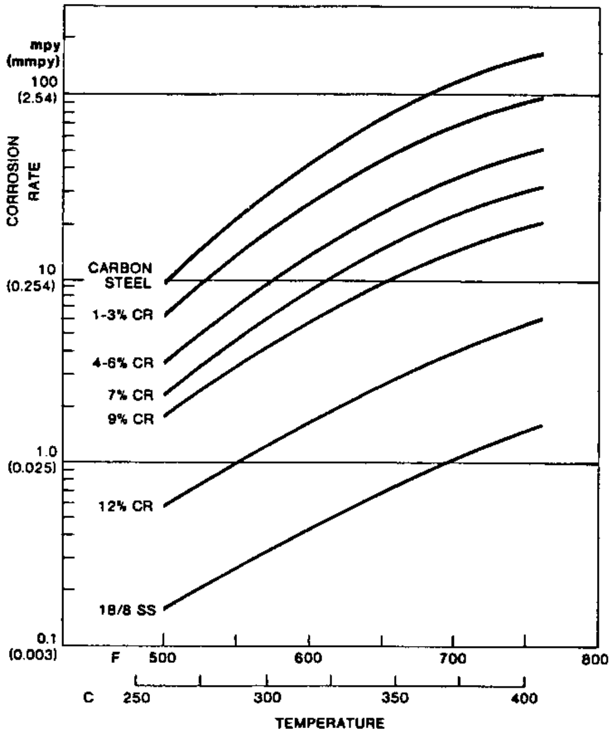


Figure 1.11 Average corrosion rates of high temperature sulfur corrosion in a hydrogen free environment as compiled from 1961 A.P.I. questionnaire data from industry-desulfurizing processes and published or reported data—nondesulfurizing processes.[9]

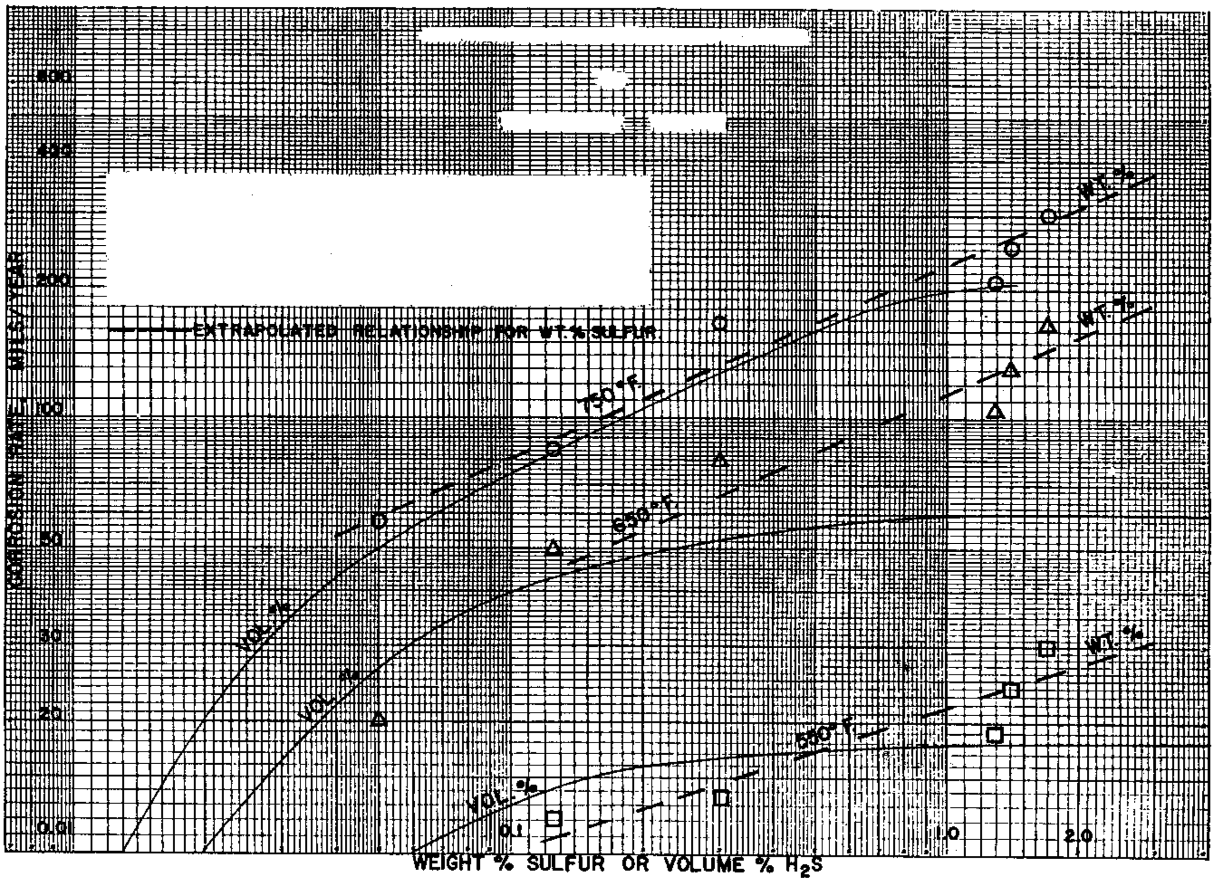


Figure 1.12 Comparison of sulfur levels vs carbon steel corrosion rates.[9]

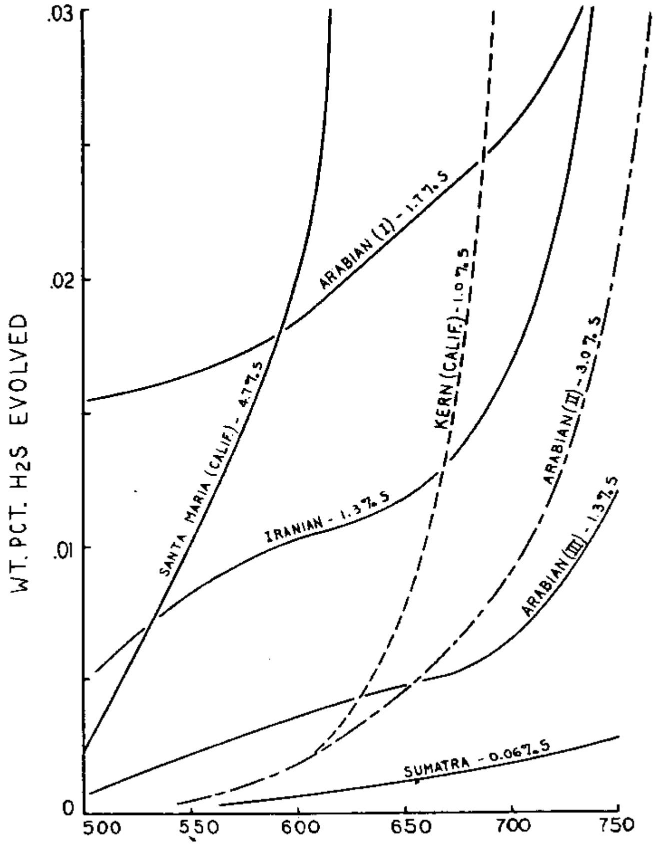


Figure 1.13 Hydrogen sulfide release from crudes.[10]

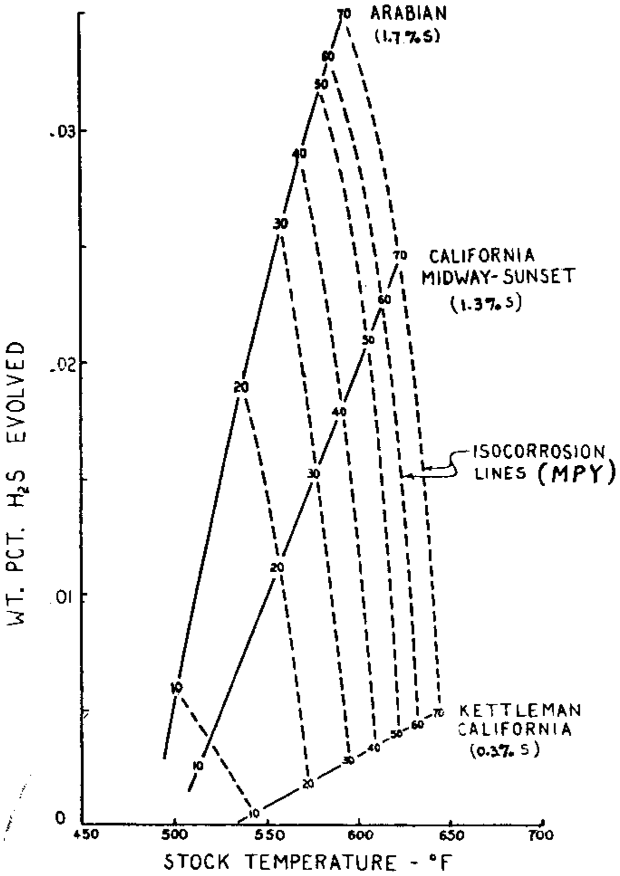
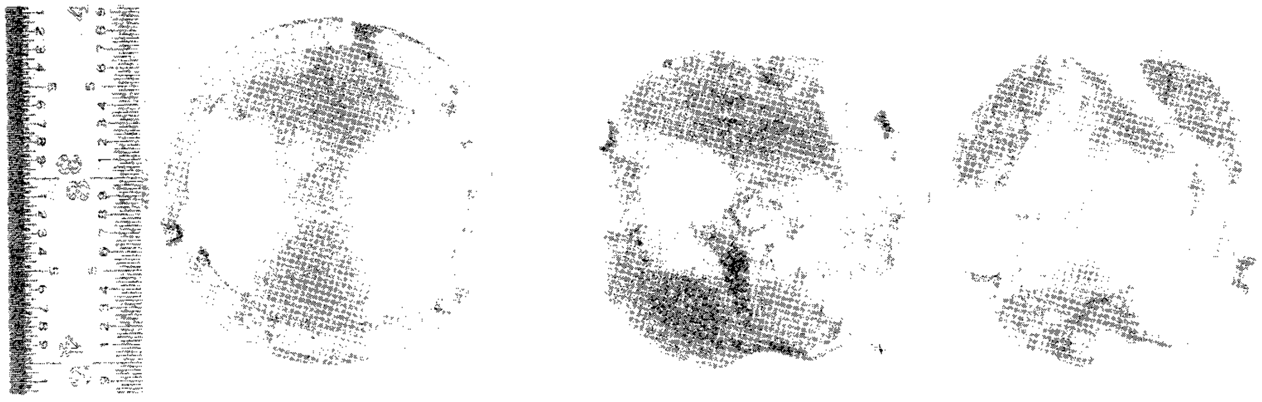


Figure 1.14 Corrosion of carbon steel furnace tubes.[10]



Type 316 Stainless Steel

Type 410 Stainless Steel

Figure 1.15 Cage tray caps exposed to oil containing naphthenic acid for six months.

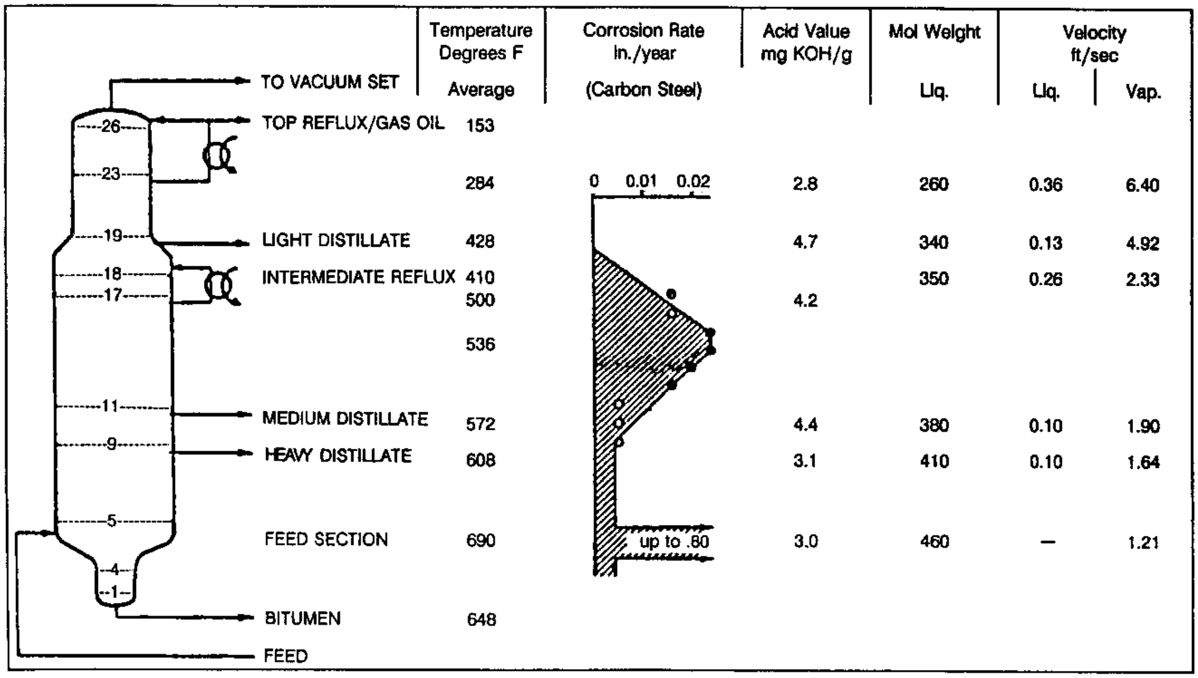
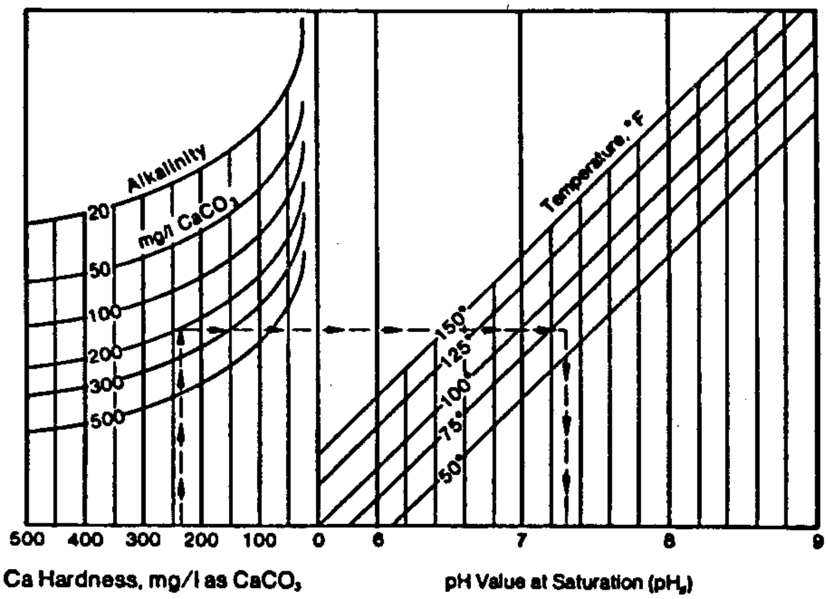


Figure 1.16 Corrosion and operating data of a high vacuum column processing a reduced crude.[11]



EXAMPLE:
Raw Water Calcium = 240 mg/l
Alkalinity = 190 mg/l
pH = 6.8
Temperature = 70°F (21°C)
From Chart: pH$_s$ = 7.3
Langelier Index = 6.8 – 7.3 = –0.5

Figure 1.17 Determination of pHs and Langelier Index from hardness, alkalinity, and temperature.[12]

| UNS NUMBER | COMMON NAME | CLEAN SEA WATER | GOOD FRESH WATER |
|---|---|---|---|
| C12200 | Copper (Phosphorus Deoxidized) | Good Up to 3 FPS | Good Up to 4 FPS |
| C23000 | Red Brass | Good Up to 4 FPS | Good Up to 5 FPS |
| C44300 | Admiralty | Good Up to 6 FPS | Good Up to 9 FPS |
| C68700 | Aluminum Brass | Good Up to 9 FPS | Good Up to 11 FPS |
| C60800 | Aluminum Bronze | Good Up to 8 FPS | Good Up to 11 FPS |
| C70600 | Copper Nickel, 10% | Good Up to 8 FPS | Good Up to 11 FPS |
| C71500 | Copper Nickel, 30% | Excellent Up to 15 FPS | Good Up to 15+ FPS |

Figure 1.18 Behavior of copper alloy condenser tubes under velocity conditions.[13]

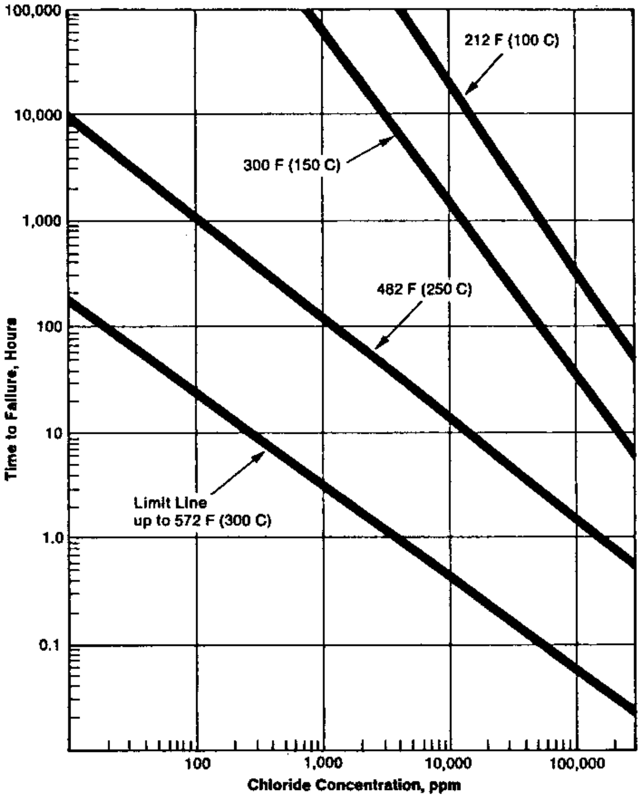


Figure 1.19 Stress corrosion cracking of 18-8 Stainless Steel in Chloride Solutions.[14]

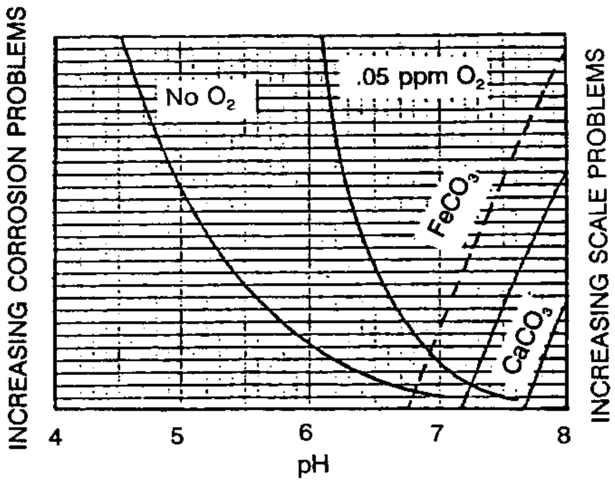
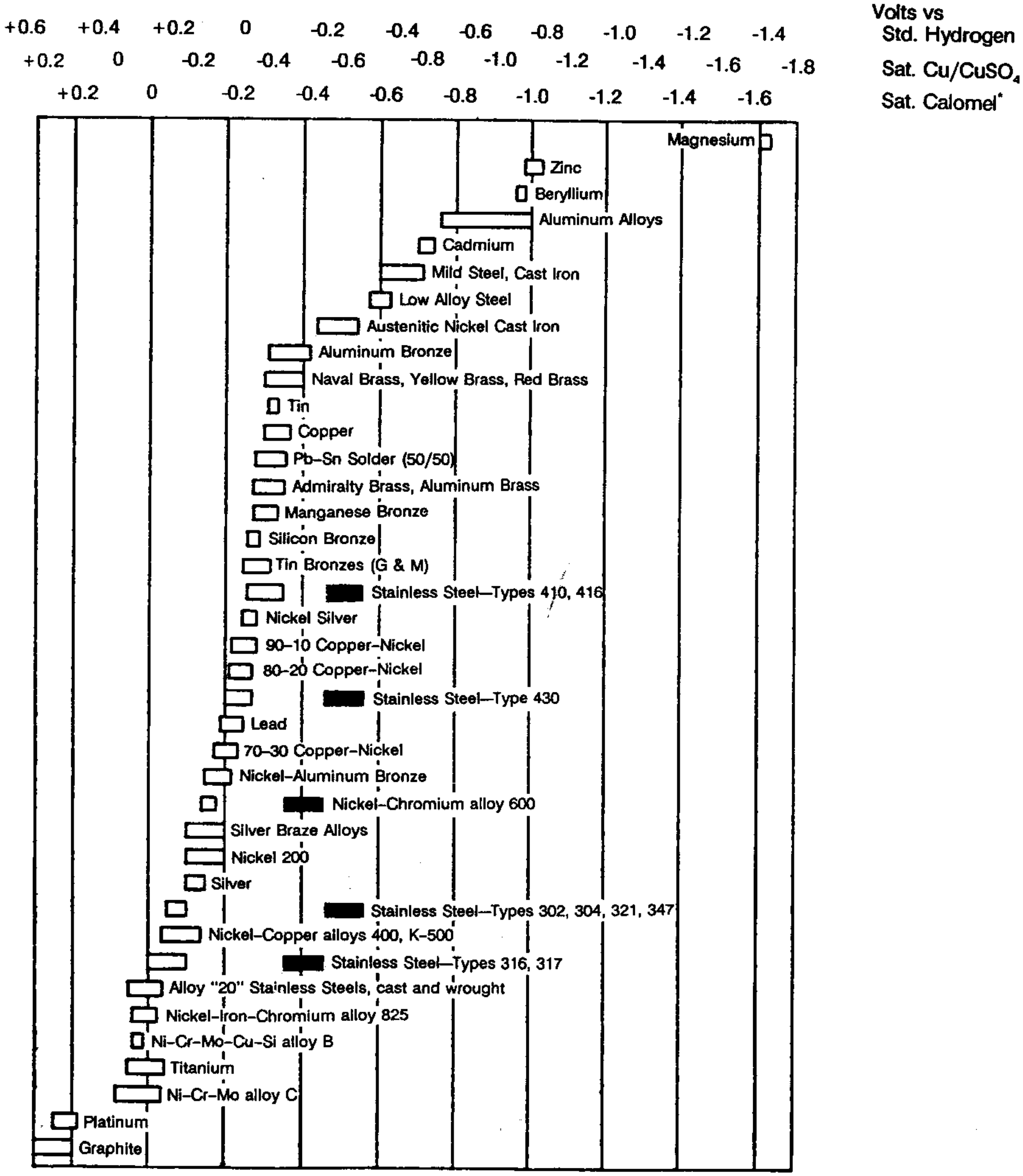


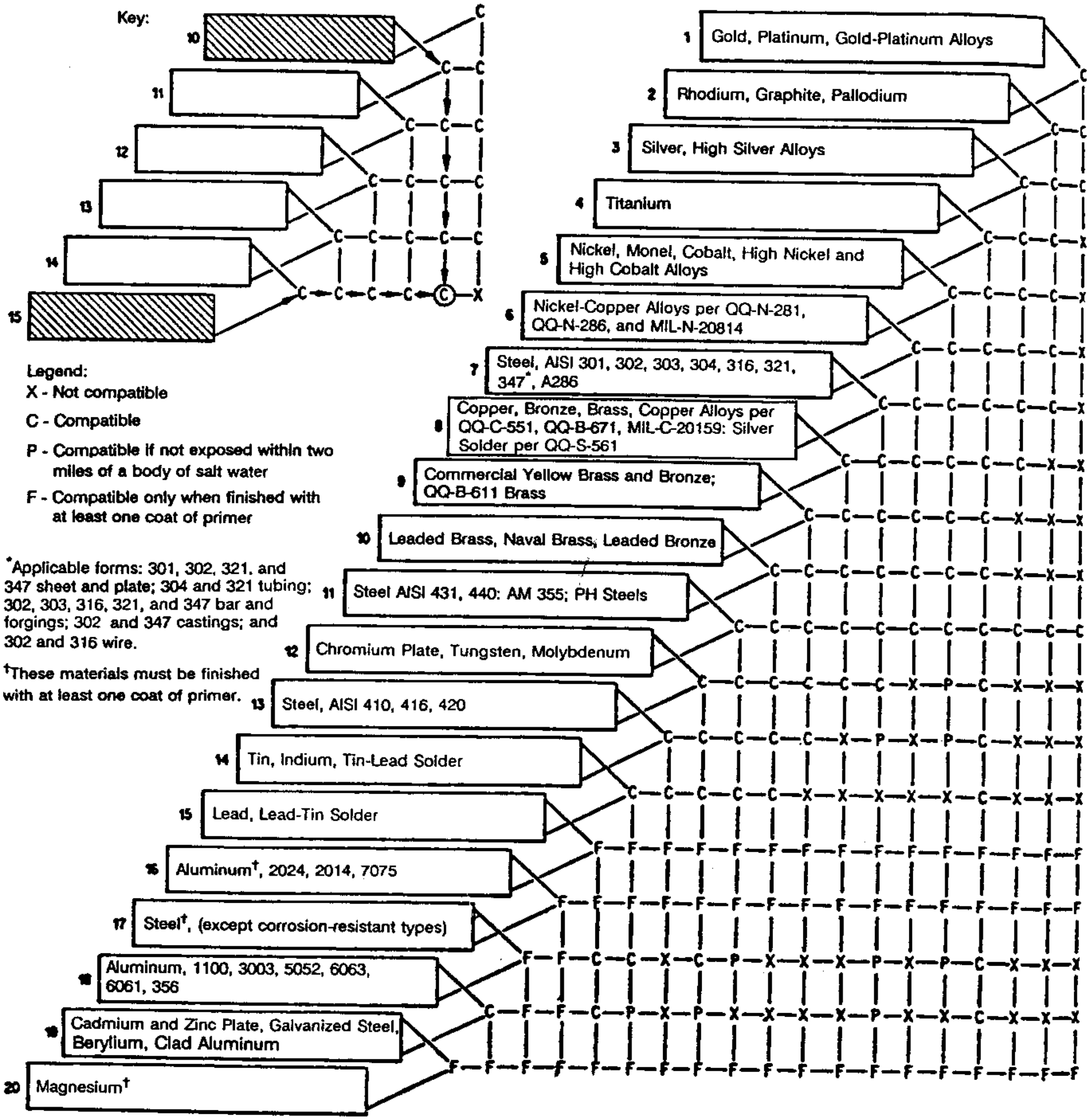
Figure 1.20 Summary of pH effects on the seawater injection system.[15]



Alloys are listed in the order of the potential they exhibit in flowing seawater. Certain alloys indicated by the symbol: ■ in low velocity or poorly aerated water, and at shielded areas, may become active and exhibit a potential near -0.5 volts.

*Also Ag/AgCl in 20 Ω-cm seawater

Figure 1.21 Corrosion potentials in flowing seawater (8 to 13 ft/sec) temperature range 50°-80°F (10°-27°C).[16]



Legend:
X - Not compatible
C - Compatible
P - Compatible if not exposed within two miles of a body of salt water
F - Compatible only when finished with at least one coat of primer

*Applicable forms: 301, 302, 321, and 347 sheet and plate; 304 and 321 tubing; 302, 303, 316, 321, and 347 bar and forgings; 302 and 347 castings; and 302 and 316 wire.

†These materials must be finished with at least one coat of primer.

| | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13 | 14 | 15 | 16 | 17 | 18 | 19 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 Gold, Platinum, Gold-Platinum Alloys | | | | | | | | | | | | | | | | | | | |
| 2 Rhodium, Graphite, Pallodium | C | | | | | | | | | | | | | | | | | | |
| 3 Silver, High Silver Alloys | C | C | | | | | | | | | | | | | | | | | |
| 4 Titanium | C | C | C | | | | | | | | | | | | | | | | |
| 5 Nickel, Monel, Cobalt, High Nickel and High Cobalt Alloys | X | C | C | C | | | | | | | | | | | | | | | |
| 6 Nickel-Copper Alloys per QQ-N-281, QQ-N-286, and MIL-N-20814 | X | C | C | C | C | | | | | | | | | | | | | | |
| 7 Steel, AISI 301, 302, 303, 304, 316, 321, 347*, A286 | X | C | C | C | C | C | | | | | | | | | | | | | |
| 8 Copper, Bronze, Brass, Copper Alloys per QQ-C-551, QQ-B-671, MIL-C-20159: Silver Solder per QQ-S-561 | X | C | C | C | C | C | C | | | | | | | | | | | | |
| 9 Commercial Yellow Brass and Bronze; QQ-B-611 Brass | X | X | C | C | C | C | C | C | | | | | | | | | | | |
| 10 Leaded Brass, Naval Brass, Leaded Bronze | X | X | X | C | C | C | C | C | C | | | | | | | | | | |
| 11 Steel AISI 431, 440: AM 355; PH Steels | X | X | X | C | C | C | C | C | C | C | | | | | | | | | |
| 12 Chromium Plate, Tungsten, Molybdenum | C | C | C | C | C | C | C | C | C | C | C | | | | | | | | |
| 13 Steel, AISI 410, 416, 420 | X | X | X | C | P | X | C | C | C | C | C | C | | | | | | | |
| 14 Tin, Indium, Tin-Lead Solder | X | X | X | C | P | X | P | X | C | C | C | C | C | | | | | | |
| 15 Lead, Lead-Tin Solder | X | X | X | C | X | X | X | X | X | C | C | C | C | C | | | | | |
| 16 Aluminum†, 2024, 2014, 7075 | F | F | F | F | F | F | F | F | F | F | F | F | F | F | F | | | | |
| 17 Steel†, (except corrosion-resistant types) | F | F | F | F | F | F | F | F | F | F | F | F | F | F | F | F | | | |
| 18 Aluminum, 1100, 3003, 5052, 6063, 6061, 356 | X | X | X | C | P | X | P | X | X | X | P | C | X | C | C | F | F | | |
| 19 Cadmium and Zinc Plate, Galvanized Steel, Berylium, Clad Aluminum | X | X | X | C | X | X | P | X | X | X | X | P | X | P | C | F | F | C | |
| 20 Magnesium† | F | F | F | F | F | F | F | F | F | F | F | F | F | F | F | F | F | F | F |

Figure 1.22 Atmospheric compatibility of metals.[17]

## REFERENCES FOR FIGURES

1. (Reprinted with permission from *The Role of Stainless Steels in Petroleum Refining*, April 1977, American Iron and Steel Institute, Washington, DC.)
2. (Reprinted with permission from "High Temperature Degradation of Structural Materials in Environments Encountered in the Petroleum and Petrochemical Industries," *Anti-Corrosion Methods and Materials*, November 1975, Sawell Publications, Ltd., London, England.)
3. (Reprinted with permission from "Crude Unit Overhead Corrosion," *Hydrocarbon Processing*, May 1972, Gulf Publishing Co., Houston, TX.)
4. (Reprinted from "Crude Oil Desalting to Reduce Refinery Corrosion Problems," *Materials Protection*, May 1962.)
5. (Reprinted from "Corrosion of Steel by Sulfides and Cyanides in Refinery Condensate Water," *Materials Protection*, December 1968.)
6. (Reprinted from "Determination of Refinery Corrosion Rates Using the PAIR Technique," *Materials Protection*, January 1969.)
7. (Reprinted from "Corrosion of Refinery Equipment by Aqueous Hydrogen Sulfide," *Corrosion*, April 1959.)
8. (Reprinted with permision from *Handbook of Chemistry*, 6th Ed., 1979, McGraw-Hill Publishing Co., New York, NY.)
9. (Reprinted from "High Temperature Sulfide Corrosion in Hydrogen Free Environment," *API Proceedings—Division of Refining*, vol. 43, May 1963, American Petroleum Institute, Washington, DC.)
10. (Reprinted from "Correlation of Corrosion in a Crude Distillation Unit with Chemistry of the Crudes," *Corrosion*, June 1960.)
11. (Reprinted from "Naphthenic Acid Corrosion—An Old Enemy of the Petroleum Industry," *Corrosion*, December 1956.)
12. (Reprinted with permission from *The Nalco Water Handbook*, 1979, McGraw-Hill Publishing Co., New York, NY.)
13. (Reprinted from the *Bridgeport Condenser and Heat Exchanger Tube Handbook*, 1964.)
14. (Reprinted with permission from "What Causes Equipment to Fail?" *Hydrocarbon Processing*, January 1975, Gulf Publishing Co., Houston, TX.)
15. (From private communication.)
16. (Reprinted with permission from "Guidelines for the Selection of Marine Materials," 2nd ed., June 1966, Ocean Science and Ocean Engineering Conference, LaQue Center for Corrosion Technology, Inc., Wrightsville Beach, NC.)

Chapter
# TWO

# Fluid Coking and Cracking, Delayed Coking, Alkylation, Sulfur Plants, and Sour Water Strippers

## *INTRODUCTION*

Fluid coking and fluid catalytic cracking (FCC) are mechanically similar. The products of fluid coking and delayed coking are the same (i.e., coke and distillate products), but the equipment is physically different. Alkylation of the three- and four-carbon molecule products from these units is commonly performed to convert them to branched chain gasoline, which increases the octane rating. As can be seen from Figure 1.1 in Chapter One, the feed to fluid catalytic crackers is a gas-oil distillate. For delayed cokers and fluid cokers, the feed is residium.

## *FLUID COKING AND FLUID CATALYTIC CRACKING*

In FCC (Figure 2.1), the feed from the vacuum column is mixed with the hot catalyst, which carries the feed up to the reactor. The reactor operates at ~900 to 1,000°F (480 to 540°C) and 40 to 50 psia (276 to 345 kPa) (25 to 35 psia [172 to 240 kPa] in a fluid coker). The cracking of the large hydrocarbon molecules occurs in the riser and the reactor. The cracked products flow out from the top of the reactor to the fractionator after the entrained catalyst is removed by the cyclones on the top. The coked catalyst passes out of the bottom of the reactor through slide valves into the stripper section. Countercurrent steam removes vapors from the catalyst before it flows to the regenerator. In the regenerator, the catalyst is regenerated by the burning of the coke at ~1,200 to 1,400°F (650 to 760°C). Entrained catalyst is again removed from the gases before the gases leave the top of the vessel. The hot regenerated catalyst passes out of the bottom of the regenerator, where it is again combined with fresh feed plus some recycle from the fractionator.

In fluid coking (Figure 2.2), the residium feed is injected into the reactor, where it is cracked thermally in a fluidized bed catalyst. Products other than coke leave the top of the reactor and are quenched in a scrubber, where residual coke is removed. The coke fines and some of the heavy fractions are recycled to the reactor. The lighter fractions are fed to conventional fractionating equipment.

The coke-laden catalyst drops to the bottom of the reactor and is circulated to the heater by steam. In the heater, the volatile products are driven off. A circulating coke stream is sent to the gasifier where 95% or more of reactor coke is gasified with steam and air.

### Reactors and Regenerator (Burner) Vessels

The mechanical designs of fluid coker and fluid catalytic cracker reactors and regenerators (called burners in fluid cokers) are essentially the same. These vessels are often 25 to 30 ft (7.6 to 9.2 m) in diameter and 80 to 100 ft (24.5 to 30.5 m) high. Walls are usually made of ½ to 1 in. (12.7 to 25.4 mm) thick carbon steel with refractory lining. The refractory lining has two layers and is applied by a spray gun technique (hence, the term gunite). The first layer against the vessel wall is an insulating refractory (the temperatures in the regenerators often reach 1,300°F [705°C]) held on by Y anchors (Nelson studs) on the wall. A 12Cr hexmesh (similar to walkway grating) is then attached to the studs, and an erosion resistant refractory is applied over the mesh. For the newer high-temperature units, stainless steel fiber reinforced refractory linings are used because the thermal expansion of the hexmesh is sufficient to cause refractory to crack. The erosion resistant lining is required to resist wear from the continual cycling of the catalyst through the two vessels. Smaller units have been made from clad construction without refractory lining. In these cases, the use of carbon steel is limited to 850°F (454°C) to avoid loss of strength resulting from long-term graphitization.(1)

The flow pattern in a fluid coker is similar to that of a fluid catalytic cracker except that the circulating solids are coke. Part of the coke is burned in the burner vessel, and hot coke is circulated to the reactor.

The cyclones in both unit types are lined with erosion resistant refractory. The cyclones in the reactors are usually made of carbon steel; the cyclones in the regenerators are made of either 2¼Cr-1Mo or type 304 (UNS S30400) or 321 (UNS S32100) stainless steel (SS). Oxidation resistance and creep strength, rather than sulfur attack, govern the selection of the cyclone material.

These vessels are often field-erected because of their large size. This means that they must be hydrostatically tested for the first time in the field; this poses the risk of brittle fracture. Figures 2.3 through 2.5 show a brittle fracture of a fluid coker burner vessel. Figure 2.3 shows an overall view of the collapsed vessel and gives an idea of the extent of the catastrophe. The debris from the failure under the support structure is shown in Figure 2.4. This gives an impression of the effect that the failure had in the immediate area. Figure 2.5 shows the numerous paths the cracks took on the bottom head, where the brittle fracture originated. The incident occurred on Feb. 17, 1956 in the Avon, California refinery during the construction of a fluid coker unit. The vessel, 36 ft (11 m) in diameter by 75 ft (23 m) high, was made from ⅝ in. (16 mm) thick ASTM(2) A285C steel. It failed in the knuckle (ASME(3) head) to skirt attachment during hydrotesting, when the ambient temperature was 45 to 50°F (7 to 10°C). For further details on this failure, refer to the *API Proceedings* from 1962, "Brittle Failure of a Large Pressure Vessel," by A.G. Harding and E.F. Ehmke.(4)

Since this failure, most designers have used only ellipsoidal or hemispherical heads that require a minimum temperature, typically 80°F (27°C), for hydrostatic tests of field-erected vessels.

The valves controlling the flow between the reactor and regenerator (or burner) are specially designed slide valves.(5) They have weld overlay hard facing (e.g., a cobalt base alloy containing 28Cr, 4CO, 1C) on the stems and sliding surfaces and erosion resistant refractory lining in the body. The hard facing weld beads should be deposited parallel to the flow direction to minimize turbulent flow.

## Associated Equipment

Type 304H (UNS S30409) SS is commonly used for the small high-temperature lines around the reactor and regenerator. Intergranular stress corrosion cracking (IGSCC) from polythionic acid has been a severe problem in these lines during shutdown. Presently, a nitrogen and ammonia purge is introduced at 200°F (93°C) above the dew point during cooldown to prevent attack.

Expansion bellows in the regenerated catalyst stand pipe have been subject to failure. Inconel(6) 625 failed as a result of loss of ductility from an aging reaction that occurs in the 1,100 to 1,500°F (595 to 815°C) range. Incoloy(7) 801 (Ti stabilized for resistance to intergranular attack [IGA]) undergoes a severe loss of ductility above 900°F (480°C). Incoloy 800 has been used successfully, although it is not immune

---

(1) Formation of graphite (free carbon) in steel by the decay of iron carbide.

(2) ASTM, Philadelphia, PA.

(3) American Society of Mechanical Engineers, New York, NY.

(4) American Petroleum Institute, Washington, DC.

(5) Box-like valves where the gate slides in guides.

(6) Trade name.

(7) Trade name.

to all failures (e.g., IGA). The International Nickel Company[8] has suggested that Inconel 617 be considered. Regardless of the alloy used for expansion bellows, the material should be solution annealed after it is formed, and careful attention to procedure details during installation is imperative to minimize failure.

In the last 10 years, as a result of more efficient operating methods, carbonate stress corrosion cracking has occurred in the fractionator overheads in fluid catalytic crackers. The problem is most severe at a pH greater than 9 and a carbonate concentration above 110 ppm. It has also occurred at a pH between 8 and 9 when the carbonate concentration is above 400 ppm. Therefore, most refiners are now specifying postweld heat treatment of carbon steel when such conditions are anticipated.

## *DELAYED COKING*

In delayed coking (Figure 2.6), the charge is fed to the fractionator. The bottom product of the fractionator is then fed to the heater, where it is heated to coking temperature. A mixture of liquid and vapor from the coker heater is fed to the coke drum that operates at ~900°F (480°C) and 50 psia (345 kPa).

The main reaction in a delayed coker occurs in pairs of vessels called coke drums. The feed temperature to a coke drum is 920 to 950°F (490 to 510°C); outlet temperatures are 800 to 820°F (425 to 440°C). Delayed coking is a batch process in which the vessels are in coking service for 24 h and then in decoking service for 24 h. This causes the vessels to cycle between room temperature and ~950°F (510°C) every 48 h. While the reaction is occurring in one vessel (i.e., while coke is filling the vessel), the other vessel is being decoked. A drum is decoked by the following:

- stripping the coke with steam;
- quenching with water—gradually filling the drum;
- draining;
- opening heads; and
- cutting the coke with a 3,200 psi (22 kPa) water system jet (i.e., a pilot hole is cut, and the remainder of the coke is cut out).

The vapor from the overhead of the coke drums is returned to the fractionator. The overhead vapor is separated into its components in the fractionator and products are withdrawn. The heavier fractions recycle to the coke drum in the fractionator bottoms.

### Coke Drum Materials

Because of the thermal cycling experienced by the coke drums, thermal fatigue is a problem. The use of C-½Mo for coke drum vessels is controversial. Cracks do develop in these vessels because of thermal fatigue; however, some refiners have blamed some of the cracking on poor toughness of C-½Mo. Although toughness does not affect fatigue crack growth (fatigue crack growth is a ductile fracture process), brittle fracture will occur in a low-toughness material quicker than in a high-toughness material. A high-toughness material can tolerate a larger fatigue crack than a low-toughness material can.

Since C-½Mo plate is supplied in the as-rolled condition in the thickness normally used for coke drums (~1 in. [25 mm] thick), the toughness is usually poor. To obtain improved toughness at minimal cost, one should specify that the C-½Mo be made to fine grain practice. Most coke drums have been made of 1Cr-½Mo materials for about the last 15 y because of the controversy over C-½Mo and the higher allowable

---

[8] International Nickel Company, New York, NY.

stress of 1Cr-½Mo. After the proper toughness requirements are specified, the ultimate choice of material should be based on cost.

Delayed cokers are usually clad with 12Cr to avoid high-temperature sulfur attack. For cladding, type 410S (UNS S41008) SS is preferred over type 405 (UNS S40500) SS because the higher chromium in type 405 SS causes problems with forming and 885°F (475°C) embrittlement (discussed in Chapter One).

Type 309 (UNS S30900) SS is normally used for clad restoration on 12Cr clad vessels. However, severe cracking occurred when type 309 SS was used for clad restoration on coke drums because of the thermal cycling of material with large differences in coefficients of thermal expansion (type 309 SS and 12Cr on low-alloy steel backing). Inconel-type (70Ni-15Cr-5Fe) electrodes perform significantly better than type 309 SS for clad restoration in coke drums because of the lower coefficient of expansion and the coke's protecting the Inconel-type electrodes from accelerated sulfur attack. This is the only high-temperature sulfur-containing environment in which high-nickel alloy materials work well. Severe sulfidation occurred in crude units when Inconel-type electrodes were used above 550°F (288°C) presumably because there was no coke to protect the Inconel-type electrodes from the environment.

## *ALKYLATION PLANTS*

### Sulfuric Acid Alkylation

In sulfuric acid (effluent refrigeration) alkylation (Figure 2.7), the feed and the recycle sulfuric acid are charged to the contractor. The reaction occurs at ~40 to 50°F (4 to 10°C) at 50 psia (345 kPa) in the presence of 98% sulfuric acid. The sulfuric acid in the effluent of the reactor is removed in the acid settler, the trap and flash drum, the caustic wash, and the water wash before sulfuric acid is fed to the fractionators. Sulfuric acid in alkylation plants is handled primarily in carbon steel, as long as the concentration of the sulfuric acid does not fall below ~80%. If the velocity exceeds 2 to 3 ft/s (0.6 to 0.9 m/s), alloy 20 (20Cr, 33Ni, 3Cu, and 2Mo) is used; type 316 (UNS S31600) SS is limited to 4 ft/s (1.2 m/s) without accelerated erosion-corrosion. Small valves (less than 6 in. [152 mm] in diameter) are usually made of alloy 20, and larger valves are made of steel with alloy 20 trim (stem and seats). Steel cases and cast iron impellers are often used for pumps; however, they only last 5 to 10 y. Critical pumps are often made of alloy 20 (the cast equivalent is ASTM A351 Grade CN7M).

### Hydrofluoric Acid Alkylation

The feed to a hydrofluoric acid alkylation unit is desiccant dried and then sent to the combined reactor settler (Figure 2.8). The reaction occurs at 90 to 100°F (32 to 38°C), at 250 psia (1,725 kPa), and in the presence of 90% hydrofluoric acid. The effluent from the combined reactor settler is fed to the main fractionator. The hydrofluoric acid goes overhead with the light ends and is condensed and collected in the accumulator. Part of the condensed overhead fluid is recycled from the feed to the combined reactor settler, part is used for reflux to the main fractionator, and the remainder is fed to the hydrofluoric acid stripper. The overhead of the stripper is returned to the main fractionator overhead condenser. The bottom product of the stripper is caustic washed to remove all traces of hydrofluoric acid. The bottom product of the main fractionator is often fed to a debutanizer fractionator column.

Carbon steel is the primary material of construction for equipment used when the concentration of hydrofluoric acid is above ~80%. Hydrogen embrittlement of high-strength steels has been a problem; steels of tensile strengths exceeding a specified minimum of 60,000 psi (413,700 kPa) are usually avoided. Flange bolts may be ASTM A193 B7, but valve bonnet bolts should be ASTM B7M or Monel(9) 400 because of leakage. Slag on the surface of welds has been reported to cause accelerated attack. Whenever possible, special attention should be given to slag removal. In higher temperature areas (e.g., the acid reboiler and the bottom of the acid regenerator), Monel 400 is used. Monel 400 is subject to stress corrosion cracking (SCC) in hydrofluoric acid if air gets into the system. As a precaution, some refiners specify stress relief of

---

(9)Trade name.

solid Monel 400. Valves are carbon steel with Monel 400 trim and Teflon[10] packing. Spot chemical testing of Monel 400 is usually specified because it is easily confused with austenitic SSs.

## *FRACTIONATION*

After the reactions have occurred in the catalytic crackers, cokers, and alkylation plants, the effluents are separated by fractionation to obtain the various products desired. The materials for the fractionation equipment are selected using basically the same criteria as those used for crude units, as discussed in Chapter One [i.e., carbon steel below 550 to 600°F (288 to 315°C) and 5Cr-½Mo piping and 12Cr clad vessels above]. However, there are some slight differences from crude units. An example is furnace tubes in delayed cokers, which are usually 9Cr-1Mo (because of the high-fluid temperatures) rather than 5Cr-½Mo.

## *SOUR WATER AND SOUR WATER STRIPPERS*

### Characteristics of Sour Water

Coking and catalytic cracking produce cyanides and hydrogen sulfide in the water condensed from these processes. Very little water is produced in the alkylation process. The traces of acid from the alkylation units and the cyanides (even though only in the ppm range) from coking and catalytic cracking cause corrosion problems in the tops of columns and the overhead piping and drums where the aqueous phase condenses. Cyanides are very active if the pH is in the alkaline range. This usually occurs because the nitrogen in the streams that produces the cyanide also produces ammonia.

The corrosion problems caused by these produced waters are blistering and hydrogen cracking. The blisters are caused by the hydrogen generated in the corrosion process recombining at voids and inclusions in the steel. The most severe hydrogen blistering has been found in de-ethanizer columns in FCC gas plants. The tendency to form blisters can be monitored by putting hydrogen probes on the system. A probe is mounted on the outside of the equipment. The current measured by the instrument is directly related to the hydrogen flow through the wall. Water (to dilute the corrosive constituents), liquid polysulfide (to react with and remove cyanides), and inhibitors are added to avoid blistering. In some catalytic crackers, sufficient excess oxygen is used in the regenerator to cause the sulfides to convert to polysulfides. As a result, corrosion in the sour water from these units is minimal.

Studies of corrosion in oil and gas fields indicate that hydrogen sulfide cracking becomes a problem when the partial pressure of hydrogen sulfide exceeds 0.05 psi (0.35 kPa) and the total pressure exceeds 65 psia (450 kPa). Figures 2.9 and 2.10 can be used to predict where sulfide stress cracking will occur for sour gas systems as a function of total system pressure vs hydrogen sulfide concentration. In refineries, 50 ppm $H_2S$ in the fluid is often used as a basis for defining sour water. Oil present in the system tends to inhibit the sulfide cracking; therefore, limits for the sulfide cracking region in the total system pressure vs hydrogen sulfide concentration are somewhat different from those in which oil is absent. The limits for sour oil and multiphase systems are shown in Figure 2.10.

To avoid hydrogen sulfide cracking, the hardness of carbon steels should be limited to 200 Brinell[11], and the hardness of low-alloy steels should be limited to ~235 Brinell. For more detailed requirements on materials resistant to hydrogen sulfide cracking, see the latest revisions of NACE Standards MR0175[12] and RP0472[13] and API Standard RP942. The latter two publications are based on refinery

---

[10] Trade name.

[11] Trade name.

[12] NACE Standard MR0175, "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment," National Association of Corrosion Engineers, Houston, TX, latest revision.

experience and require a maximum of 200 Brinell for carbon steel welds; MR0175 is based on oil and gas field experience and requires a maximum of 241 Brinell for carbon steel. The difference may have arisen because submerged arc and other automatic welding processes are commonly used for refinery equipment; whereas, most carbon steel oil and gas field equipment is welded by the manual metal arc process that tends to deposit softer welds than do automatic welding processes. Recent experience has shown that alkaline solutions of $H_2S$ and carbonates are particularly aggressive. Refiners are now specifying postweld heat treatment in these services. This phenomenon is referred to as a hydrogen-induced cracking (HIC) or stress-oriented hydrogen-induced cracking (SOHIC). In addition to postweld heat treatment, some steel companies are suggesting limiting sulfur in steel to 0.001 percent to minimize failures. Niobium-vanadium steels are used so that the high strength can be maintained without the need for high carbon. Conversely, there have been cracking problems with steels of normal carbon contents containing microalloying elements. Calcium treating the steel and limiting the oxygen to less than 10 ppm have also been suggested as ways to minimize HIC and SOHIC.

### Sour Water Strippers

The sour or foul water from all units in a refinery is collected and sent to a stripper for purification before it is discharged into the environment. A typical process flow diagram of a nonacidified condensing sour water stripper is shown in Figure 2.11. In this unit, the sour water enters the stripper vessel through the feed bottoms exchanger. The hydrogen sulfide and other corrosive gases are removed by the heat supplied by the reboiler connected to the bottom of the stripper vessel. The overhead stream is condensed and then collected in the reflux drum. The liquid from the reflux is recycled to the stripper, and the gases are either burned or fed to a sulfur plant.

### Corrosion in Sour Water Strippers

The main corrosion problems in a nonacidified condensing sour water stripper occur in the overhead system. Exchanger tubes in the overhead condenser are often made of commercially pure titanium. The reflux pump is often alloy 20 (CN7M). In very corrosive waters, such as those containing phenols or large quantities of salts, Hastelloy[14] C276 is used. Two API surveys (API Standards 944 and 950) concluded that the location and severity of corrosion vary with the type of unit as follows:

Acidified: severe corrosion in the feed section, bottom section, and stripper tower;
Nonacidified Condensing: severe corrosion and erosion-corrosion in the overhead section; and
Nonacidified, Noncondensing: negligible corrosion.

## *SULFUR PLANTS*

### Process

Sulfur is quite versatile; it can be used as an agricultural insecticide or as a raw material for making sulfuric acid, as shown in Figure 2.12. To make sulfur, acid gas (hydrogen sulfide, sulfur dioxide, and carbon dioxide) from the various refinery amine units is collected and fed to a sulfur plant. In a typical sulfur plant, the acid gas is fed to a reaction furnace. The hydrogen sulfide is first partially burned at ~2,500°F (1,370°C) and 15 psia (103 kPa) in the reaction furnace to form sulfur dioxide; next, it is passed through a waste heat boiler and then passed over catalyst beds at ~500°F (260°C) and 15 psia (103 kPa) in the converters. Sulfur is condensed from the effluent of successive converters and solidified in pits.

---

[13] (...continued)

[13] NACE Standard RP0472, "Methods and Controls to Prevent In-Service Cracking of Carbon Steel (P-1) Welds in Corrosive Petroleum Refining Environments," National Association of Corrosion Engineers, Houston, TX, latest revision.

[14] Trade name.

## Materials

The effluent from the reaction boiler is handled in type 310 (UNS S31000) SS above 800°F (425°C), type 321 or 347 (UNS S34700) SS above 500°F (260°C), and carbon steel below 500°F (260°C). Molten sulfur is handled in steam-traced steel or aluminum. At the discharge to the pits, oxygen causes severe attack on steel, so the discharge end of the steel line often contains a short piece of alloy 20.

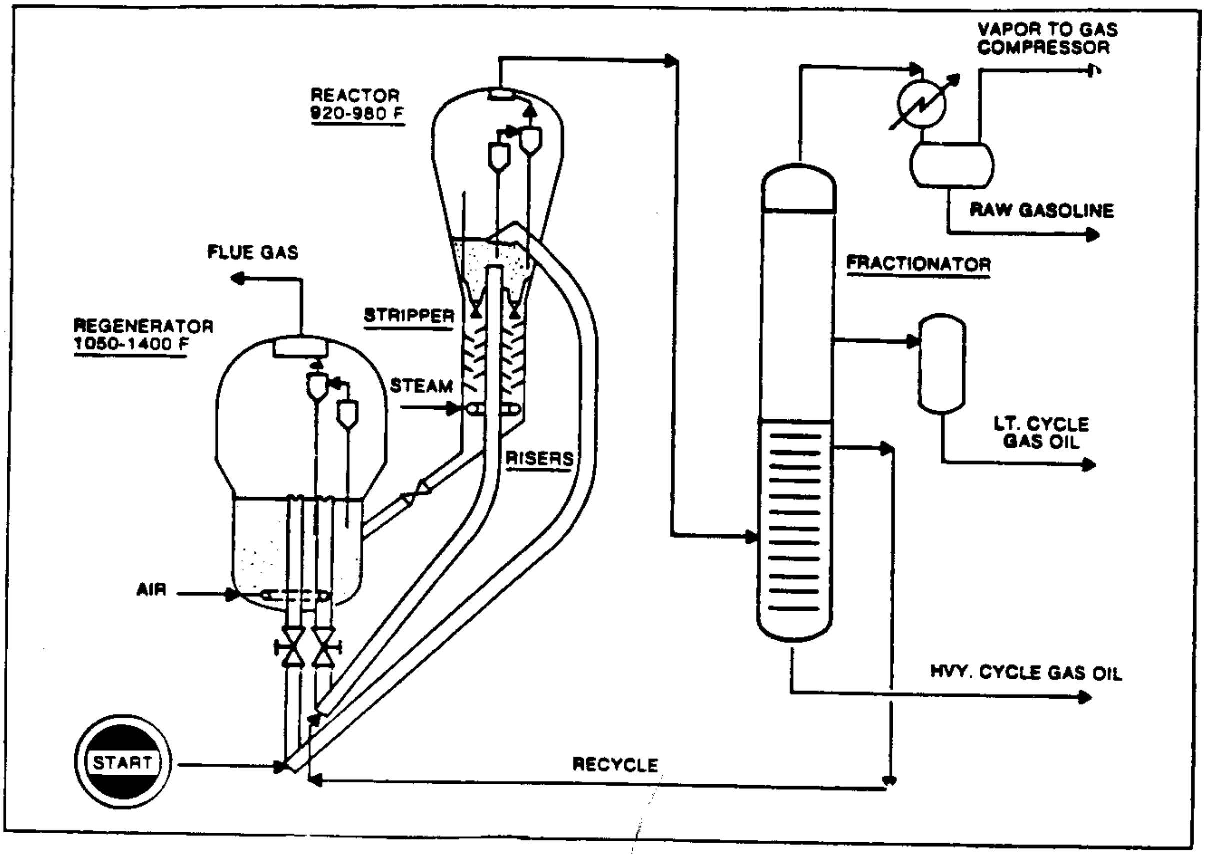


Figure 2.1 Fluid catalytic cracking[1]

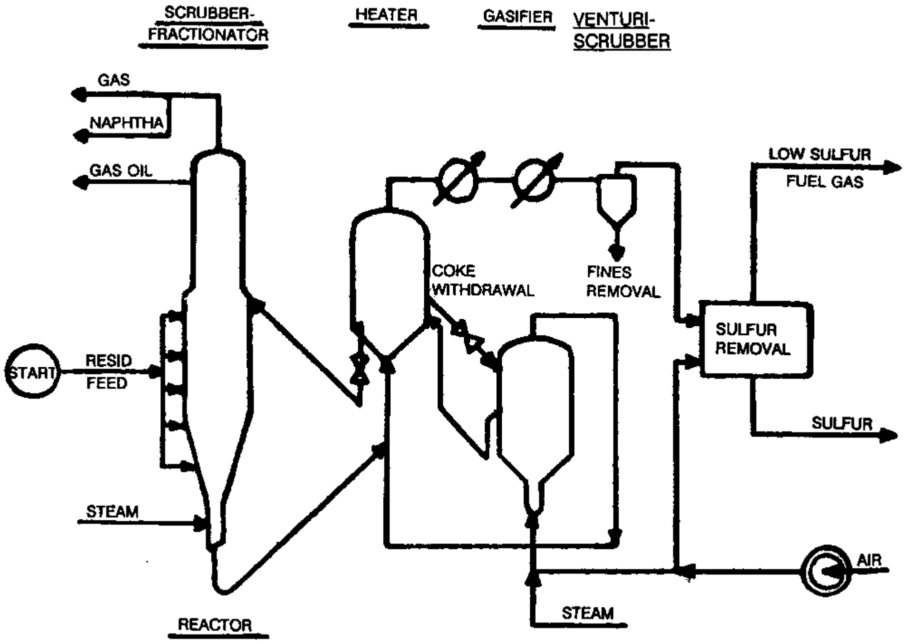


Figure 2.2 Flexicoking[2]

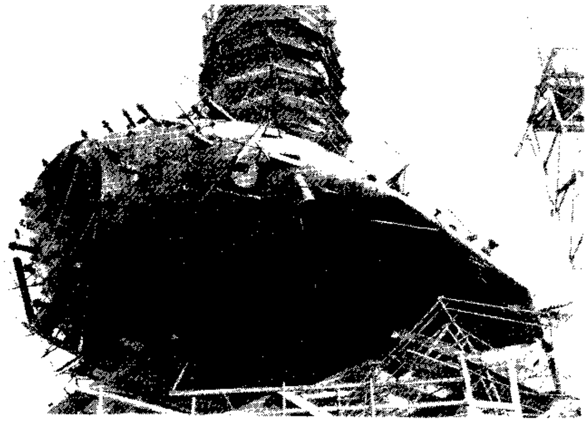


**Figure 2.3** Front view of collapsed vessel. Test closure for vapor line opening in top center of top head at upper left.[3]

**Figure 2.4** Heat fragments directly below collapsed shell.[3]

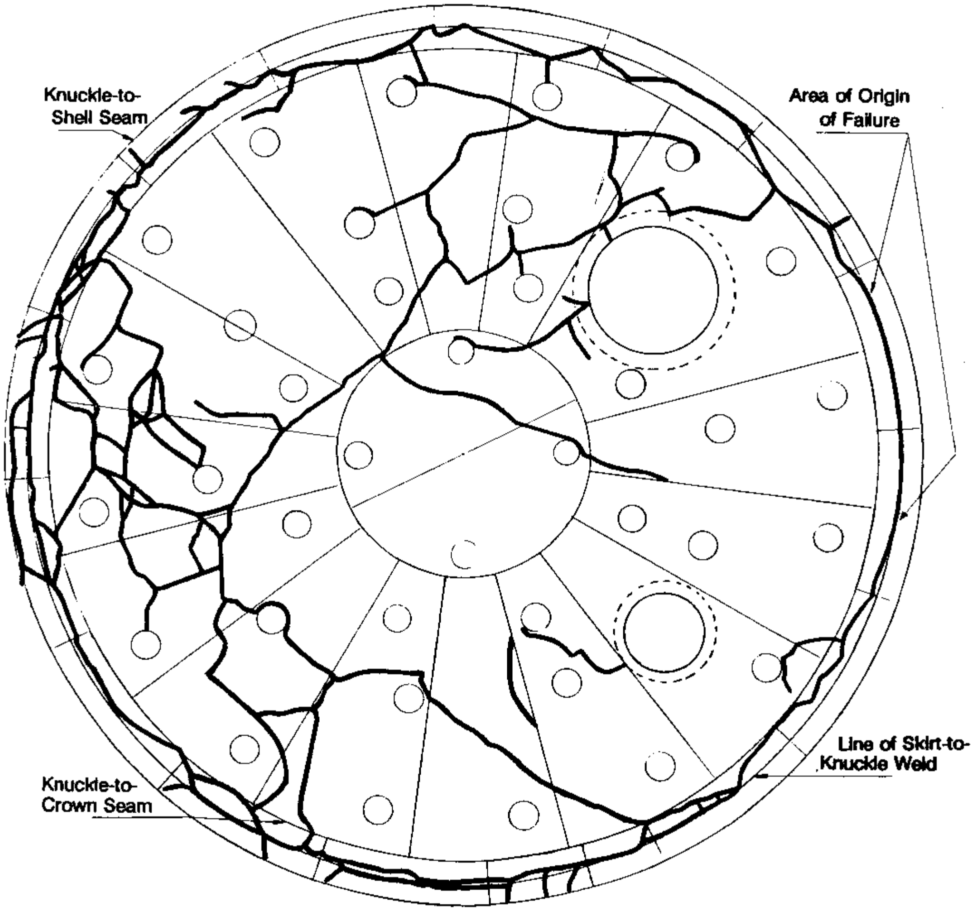


**Figure 2.5** Layout of failed bottom head showing 34-piece construction and brittle fracture lines.[3]

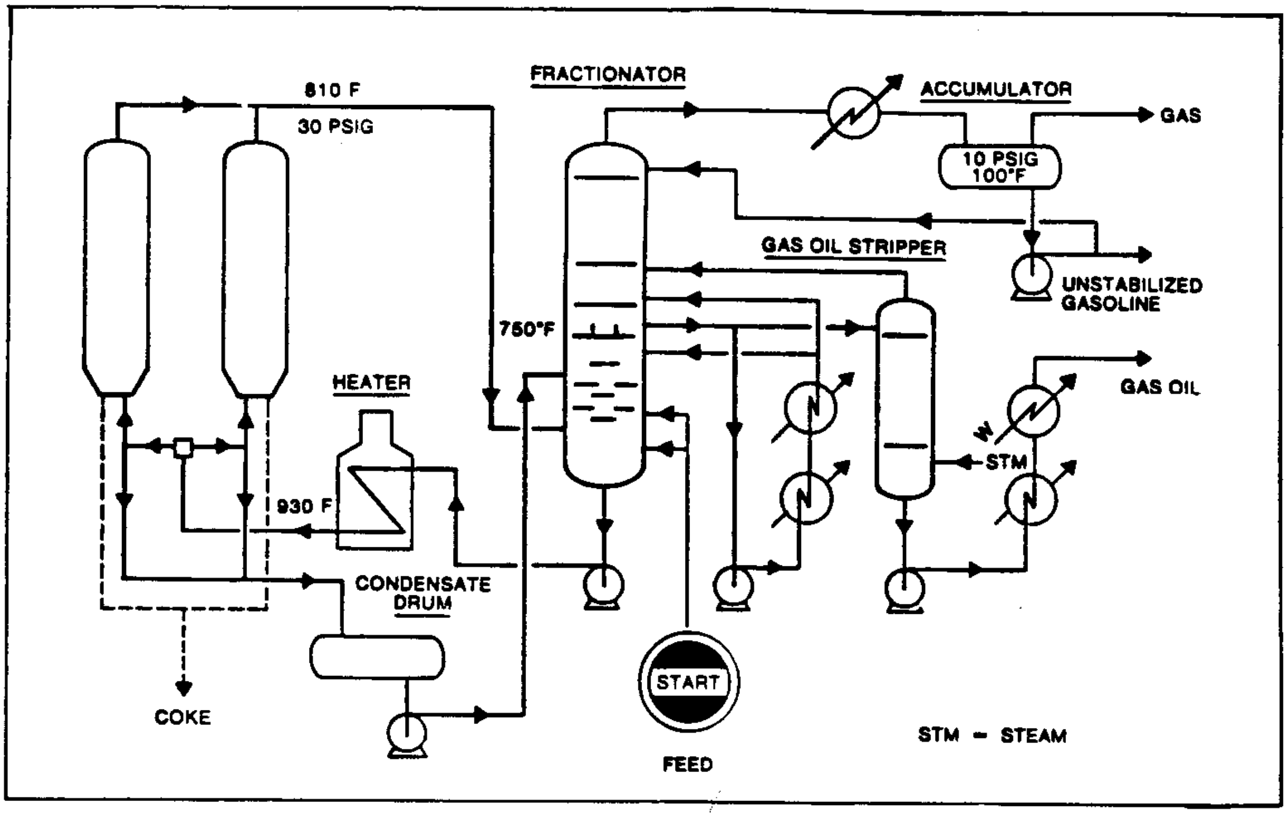


Figure 2.6 Delayed coking[1]

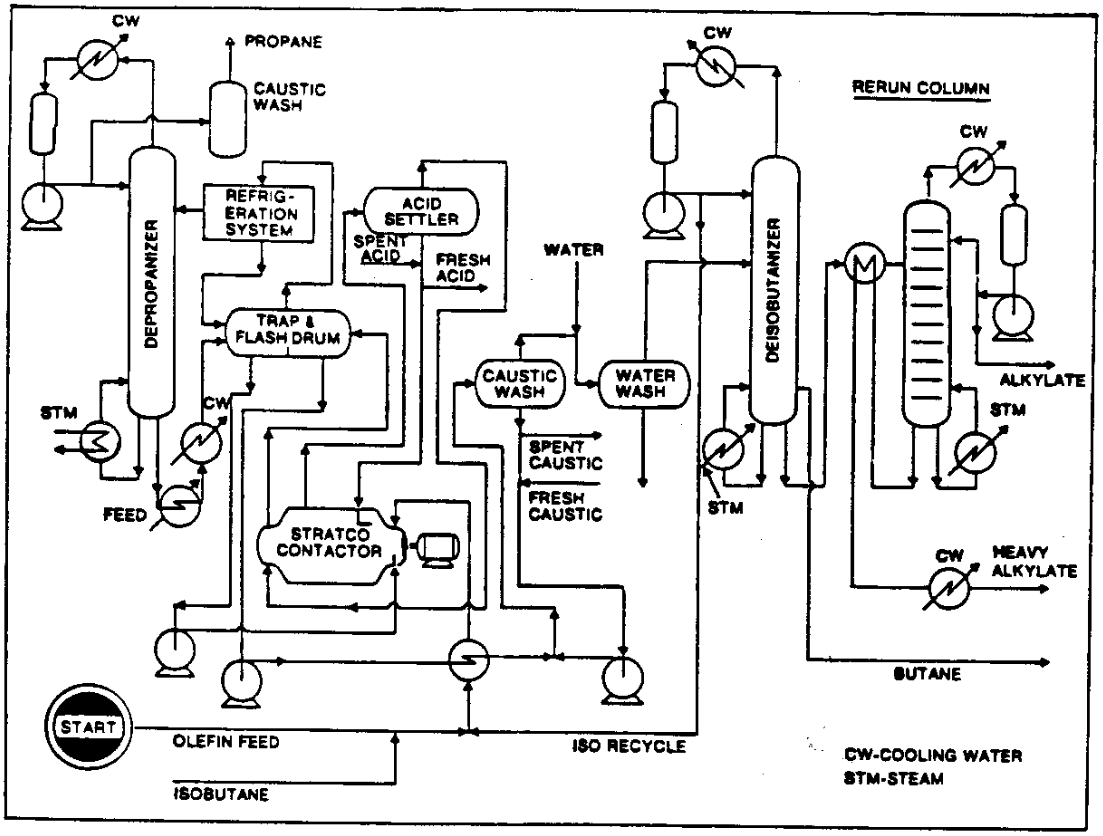


Figure 2.7 Sulfuric acid alkylation[1]

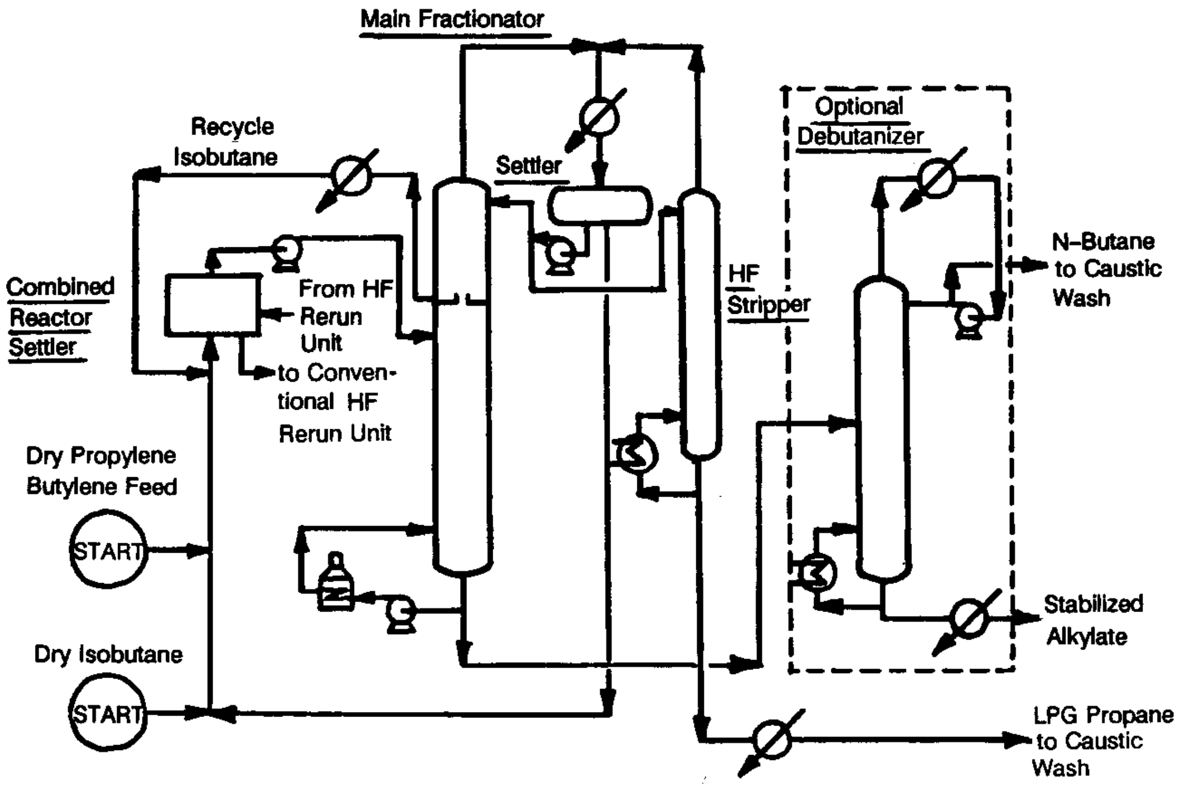


Figure 2.8 Hydrofluoric acid alkylation[2]

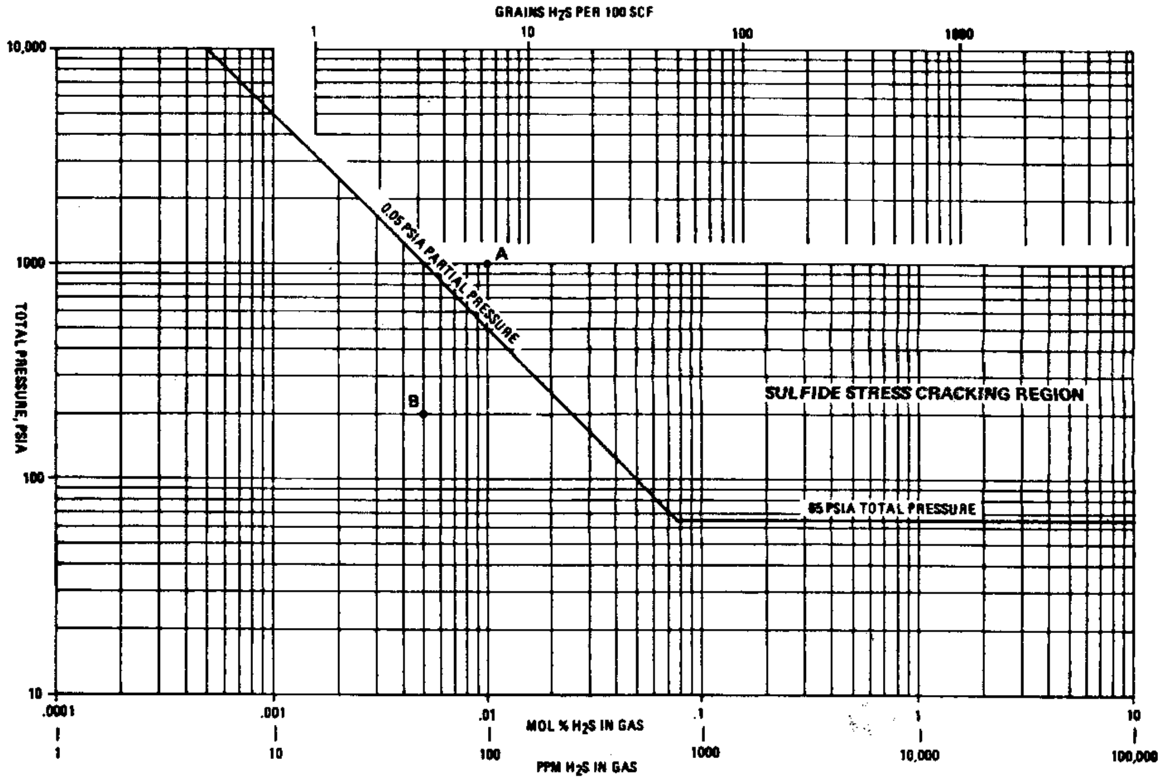


Figure 2.9 Sour gas systems[4]

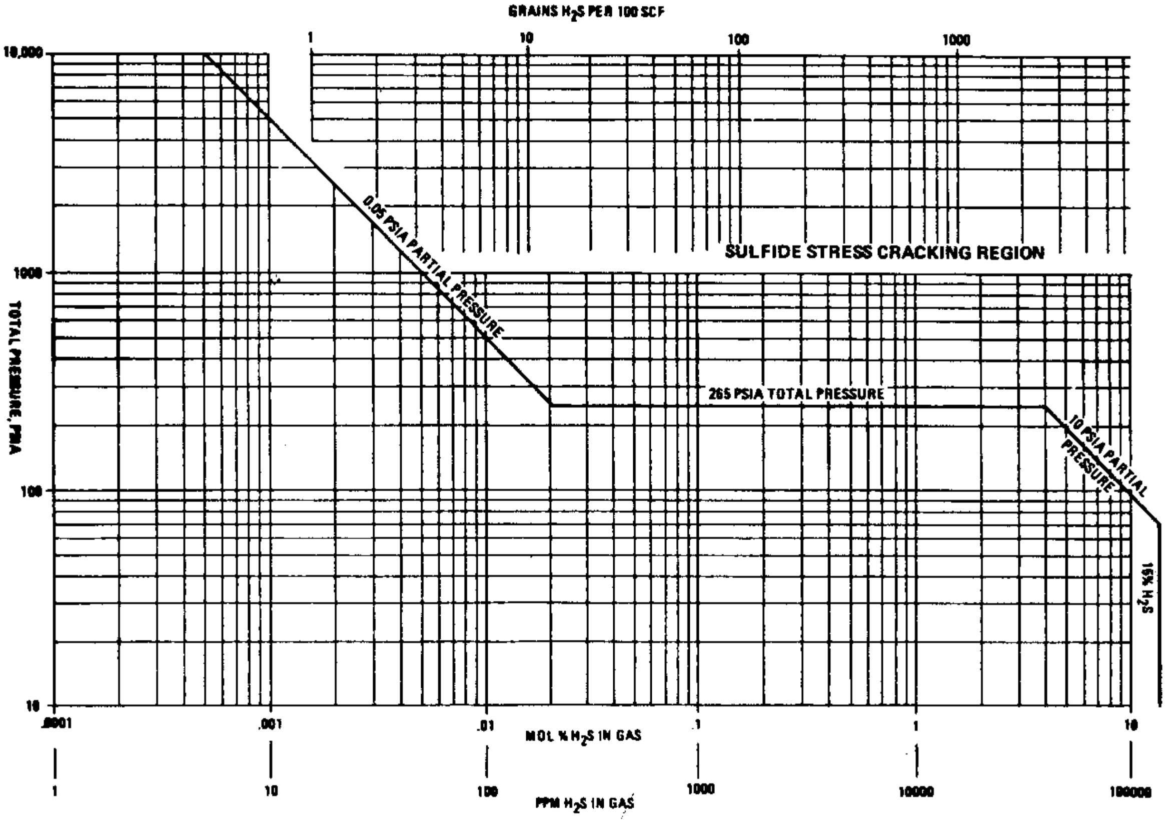


Figure 2.10 Sour multiphase systems[4]

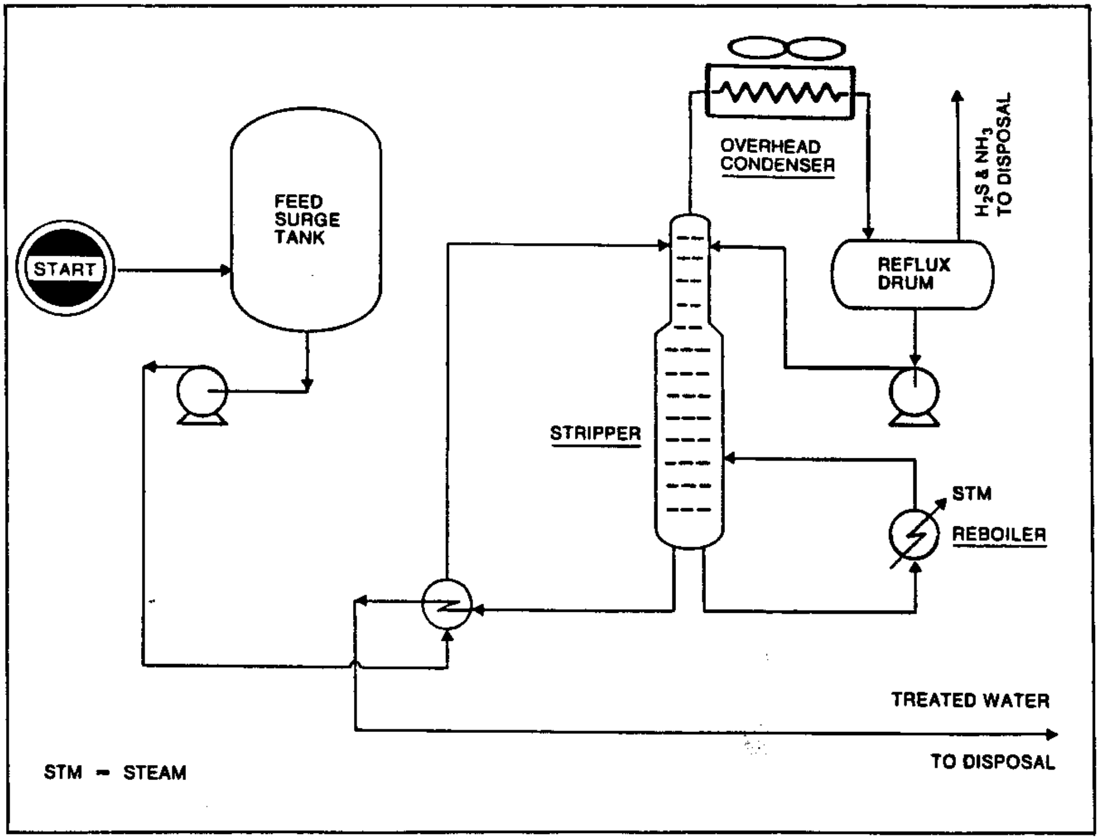


Figure 2.11 Sour water stripper (non-acidified)[1]

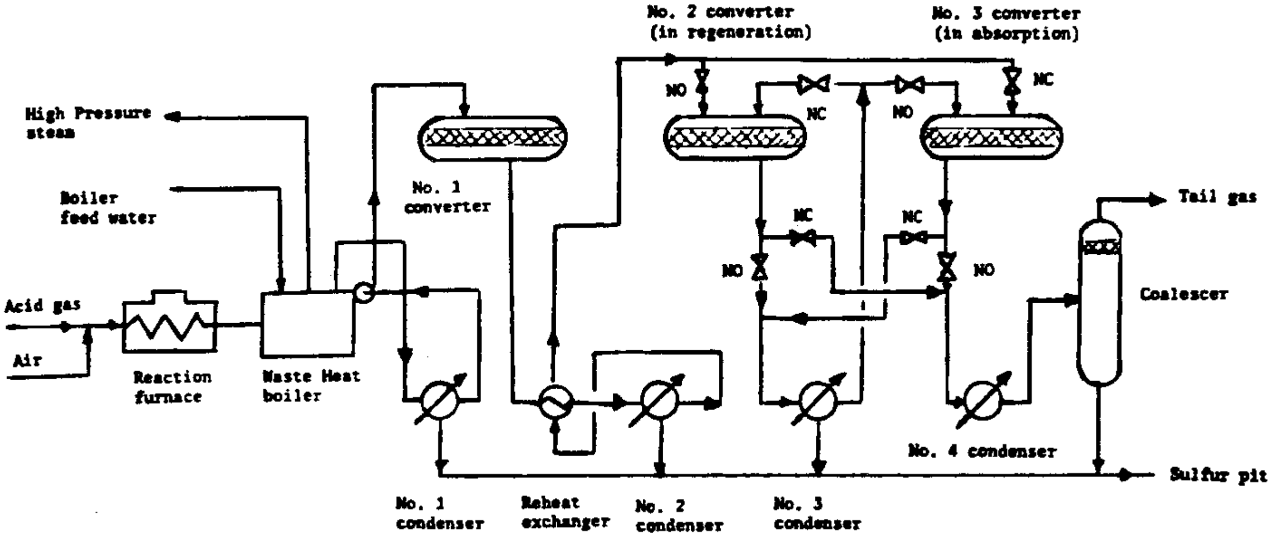


Figure 2.12 Sulfur plant[2]

## REFERENCES FOR FIGURES

1. (*The Role of Stainless Steels in Petroleum Refining*, vol. 4. Washington, DC: American Iron and Steel Institute, 1977.)

2. (*Refinery Process Handbook, Hydrocarbon Processing*. Houston, TX: Gulf Publishing Co., 1968.)

3. (A.G. Harding, E.F. Ehmke, "Brittle Failure of a Large Pressure Vessel," *API Proceedings—Division of Refining*. Washington, DC: American Petroleum Institute, 1962.)

4. (NACE Standard MR0175-80, "Sulfide Stress Cracking Resistant Metallic Material for Oilfield Equipment." Houston, TX: NACE, 1980.)

## BIBLIOGRAPHY

API Standard 942. "Recommended Practice for Welded, Plain Carbon Steel Refinery Equipment for Environmental Cracking Service." Washington, DC: American Petroleum Institute, latest revision.

API Standard 944. "Survey of Materials Experience and Corrosion Problems in Sour Water Equipment." Washington, DC: American Petroleum Institute, latest revision.

API Standard 950. "Survey of Construction Materials and Corrosion in Sour Water Strippers." Washington, DC: American Petroleum Institute, latest revision.

Bergman, D.J., G.W.G. McDonald. "Solving Problems in HF Alkylation Units." *Corrosion* 17, 4(1961): p. 9.

Bradbury, W.A. "Monolithic Linings for Refinery Service." *Pet. Refiner.* 33, 3(March 1954): p. 167.

Copson, H.R., C.F. Cheng. "Stress Corrosion Cracking of Monel in Hydrofluoric Acid." *Corrosion* 12, 12(1956): p. 647t.

Dean, S.W., G.D. Grab. "Corrosion of Carbon Steel Tanks in Concentrated Sulfuric Acid Service." *Materials Performance* 25, 7(1986): p. 48.

Degnan, T.F. "Effect of Velocity on Life Expectancy of Steel Pipelines in Commercial Strengths of Sulfuric Acid." *Corrosion* 15, 7(1959): p. 326t.

Ehmke, E.F. "Polysulfide Stops FCCU Corrosion." *Hydroc. Proc.* 60, 7(July 1981): p. 149.

Gutzeit, J. "Corrosion of Steel by Sulfides and Cyanides in Refinery Condensate Water." *Materials Protection* 7, 12(1968): p. 17.

Hansen, R.D. "FCC Slide-Valve Problems Can Be Remedied." *Oil and Gas J.* 8, 16(April 18, 1983): p. 139.

Harding, A.G., E.F. Ehmke. "Brittle Failure of a Large Pressure Vessel." *API Div. Refining* 42, 3(1962): p. 107.

Hildebrand, R.L. "Sour Water Strippers—A Review of Construction Materials." *Materials Performance* 13, 5(1974): p. 16.

Holmberg, M.E., F.A. Prange. "Corrosion in Hydrofluoric Acid Alkylation." *Ind. Eng. Chem.* 37, 11(Nov. 1945): p. 1,030.

INCO Corrosion Engineering Bulletin CEB-1. "Resistance of Nickel and High Nickel alloys to Corrosion by Sulfuric Acid." New York, NY: International Nickel Company, 1983.

INCO Corrosion Engineering Bulletin CEB-5. "Corrosion Resistance of Nickel-Containing Alloys in Hydrofluoric Acid, Hydrogen Fluoride and Fluorine." New York, NY: International Nickel Company, 1968.

Mason, J.F., Jr., C.M. Schillmoller. "Corrosion in Sour Water Strippers." *Corrosion* 15, 7(1959): p. 358t.

McGowin, T.S., R.A. White. "Coke Drum Fracture Experience." *API Div. Refining* 52, 3(1972): p. 778.

Merrick, R.D. "Refinery Experience with Cracking in Wet $H_2S$ Environments." *Materials Performance* 27, 1(1988): p.30.

Moore, K.L. "Alloy Stops Corrosion in Fluid Coker." *Pet. Refiner.* 39, 5(May 1961): p. 1949.

NACE Task Group Report T-5A-6. "Summary of Questionnaire Replies on Corrosion in HF Alkylation Units." *Corrosion* 15, 5(1959): p. 237t.

NACE Standard RP0472. "Methods and Controls to Prevent In-Service Cracking of Carbon Steel (P-1) Welds in Corrosive Petroleum Refinery Environments." Houston, TX: NACE, latest revision.

NACE Standard MR0175. "Sulfide Stress Cracking Resistant Metallic Material for Oilfield Equipment." Houston, TX: NACE, latest revision.

Neumaier, B.W., C.M. Schillmoller. "What To Do About Hydrogen Blistering." *Pet. Refiner.* 36, 9(September 1957): p. 319.

Thornton, D.P., Jr. "Corrosion-Free AF Alkylation." *Chem. Eng.* 77, 14(July 13, 1970): p. 108.

Weil, N.A., F.S. Rapasky. "Experience with Vessels of Delayed Coking Units." *API Div. Refining* 38, 3(1958): p. 214.

Chapter
# THREE

# Hydrodesulfurizers, Catalytic Reformers, Hydrocrackers, and Flue Gas

## *INTRODUCTION*

Some sulfur compounds are cracked to hydrogen sulfide and removed in the crude unit. The sulfur remaining in the processed crude must be removed if the lighter petroleum fractions are to be reformed into products such as gasoline, etc. Desulfurizing is also necessary to meet the sulfur limits placed on kerosene and diesel products and for the feed to the fluid catalytic cracker to reduce sulfur dioxide emissions from the regenerator flue gas. Sulfur compound-bearing petroleum fractions from distillation columns of coker and catalytic cracking units are also fed to the hydrodesulfurizers.

## *HYDRODESULFURIZERS AND HYDROCRACKERS*

### General

In both hydrodesulfurizers (Figure 3.1) and hydrocrackers (Figure 3.2), the feed is first passed to exchangers where it is heated by the reactor effluent. It next goes to a fired heater and then to the reactors at ~700 to 750°F (370 to 400°C). The pressures in hydrodesulfurizers normally range from 350 to 500 psia (2,415 to 3,450 kPa); the pressure in the hydrocracker ranges from ~1,500 to 2,000 psia (10,340 to 13,790 kPa).

The sulfur (and the nitrogen in a first stage hydrocracker) is removed by adding hydrogen to the feed, heating this mixture in a furnace, and passing it over a catalyst at high pressure in reactor vessels. The molecules are broken down in the reactor, and the released sulfur reacts to form hydrogen sulfide and mercaptans. In addition, some ammonia and some hydrogen cyanide (in first stage hydrocrackers) is formed. In hydrodesulfurizers, the reactor effluent is cooled through a series of exchangers and then sent to a high-pressure separator vessel in which the gas is taken off the top and sent to a unit to remove the hydrogen sulfide. The hydrogen sulfide-free gas is recycled to the feed. The liquid from the high-pressure separator is passed through a letdown valve to a low-pressure separator. The liquids from the low-pressure separator are then fed to a fractionator.

In a hydrocracker, the effluent of the first stage is also cooled and sent to a high-pressure separator. In many of the hydrocracking processes, the liquid from the high-pressure separator is fed to a heater and to a second stage reactor. The effluent from the second stage follows the same scheme as that in a hydrodesulfurizer (i.e., exchange cooling, high- and low-pressure separation, and fractionation). The bottom product of the fractionator is often recycled to the feed of the second stage hydrocracker.

For materials selection, hydrocrackers are treated the same as hydrodesulfurizers, particularly in the first stage. From a materials standpoint, the demarcation between low-pressure units (hydrodesulfurizers) and high-pressure units (usually hydrocrackers) is 650 psia (4,480 kPa).

## Hydrogen Attack

Carbon steel is used until the temperature exceeds that at which an alloy is required by API Standard 941.(1) Figure 3.3 shows the temperature vs hydrogen partial pressure limits in API 941 for carbon and alloy steels. Solid lines indicate where internal decarburization and fissuring will occur. Dashed lines indicate where the less harmful surface decarburization will occur. API 941 was derived from laboratory work conducted by Naumann in Germany in the early 1940s. Since then, it has been revised periodically, based on operating experience. Because experience with C-½Mo steels (particularly in catalytic reformers) has been poor, the 1990 edition of API 941 has removed C-½Mo from the design curve and produced a separate *experience* curve for C-½Mo steels (Figure 3.4). As a result, most refiners to specify a minimum of 1Cr-½Mo when API 941 indicates that the limits for carbon steel have been exceeded. Recent work has indicated that some failures in C-½Mo can be attributed to the lack of (or improper) heat treatment after forming or welding. Heat treatment should be at a minimum of 1,200°F (650°C) to prevent hydrogen attack in C-½Mo steels.

When high-pressure hydrogen is to be in contact with metals for only a short period of time, carbon steel may be used at higher temperatures than those indicated by Figure 3.3. Figure 3.5 gives the permissible times that carbon steels may be used as a function of temperature and hydrogen partial pressure. High temperatures can be tolerated for short time periods because hydrogen attack has an incubation period. Hydrogen attack is also cumulative; therefore, the total anticipated time at temperature must be used as a basis for alloy selection.

When steel is exposed to hydrogen at high temperatures, the hydrogen enters the steel, forming a concentration gradient through the steel, as indicated in Appendix C. If insufficient carbide-forming alloying elements (e.g., Cr, Mo, and Cb) are present, or the microstructure is in the wrong condition from improper heat treatment, the hydrogen that has entered the steel will react with the carbon in the steel to form methane. Since the methane molecules are too large to diffuse through the steel lattice, they cause microfissures to form. These fissures eventually combine to form cracks, as shown in Figure 3.6(a). Figures 3.6(b) and (c) show the microstructures of fissured and unattacked base metal respectively. Note the absence of the dark (pearlite) constituent in Figure 3.6(b) that is present in Figure 3.6(c).

## Sulfidation by Hydrogen-Hydrogen Sulfide Mixtures

When the temperature exceeds 550°F (288°C) in hydrogen-hydrogen sulfide mixtures, severe corrosion occurs on carbon and low-alloy steels. Corrosion rates of various materials as a function of mole percent (mol%) hydrogen sulfide (based on only the constituents in the vapor phase) vs temperature for both gas oil and naphtha streams are shown in Figures 3.7(a) through (j). Although desulfurization occurs in the first stage of hydrocrackers, the feed to many second stage hydrocrackers still contains sufficient sulfur compounds to require that materials be identical to those in the first stage hydrocrackers. Before hydrogen enters the process stream, 5Cr-½Mo and 12Cr clad steels can be used above 550°F (288°C). When hydrogen is present, 18Cr-8Ni stainless steel (SS) is usually selected; stabilized grades are commonly used to prevent intergranular attack (IGA) during downtime. The 12Cr alloy is occasionally used up to 650°F (345°C) when the hydrogen sulfide concentration is less than 1 mol%. Aluminized (hot-dipped aluminum-coated) carbon and low-alloy steel also display excellent resistance to hydrogen sulfide in these environments; however, rapid attack can occur at breaks in the coatings. Aluminizing is therefore usually selected primarily to reduce fouling from scale formation rather than to protect from corrosion.

## Reactors

Reactors are normally made of low-alloy steel (selected per API Publication 941) and clad or weld overlaid with type 347 (UNS S34700) SS. The stabilized grades (i.e., type 347 or 321 [UNS S32100] SS) are normally used for all stainless equipment in these units to avoid intergranular stress corrosion cracking (SCC) during downtime. Downtime corrosion is discussed in the next section of this chapter, "Feed-Effluent Exchangers."

---

(1) American Petroleum Institute, Washington, DC.

A number of potential problems with reactors exist because of the heavy walls [up to ~10 in. (254 mm) thick] and the high-operating temperatures [up to ~850°F (455°C)]. The most commonly used low-alloy steel for reactors is 2¼Cr-1Mo. High-strength steels for reactors are covered by ASME[2] Code, cases 1960 and 1961. Welding of Cr-Mo steels requires both preheat and postweld heat treatment (PWHT). The 2¼Cr-1Mo material is usually quenched and tempered to produce the best combination of strength and toughness possible. The tensile strength is usually controlled from 75 to 100 ksi (517,000 to 690,000 kPa). The total amount of PWHT must be controlled so the strength will not be reduced to below the required minimum. The maximum amount of PWHT permitted is estimated by plotting strength vs the tempering parameter $T(20 + \log t) \times 10^{-3}$ (Figure 3.8), where T is temperature in degrees rankine and t is time in hours. Coupons heat-treated with the material are commonly used to confirm the estimates of the tempering parameter.

If the chromium content of the steel exceeds 1.75%, the preheat is normally held until an intermediate PWHT is performed. Stress relief cracking (SRC) may occur if the sulfides are not controlled by adding cerium or zirconium, for example. Steels with more than 2.5% chromium are resistant to SRC. An empirical equation has been developed to predict the SRC of steels with less than 2.5% chromium. Cracking is predicted when $\Delta G$ is greater than zero where $\Delta G$ is defined as:

$$\Delta G = [\%Cr] + 3.3[\%Mo] + 8.1[\%V] - 2 \tag{3.1}$$

Other phenomena that may occur during PWHT are sigma phase embrittlement of the type 347 SS weld overlay, secondary hardening of the base metal, and cracking of internal attachment welds to the shell. Ferrite and sigma phase are also susceptible to hydrogen embrittlement. The detrimental effects of sigma phase (a brittle FeCr compound) can be limited by specifying that the overlay have no more than 10% ferrite[3] (which transforms to sigma phase). A minimum ferrite content of 2 is required to avoid weld cracking. The DeLong diagram (Figure 3.9) shows how the ferrite content can vary significantly by varying the nickel equivalent and the chromium equivalent in the SS alloy. Secondary hardening resulting from precipitation of a phase during PWHT is minimized by limiting copper to 0.2% in 2¼Cr-1Mo. Nickel is sometimes limited to 0.2 to 0.3% to minimize hardenability and reduce temper embrittlement. Internal attachment weld cracking is minimized by putting the type 347 SS (second pass of the overlay) on after PWHT.

Long-term potential problems are weld overlay disbonding, temper embrittlement, and flaking. Disbonding of weld overlay is caused by carbides in the overlay embrittling in the presence of hydrogen. It is a problem primarily with low-penetration processes such as strip overlay, particularly when the strip overlay is put on forging rather than on plate. This is because the surfaces of plate are decarburized, but the surfaces of forgings are not since they are machined after forming. Therefore, the machined surfaces of forgings are more hardenable (i.e., more crack sensitive). Disbonding in forging (and plate) can be avoided by limiting the carbon on the surface to be overlaid to 0.15% and by using low-carbon stainless steel in the first overlay pass. The resultant overlay should not have more than 0.03% carbon.

The major cause of temper embrittlement is segregation of phosphorus to the grain boundaries. A common way to minimize temper embrittlement of 2¼Cr-1Mo base metal is to limit the "J" factor to a maximum of 180 where J is defined as:

$$J = (Si + Mn) \times (P + Sn) \times 10^4 \tag{3.2}$$

---

[2] American Society of Mechanical Engineers, New York, NY.

[3] Ferrite is a magnetic phase that forms upon cooling in an otherwise nonmagnetic phase called austenite. Its formation depends on alloy content.

where concentrations are in wt%. For example, the increase in the transition temperature resulting from temper embrittlement is 0 to 35°F (0 to 19°C) for a J factor below 180; a 75°F (42°C) increase can be expected with a J factor of 260. More recent studies indicated that limiting the (P + S) to less than 0.01% is sufficient because Si + Mn only control the embrittlement rate.

For weld metal, the X factor has been developed in which

$$X = \frac{10P + 5Sb + 4Sn + As}{100} \tag{3.3}$$

Concentrations are in parts per million (ppm). When the X factor is plotted against the Mn + Si in ppm, the X factor should decrease from 20 to 12 as the Mn + Si increases from 0.8 to 1.4.

Some users specify a step cooling test of 2¼Cr-1Mo. Step cooling simulates about half the increase in the ductile-brittle transition that will occur after a long-term service. A typical step cooling sequence is as follows:

- 1,100°F (595°C) for 1 h
- 1,000°F (540°C) for 15 h
- 975°F (525°C) for 24 h
- 925°F (495°C) for 60 h
- 875°F (470°C) for 100 h

Step cooling will not simulate embrittlement of 1¼Cr-1Mo, though it occurs (e.g., a 100°F [38°C] increase in transition temperature was reported after 8 y at 930°F [500°C]). This is because the embrittlement in 1¼Cr-1Mo is caused by precipitation of carbides in the ferrite phase rather than segregation of impurities to the grain boundaries. Temper embrittlement can be reversed by heating at 1,150°F (620°C) for 2 h per inch of thickness.

Hydrogen flaking or cracking, which result when the steel becomes supersaturated in hydrogen, can be avoided by using careful shutdown procedures, including slow cool down rates after depressurizing the equipment. It is important to recognize that the fracture toughness $K_{Ic}$ in the presence of hydrogen ($K_{IH}$) does not increase significantly with temperature, whereas the fracture toughness in the absence of hydrogen increases significantly with temperature.

Whether or not there are harmful effects during operation from laminations is controversial; however, most users specify the plate to meet the ultrasonic testing requirements in ASTM(4) A435 or A578. This minimizes delays during fabrication by screening out large laminations that otherwise could wind up at undesirable locations.

Brittle fracture is always a concern with heavy wall vessels. An 80 to 100°F (27 to 38°C) minimum hydrostatic test temperature is often specified to minimize the possibility of brittle fracture during hydrostatic testing. To minimize the possibility of brittle fracture of heavy wall reactors during start up and shutdown, reduced pressure below 200 to 300°F (90 to 150°C) is usually specified. Typical limitations are 40% of the design pressure or 20% of the original hydrostatic test pressure. With the advent of temper embrittlement resistant steels and weld metal, some refiners feel reduced pressure is only required below 100°F (38°C).

## Feed-Effluent Exchangers

Feed-effluent exchangers are made of materials similar to those used in the reactors because they are exposed to the same environments. Tubes are usually type 321 or 347 SS, although type 304 (UNS S30400) SS has been used. Because of thin walls and high stresses on tubes as well as thermal stress, crevices, etc., both transgranular and intergranular SCC of austenitic SS tubes occur frequently in exchangers, as indicated in Table 3.1. Type 304, 321, and 347 SS's have failed from transgranular SCC.

---

(4) ASTM, Philadelphia, PA.

Intergranular SCC has occurred primarily in type 304 SS, although type 321 and 347 SS's may fail intergranularly when improper heat treatments are applied, as discussed below in this section.

To minimize transgranular SCC, U-bent tubes are stress relieved at 1,650°F (900°C) or annealed at 1,800°F (980°C). Using resistance coil heating for 5 seconds on the U-bends is a satisfactory method of relieving stresses in type 321 and 347 SS exchanger tubing. This is not recommended for type 304, 316 (UNS S31600), etc., SS's because a zone is created adjacent to the area in which the bend is heated that is subject to intergranular SCC. Intergranular SCC can occur during downtime as a result of exposure to polythionic acid or sulfurous acid. These corrosives are formed by the reaction of iron sulfide, water, and oxygen. Some refiners think that the use of stabilized grades is sufficient to avoid attack. Others think that a stabilizing heat treatment at 1,650°F (900°C) for 4 h is required, even if stabilized grades are used. Still others think that specifying a 1,950°F (1,065°C) maximum annealing temperature will ensure that niobium or titanium carbides form. Since failure occurs during downtime, NACE has issued a recommended practice on the protection of austenitic SS's during downtime. NACE Standard RP0170(5) recommends using neutralizing solutions and other precautions during downtime. Where deposits occur, it is necessary to remove them to allow the neutralization solution to be effective. For example, failures have occurred in tubes in which a coke deposit was not removed.

## Coolers

In desulfurizers and first stage hydrocrackers, wash water is injected between exchangers, cooling the process fluid. The water that condenses contains varying amounts of hydrochloric acid, ammonia, and hydrogen sulfide. Depending on the amounts of these constituents, varying amounts of general corrosion, pitting, and blistering can occur. From Figure 3.10, the pH of condensed water can be predicted from the ppm level of hydrochloric acid, hydrogen sulfide, and ammonia at room temperature. Note that the hydrogen sulfide content has little effect on the pH. Figures 3.11 and 3.12 show the effect on corrosion of these constituents without and with air, respectively, at room temperature. As can be seen, the corrosion rate is roughly a function of pH. Also note that oxygen from the air increases corrosion greatly. The effect of ammonia neutralization on corrosion at room temperature is shown in Figure 3.13. Air (oxygen) accelerates corrosion greatly. A pH greater than 8 must be reached to obtain maximum benefit from ammonia additions. Figures 3.14 and 3.15 show the effect of ammonia additions on corrosion at 300°F (150°C). When a tenacious oxide film is formed on steel (Figure 3.14), corrosion is much greater than when only a thin iron sulfide film is present. Corrosion control is not maximized until a pH above 8 is reached.

Corrosion in hydrocracker air coolers is particularly severe if velocities exceed 20 ft/s (6 m/s) and the product of the mol% hydrogen sulfide and the mol% ammonia is high. As can be seen in Figure 3.16, the higher the product of the mol% hydrogen sulfide and the mol% ammonia (based on total stream analysis), the higher the probability of severe corrosion. An ammonium bisulfide concentration of greater than 2% in the separator also indicates potential corrosion problems. Water injection rates to keep the ammonium bisulfide concentration below 2% have been successful in preventing severe corrosion of carbon steel tubes, provided the pH of the water draw-off can be maintained between 8.3 and 9.0. Severe corrosion has been experienced on air coolers when the pH levels were below 8.0. Carbon steel tubes can be used if the above limits are maintained, the flow is distributed evenly in multiple pass units, and the velocity is kept below 20 ft/s (6 m/s). When this cannot be done or is not done, alloys such as Monel(6) 400 and Incoloy(7) 800 have been used. Recently, duplex SS's such as UNS S31803 have been used. Waterside corrosion is usually controlled by inhibitors, and scaling is prevented by adjusting the Langelier Saturation Index of the water to zero by acid or base additions, as discussed in the section on utilities in Chapter One.

---

(5) NACE Standard RP0170, "Protection of Austenitic Stainless Steel from Polythionic Acid Stress Corrosion Cracking During Shutdown of Refinery Equipment," NACE, Houston, TX, latest revision.

(6) Trade name.

(7) Trade name.

## Other Corrosion and Materials Problems

Corrosion problems have also occurred in compressors, sour water valve trims, expansion bellows, and hydrocracker fractionators. Type 4140 (UNS G41400) compressor impellers have sulfide cracked in sour gas when the hardness exceeded 235 Brinell(8). Hardened 12Cr valve trim has sulfide cracked; to prevent this problem, 18Cr-8Ni SS trim in sour water service is commonly used. Sulfide cracking has not occurred significantly in pumps.

In addition to the potential for SCC from the inside as a result of the process fluids, austenitic SS's can experience SCC from the outside. If the austenitic SS is neither low carbon nor stabilized, intergranular SCC can occur as low as at room temperature as a result of either chlorides or sulfur dioxide in the atmosphere. In the 140 to 220°F (60 to 104°C) range, transgranular SCC of stabilized, low carbon, and regular grades of austenitic SS's has occurred as a result of chlorides from seacoast atmospheres.

Above ~220°F (104°C), moisture needed for SCC does not form on the surface in the absence of hygroscopic salts. SCC from the atmosphere is most common in warm climates. It also can occur under insulation, particularly where a steam leak supplies moisture to leach out chlorides from the insulation or to dissolve salts from the atmosphere.

To prevent SCC under these conditions, specify that insulation meet ASTM C795 and use organic coatings. Both epoxies and silicone coatings have given good results. One report indicates that aluminum foil is superior to coatings for preventing atmospheric SCC.

Cracking of weld overlays in ring gasket grooves of flanges has also been a problem. The cause is hydrogen embrittlement of the ferrite phase in the overlay. The preventive measures used include two pass overlay with the first pass of type 309 (UNS S30900) and minimizing the overlay thickness.

Expansion bellows are thin, highly stressed material. They are commonly made of 18Cr-8Ni SS's, high-nickel alloys such as Monel 400, Incoloy 800, and Inconel(9) 625. Some manufacturers claim that the fatigue life is enhanced if the bellows are not annealed after forming. Independent studies by the International Nickel Company(10) and others concluded that all bellows, regardless of alloy, should be annealed after forming.

The fractionation equipment in a hydrocracker is generally carbon steel; however, not all the sulfur has been removed. If the temperature will exceed 500°F (260°C), the sulfur content should be checked to determine whether SS is required. Severe corrosion of carbon steel has occurred in hydrocarbon fractionator furnace tubes and transfer lines as a result of the introduction of residual hydrogen sulfide in recycle gas from an amine unit.

## *CATALYTIC REFORMERS*

A typical process flow diagram of a catalytic reformer is shown in Figure 3.17. Desulfurized naphtha is heated in feed-effluent exchangers and then passed to a fired heater, where it is heated to 850 to 1,000°F (455 to 540°C) at 500 psia (3,450 kPa) in a series of reactors and fired heaters. In the reactors, the hydrocarbon and hydrogen are passed over a catalyst (often platinum/rhenium based) to produce rearranged molecules, which are primarily aromatics with some isoparaffins. The reactor effluent is cooled by exchange and then passed to a separator vessel. The gas from the separator is recycled to the reactors. The liquid is fed to a fractionator.

Because hydrogen is used in the reforming reaction, materials must be selected according to API 941, except that C-½Mo should not be used (i.e., the minimum alloy for hydrogen service should be 1Cr-½Mo). As mentioned previously, this is because of C-½Mo failures in catalytic reformers that some refiners have related to the catalytic reformer process regeneration. When selecting furnace tubes, for example, it is important to select the steel with the hydrogen resistance based on the metal temperature,

---

(8)Trade name.

(9)Trade name.

(10)International Nickel Company, New York, NY.

which is often 100°F (38°C) greater than the process temperature. There is no hydrogen sulfide in catalytic reformers, so SS's are not required for sulfidation resistance.

The catalytic reformer reactors are normally refractory-lined steel because the reaction temperatures are ~1,000°F (540°C). Often there is an austenitic SS shroud covering the refractory lining to prevent the process fluids from channeling through the refractory lining rather than from passing through the catalyst bed. Some refiners prefer to use low-alloy shells under the refractory lining because of concern about *hot spots* that can form when the refractory cracks or spalls locally. Other refiners simply *cool* these hot spots, if they appear, by directing steam on the affected area. The reactor catalyst is activated by organic chlorides; some of these break down to hydrogen chloride. Some of the hydrogen chloride in the reactor effluent travels to the stabilizer, and the remainder is recycled with the hydrogen to the heaters and reactors. To combat corrosion from the chlorides in the system, some refiners use Monel 400 trim steel valves, while others use alloy 20 trim. Others have found that standard 12Cr trim works well. Ammonia injection and caustic wash are used to reduce corrosion in the stabilizer. The ammonium chloride formed in the reactor effluent is sufficiently aggressive to cause SCC of Monel K-500, which was originally selected for compressor impellers. Currently, carbon or low-alloy steel impellers are used if the gas is dry. Where there is a possibility of some moisture, 17-4 PH (UNS S17400) in the H1150 condition (maximum hardness of Rockwell C33) has been used.

## *FLUE GASES CONTAINING OXIDES OF SULFUR*

Some of the high-sulfur residuum from the crude towers is sold directly as residual fuel oil rather than being desulfurized. Burning this high-sulfur fuel oil creates a pollution problem and stimulates oxidation above 1,000°F (540°C). These residual fuel oils (particularly from Venezuela) contain vanadium, and when the fuel is burned, vanadium pentoxide is formed. This deposits on tube hangers, etc., and can cause catastrophic oxidation resulting from the low-melting eutectic that forms around 1,200°F (650°C). Solutions to this problem are to (1) keep the temperature below 1,200°F (665°C); (2) design the furnace with soot blowers; (3) keep the excess air to 1 to 2%; or (4) use a 50Cr-50Ni alloy for tube hangers.

The sulfur dioxide and trioxide that go up the stack can cause severe corrosion if the metal temperature falls below the dew point (usually below 400°F [205°C]). In mild concentrations of sulfur oxides, type 316L (UNS S31603) SS usually performs well below 140°F (60°C) and at somewhat higher temperatures in the absence of chlorides. For scrubbers that operate below 140°F (60°C), the choice between type 316L SS and the high-molybdenum alloys such as type 317LM (UNS S31725) SS, type 904L SS, Inconel 625, etc., depends on the chloride ion concentration and on the pH (i.e., increasing molybdenum is required as the chloride ion increases and the pH decreases), as shown in Figure 3.18. For example, at pH 4, type 316L SS could be used up to 60 ppm chlorides; but for 700 ppm chloride at pH 4, type 904L SS would be required.

Ducts containing flue gases that produce corrosive condensate can be made of the following materials:

- refractory-lined carbon steel;
- organic-coated carbon steel;
- organic-lined carbon steel;
- Inconel 625 clad carbon steel;
- high-alloy strip-lined carbon steel; and
- titanium (either solid or clad on carbon steel).

Maintenance is difficult for both refractory-lined and organic-coated steel. Corrosion on the steel behind a refractory lining can occur because of the porosity of refractory linings. Organic coatings are reported to last from 1 to 10 y, depending on the application and on temperature excursions. If temperature excursions do not occur, fiber-reinforced plastic is a good choice. In general, organic sheet linings are costly and subject to failure in temperature excursions; Inconel 625 clad steel is usually cost competitive and is not affected by temperature excursions. There is limited experience with solid titanium and high-alloy strip-lined carbon steel. Both require careful attention to welding details. Therefore, environment, cost, and experience should be evaluated on a case-by-case basis before selecting a ducting material.

Fine particle solid erosion may also be a problem in flue gas. Refractory linings such as AA-22(11) and hard facings such as 100HC(12) are often used where severe erosion occurs. Where milder erosion or alternate wetting and drying is expected, low-alloy steels (e.g., Cor-ten(13)) can be used. Stresses (including secondary stresses) on Cor-ten should be limited to 8 ksi (55,160 kPa) to avoid downtime cracking from temper embrittlement. When stresses higher than 8 ksi (55,160 kPa) will be experienced, 1¼Cr-½Mo should be used in place of Cor-ten.

---

(11)Trade name.

(12)Trade name.

(13)Trade name.

## TABLE 3.1

### Distribution of Cases of Stress Corrosion Cracking Among Various Refinery Units

| Equipment | Failures | Onstream Cracking |  |  |  | Shutdown Cracking |  |  |  | Cracking Service Uncertain |  |  |  |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
|  |  | Crude Still | Hudrode-sulfurizer and Reformer | Chem-ical | Mis-cella-neous | Crude Still | Hudrode-sulfurizer and Reformer | Chem-ical | Mis-cella-neous | Crude Still | Hudrode-sulfurizer and Reformer | Chem-ical | Mis-cella-neous |
| Exchanger tubes . | 31 | 2 | 4 | 6 | 7 | 0 | 10 | 0 | 1 | 0 | 1 | 0 | 0 |
| Piping . . . . . . . . . | 9 | 0 | 0 | 2 | 1 | 1 | 4 | 0 | 0 | 0 | 1 | 0 | 0 |
| Thermowells . . . . | 9 | 5 | 0 | 0 | 0 | 0 | 3 | 0 | 1 | 0 | 0 | 0 | 0 |
| Bellows . . . . . . . . | 5 | 1 | 1 | 0 | 2 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| Cladding . . . . . . . | 4 | 0 | 0 | 0 | 0 | 0 | 4 | 0 | 0 | 0 | 0 | 0 | 0 |
| Springs . . . . . . . . | 2 | 0 | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Bubble caps . . . . . | 2 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 |
| Wire screen . . . . . | 2 | 0 | 0 | 0 | 0 | 0 | 1 | 1 | 0 | 0 | 0 | 0 | 0 |
| Level controller . . . | 1 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Channel . . . . . . . . | 1 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Stud . . . . . . . . . . | 1 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 |
| Flange . . . . . . . . . | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| Shell . . . . . . . . . . | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Bolt . . . . . . . . . . . | 1 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Elbow . . . . . . . . . | 1 | 0 | 0 | 0 | 1 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Subtotal . | 71 | 9 | 8 | 10 | 12 | 1 | 24 | 1 | 3 | 0 | 3 | 0 | 0 |
| Total . . . . | 71 | 39 |  |  |  | 29 |  |  |  | 3 |  |  |  |

**Notes:** Chemical units—polyethylene, naphthalene, ammonium sulfate.
Miscellaneous units—fluid catalytic cracking, monoethanolamine (MEA) extraction.
HF alkylation, boiler, propylene polymerization, propane deasphalting.

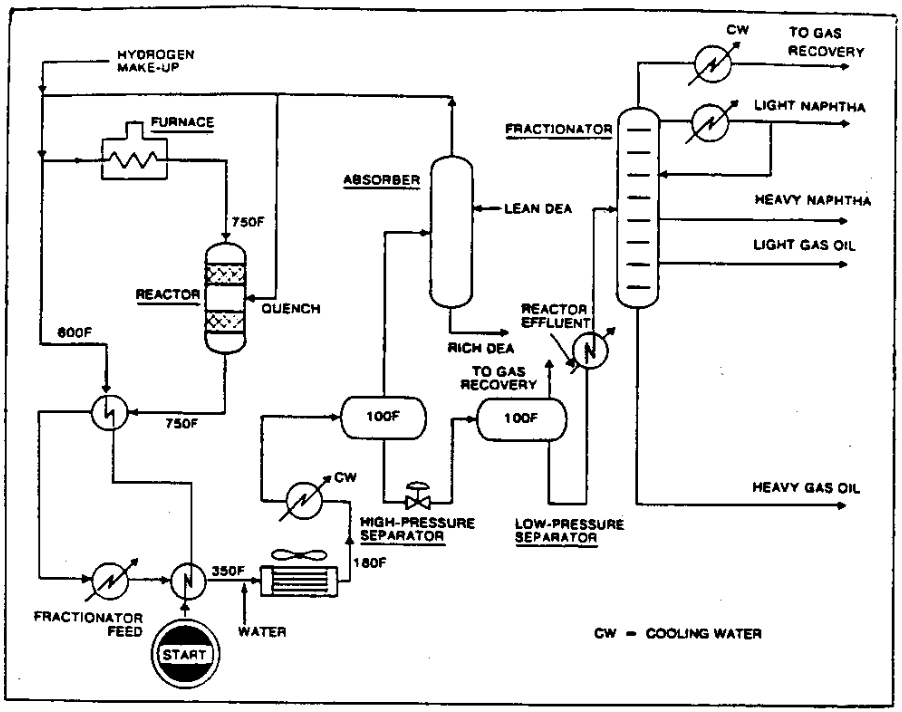


Figure 3.1 Hydrodesulfurizer[1]

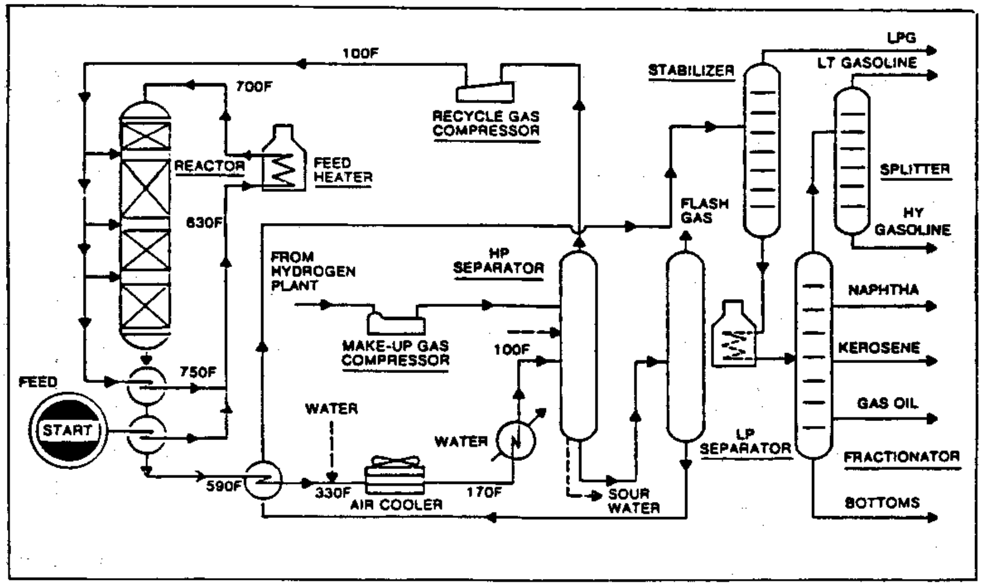
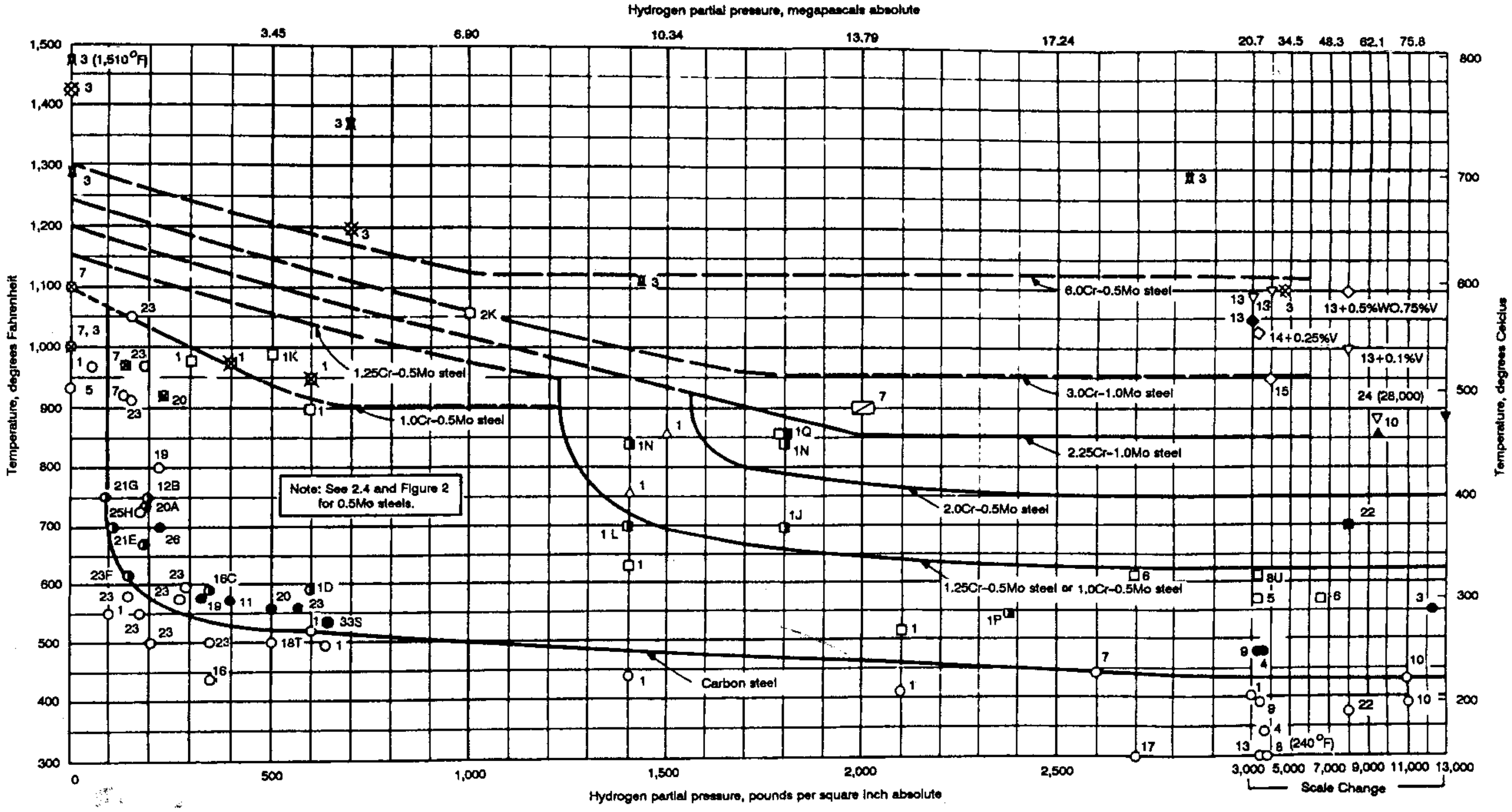


Figure 3.2 Hydrocracking[1]



**Legend:**

Surface decarburization - - - - - - -

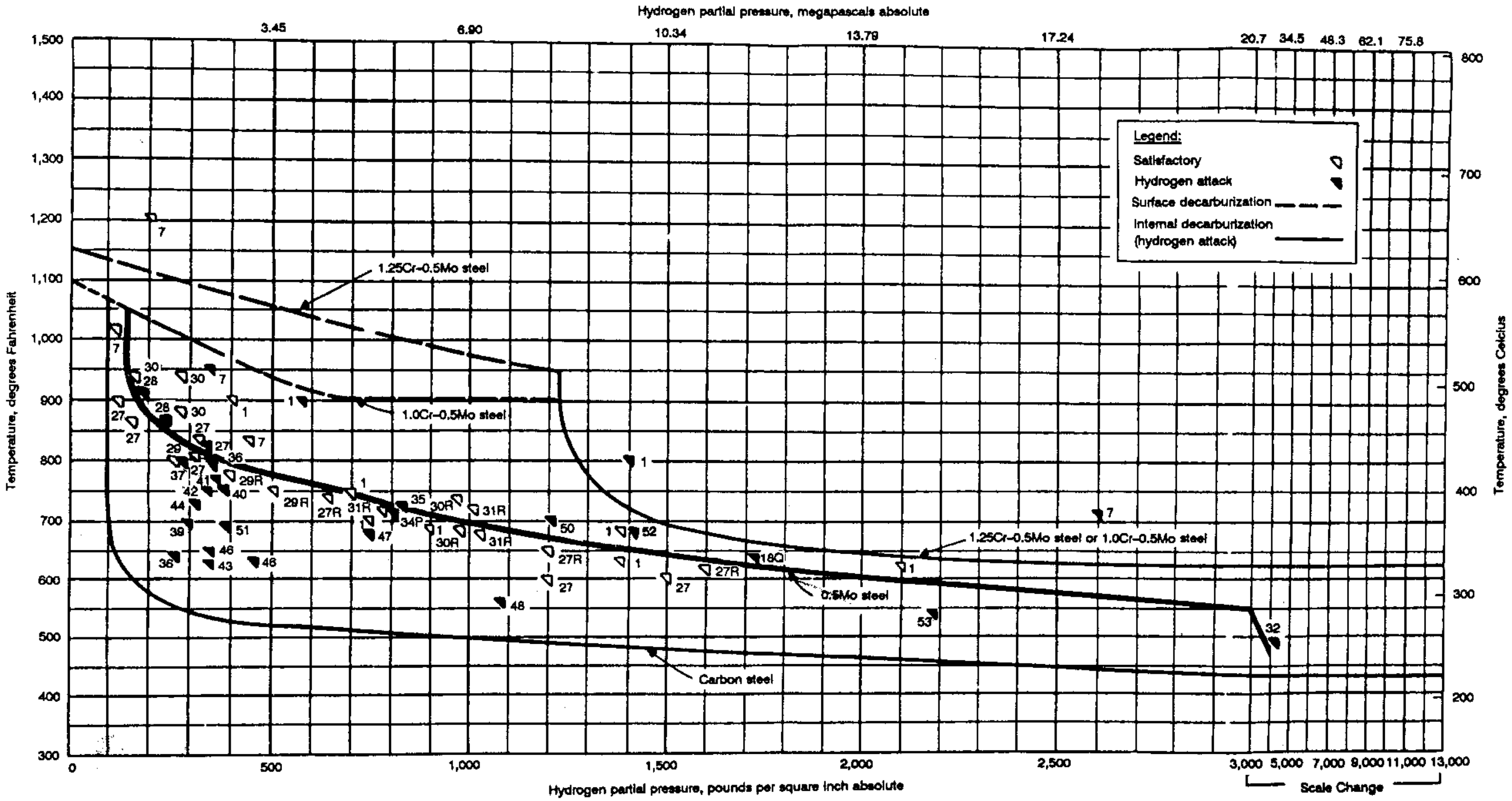
Internal decarburization (Hydrogen attack) ————————

| | Carbon steel | 1.0 Cr 0.5 Mo | 2.0 Cr 0.5 Mo | 2.25 Cr 1.00 Mo | 3.0 Cr 0.5 Mo | 6.0 Cr 0.5 Mo |
|---|---|---|---|---|---|---|
| Satisfactory | ○ | □ | △ | ▭ | ◇ | ▽ |
| Hydrogen attack | ● | ■ | ▲ | ▬ | ◆ | ▼ |
| Surface decarburization | ▨ | ⊠ | ⧗ | ▧ | ⊗ | ⧗ |
| See comments | ◐ | ◧ | ◭ | ◧ | ◈ | ⯆ |

Notes:

1. The limits described by these curves are based on service experience originally collected by G.A. Nelson and on additional information gathered by or made available to API.
2. Austenitic stainless steels are generally not decarburized in hydrogen at any temperature or hydrogen pressure.
3. The limits described by these curves are based on experience with cast steel as well as annealed and normalized steels at stress levels defined by Section VIII, Division I of the ASME Code. See 2.7 and 2.8 in text for additional information.

Figure 3.3 Operating limits for steels in hydrogen service to avoid decarburization and fissuring[2]



Notes:

1. References and comments are shown on page 8.

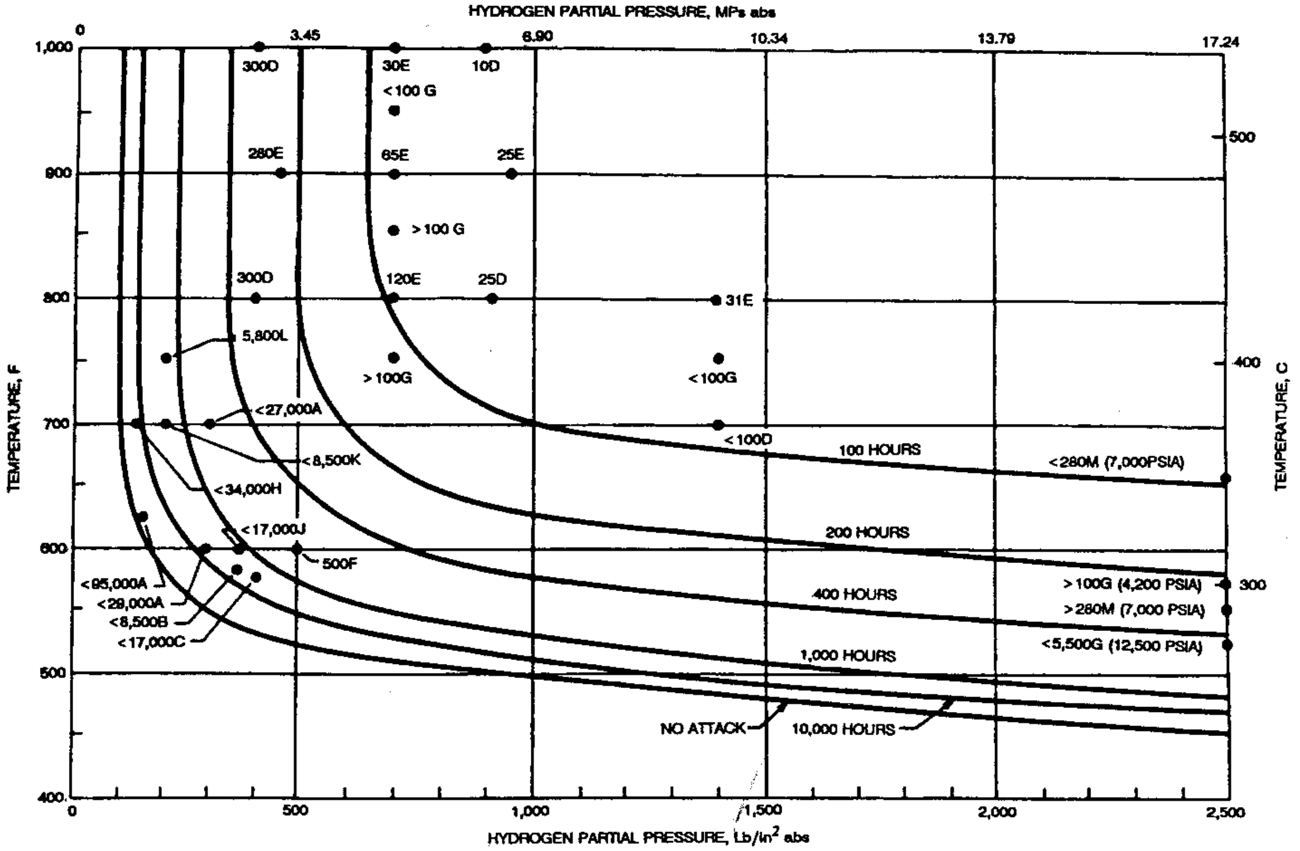
2. Curves for carbon steel, 1.0Cr–0.5Mo steel, and 1.25Cr–0.5Mo steel are included for reference.

3. The symbol ◁ is retained as a reference against previous revisions of this publication.

4. Reference numbers are the same as in previous editions of this publication.

5. The 0.5Mo steel curve is the same as the one shown in the third edition of this publication (1983).

Figure 3.4 Experience with C–0.5Mo and Mn–0.5Mo steels in hydrogen service[2]



**References**

A. AMOCO Oil Co., 1960.*

B. A.R. Ciuffreda and W.D. Rowland, "Hydrogen Attack of Steel in Reformer Service," *Proc. API*, 37[III], pp. 116-28, 1957.

C. C.A. Zapffe, "Boiler Embrittlement," *Trans. ASME*, 66, pp. 81-126, Feb., 1944.

D. R.E. Allen, R.J. Jansen, P.C. Rosenthal, and F.H. Vitovec, "The Rate of Irreversible Hydrogen Attack of Steel at Elevated Temperatures," *Proc. API*, 41[III], pp. 74-84, 1961.

E. L.C. Weiner, "Kinetics and Mechanism of Hydrogen Attack of Steel," *Corrosion*, 17, pp. 109-15, 1961.

F. J.J. Hur, J.K. Deichler, and G.R. Worrell, "Building a Catalytic Reformer?" *Oil and Gas J.*, 54[78], pp. 103-7, Oct. 29, 1956.

G. F.K. Naumann, "Influence of Alloy Addition to Steeel upon Resistance to Hydrogen under High Pressure," *Tech. Mitt. Krupp*, 1[12], pp. 223-34, 1938.

H. M. Hasegawa and S. Fujinaga, "Attack of Hydrogen on Oil Refinery Steels," *Tetsu To Hagane*, 46[10], pp. 1349-52, 1960.

J. T.C. Evans, "Hydrogen Attack on Carbon Steels," *Mech. Eng.*, 70, pp. 414-16, 1948.

K. Air Products, Inc., Mar., 1960.*

L. API Refinery Corrosion Comm. survey, 1957.

M. I. Class, "Present State of Knowledge in Respect to the Properties of Steels Resistant to Hydrogen under Pressure," *Stahl Eisen*, 90 Aug. 18, 1960.

---

*Private communication to Subcommittee on Corrosion

Figure 3.5 Time for incipient attack of carbon steel in hydrogen service[2]

Figure 3.6a Cross section of channel of exchanger. Note cracking in weld metal at right (light colored area) of specimen.[3]

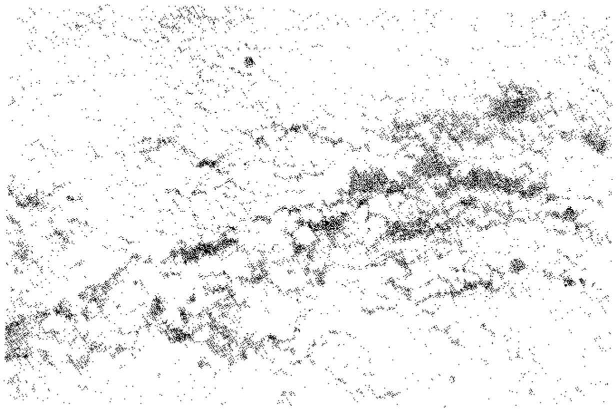


Figure 3.6b Photomicrograph showing fissuring in weld metal. Nital etch, 100X[3]

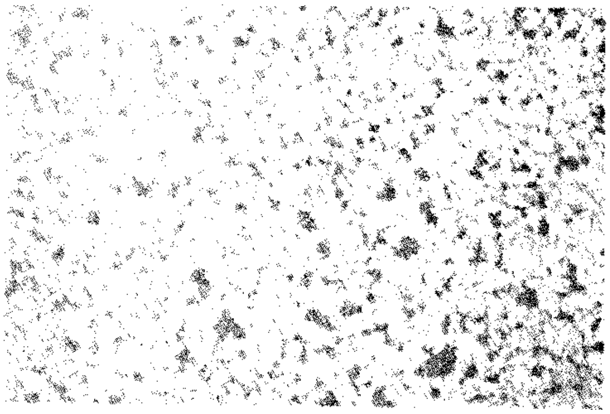


Figure 3.6c Photomicrograph showing structure of parent metal. Nital etch, 100X[3]

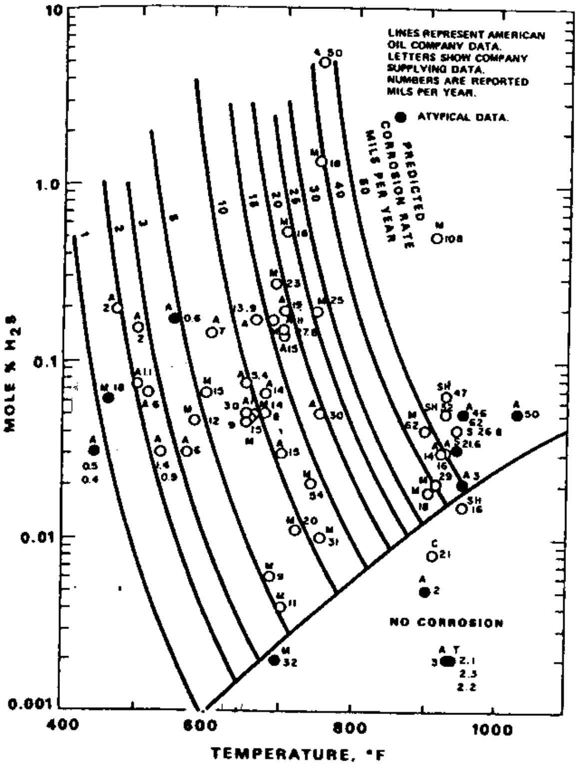


Figure 3.7a Carbon steel—naptha diluent

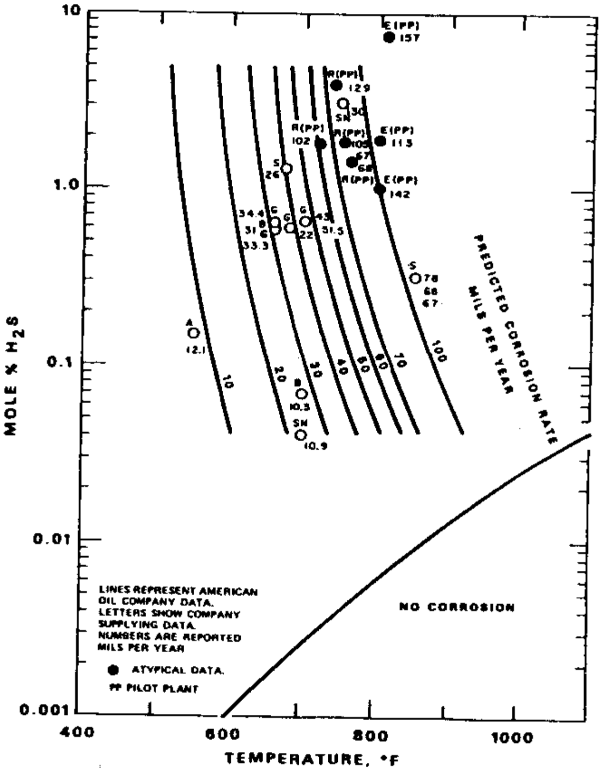


Figure 3.7b Carbon steel, gas oil diluent

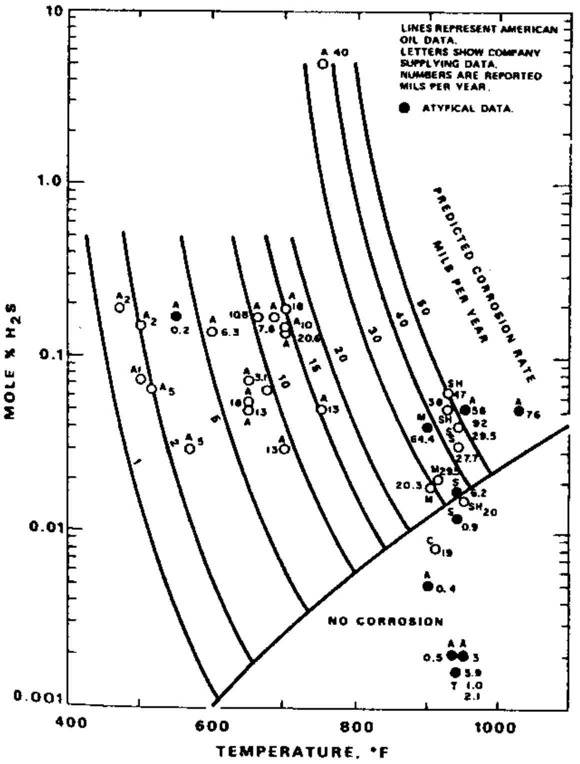


Figure 3.7c 5% Cr steel, naptha diluent

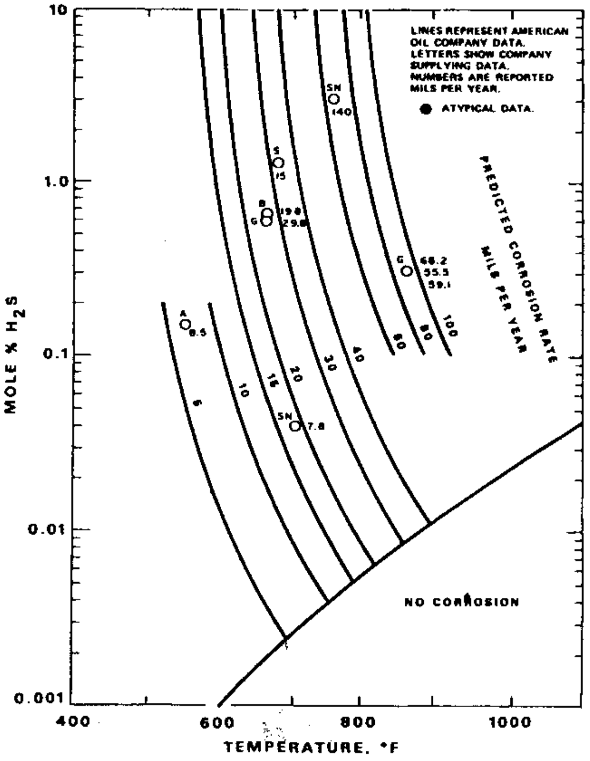


Figure 3.7d 5% Cr steel, gas oil diluent

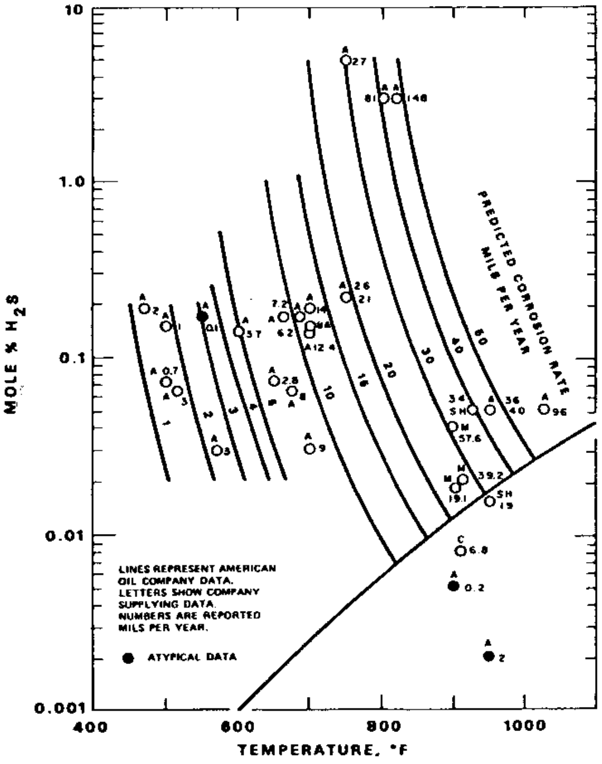


Figure 3.7e 9% Cr steel, naptha diluent

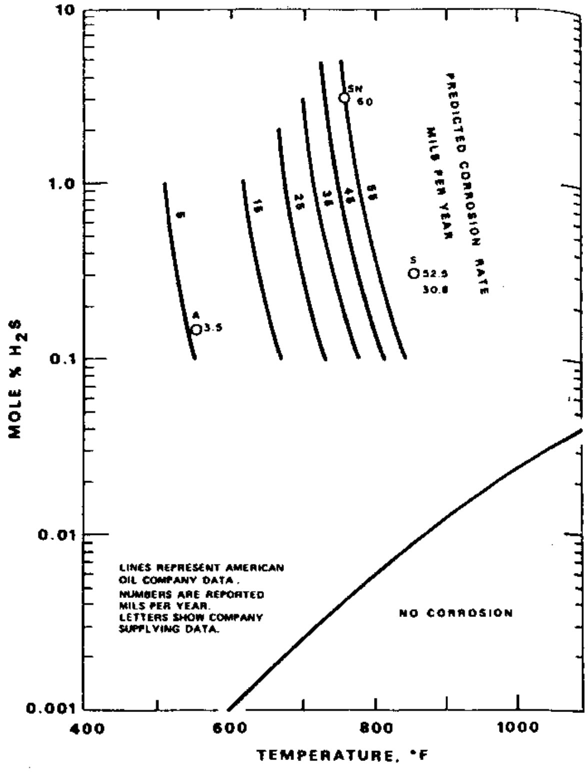


Figure 3.7f 9% Cr steel, gas oil diluent

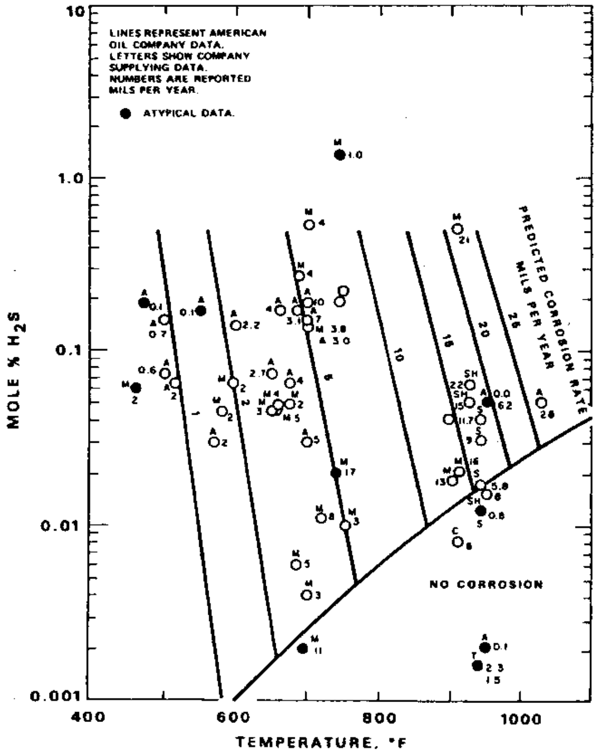


Figure 3.7g 12% Cr stainless steel, naptha diluent

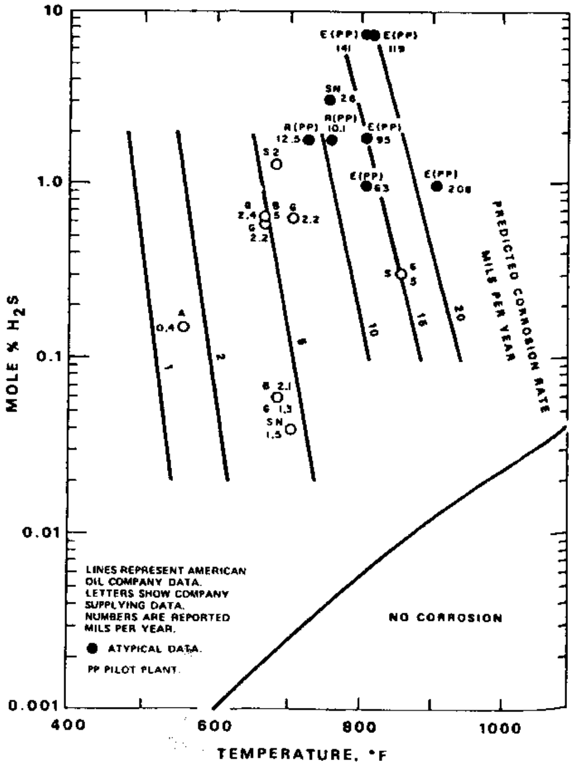


Figure 3.7h 12% Cr stainless steel, gas oil diluent

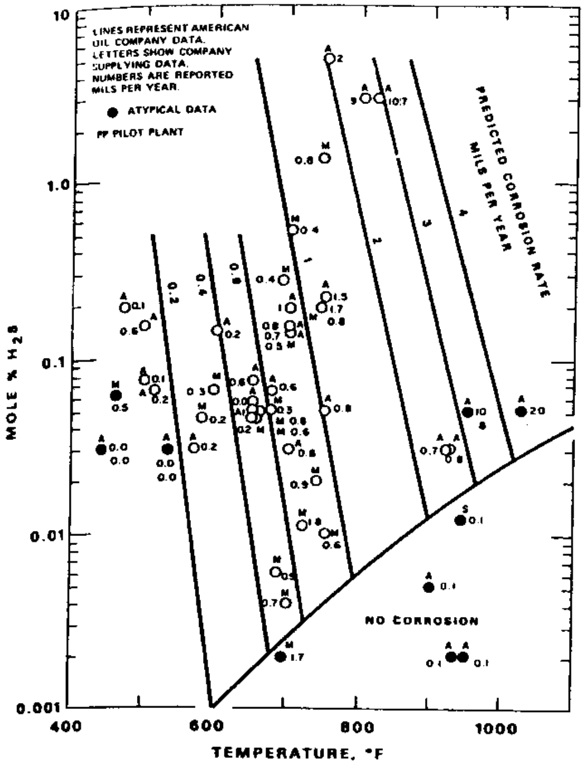


Figure 3.7i 18-8 stainless steel, naptha diluent

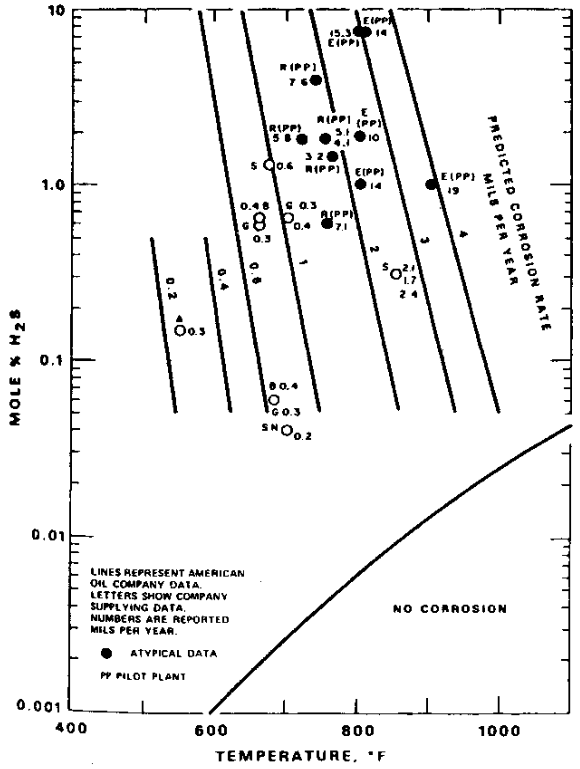


Figure 3.7j 18-8 stainless steel, gas oil diluent

Figure 3.7 Isocorrosion curves for carbon, low alloy, and stainless steels as a function of mole percent $H_2S$ and temperature.[4]

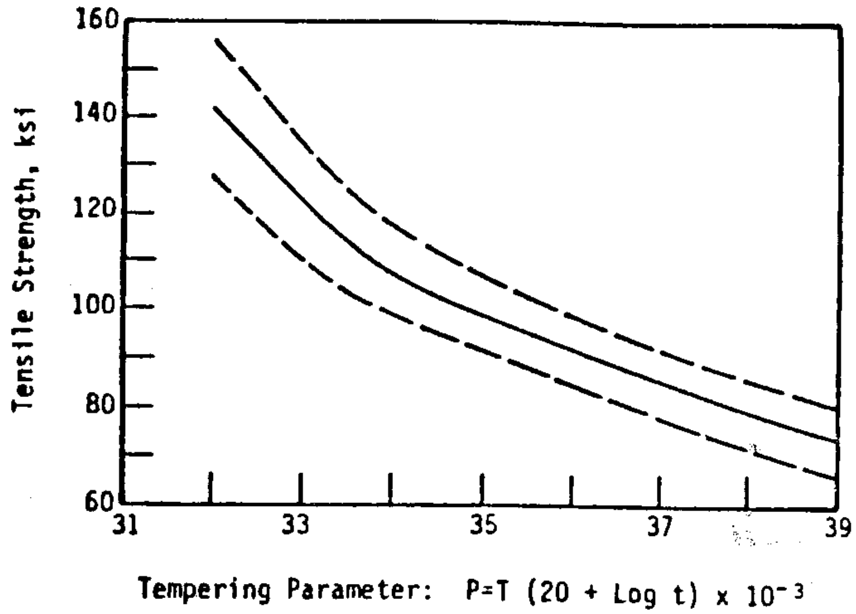
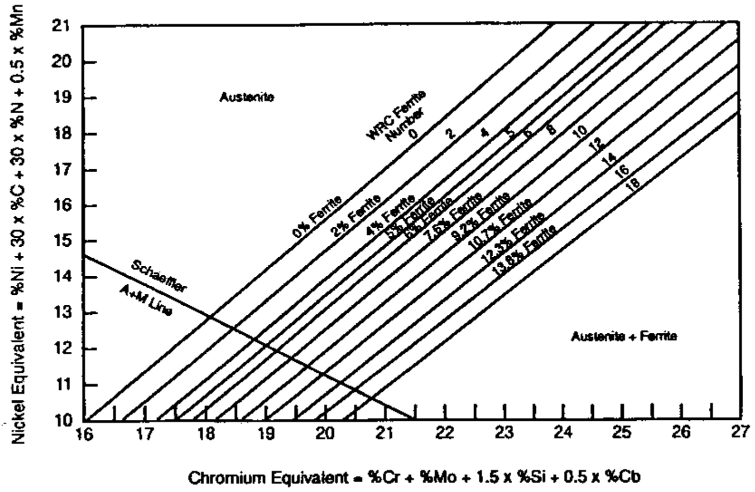


Figure 3.8 Tempering parameter vs tensile strength for quenched and tempered 2¼Cr–1Mo steel.[5]



GENERAL NOTE:
The actual nitrogen content is preferred. If that is not available, the following applicable nitrogen value shall be used:

(a) GMAW welds – 0.08% (except self-shielding flux cored electrode GMAW welds 0.12%)
(b) welds of other processes – 0.06%

Figure 3.9 Delta ferrite content[8]

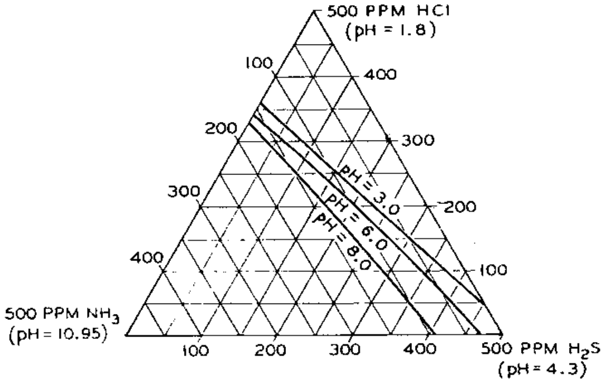


Figure 3.10 Iso–pH lines for the aqueous HCl–$H_2S$–$NH_3$ system (500 ppm total)[7]

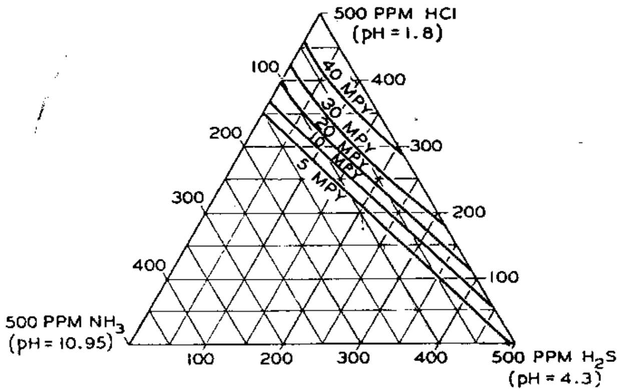


Figure 3.11 Iso-corrosion lines for carbon steel in aqueous HCl-$H_2S$-$NH_3$ system (500 ppm total; nitrogen atmosphere, room temperature, and atmospheric pressure)[7]

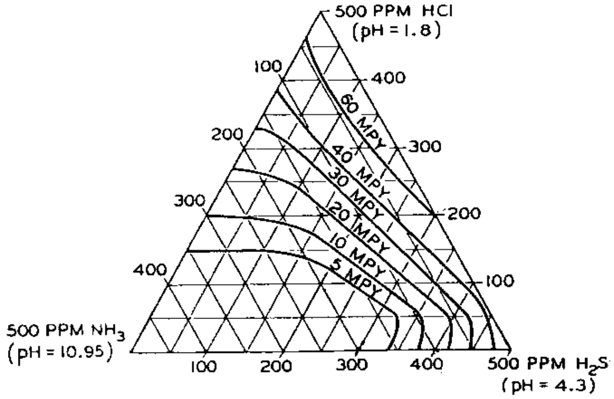


Figure 3.12 Iso-corrosion lines for carbon steel in aqueous HCl-$H_2S$-$NH_3$ system (500 ppm total; air atmosphere, room temperature, and atmospheric pressure)[7]

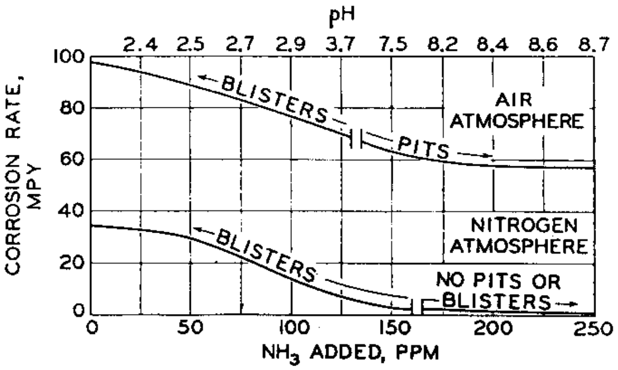


Figure 3.13 Effect of $NH_2$ neutralization on corrosion of carbon steel in an aqueous solution containing 400 ppm HCl, 50 ppm $H_2S$, 50 ppm $NH_3$ at room temperature and atmospheric pressure[7]

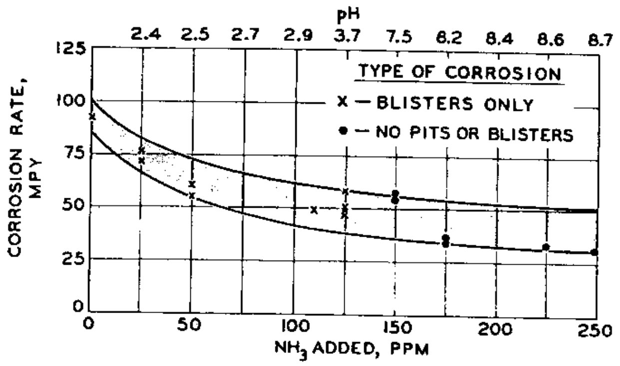


**Figure 3.14** Effect of $NH_3$ addition on corrosion when only a sulfide film formed on the test coupons. Carbon steel coupons were in aqueous $HCl-H_2S-NH_3$ solutions for 24 hours at 300°F (150°C) and 625 psig under nitrogen.[7]

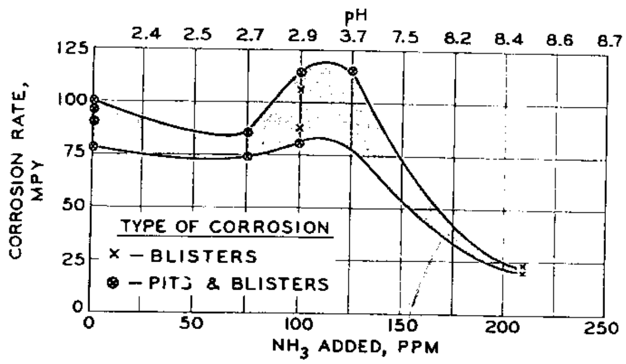


**Figure 3.15** Effect of $NH_3$ addition on corrosion when nonremovable oxide film formed on the test coupons. Carbon steel coupons were in aqueous $HCl-H_2S-NH_3$ solutions for 24 hours at 300°F (150°C) and 625 psig under nitrogen.[7]

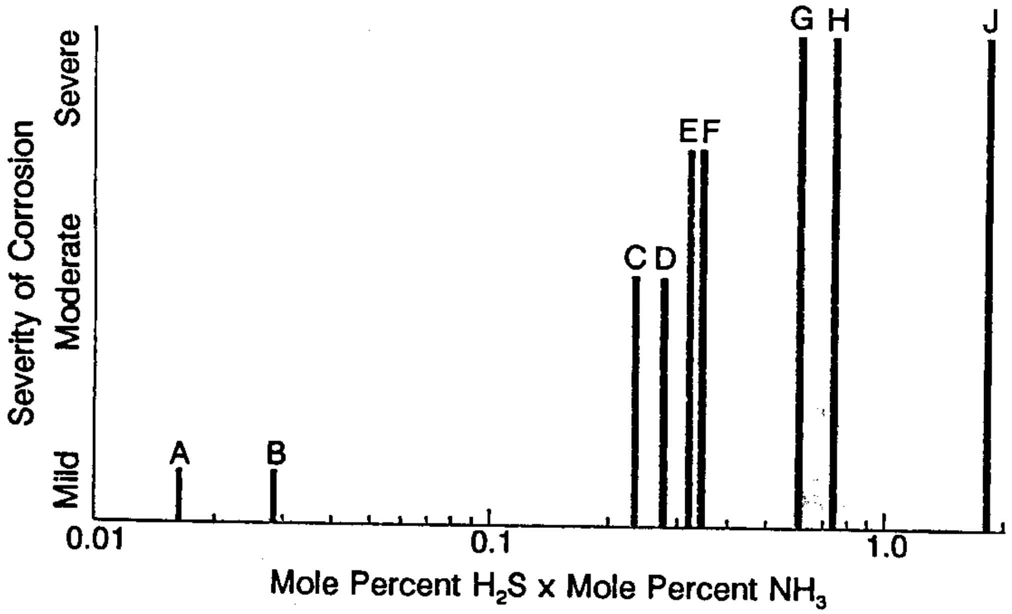


**Figure 3.16** Effect of stock composition on corrosivity for hydrocracker air coolers[8]

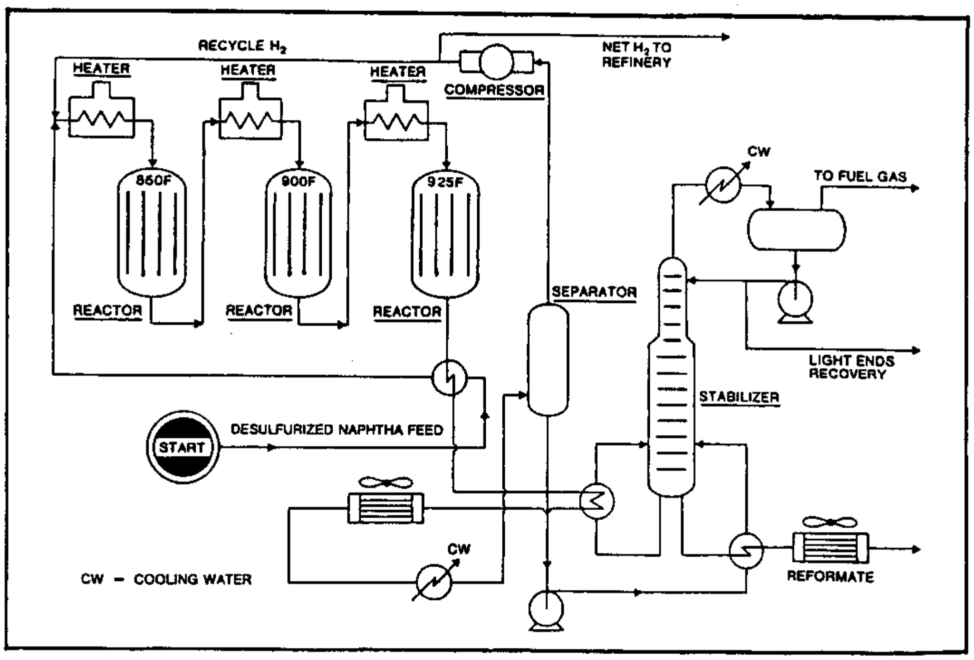


Figure 3.17 Catalytic reforming[1]

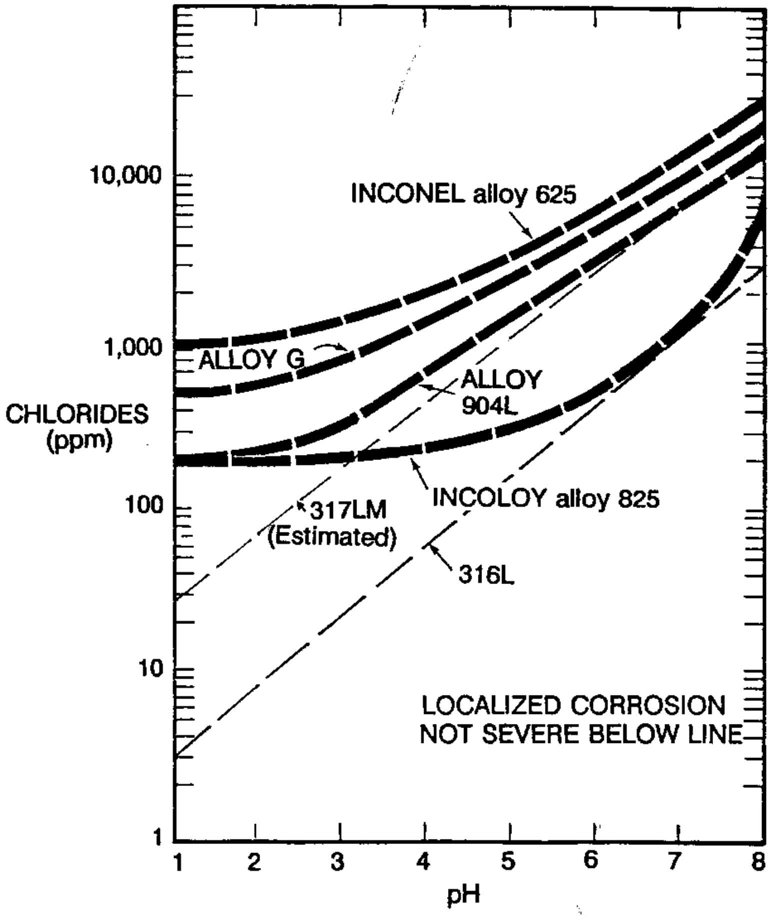


Figure 3.18 Predicted corrosion behavior of alloys in $SO_2$ scrubber environments from field tests (125-160°F [50-70°C] oxidizing)[9]

Chapter
# THREE

## REFERENCES FOR FIGURES

1. (Reprinted with permission from *Petroleum Refinery Engineering,* 4th ed., 1958, McGraw-Hill Publishing Co., New York, NY.)

2. (Reprinted with permission from API Standard 941, *Steels for Hydrogen Service at Elevated Temperatures and Pressures in Petroleum Refineries and Petrochemical Plants,* 3rd ed. May 1983, American Petroleum Institute, Washington, DC.)

3. (Reprinted from "Hydrogen Service Failures of Welds with Insufficient Alloy Content," *Corrosion*, September 1961.)

4. (Reprinted from "Computer Correlations to Estimate High Temperature Hydrogen Sulfide Corrosion in Refinery Streams," *Materials Protection,* January 1971.)

5. (Reprinted from "The Use of Quenched and Tempered 2¼ Cr-1 Mo Steel for Thick Wall Reactor Vessels in Petroleum Refinery Processes: An Interpretive Review of 25 Years of Research and Application," *WRC Bulletin 275*, February 1982, Welding Research Council, New York, NY.)

6. (Reprinted with permission from ASME Boiler and Pressure Vessel Code, Section III, Subsection NB, 1983 ed., American Society of Mechanical Engineers, New York, NY.)

7. (Reprinted from "Chloride Corrosion and Fouling in Catalytic Reformers with Naphtha Pretreaters," *Corrosion*, March 1961.)

8. (Reprinted with permission from "Corrosion by Sulfide Containing Condensate in Hydrocracker Effluent Coolers," *API Division of Refining*, May 1968, American Petroleum Institute, Washington, D.C.)

9. (Reprinted from "Effect of pH, Chloride, and Temperature on Localized Corrosion of Nickel Alloys in $SO_2$ Scrubber Environments," CORROSION/82, paper no. 196, 1982, NACE, Houston, TX.)

10. (Reprinted with permission from "Cracking Failures of Austenitic Steel," May 1966, *Hydrocarbon Processing*, Gulf Publishing Co., Houston, TX.)

Chapter
# FOUR

# Hydrogen, Methanol, Ammonia, Gas Treating, Hydrodealkylation, Polymerization, Phenol, and Solvent Treating

## *INTRODUCTION*

Hydrogen, methanol, and ammonia plants are very similar. Methane or naphtha feed stock is first desulfurized and then combined with steam in a reformer furnace. Hydrogen and carbon dioxide are produced at ~1,500°F (820°C) in the reformer as the starting point for all three processes.

In a hydrogen plant (Figure 4.1), the process gas (hydrogen and carbon dioxide) from the reformer furnace is cooled to ~850°F (450°C) in a quench steam generator, then cooled further to ~700°F (370°C) and sent to a shift converter where additional hydrogen is formed. The process gas is cooled again and then fed to a pressure swing adsorption (PSA)$^{(1)}$ unit, a hot potassium carbonate absorption system, or a monoethanolamine (MEA) absorption system to purify the hydrogen by removing the carbon dioxide.

In an ammonia plant (Figure 4.2), the synthesis gas from the reformer furnace is fed into a secondary reformer vessel, where air is added through a burner to create outlet vessel temperatures of ~1,800°F (980°C). The outlet of the secondary reformer vessel is cooled in a quench steam generator and sent to a shift converter; this is followed by a carbon dioxide removal system such as the one in a hydrogen plant. The purified nitrogen from the air added in the secondary reformer vessel and hydrogen synthesis gas is fed to a methanator to convert residual oxides of carbon back to methane (which is inert in the ammonia conversion); the gas is then compressed to ~3,000 psia (2,070 kPa). The compressed synthesis gas is fed to an ammonia converter vessel. As the synthesis gas passes over catalyst beds, ammonia is formed. The ammonia product is then cooled and refrigerated to separate out impurities.

In a methanol plant (Figure 4.3), the synthesis gas passes from the reformer furnace to a heat recovery section where it is cooled to room temperature. The synthesis gas is then compressed to 750 to 1,500 psia (5,170 to 10,345 kPa) and fed to the converter vessel through preheat exchangers. Methanol is formed as the gas passes over catalyst beds in the converter vessel at 400 to 600°F (205 to 315°C). The methanol product is then cooled and fed to separators and then to fractionators to complete the purification.

## *MATERIALS OF CONSTRUCTION*

### High-Temperature Front End

The front end section of hydrogen, methanol, and ammonia plants is shown in Figure 4.4. The secondary reformer is used only in an ammonia plant. The feed gas is desulfurized in carbon steel equipment. When the metal temperature exceeds 800 to 850°F (425 to 455°C), 1Cr-½Mo$^{(2)}$ or 1¼Cr-½Mo are used to avoid long-term deterioration of the mechanical properties by graphitization. Preheat coils in the top of the reformer furnace are usually 2¼Cr-1Mo up to 1,200°F (650°C) metal temperature and type 304H

---

(1) Proprietary process of Union Carbide, Indianapolis, IN.

(2) Not normally available in tubular or pipe form.

(UNS S30409) stainless steel (SS) for metal temperatures above 1,200°F (650°C). Caustic stress corrosion cracking (SCC) from solids can occur in the steam preheat coils if solid carry-over is excessive (see Chapter One, Steam and Condensate section). The inlet connections to the steam methane reformer furnace tubes are either 1¼Cr-½Mo (1,100°F [595°C] maximum) or 2¼Cr-1Mo (1,200°F [650°C] maximum).

The methane (or naphtha) and steam are converted to hydrogen and carbon dioxide over a nickel catalyst in the ACI[3] Grade HK 40 (0.4C, 25Cr, and 20Ni) or ACI Grade HP modified (0.4C, 25Cr, 30Ni, and Nb) primary reformer tubes. HP modified has largely replaced HK because of superior stress-to-rupture strength (e.g., 1.82 ksi [12,550 kPa] vs 1.2 ksi [8,275 kPa] at 1,800°F [980°C]). Skin temperatures on these tubes are ~1,800°F (980°C), and the outlet process temperature is ~1,500°F (820°C). Sulfur content in the fuel gas is limited to 2,000 to 3,000 ppm hydrogen sulfide to avoid accelerated oxidation. The tubes are centrifugally cast and have been used in the as-cast condition that includes ~3/32 in. (2.4 mm) dross and unsoundness on the inside diameter. Currently, most tubes are bored to remove the dross and unsoundness. Since the tubes are operating in the range in which sigma phase (a brittle FeCr compound) forms, the Cr, Ni, and C are *balanced* to minimize sigma formation. The welds must be blasted to remove all residual slag; if the residual slag forms a eutectic with the metal oxides, catastrophic oxidation will occur.

The outlets of the primary reformer furnace tubes are connected to either a refractory-lined steel or (occasionally) an Incoloy[4] 800H outlet header with Incoloy 800H *pigtails*. Pigtails are tubes (~1 in. [25.4 mm] in diameter) connected to a reducing cone or a side boss at the bottom of the centrifugally cast tube. They are called pigtails because they were originally made in a double loop configuration to compensate for thermal expansion. More advanced designs have eliminated the need for the loops. Premature failure of Incoloy 800 pigtails has occurred because of too fine a grain size (smaller in size than ASTM[5] No. 5); however, these problems can be avoided by specifying Incoloy 800H. Some refiners prefer single row reformer tubes to minimize the thermal stresses on the pigtails. For temperatures above 1,200°F (650°C), INCO[6] 82 or INCO A weld filler metal should be used (although INCO A has a somewhat lower creep strength than INCO 82). Neither INCO 92 nor INCO 182 should be used above 900 to 950°F (482 to 510°C) because they embrittle when exposed to high temperatures. INCO 182 has a significantly lower creep strength than INCO 82. Weld filler metal from other sources should be examined very carefully because some filler metals are subject to *green rot* (preferential oxidation of chromium that occurs at ~1,350°F [730°C], resulting in rapid deterioration). For the same reason, Inconel[7] 600 (wrought or cast) should not be used above 1,350°F (730°C) in this service.

A transfer line connects the primary reformer to the quench steam generator in a hydrogen plant and to the secondary reformer in an ammonia plant. The secondary reformer in an ammonia plant is connected to the quench steam generator by another transfer line. Transfer lines normally operate at 1,450 to 1,800°F (788 to 980°C) and are usually made of either Incoloy 800H or refractory-lined carbon steel. Above ~1,500°F (820°C), the combination of low-strength and high-thermal expansion of metals makes refractory linings attractive; however, refractory linings can develop hot spots from cracks and can sometimes deteriorate as a result of condensation of corrosive gases at the metal wall.

The secondary reformer in an ammonia plant is a carbon steel vessel with a dual layer refractory lining. Internal temperatures reach ~2,000°F (1,090°C) from burning as a result of air added through a burner at the top of the vessel to the feed gas (hydrogen, carbon monoxide, carbon dioxide, and steam). The burner is a refractory-lined device that is subject to failure if not carefully designed. Quench steam generators have refractory-lined inlet channels and tube sheets. Tubes are often made of carbon steel because the heat transfer from the steam on the outside of the tube is markedly better than that from the synthesis gas inside the tube. As a result, the metal temperature closely approaches the temperature of the steam. The inlet ends of the tubes are protected from the inlet gas by ferrules, usually made of type 310 (UNS S31000) SS with insulation between the ferrule and the tube. The tube material should be selected

---

(3) Alloy Coatings Institute, Des Plaines, IL.

(4) Trade name.

(5) ASTM, Philadelphia, PA.

(6) Trade name.

(7) Trade name.

according to the maximum anticipated metal temperature and to API[8] Standard 941. The outlet channels are usually made of low-alloy steel selected by using API 941.

## Carbon Dioxide and Hydrogen Sulfide Removal

After the synthesis gas leaves the quench steam generator, it goes through a shift converter to convert more of the synthesis gas to hydrogen. Some ammonia is formed in this unit when nitrogen is present. Alloy selection is based on API 941 until the synthesis gas is cooled below the dew point (usually ~325°F [160°C]). When wet carbon dioxide condenses out of the synthesis gas, severe corrosion of carbon and low-alloy steel results, particularly in the turbulent areas. Type 304L (UNS S30403) SS is normally used to resist this attack. Figure 4.5 shows the relationship between pH and carbon dioxide partial pressure. As can be seen in Figure 4.5, the corrosion rate of carbon steel at 100°F (38°C) increases as the carbon dioxide partial pressure increases. The variation in corrosion rate results from the strong effect of the turbulence. The following rates were measured in a two phase gas-water system containing carbon dioxide at a partial pressure of 18 psi (125 kPa):

| | Corrosion Rate (mpy [mm/y]) | |
|---|---|---|
| | Location A | Location B |
| Material | 280°F (138°C) | 320°F (160°C) |
| carbon steel | 50 (127) | 50 (127)[9] |
| 5 Cr | 11.5 (0.29) | 2.2 (0.06) |
| type 405 (UNS S40500) | 1.14 (0.03) | 0.7 (0.02) |
| type 304 (UNS S30400) | 0.01 (0.0003) | 0.06 (0.0015) |

In ammonia and hydrogen plants, part of the carbon dioxide is removed in the condensate in the knockout pots, which are made of type 304L SS or type 304L SS clad (Figure 4.6). The overhead lines of the knockout pots may be made of carbon steel if no condensation occurs. This is particularly true in those ammonia plants in which some of the ammonia formed in the shift converter is present in the stream. In general, the overhead lines of the knockout pots used in hydrogen plants are made of type 304L SS. The remainder of the carbon dioxide is removed by absorption in a potassium carbonate solution, an amine solution, or a low-temperature PSA unit.

Carbon steel is the predominant construction material for carbonate and amine solution containers. Corrosion in the overhead lines (hydrogen sulfide or carbon dioxide plus water from the regenerator) is prevented by adding corrosion inhibitors. Although amine carry-over can act as a corrosion inhibitor in the overhead line, SCC of carbon steel has occurred when amine added as a corrosion inhibitor became concentrated. Copper and copper base alloys should be avoided in amine service and are questionable in carbonate service. Nickel or cobalt base alloys (e.g., Monel[10] 400 and Inconel 600) except for Stellite[11] should be avoided in carbonate service. Monel 400 should be avoided in amine service if UCC Amine Guard[12] corrosion inhibitor is used.

---

[8] American Petroleum Institute, Washington, DC.

[9] Rates of the corrosion probe were above 1,000 mpy (25.4 mm/y).

[10] Trade name.

[11] Trade name.

[12] Trade name.

In amine units, absorption typically occurs at 130°F (55°C); in carbonate units, absorption typically occurs at 200°F (93°C). Absorption pressures are typically 100 to 400 psia (690 to 2,760 kPa), although units can be designed to handle pressures at ~1,000 psia (6,895 kPa). Amine and carbonate strippers (regenerators) typically operate at 240°F (115°C) and 25 to 30 psia (172 to 207 kPa). In the past, stress relief of carbon steel welds and cold bends was usually required when the process temperature exceeded 140°F (60°C) in both amine and carbonate solutions. Past practices for amine service varied from requiring stress relief when hydrogen sulfide was present to using 176 to 200°F (80 to 93°C) as the process temperature above which stress relief was required. As a result of a severe failure in an amine unit, many operators examined equipment that was exposed to amine service. Cracking was found to be independent of process temperature. Therefore, many operators now require stress relief for all equipment exposed to amine solutions, regardless of process temperature.

Recent work reveals that SCC occurs only in hot MEA solutions when the electrochemical potential of the steel surface is more negative than -700 mV vs a silver-silver chloride electrode. The tendency for SCC increases with an increase in solution concentration and in temperature. Saturating the hot MEA solution with hydrogen sulfide makes the potential of the steel more positive (i.e., decreases the tendency for SCC). This latter result raises a question about the practice of some operators who require stress relief only for steels exposed to amine solutions containing hydrogen sulfide.

There is some question about the need to stress relieve carbon steel in a carbonate solution, which normally contains corrosion inhibitors. Oxygen is usually added to maintain the inhibitor, which is often vanadium pentoxide in the active (oxidized) state; otherwise, SCC can occur.

Threaded connections should be avoided in an acid gas amine solution because the turbulence created by the threaded area causes severe corrosion of the threads. Where turbulent areas cannot be avoided by design (e.g., pumps and control valves or equipment to be used where the velocity exceeds 8 ft/s [2.4 m/s]), type 304L SS should be used. Reboiler tubes should be made of type 304 (UNS S30400) SS (type 304L SS if seal welded). The PSA unit operates at 50 to 100°F (10 to 38°C) and undergoes pressure cycles as part of the normal operating cycle. The only material problem presently known is fatigue cracking, which is accelerated by the presence of hydrogen; this occurs as a result of the cycling of the vessels. Therefore, stress raisers should be avoided in the equipment design.

## High-Pressure Ammonia Conversion

After the hydrogen is purified, it is ready for use in a refinery hydrogenation process. In an ammonia plant, the hydrogen-nitrogen mix is sent to an ammonia converter (Figure 4.7), which requires a start-up heater. Since the material in the heater will be exposed to hydrogen only for a short period, the time dependent curves in API 941 should be consulted when selecting an alloy for the heater tubes.

The ammonia reaction occurs in an internal type 304 SS basket where the temperature is ~900°F (480°C). Even though the pressure is ~3,000 psi (20,685 kPa), the converter wall (usually multilayer) does not often require alloy materials to resist hydrogen because cool gas is circulated on the outside of the basket. When alloy materials are required to resist hydrogen attack, they are only required on the inner converter wall layer because the outer layers are vented to the atmosphere. The outlet connection is usually hot enough to require chrome steel alloys to resist hydrogen attack. Nitriding should also be considered at temperatures above 750°F (400°C). Using a nitriding allowance (usually 1/16 to ⅛ in. [1.6 to 3.2 mm]) is all that is usually required; however, Inconel 600 is used for basket screens and occasionally for overlaying very high-temperature parts.

After the ammonia leaves the converter, it is cooled and purified. Although SCC has occurred in anhydrous ammonia, it has not been a problem in the process plant because no oxygen is introduced until the ammonia enters the storage equipment. The ammonia is stored at -28°F (-33°C). It used to be thought that this temperature was too low to cause SCC; however, recently cracking has been observed in ammonia storage vessels. Therefore, stress relief of these vessels is being specified. At least 0.2 wt% water is required to avoid SCC during shipment and subsequent storage.

## Methanol Plants

Methanol plants are very similar to ammonia plants; high-temperature reformer furnaces and high-pressure (multilayer) converters are used. High-corrosion rates on carbon steel occur at ~500°F (260°C) in the carbon monoxide, carbon dioxide, and hydrogen environments found in methanol plants; therefore, corrosion resistant alloys are required in this range. Figure 4.8 shows the corrosion rates of 11 alloys as a function of temperature in the 50-50 carbon dioxide-hydrogen mixtures that are common in methanol plants. In addition, metal dusting has been reported in the process boiler of a methanol plant. See the following section.

## Other Common Processes

The feedstock in hydrodealkylation units is heated to ~1,200°F (650°C) in a preheat furnace before entering the reactor. Above ~1,100°F (590°C), metal dusting or catastrophic carburization occurs on all alloys that are otherwise suitable for the temperature conditions. The attack is very rapid and takes the form of round bottom pits. The surface of the remaining metal is heavily carburized. A small quantity of sulfur (0.05 to 0.5 wt%) in the form of hydrogen sulfide or mercaptan added to the feed will prevent attack. Aluminizing has also been used to prevent attack.

Polymerization units use phosphoric acid as a catalyst in the reactor. Because solid phosphoric acid catalysts do not cause corrosion, carbon steel can be used. However, liquid phosphoric acid is very corrosive to carbon steel, so corrosion resistant materials are required. At a phosphoric acid concentration of 100%, type 304L SS is satisfactory up to 120°F (50°C), and type 316L SS is required from 120 to 225°F (50 to 107°C).

Phenol is produced by the oxidization of cumene and is followed by cleavage of the oxidation product of phenol and acetone. Type 304L SS (clad) is required to resist corrosion in the oxidation vessel, and alloy 20 (clad) is often used in the cleavage vessel.

Two common solvent treating processes are solvent deasphalting and solvent treating. In solvent deasphalting, propane, butane, or a mixture of the two is used to dissolve all hydrocarbons but asphalt. In general, no corrosion occurs from the process side in these units. In solvent treating with furfural, some corrosion occurs when the furfural is mixed with water and in the portions in which furfural is heated above 420°F (215°C). Where these conditions exist, type 304L SS is used below 160°F (70°C), and type 316L SS is used above 160°F (70°C). Where there is a potential for chloride SCC of SS, red brass or 70Cu-30Ni is used at temperatures up to ~200°F (93°C), and Monel 400 is used above.

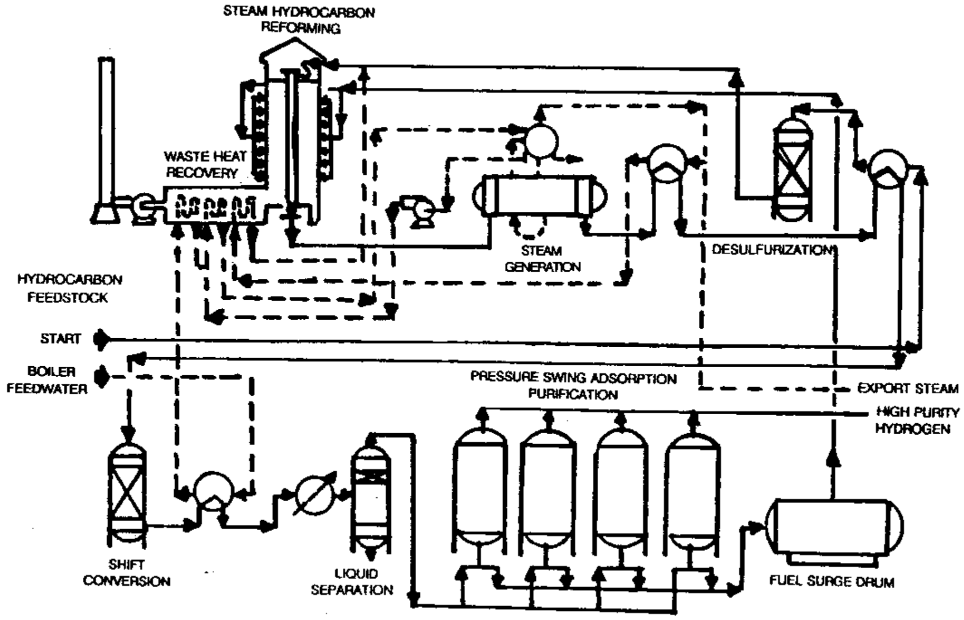


Figure 4.1 Hydrogen[1]

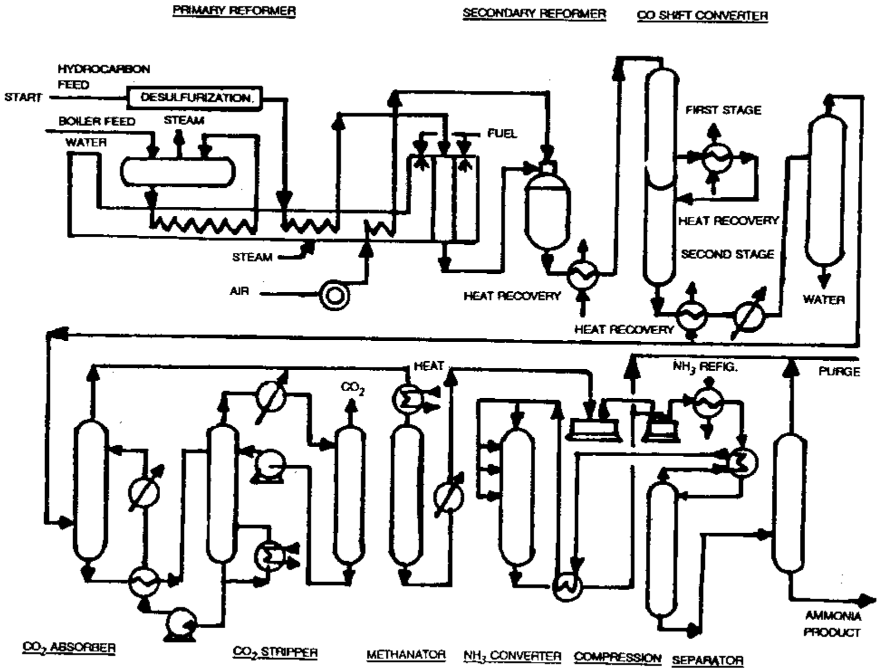


Figure 4.2 Ammonia[1]

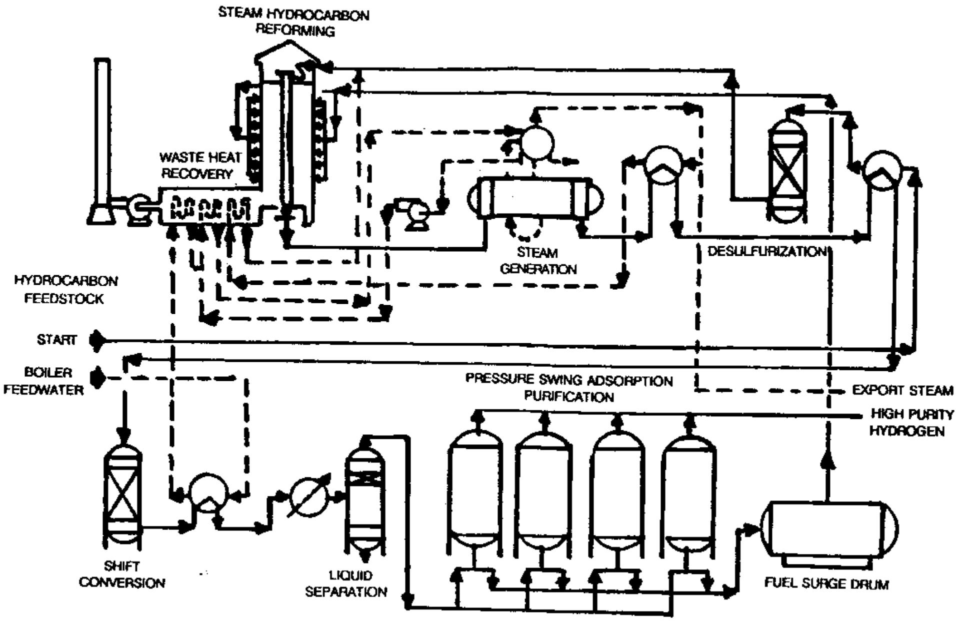


Figure 4.1 Hydrogen[1]

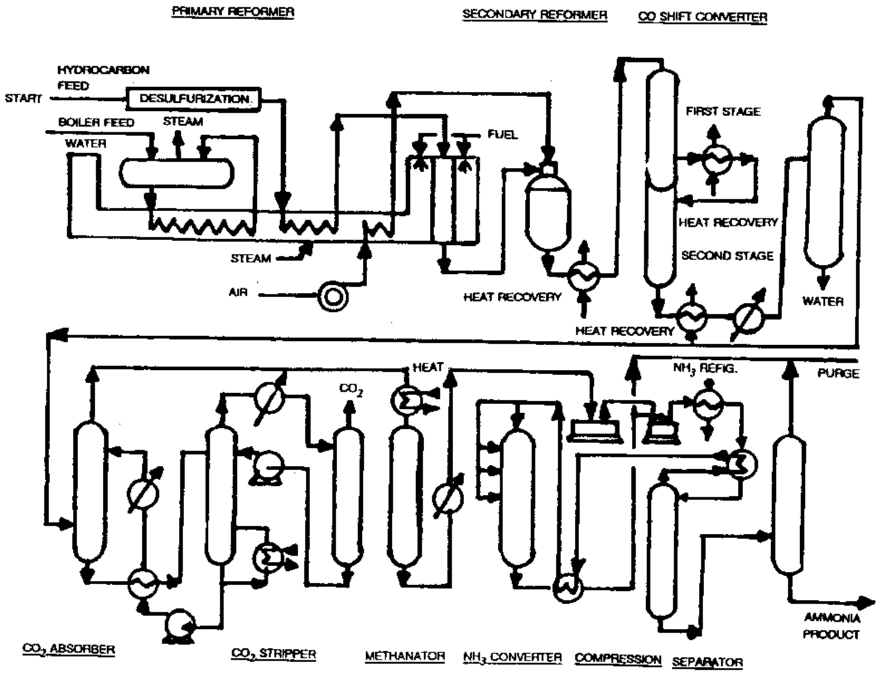
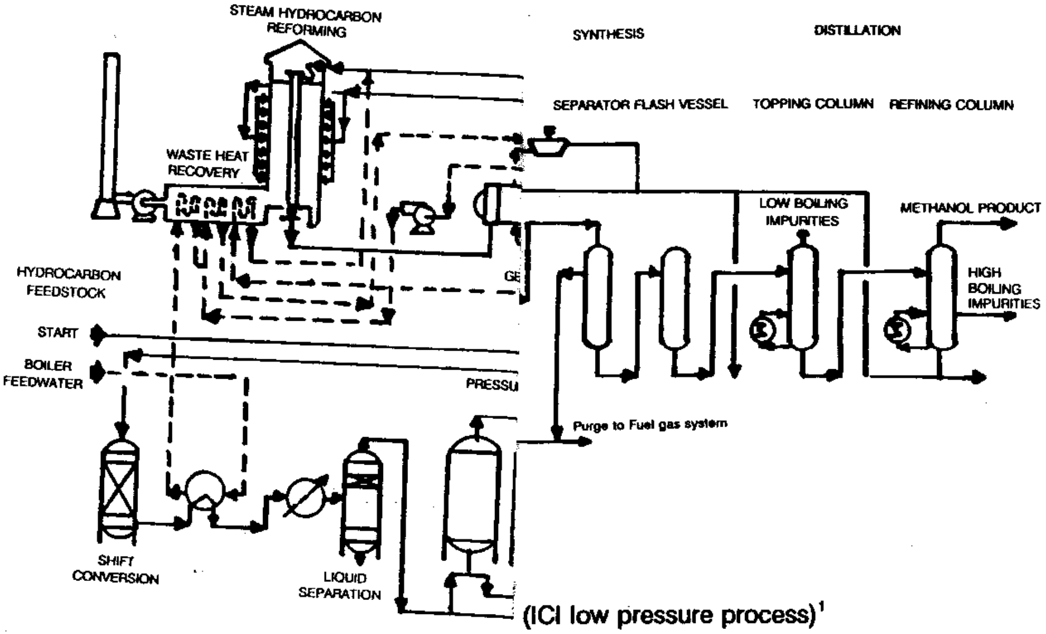
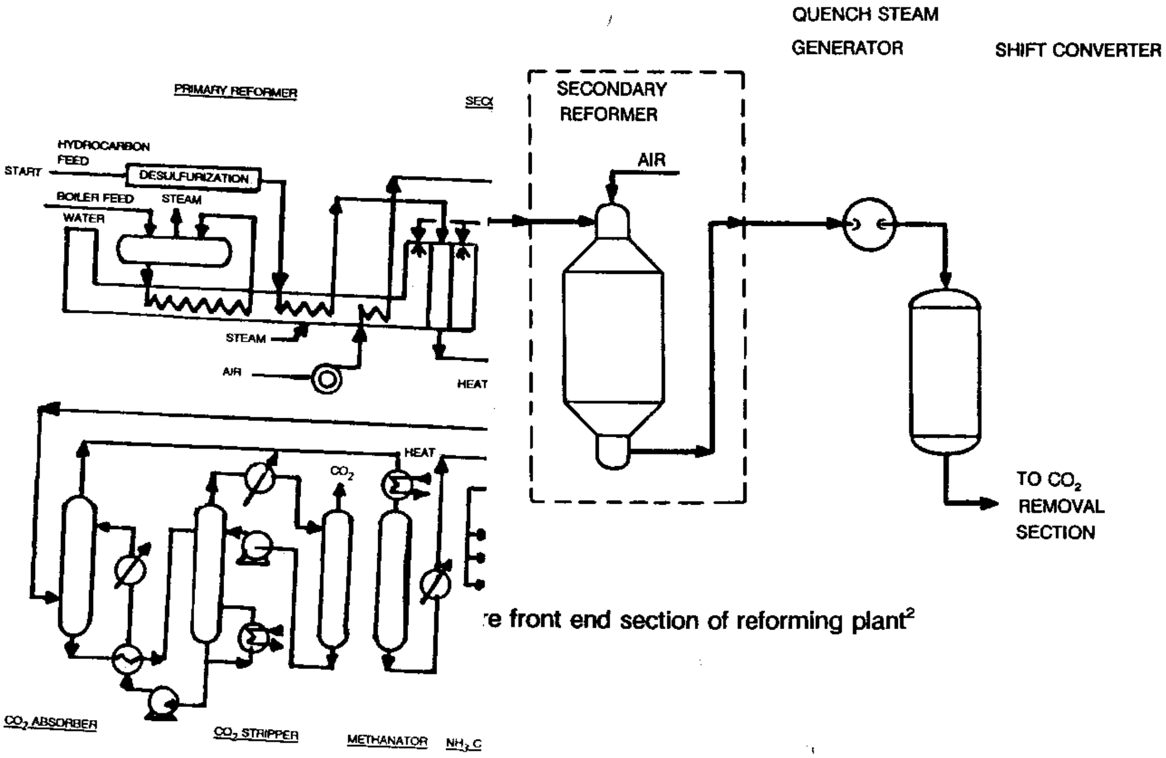


Figure 4.2 Ammonia[1]



(ICI low pressure process)[1]

Figure 4.1 I



re front end section of reforming plant[2]

Figure 4.2 An

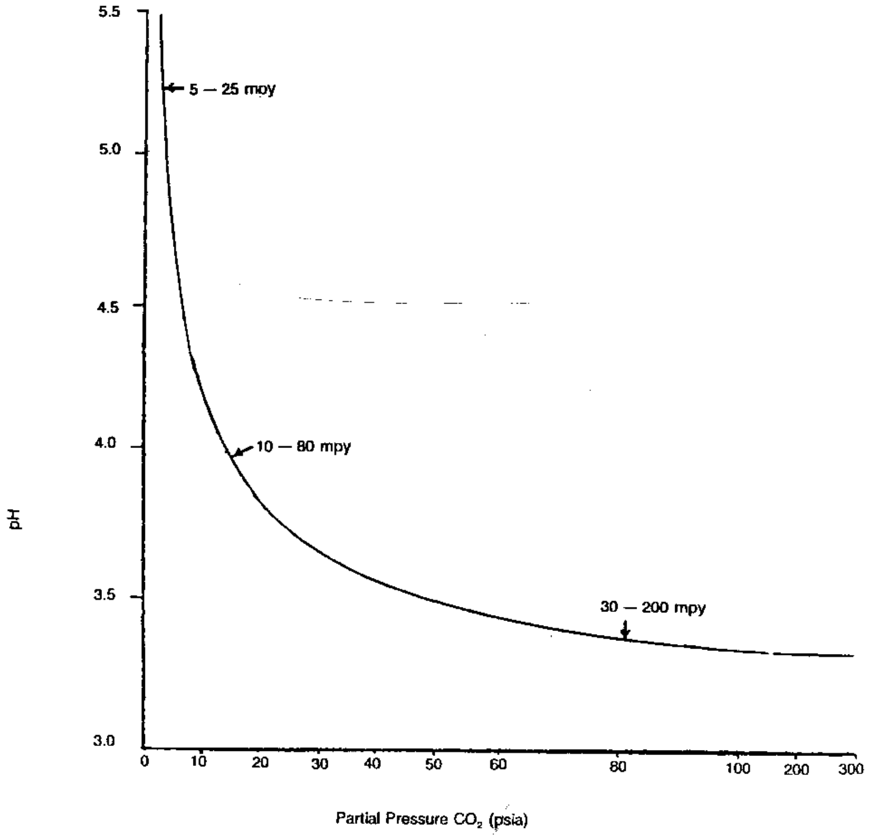


Figure 4.5 Relationship between pH, carbon dioxide partial pressure, and estimated corrosion rate on carbon steel at 100°F (38°C)[2]

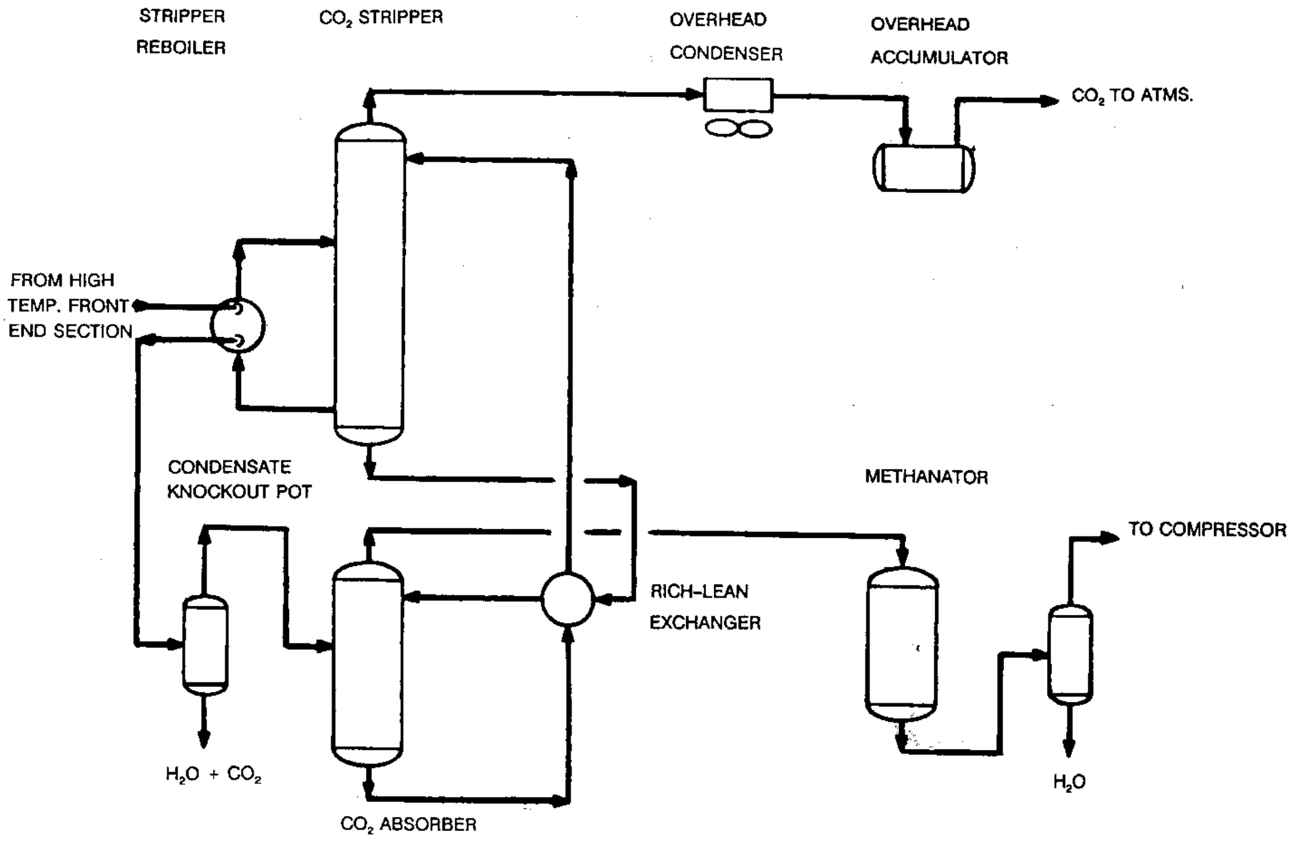


Figure 4.6 Carbon dioxide removal section of reforming plant[2]

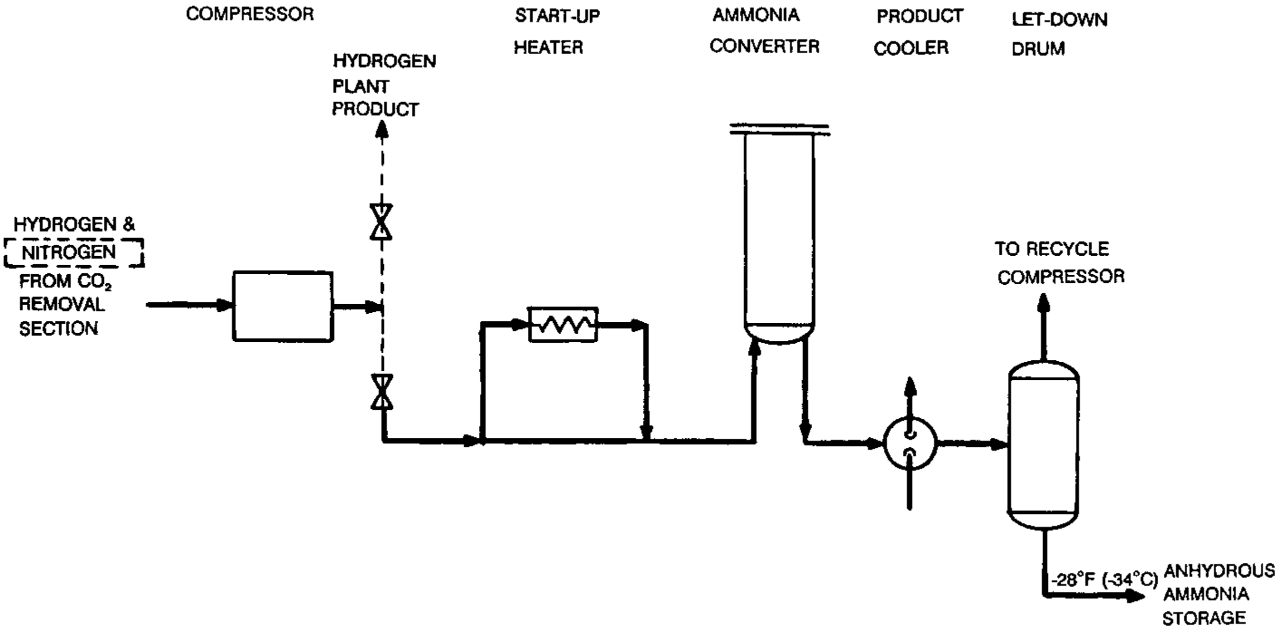
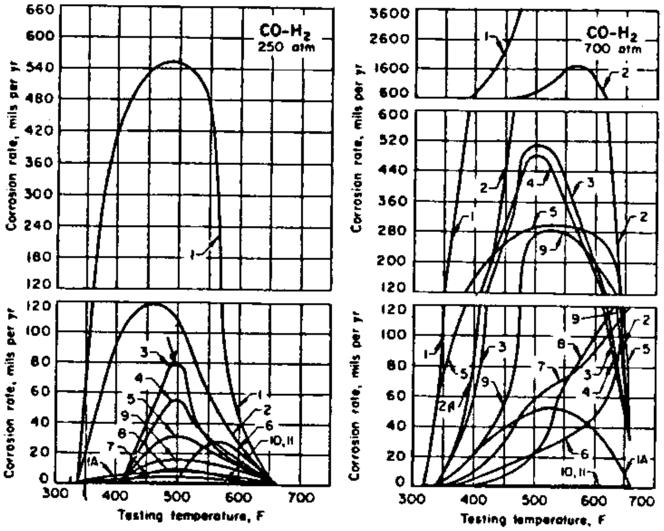


Figure 4.7 High pressure section of reforming plant[2]



| Metal | C | Mn | Si | Cr | Ni | Other |
|---|---|---|---|---|---|---|
| 1 ............ | 0.09 | ... | ... | ... | ... | 0.016 P |
| 1A[a] .......... | 0.09 | ... | ... | ... | ... | 0.016 P |
| 2 ............ | 0.12 | 0.75 | 0.25 | 3.36 | 0.08 | 0.30 Mo |
| 3 ............ | 0.095 | 0.38 | 0.35 | 13.70 | 0.37 | 0.34 Mo |
| 4 ............ | 0.17 | 0.52 | 0.46 | 13.90 | 0.57 | 0.24 Mo |
| 5 ............ | 0.08 | 0.58 | 0.60 | 16.20 | 0.20 | .... |
| 6 ............ | 0.49 | 17.80 | 0.63 | 2.89 | 0.05 | .... |
| 7 ............ | 0.09 | ... | ... | 17.3 | 8.22 | 0.59 Ti |
| 8 ............ | 0.106 | 0.40 | ... | 17.5 | 9.20 | 2.30 Mo |
| 9 ............ | 0.10 | 0.34 | 0.50 | 17.9 | 8.90 | 2.40 Cu |
| 10 ........... | 0.35 | ... | ... | 30.25 | 0.20 | .... |
| 11 ........... | 0.09 | 0.70 | 2.40 | 25.20 | 20.10 | 0.023 P |

[a] Same as item 1 except galvanized.

Figure 4.8 Effect of temperature and pressure on corrosion rate of several steels by 50-50 CO-$H_2$. Steels were manufactured in Germany and tested in pilot plants at the I.G. Farbenindustrie Ammonia Werke, Merseburg.[3]

Chapter
# FIVE

# Underground Piping, Production Equipment, and Tankage

## *INTRODUCTION*

Refinery and production piping are usually designed to ASME/ANSI[1] B31.3 specifications. Atmospheric storage tankage is designed to API[2] 650 specifications, and low-pressure tankage is designed to API 620 specifications. The design of pipelines containing liquids is covered by ASME/ANSI B31.4. Gas transmission pipeline design is covered by the ASME *Guide for Gas Transmission and Distribution Piping Systems*. Formerly, ASME/ANSI B31.8 was used for the design of gas lines; however, because of public concern over the large amount of stored energy in gas transmission lines, the U.S. Department of Transportation (DOT) asked ASME to incorporate its regulations and many provisions of ASME/ANSI B31.8 into an ASME code. The DOT has issued regulations for both gas lines (Title 49, Part 192) and liquid lines (Title 49, Part 195).

For refineries and production equipment, pipe is purchased according to an ASTM[3] or API specification, and supplementary requirements are vary rarely added. Supplementary requirements for pipelines are almost always included because pipelines consist of miles of identical material; specifications can thus be tailored to the job needs in dimensions, chemistry, and mechanical properties. When the pipeline is to be purchased in large tonnages, supplementing the API specification usually entails little or no cost penalty when using competitive bidding.

## *LINE PIPE*

### General

Most line pipe is manufactured by one of the following four methods:

- UOE (one pass of submerged arc welding on each side of a long seam);
- electric resistance welded long seam;
- seamless; or
- helical seam (most commonly made by using one pass of submerged arc welding on each side).

To minimize damage during handling, a minimum practical wall thickness has been established by some organizations (Table 5.1). Other organizations limit the diameter to wall thickness ratio of 100 to 105.

---

[1] American Society of Mechanical Engineers, New York, NY/American National Standards Institute, New York, NY.

[2] American Petroleum Institute, Washington, DC.

[3] ASTM, Philadelphia, PA.

### *UOE Line Pipe*

The UOE process for double submerged arc welded (DSAW) line pipe is shown schematically in Figure 5.1. Plate is prepared and formed into a "*U*." It is then pressed round into an "*O*," submerged arc welded, and expanded (E). Hence the label UOE. Figure 5.2 shows a typical cross section of a DSAW, plus an example of a toe crack that was found by nondestructive examination. A minimum of weld passes in this case, two is used to maximize production. UOE pipe is available in 16 to 64 in. (406 to 1,625 mm) diameters. It is the most commonly used pipe, particularly in large diameters, because of its high reliability when the long seam is inspected properly. The cost varies because the larger the diameter, the more cost competitive the pipe. Hydrostatic test records reveal that only about one failure occurs every 500 mi. (800 km) of test.

### *Electric Resistance Welded Line Pipe*

The process for manufacturing electric resistance welded (ERW) pipe is shown schematically in Figure 5.3. In this process, coils, rather than plate, are formed and then continuously electric resistance welded. Figure 5.4 shows a typical cross section of an ERW weld. In contrast to the submerged arc weld, the ERW weld is very narrow. The dark area between the weld and the remainder of the pipe is the heat-affected zone; only the light area in the very center is the weld. ERW line pipe is available in 4 to 48 in. (100 to 1,220 mm) diameters, with a 0.562 in. (14 mm) maximum wall thickness. However, it is only cost competitive in 6 to 26 in. (152 to 660 mm) sizes. Although its reliability is often relatively low (hydrostatic test records reveal that about one failure occurs every in 10 mi. [16 km] of test), it is commonly used because of low cost. With adequate specifications, good mill inspection, and selection of the best suppliers, one can improve its reliability significantly. The suppliers who offer a quality product have been able to get gas companies to permit the use of ERW in high-pressure gas (1,400 psi [9,653 kPa]) vs the old 200 psi (1,380 kPa) limit. Although the introduction of high-frequency welding currents has minimized the defects common to low-frequency current welded EWR pipe, they still occur. Therefore, inspection techniques should be stringent enough to make sure the following defects can be identified:

- hook cracks: caused by nonmetallic inclusions at the edge of the material that follow flow lines of the material as the weld is pushed together during welding (Figure 5.5);
- penetrators: areas of no weld caused by (1) nonmetallic materials on the edge to be welded that are not squeezed out; (2) arcing of electrical contacts; (3) insufficient or excessive upset during welding; or (4) short circuiting of welding current caused by burrs on welding surfaces (Figure 5.6);
- stitch welds: intermittent fusion caused by short repetitive variations in the welding heat (Figure 5.7).

### *Seamless Line Pipe*

The process for manufacturing seamless line pipe is shown schematically in Figure 5.8. In this process, a heated metal cylinder is pierced and then formed into the proper diameter and wall thickness. Seamless pipe is available through 26 in. (660 mm) diameter, but it is normally used only up to 16 in. (405 mm) diameter. Although seamless line pipe is the most expensive (15 to 25% above ERW), it is the most reliable. Even so, failures do occur. Hydrostatic test records reveal that about one failure occurs every 500 mi. (800 km) of test. Some mills produce seamless pipe that has a significantly higher failure rate; thus, it is important to ensure adequate quality control.

### *Helical Seam Line Pipe*

The process for manufacturing helical seam line pipe (previously called *spiral weld*) is shown schematically in Figure 5.9. As in ERW pipe, steel strip in coil form is used, but the coil is formed into a spiral. The seams are welded by the DSAW process as in UOE pipe. Some early prejudice against helical seam pipe resulting from unravel failures that occurred many years ago has been overcome. It is available from 6 to 100 in. (152 to 2,540 mm) diameters, but the smallest diameter commonly used for line pipe is 24 in. (610 mm). Problems are sometimes encountered in bending and lining up. Strict adherence to dimensional tolerances during manufacture can significantly reduce costs of line-up, clamping, and fabrication. As a result, large quantities of helical seam pipe have been used.

*Other Pipe Manufacturing Processes*

Induction welded long seam pipe (similar to ERW) is normally used for 2 to 4 in. (50 to 100 mm) pipe. Continuous (furnace) butt weld pipe is available in ¾ to 4½ in. (20 to 115 mm) pipe; however, it is never used in critical applications because of its very low reliability.

## Specifications for Line Pipe

API specification 5L is currently the principal line pipe specification. It combines the previous API 5L, 5LX, and 5LS. The selection of a grade depends on the strength-to-weight ratio and the pumping costs. ASTM specifications (e.g., ASTM A381) are often used for compressor station pipe, particularly for extruded headers.

The low-strength grades in API 5L are Grades A and B. Grade A has a 30 ksi (207,000 kPa) minimum yield strength, and Grade B has a 35 ksi (241,000 kPa) minimum yield strength. The seamless and welded (ERW, DSAW, GMA, or FBW) manufacturing processes are permitted.

The extra strength (X) grades in API 5L range from X42 to X70 grades. The number after the "X" refers to the specified minimum yield strength (i.e., X42 means line pipe with 42 ksi [290,000 kPa] minimum yield strength). The seamless and welded (ERW, DSAW, and GMA) manufacturing processes are permitted by API 5L. All grades are normally cold expanded to achieve dimensional uniformity and increased strength from strain hardening. API X52, one of the most commonly used grades, is about the maximum strength material that can be obtained by cold expansion without alloying additions, although alloying additions are also permitted. In the last six to seven years, 90% of the large diameter line pipe has been the X60 to X70 grades. The X70 grade is beginning to be used in the United States, and significant amounts of it have been produced in Europe and Japan because of the high pressures used in large diameter pipe and the consequent need for resistance to fracture. Small amounts of grain-refining alloying additions are used to obtain the desired strength and impact strength. In general, a minimum preheat (depending on composition and conditions) is required for welding the X60 and higher yield strength grades. Matching strength E8010G welding electrodes are available for welding the round seams.

The helical seam grades in API 5L range from A to X70. Cold expansion is not normally performed; however, some mills have installed and used expanders successfully.

## Common Supplementary Requirements for Line Pipe

As mentioned previously, specifications to supplement the API requirements are normally written to tailor the line pipe to the specific operating conditions (Appendix D). Typical requirements are as follows:

- limit cold expansion to 1.5% to avoid the degradation of impact properties;
- require the hydrostatic test to be at 90 to 100% of the specified minimum yield strength to maximize reliability. Often, the mills will pay for the pipe that fails in the field even when the pipe is tested at 100% of the specified minimum yield strength;
- require radiography of the end of long seams and of all jointer welds (when permitted) per API 1104;
- perform ultrasonic examination of long seams at the mill;
- require magnetic particle, liquid penetrant, or individual ultrasonic testing of the end 6 in. (150 mm) of the inside (sometimes the end 6 in. [150 mm] of the outside as well) for X60 and stronger pipe;

- prohibit the repair of parent pipe after cold expansion because the heat of welding reduces the strength gained from the cold expansion;
- require any repairs to be made using preheat and low-hydrogen electrodes to avoid underbead cracking. (Historically, a Vickers hardness of 350 has been considered the threshold for underbead cracking when cellulosic electrodes are used.);
- when repair is permitted, require radiography for through-wall repairs, magnetic particle examination for other repairs, and rehydrostatic test for all repaired pipe;
- require radiography per API 1104 after forming for skelp welds in helical seam pipe;
- in designing, limit weldolets to a maximum of 4 in. (100 mm) to minimize stress concentrations and avoid excessive heat input, which destroys the benefits of cold expansion; and
- induction bending should be per IPA-VIBS(4)-86. The weld in longitudinally welded pipe should be on the neutral axis. Ultrasonic wall thickness measurements should be made after bending. Copper bending shoes should be prohibited to avoid contamination that can cause cracking.

## *FITTINGS AND VALVES*

Fittings, including extruded multi-outlet headers, are usually made from material similar to pipe in chemical composition and heat treated to attain mechanical properties that match the pipe. Quenching and tempering are frequently necessary to meet fracture toughness requirements, particularly in the 60 ksi (414,000 kPa) and higher yield strength grades. Typical specifications governing pipe fittings are as follows:

| **Specification** | **Product Forms** | **Scope** |
|---|---|---|
| ANSI B16.5 | All (also valves) | Standard ASTM materials, dimensions, and pressure-temperature ratings |
| MSS(5)-SP-44 | Flanges | Grades F36 through F65, dimensions, chemistry, and mechanical properties, but no impacts |
| MSS-SP-75 | All welded fittings except flanges (includes headers) | Grades Y42 through Y65, full materials specification |
| ASTM A381 | Welded pipe(a)<br>(starting form for welded headers, tees, and elbows) | Grades Y35 through Y65, full materials specification |
| ASTM A694 | Forged flanges, fittings, and valves | Grades F42 through F65, full material specification, but no impacts required |
| ASTM A707 | Forged flanges | Yield strength 42 ksi (289,590 kPa) through 75 ksi (517,125 kPa), full material specification |

---

(4)International Pipe Association's Voluntary Standard for Induction Bending of Pipe.

(5)Manufacturers Standardization Society of the Valve and Fittings Industry, Inc., Vienna, VA.

[a] Usually fabricated from high-strength low-alloy plate such as ASTM A633, Grades C and E, or ASTM A737.

NOTE: Other standard specifications exist for low carbon, manganese, molybdenum, columbium and low carbon, nickel, chromium, molybdenum, and copper high-yield strength steels.

Valves are either cast or fabricated from plate. Specific requirements are covered in API 6D. Radiography of weld ends and repair welds is often specified.

## *ALLOYING ELEMENTS*

Requirements are placed on alloying elements in steel to control strength, weldability, and notch toughness.

### Chemistry

Typical limits for chemistry are as follows:

- carbon is usually limited to 0.20% in API X60 to X70 pipe and 0.26% in API X52 pipe to enhance weldability. Steels with 0.08% maximum carbon (low carbon martensite) are used to avoid the need to postweld heat treat in heavy sections;

- silicon is usually specified as 0.13 to 0.33% in the United States when notch toughness is required. Semikilled (no minimum silicon) steel is still commonly used in the United States;

- manganese is often limited to 0.8 to 1.6%. With less than 0.8% manganese, there is not enough manganese to tie up sulfur although, theoretically, a minimum of 0.4% manganese is needed. Also, a manganese-to-carbon ratio of 4-to-1 minimum is required for good notch toughness. Weldability decreases with a manganese content above 1.6%. Some specifications limit the manganese-to-silicon ratio to 3-to-1 minimum to maximize weldability;

- nitrogen is often limited to 0.009% maximum; however, this is usually possible only with basic oxygen steel. The limit on nitrogen is usually 0.012%. Although some nitrogen is desirable to increase strength, poor notch toughness and weld cracking occur as a result of nitride formation when nitrogen is too high. For nitrogen-bearing grades, a 250°F (120°C) preheat for welding is usually required. When specifications permit nitrogen in excess of 0.01%, the vanadium-to-nitrogen ratio should be specified as a minimum of 4-to-1 to avoid embrittlement. Some specifications require the aluminum-to-nitrogen ratio to be 2-to-1 or greater (to minimize strain age embrittlement), and they limit the aluminum to a maximum of 0.032% (to maximize toughness);

- vanadium and niobium (columbium) are the most commonly added grain refiners. Many users limit the sum of vanadium and niobium to 0.10% maximum. Vanadium provides the best increase in strength for the amount added. Vanadium and niobium cause strengthening from grain refinement and increase the strength by forming carbides and nitrides. Niobium also causes strengthening from precipitation hardening. Unless the niobium is greater than 0.025%, induction bending may drop the yield strength below the minimum in API X60 and higher grades. Niobium additions are usually limited by cost because double inoculation is often required. Vanadium additions are limited because of poor low-temperature properties, temper embrittlement, and underbead cracking when the concentration becomes too high. Postweld heat treatment will lower the fracture toughness of vanadium-bearing steels and weld metal, but it only reduces the fracture toughness of niobium-bearing weld metals;

- titanium and zirconium are occasionally used as grain refiners. Titanium is also a carbide former and is usually limited to 0.02%. Titanium is harmful to notch toughness when it exceeds 0.02%.

The zirconium content is usually limited to less than 0.2% to minimize martensite and massive upper bainite formation.

- molybdenum causes the formation of fine acicular ferrite in preference to polygonal ferrite in low-carbon steels. The molybdenum content is usually limited to less than 0.2% to minimize martensite and massive upper bainite formation; and
- rare earth metal (REM) additions and calcium-argon blowing are used to control sulfide amounts and shapes to increase notch toughness. Rare earth metals are cerium, lanthanum, and misch metal, which is a mixture of elements with atomic numbers of 57 to 71 that contain ~50% cerium. Usually, 1½ times the sulfur level is added. Problems with gas metal-arc welding have been reported when REMs exceed 0.02%.

**Weldability**

As discussed in the above section on chemistry, carbon and, to a lesser extent, other alloying elements have a significant effect on weldability. The effect is commonly expressed as the carbon equivalent (CE), which is defined as either:

$$CE = C + \frac{Mn}{4} \qquad (5.1)$$

or

$$C + \frac{Mn}{6} + \frac{(Cr + Mo + V)}{5} + \frac{(Ni + Cu)}{15} \qquad (5.2)$$

Preheat is not required for grades up to API X52 when the CE is less than 0.5 to 0.55 [by Equation (5.1)]. Equation (5.2) is commonly used in specifications. Limiting the Equation (2) CE to 0.42 for X60 through X70 grades is usually required. The maximum CE, based on preheat and interpass temperature, wall thickness, and heat input (travel speed), can be estimated from Figure 5.10. For example, for 0.42 CE and 1 in. (25 mm) wall pipe, a preheat of 68°F (20°C) would be required for a 12 KJ/cm heat input; however, if the heat input was reduced to 9 KJ/cm, then a 140°F (60°C) preheat would be required.

A refinement to the CE is the parameter Pcm, which has been developed to predict hydrogen cracking susceptibility as it relates to weldability. The Pcm chemistry parameter, applicable to most low-alloy steels having less than ~0.18% carbon, is defined as:

$$Pcm = C + \frac{Si}{30} + \frac{(Mn + Cu + Cr)}{20} + \frac{Ni}{60} + \frac{Mo}{15} + \frac{V}{10} + 5B \qquad (5.3)$$

Recently, this approach has been refined further by using a Phm parameter defined as:

$$Phm = Pcm + 0.075\log(Hef) + 0.15\log(0.017KtSw) \qquad (5.4)$$

where Hef = 0.50 Hf for cellulosic electrodes
Hef = Hf for low-hydrogen electrodes
where Hf = diffusible hydrogen content per 100 g of fused metal

Kt = stress concentration factor
= 3.5 for the root pass of a double V-groove
= 1.5 for the root pass of a simple V-groove

Sw = nominal stress acting on the weld metal (kgf/mm x mm)
= ksi/1.42
= 0.050 Rf for Rf less than 20 Sy
= Sy + 0.005 (Rf - 20 Sy) for Rf greater than 20 Sy
where Sy = yield strength (kgf/mm x mm)

Rf = intensity of restraint (kgf/mm x mm)
= 69 h
where h = thickness (mm)

After Phm is calculated, the time necessary to cool a weld to 212°F (100°C), called critical T100, is calculated where:

$$\text{Critical T100 (degrees C)} = 105{,}000(\text{Phm} = 0.276)^2 \tag{5.5}$$

The critical (minimum) preheat temperature (CT) is then calculated as follows:

$$CT = 52 - \frac{1{,}011}{(T)^{0.5}} + 74.2\exp(0.00054T) \tag{5.6}$$

where CT = critical preheat temperature (degrees C)
T = T100 cooling time to 212°F (100°C) in seconds

## *PROCESSING LINE PIPE*

Three major kinds of steel are used for large diameter line pipe operating under extreme climatic conditions:

- controlled rolled plate of a precipitation-hardening type containing columbium and vanadium;
- controlled rolled plate of an acicular-ferrite type; and
- superfine grain quenched and tempered plate.

Controlled rolling is most common and consists of the following three stages:

- simultaneous deformation and recrystallization;
- low temperature austenite deformation; and
- deformation in the mixed austenite-ferrite region.

In the first stage above 1,830°F (1,000°C), austenite grain size is reduced by repeated deformation and recrystallization. In the second stage, between 1,740°F (950°C) and the Ar transformation temperature, austenite grains are elongated and numerous deformation bands are produced, resulting in a very fine ferrite grain size. In the third stage, slightly below the Ar temperature, newly formed ferrite is deformed, providing higher strength and lower ductile-to-brittle transition temperatures.

As the finishing temperature decreases, the strength and toughness increase, as shown in Figures 5.11 and 5.12; however, optimum mechanical properties occur at a finish rolling temperature of ~1,490°F (810°C). At higher finish rolling temperatures, bainitic structures appear, causing a deterioration of the fracture appearance transition temperature. With finish rolling temperatures below 1,380°F (750°C), the brittle fracture resistance also deteriorates.

## *FRACTURE*

Long pipeline fractures such as that shown in Figure 5.13 can occur in either a brittle or a ductile manner. The fracture appearance and the fracture speed of ductile and brittle modes are quite different (as shown in Figure 5.14). Various standards have minimum requirements for fracture control. The common ones in the United States and Canada are as follows:

- API Appendix SR 6 requires 40% minimum shear in a dropweight tear test on 50% of the heats for 20 in. (508 mm) diameter API X52 or stronger pipe;
- API Appendix SR 8 covers Charpy V-notch testing on pipe with diameters of 16 in. (405 mm) or greater. The minimum energy acceptance level is specified by the purchaser; and
- Canadian Standards Association(6) Z184 requires 50 to 75% shear average, 35% minimum in a dropweight tear test.

These requirements are, of course, subject to change. In addition to the United States and Canada, many other countries have regulations containing specific requirements. Most users specify more than the minimum toughness required by the governing codes or regulations.

### Brittle Fracture

Brittle fractures of pipe typically follow a sinusoidal path, as shown in Figure 5.15. A high-speed photograph of brittle fracture reveals that the advancing tip is well ahead of any significant deformation on the pipe (Figure 5.16); the crack travels faster than the energy in the pipe can be released. The longest recorded brittle fracture was 8.1 mi. (13 km). It occurred in 1960 on a 30 in. (760 mm) diameter API X56 line that was being gas tested at 60% yield. Research by Battelle(7) reveals that brittle fractures can be avoided in steels other than quenched and tempered ones by specifying 85% average shear area in a dropweight tear test (DWTT) at the minimum service temperature. This is considerably more stringent than API 5L Appendix SR 6. Figure 5.17 shows that the percent shear in a DWTT differs only slightly from that observed in full scale tests. Meeting the 85% shear criterion also ensures that propagating ductile fracture will be arrested. Since the DWTT is applicable only to the pipe base metal, Charpy V-notch test criterion used to ensure that ductile fracture will not propagate. The Charpy V-notch approach is discussed in the next section.

### Ductile Fracture

Figure 5.18 shows a high-speed photograph of a ductile fracture. The energy release does not lag behind the crack tip as it does in brittle fracture. Ductile fracture follows essentially a straight path along the pipe rather than the sinusoidal path of brittle fracture. The scalloped fracture edges of a typical ductile fracture are shown in Figures 5.19 and 5.20. Ductile fractures do not normally propagate; however, if the

---

(6)Canadian Standards Association, Rexdale, Ont.

(7)Battelle-Columbus, Columbus, OH.

pipe material has low-energy absorption characteristics (e.g., low-shelf energy in impact tests), *propagating shear* can occur. The longest recorded ductile fracture was 1,000 ft (30 m). It occurred in the late 1960s on a 36 in. (915 mm) diameter API X65 pipe during testing. Research by Battelle shows that ductile fracture initiation can be avoided by specifying a minimum Charpy V-notch energy value, calculated by the following equation:

$$CVN = \frac{8Ac(\bar{\sigma})^2}{12\pi E} \ln \sec \frac{\pi}{2} \times \frac{M_T \sigma_H}{\bar{\sigma}} \tag{5.7}$$

where the terms are defined as:

CVN = Charpy V-notch upper shelf energy (ft-lbs)
A = section area or Charpy specimen beneath the notch ($in.^2 = 0.0827\ in.^2$ for a ⅔ size Charpy specimen)
c = one-half the total axial critical through-wall flaw length (total length = 2c [in.])
E = Young's modulus of elasticity (use $30 \times 10^6$ psi)
$M_T$ = the *bulge factor* correction; $M_T$ is closely approximated by $[1 + 1.255 (c^2/Rt) - 0.0135 (c^4/R^2/t^2]^{½})$
R = pipe radius (in.)
t = pipe wall thickness (in.)
$\sigma_H$ = hoop stress, psi
$\bar{\sigma}$ = flow stress (yield strength + 10,000) psi

Research by Battelle also shows that the Charpy V-notch energy required to prevent ductile fracture propagation can be calculated by the following equation:

$$E_{req} = 0.0108\,\sigma^2 (Rt)^{\frac{1}{3}} \tag{5.8}$$

where $\sigma$ = hoop stress, ksi
R = pipe radius, in.
t = pipe wall thickness, in.
$E_{req}$ = Charpy V-notch plateau energy for full size specimen, ft-lbs

The Charpy V-notch energy needed to arrest ductile fracture as a function of stress level for API X60 and X70 material in a 30, 36, and 42 in. (760, 915, and 1,065 mm) diameter pipe calculated from this equation is shown graphically in Figure 5.21 (A = 0.1237). The limitation of the Charpy V-notch test is that it is not a full thickness test, whereas the DWTT is. This means in thicknesses more than ~⅝ in., compensation in the form of increased energy absorption requirements is often specified for thick pipe.

When a submarine pipeline is to be installed using a lay barge, the yield strength is usually used for the stress in equations calculating the required impact strength. In addition, when the longitudinal stress due to laying exceeds ¾ of the maximum specified yield strength of the pipe, the minimum yield strength of the weld metal has been required to be 5 to 10 ksi above the minimum yield strength of the pipe. This prevents concentration of the strain in the weld metal that has resulted in fractures occurring during pipe laying.

Work sponsored by the AISI[8] Committee of Large Diameter Line Pipe Producers has produced an equation similar to Battelle's. The Committee points out that the impact energy required by these equations is insufficient to stop propagation when splits occur. Splits are parallel to the plane of the original plate surface and generally include groups that form a chevron pattern. To date, the exact metallurgical mechanism that causes splitting has not been established, but it is associated with low-finishing temperatures and high levels of mechanical working. *On-Line Accelerated Cooling* (OLAC), developed by Nippon Kokan K. K.,[9] appears to reduce the incidence of splitting or separating. Where splits cannot be avoided, crack arrestors (such as pipe sleeves) have been proposed. Using the above equation, one can see that crack arrestors reduce the rupture stress below the critical value. The distance between sleeves is a function of the cost and ease of replacing pipe, should it fail.

## INTERNAL CORROSION OF PIPING

High strength line pipe is often used for transporting oil or natural gas, whereas lower strength pipe is often used for water lines. Corrosion in water lines is primarily a function of oxygen content. If oxygen is removed mechanically (by deaeration) or chemically (by oxygen scavengers such as sodium sulfite), and if other corrosive gases (such as carbon dioxide and hydrogen sulfide) are not present, corrosion will not occur. Where oxygen or other corrosive gases will not be removed, internal coatings such as chemically cured epoxies, vinyls, and cement linings are normally used for corrosion protection. Organic coatings have a limited life because they contain pinholes and are subject to mechanical damage. Organic coatings require repair in 5 to 15 y, depending on the adequacy of the initial surface preparation and the specific type of coating. Internal cathodic protection is usually impractical because the limitations of the anode throwing power require anodes at approximately every 10 diameters. Other problems with internal cathodic protection are maintenance of the system inside the pipe and ability to pass a pig through the line because the anodes interfere with flow.

For cross country lines containing oil or gas, the corrosive constituents such as water, carbon dioxide, and hydrogen sulfide are usually reduced to a very low level before the fluid enters the line. The lost efficiency required to pump the unwanted constituents and the extra wall thickness required for corrosion allowance usually cannot be economically justified. Even with cleanup systems, some water will get into pipelines. In oil lines, oil soluble corrosion inhibitors usually prevent attack by water settling in low spots, etc. Gas lines are usually dehydrated to 60% of saturation to avoid corrosion from condensing water containing dissolved carbon dioxide. Molecular sieves that reduce water to 5 ppm have proved necessary in lines containing 100% carbon dioxide.

Whether corrosive constituents are removed at the oil or gas well or just before they enter cross country lines is a matter of economics (i.e., cost of the line, ease of replacement, etc). When dehydration or gas purification is not performed at the wellhead, severe corrosion may occur. Laboratory data on the corrosion rate vs partial pressure of carbon dioxide (Figure 4.5 in Chapter Four) often do not give a good estimate of the corrosiveness of the fluid because variables other than carbon dioxide partial pressure also affect metal loss. When the gas contains less than 15% oil (corrosion is low when there is more than 15% oil in the gas) and velocities are high, the chemical composition of the water, rather than the carbon dioxide partial pressure, appears to control the corrosion. The pH of the system calculated from the water composition has been used to determine whether or not a well is corrosive. To date, however, there is not a one-to-one correlation between the *in situ* pH and corrosiveness.

The limiting velocity to avoid erosion-corrosion according to API RP 14E is:

$$Ve = \frac{C}{\sqrt{\rho m}} \tag{5.9}$$

---

[8] American Iron and Steel Institute, Washington, DC.

[9] Nippon Kokan K.K., Fukuyama, Japan.

where $Ve$ = velocity in ft/s
$\rho m$ = gas/liquid mixture density in lbs/ft$^3$
$C$ = empirical constant usually taken as 100 for continuous service, although some companies use a constant as high as 160

Sand entrainment will reduce the C value greatly. The applicability of this equation to high-pressure gas-oil-water mixtures is highly questionable. No account is taken of the relative velocities or relative amounts of the phases. Currently, the best approach to minimize erosion-corrosion is to select conditions that maintain annular flow by use of the graph in Figure 5.22, in which the parameters are the following:

- $G$ = mass velocity of the gas phase in lbs/h/ft$^2$ of total pipe cross sectional area;
- $\lambda$ = $[(P_G/0.075)\ (P_L/62.3)]^{1/2}$;
- $P_G$ = density of gas in lbs/ft$^3$;
- $P_L$ = density of liquid in lbs/ft$^3$;
- $L$ = mass velocity of the liquid phase in lbs/h/ft$^2$ of total pipe cross sectional area;
- $\psi$ = $(73/\nu)\ [\mu_L\ (62.3/P_K)^2]^{1/3}$;
- $\nu$ = liquid surface tension in dynes/cm; and
- $\mu_L$ = liquid viscosity in centipoise.

Even when the system is designed for annular flow, large radius elbows and dead-leg tees should be used to minimize turbulence. When the system operates in the annular flow region, corrosion is low enough (because of the film on the wall) to permit the use of carbon steel. Although the velocities where annular flow exists must be calculated for each system, annular flow usually occurs at ~10 to 20 ft/s (3.0 to 6.1 m/s). Below the annular flow range, where stratified, wavy, plug, or slug flow occurs, corrosion inhibitors are required if the partial pressure of carbon dioxide exceeds 4 psi (28 kPa). Three phase corrosion inhibitors often prove most practical in gas-oil-water systems. Regardless of the type of inhibitor selected, a monitoring system should be installed to verify the effectiveness of the inhibitor.

When velocities exceed ~20 ft/s (6.1 m/s), bubbles or dispersed flow conditions result; SS's are used with these conditions. The martensitic SS's have performed well, but austenitic SS's (e.g., type 304L [UNS S30403] SS) are required for complete immunity to metal loss unless oxygen is completely absent.

There is some indication that the presence of mercury in the system reduces the corrosion resistance of martensitic SS's. In addition, the corrosion resistance of martensitic SS's is greatly reduced when they are tempered in the 750 to 1,100°F (400 to 590°C) range. Where the danger of pitting or stress corrosion cracking (SCC) from chlorides makes the use of austenitic SS's (e.g., type 304L SS) questionable, super SS's such as UNS S31803 (duplex) and UNS S31254 can be used. The suitability of super SS for service is a function of pH, $H_2S$, chloride ion concentration, and temperature. For example, UNS S31803 is reported to be limited to a maximum hydrogen sulfide partial pressure of about 5 psi at a sodium chloride concentration of 1 g/L at 176°F (80°C) and a pH of 2.7. Therefore, the suppliers of the particular type of super SS should be consulted when selecting one of these materials.

Both austenitic and super SS's have excellent resistance to erosion-corrosion in velocities up to 85 ft/s (26 m/s). Usually, copper base alloys are not considered because of poor resistance to hydrogen sulfide,(10) poor resistance to erosion, and low strength. Prevention of corrosion by coatings is usually impractical in production equipment because of limited life, as described previously, and because the coating can be blown off by sudden depressurization when the operating pressure is above ~650 psi (4,480 kPa).

## Internal Stress Corrosion Cracking by Aqueous Solutions Containing Carbon Monoxide and Carbon Dioxide

Transporting synthetic gas has resulted in SCC in some pipelines. For SCC to occur, carbon dioxide, carbon monoxide, and water must be present. The presence of oxygen greatly increases the severity of SCC. Dehydration is the most effective method of preventing this type of SCC.

---

(10) In copper alloy gas lines, hydrogen sulfide should be limited to 0.3 grains per 100 standard ft$^3$ (2.83 m$^3$), and the water dew point should be below the pipeline temperature at all times. In copper base alloy oil lines, the hydrogen sulfide should be limited to 1 ppm.

## Hydrogen Sulfide Cracking

Hydrogen sulfide cracking occurs in pipelines as well as in refineries and production wells, as discussed in the previous chapters. The same methods discussed previously (i.e., limiting the macrohardness of welds to Rockwell C 22 or the microhardness of welds to 260 to 280 Vickers) are used to avoid failure. These limits must be used with caution, as adherence will not prevent all forms of hydrogen cracking. The microstructure (quenched and tempered steel is more resistant than annealed or normalized steel) and the stress level (the higher the stress level, the greater the susceptibility) should be considered in marginal cases. Susceptibility to sulfide stress cracking can be estimated by following the procedure in NACE Standard TM0177.(11) This test consists of exposing a stressed specimen to acidified (with acetic acid to pH 3) sodium chloride saturated with hydrogen sulfide at ambient pressure and temperature. The specimen is considered resistant if it does not fail within 30 days.

Hydrogen generated from corrosion can cause problems when it recombines in the steel. This results in blisters in low-strength steel (e.g., API X42) or a cracking phenomenon called hydrogen-induced cracking (HIC), which is similar to lamellar tearing, in medium strength steels (e.g., API X60). In contrast to sulfide cracking (which is a form of hydrogen embrittlement unique to high-strength steels), hardness limits do not prevent HIC. A photomicrograph of this type of failure in medium strength steel is shown in Figure 5.23, and a schematic representation of this stepwise cracking phenomenon is shown in Figure 5.24. The susceptibility to attack is a function of the manganese sulfide stringer morphology. Elongated stringers (wafers) are most susceptible, whereas lozenge (ellipsoidal) shapes (Type I) are least susceptible. Susceptibility to stepwise cracking can be estimated by following the procedure in NACE Standard TM0284,(12) which consists of exposing an unstressed specimen in hydrogen sulfide-saturated (pH 5) synthetic seawater at an ambient temperature and pressure for 96 h. Low-finishing temperatures in thermomechanical rolling can be easily detected by this method. Typical acceptance standards are crack sensitivity ratio 10% maximum, crack length ratio 10% maximum, and crack thickness ratio 5% maximum.

Susceptibility to HIC can be minimized by:

- adding corrosion inhibitors;
- adding 0.25 to 0.3% copper and limiting the sulfur to 0.015% in steel for environments with a pH greater than 5; and
- calcium-argon treating the steel to control the shape and amount of inclusions and to produce material with maximum sulfur contents of 0.001% (9 ppm) and hydrogen of 1.5 ppm; unfortunately, steels with very low sulfur levels are more susceptible to cracking during welding than steels with high sulfur levels (0.005% and above).

## *EXTERNAL CORROSION OF PIPING*

Buried pipelines are subject to external corrosion from ground water and highly conductive soils. The corrosiveness of soils is often estimated based on soil resistivity measurement. The measurement is made with the *Wenner* four-pin method, which is used in conjunction with a *Vibroground*(13) and a *Miller*(14) 10-pin conductor set to determine the average electrical resistivities. A general relationship between corrosion and soil resistivity is as follows:

---

(11) NACE Standard TM0177, "Testing of Metals for Resistance to Sulfide Stress Cracking at Ambient Temperatures," NACE, Houston, TX, latest revision.

(12) NACE Standard TM0284, "Evaluation of Pipeline Steels for Resistance to Stepwise Cracking," NACE, Houston, TX, latest revision.

(13) Trade name.

(14) Trade name.

| Soil Resistivity (ohm-centimeter) | Corrosion Classification | Corrosiveness Constant (g) |
|---|---|---|
| less than 2,000 | very corrosive | 40 |
| 2,000 to 5,000 | corrosive | 30 |
| 5,000 to 10,000 | moderately corrosive | 20 |
| greater than 10,000 | progressively less corrosive | 10 or less |

Maximum pit depths as a function of time can be estimated by using the following equation:

$$D = g(t)^{\frac{1}{2}} \tag{5.10}$$

where D = pit depth (mil)
g = corrosiveness constant
t = time (y)

The most economical way to prevent external corrosion of underground piping is to coat the pipe and use cathodic protection.

## Coatings for External Corrosion Prevention

The generic coating systems commonly used for cross country pipelines are as follows:

- asphalt mastic (somastic);
- coal-tar enamel;
- asphalt enamel;
- polyvinyl chloride tape;
- polyethylene tape;
- polyethylene extrusions; and
- fusion-bonded epoxy.

Asphalt mastic is a heavy duty system that is shop-applied in thicknesses up to 1 in. (25.4 mm). Although asphalt mastics perform well, they are very costly. Their use is usually limited to river crossing and swamp areas. Coal-tar enamel has more than 50 y of successful performance underground, but it is subject to cracking when the temperature is below 20°F (-7°C), and there are environmental constraints. The EPA has shut down applicators in the middle of production because of air pollution. These problems rule out asphalt mastic and coal-tar enamel as feasible materials for most pipelines. In addition, coal-tar enamels are often ruled out because of long-term deterioration. Asphalt enamel is generally considered inferior to coal-tar enamel; therefore, its use is limited. Polyvinyl chloride tape is becoming obsolete because of the superior performance of polyethylene tape.

Polyethylene tape, polyethylene extrusions, and fusion-bonded epoxy are the remaining viable choices. All have been applied successfully, and all have had problems. To obtain a satisfactory coating, careful attention must be given to the following:

- materials specifications;
- coating application and procedures;
- coating inspection; and
- shipping and handling.

Failure to follow good practice in any of the above areas can result in an unacceptable coating. The special factors associated with these pipeline coating systems are as follows:

<u>Polyethylene tape</u>. There are more than 30 y of experience with polyethylene tape. It has been applied over the ditch, at the railhead, and in the shop. Surface preparation, an indispensable element in proper coating adhesion, is very difficult in an over-the-ditch operation. The generally poor performance of over-the-ditch tape applications has caused most pipeline companies to abandon them. Occasionally, however, one still hears of a pipeline company that has used its own highly trained crews and has obtained a good over-the-ditch application.

The most successful polyethylene tape applications are shop or railhead applied. The best results are obtained when handling is minimized, and some pipeline companies will not permit the application to be more than 100 mi. (160 km) from where the pipe is to be buried. The most practical method of minimizing handling is to position the application at a railhead. Even with railhead application, care must be taken to minimize damage. Cathodic protection current requirements will be minimized by reducing initial damage to the coating. Tapes are more susceptible to cathodic disbondment (loss of bond to the pipe resulting from hydrogen evolution, which is caused by the cathodic protection current) than other types of pipeline coating if the current densities become too high.

Cathodic disbondment is associated with over-the-ditch applications of tape and, to a lesser extent, with shop- or railhead-applied tape. Moisture penetration into the overlap is also a potential problem. For this reason, and to minimize damage during handling, a double wrap is preferred. The potential problems with polyethylene tape have been avoided in many cases, and there is a long history of successful applications.

The operating temperature range is from -10 to 150°F (-23 to 66°C); however, some tapes (e.g., Tapecoat High Temperature Machine Applied(15)) can be used up to 200°F (93°C).

<u>Extruded polyethylene</u>. Extruded polyethylene has been in general use for ~25 y. The polyethylene is applied by either a forward extrusion or a side extrusion process. The forward extrusion is presently limited to ~24 in. (610 mm) outside diameter pipe. The side extrusion can be used for sizes up to ~120 in. (3,050 mm). Extrusions are usually shop-applied but can be applied at the railhead if economics permit. In addition to excellent temperature (-40 to 150°F [-40 to 66°C]) and water resistance, the extruded polyethylene coatings exhibit excellent resistance to disbonding and soil stresses. The commonly used 50 mil (1.3 mm) thickness offers excellent resistance to handling damage. The bonding problems with early applications of the side extrusion appear to be solved. Field joints are often made with heat-shrinkable sleeves.

<u>Fusion-bonded epoxy</u>. Fusion-bonded epoxy has been widely used since the mid-1970s. The information available to date from cathodic protection current requirement data indicates little deterioration in properly applied fusion-bonded epoxy (or properly applied polyethylene tapes or extrusions). Fusion-bonded epoxy displays excellent chemical resistance, excellent resistance to cathodic disbonding, and excellent temperature resistance (-100 to 150°F [-73.3 to 66°C]). Some formulations can be used up to 200°F (93°C), though there are recent indications of problems with fusion-bonded epoxies on hot lines. Good temperature resistance is associated with good impact resistance, which minimizes handling damage. A near-white metal-blasted surface (SSPC(16)-10) is required. Since the fusion-bonded epoxy film is relatively thin (12 to 16 mil [0.3 to 0.4 mm]), it is more susceptible to slivers and other imperfections on the steel surface than thicker coatings. Because of this, a specific pinhole density is permitted, although other coatings are required to be pinhole-free. There have been problems meeting the pinhole limitations on some pipelines, which has led to costly repairs. The coating must be cured (~400°F [200°C]), and problems have occurred as a result of improper curing. Curing at a lower temperature results in a more flexible coating, but the softer coating is more prone to disbonding. Field joints are either epoxy-coated or taped. Concern has been expressed over strain aging occurring during the curing of the epoxy, which reduces the toughness of the steel pipe. To date, the seriousness of the potential strain aging problem is controversial. While some

---

(15)Trade name.

(16)Steel Structures Painting Council, Pittsburgh, PA.

companies have abandoned the use of fusion-bonded epoxy because of the problems associated with it, there is still a trend in the pipeline industry toward its use.

### Cathodic Protection for External Corrosion Prevention

All coating systems mentioned above will exhibit some damage and pinholes. To prevent corrosion in these areas, cathodic protection is applied to cross country pipelines. Table 5.2 shows how current density ranges vary depending on the type of coating used and the percent of bare surface anticipated. It must be emphasized that to ensure a cathodic protection system is operating properly, potential measurements must be taken along the system. NACE Standard RP0169[17] contains recommendations on minimum requirements for control of external corrosion on underground or submerged metallic piping systems. Recently, there has been discussion that the NACE recommended practice should be revised so the errors arising from soil path IR drop are eliminated before using the -0.85 volts vs $Cu/CuSO_4$ half-cell criterion for protection. This is because significant reduction in the corrosion rate is not obtained until the electrochemical potential of the metal surface is within about 0.05 volt of the protection criterion voltage.

Although using cathodic protection does provide some latitude for coating quality, cathodic protection will not compensate for poor coating quality. The cathodic protection current requirements become excessive on poorly coated lines. Improperly applied polyethylene tapes and fusion-bonded epoxy coatings have resulted in the lines having to be dug up and recoated. The same thing could happen to any improperly applied coating.

### External Stress Corrosion Cracking of Underground Piping

Throughout the past decade, there have been about two to three reports per year on SCC of buried pipelines. The cracking occurs on the outside of the pipe under disbonded coatings of lines that are under cathodic protection. The failures have been located where the line is warmest (greater than 100°F [38°C]) (e.g., within 10 mi. [16 km] downstream from compressor stations). Research indicates that the sodium carbonate- bicarbonate environment caused by the cathodic protection will cause SCC if sufficient protective current cannot get to the surface to polarize it below the narrow potential-pH band at which the material is susceptible (see Figure 5.25). This is often the case under disbonded coatings. Most of the failures have been under coal-tar enamel coatings. To date, no failures of fusion-bonded epoxy-coated pipelines have been reported. Hydrostatic testing is presently the best means for detecting leaks from stress corrosion cracks. Good surface preparation, which is most easily attained with shop-applied coatings, is currently the best preventive measure.

## *TANKAGE*

Storage tanks built in accordance with API 650 are commonly made of mild steel. Notch tough steel is required when the design metal temperature is 50°F (10°C) or below (lowest one day mean temperature of 35°F [2°C] or below). High-strength steels are sometimes used in large diameter tanks to minimize cost by reducing the required thickness. Care should be exercised when selecting high-strength steels for fluids containing hydrogen sulfide because of the potential for sulfide stress cracking. As a minimum, the hardness of the welds should meet NACE Standard RP0472.[18]

### Corrosion in Petroleum Storage Tanks

Corrosion in atmospheric storage tanks can be divided into three zones: the tank roof, the walls, and the bottom. Corrosion on the underside of the tank roof is controlled by the relative amount of air and

---

[17] NACE Standard RP0169, "Control of External Corrosion on Underground or Submerged Metallic Piping Systems," NACE, Houston, TX, latest revision.

[18] NACE Standard RP0472-87, "Methods and Controls to Prevent In-Service Cracking of Carbon Steel (P-1) Welds in Corrosive Petroleum Refining Environments," NACE, Houston, TX, latest revision.

hydrogen sulfide as well as the temperature. As can be seen in Figure 5.26, the worst condition is 0.5% hydrogen sulfide. Inorganic zinc coatings are used most commonly for corrosion protection of the roof area. Inert gas blankets can also be used to prevent corrosion in cone roof tanks.

The corrosion rate as a function of tank wall height is shown in Figure 5.27. Corrosion in light refined products (API density, 50 degrees or lighter) is higher than that in heavier products because oxygen solubility is higher. Corrosion is high in the 80 to 90% level of the side wall as a result of the mechanism shown in Figure 5.28.

Tank bottom corrosion is a function of the water layer that exists on the bottom of most tanks. The presence of sulfate-reducing bacteria, characterized by shiny pits, is more of a problem in heavy stocks because oxygen cannot reach the bottom. The most common way to control tank bottom corrosion is to drain the water from the tank bottom periodically. Both epoxy and polyester coatings reinforced with chopped glass fiber have been used successfully in places where severe corrosion has occurred. For new tanks in which corrosion is expected, coal-tar epoxy is usually specified for the bottom. Corrosion of the underside of the tank bottom does not usually occur if a proper oil and sand base is used. Cathodic protection is used when water cannot be prevented from contacting the underside of the tank bottom.

## Low-Pressure, Low-Temperature Tanks

Liquid ammonia, liquefied propane gas (LPG), and liquefied natural gas (LNG) would not be expected to cause corrosion problems since they are stored at low temperatures (-28, -44, and -260°F [-33, -42, and -162°C] respectively). However, there have been reports of SCC in fully refrigerated ammonia storage tanks. There have also been reports of sulfide cracking in the heat-affected zones of LPG spheres as a result of trace amounts of hydrogen sulfide in the LPG. The primary concern in storing these fluids is resistance to brittle fracture. Appendix A lists common materials suitable for the low temperatures at which these fluids are stored. More detailed requirements for liquid ammonia and LPG tanks are included in Appendix R of API 620 and BS(19) 4741. More detailed requirements for LNG tanks are contained in Appendix Q of API 620 and BS 5387. Liquid ammonia tanks and small LPG tanks are usually single walled, and large LPG tanks are usually double walled (Figure 5.29). Ultrafine grain materials for LPG tanks must be used with caution because failure can result from excessive weld repair, which causes strain damage in the base metal.

There have been a few steel wire-wrapped concrete tanks used for LNG; however, the majority are of double wall construction. As shown in Figure 5.29, the inner tank is separated from the outer tank by insulation. The inner tank is made of either 9% nickel steel (usually economical for large tanks), type 304 (UNS S30400) SS, or aluminum (usually economical for small tanks).

Nine percent nickel steel is usually used in the quenched and tempered condition. For the most reliable construction, carbon should be limited to 0.08% (0.05% over 1½ in. [3.8 cm]). This is a compromise between toughness (which requires low carbon) and strength (which requires high carbon). Sulfur should be limited to 0.01% to enhance toughness. To minimize temper embrittlement, the following limits should be considered: 0.1% molybdenum; 0.012% phosphorus; and 0.4 to 0.7% manganese. Tempering should be performed at 1,075°F ±10°F (580°C ±12°C). Below 1,050°F (565°C), temper embrittlement can result; above 1,100°F (595°C), austenite will form, and upon cooling, transform to martensite, thereby lowering the toughness. In addition, Charpy V-notch impact strength should be 60 ft/lb (81 J) average transverse at -30°F (-34°C). For 9% nickel steel with thicknesses greater than 1 in. (25.4 mm), fracture mechanics testing should be considered to determine the maximum allowable flaw size. The maximum thickness at which good properties can be obtained is 2 in. (51 mm). The minimum thickness should be ⅜ in. (9.5 mm) because of the potential for warpage from the severe blasting required for descaling 9% nickel steel.

Using fracture mechanics testing or API BS 5387, design stresses can exceed those allowed by API 620 (Appendix Q) (31.7 ksi [218,600 kPa]). In these cases, the allowable stress is limited to two-thirds of the yield strength. Since the Inconel(20) weld metal normally used to join 9% nickel is weaker than the base metal, the yield strength of the weld metal limits the allowable design stress. The maximum yield strength currently attainable with Inconel-type electrodes is 60 ksi (414,000 kPa). The 60 ksi (414,000 kPa) minimum yield strength Inconel-type electrodes minimize the thickness required in the tank wall and, consequently,

---

(19)British Standards Institute, London, England.

(20)Trade name.

the cost. Experimental ferritic 13% nickel electrodes with strength matching the 9% Ni-base material are now being tested.

## TABLE 5.1
## Minimum Practical Wall Thickness for Thin Wall Pipe

| Diameter (inches) | Minimum Wall Thickness[a] (inches) |
|---|---|
| 2.315[b] | 0.125 (0.154) |
| 4.5 | 0.154 |
| 8.625 | 0.156[c] |
| 10.750 | 0.188 |
| 12.750 | 0.188 |
| 14. | 0.203 |
| 16. | 0.203 |
| 18. | 0.219 |
| 20. | 0.250 |
| 24. | 0.250 |
| 26. | 0.250 |
| 30. | 0.250 |
| 32. | 0.281 |
| 36. | 0.312 |
| 38. | 0.312 |
| 40. | 0.344 |
| 42. | 0.344 |
| 48. | 0.375 |

---

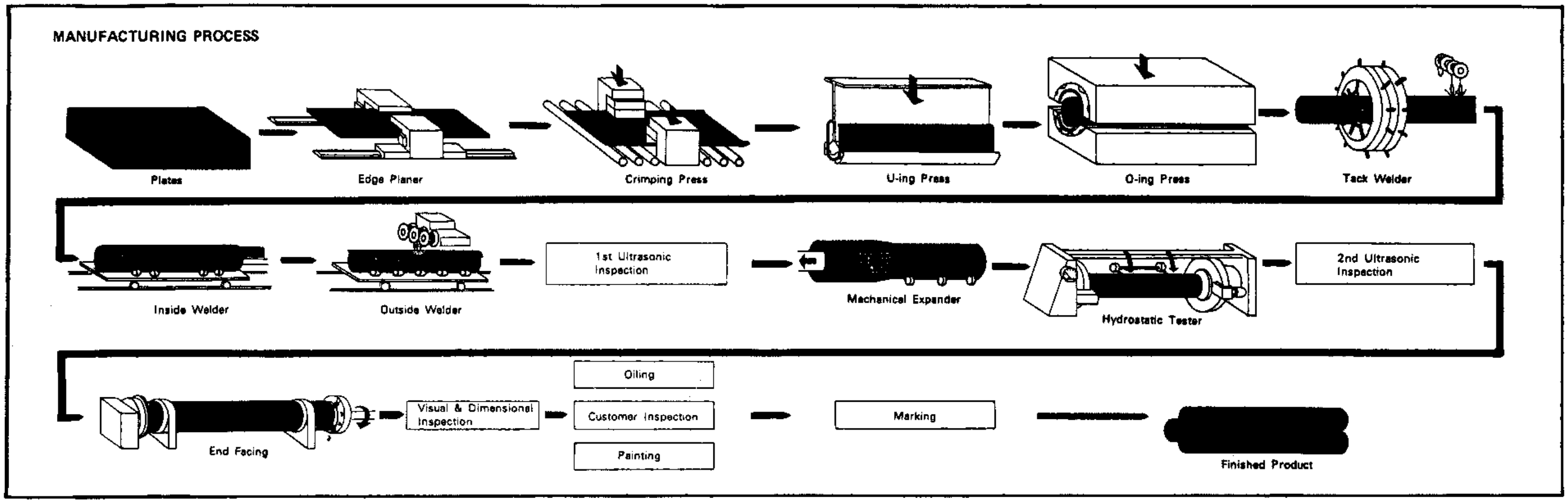
[a] The minimum the mills will offer for submerged arc welded pipe is 0.250 in.

[b] Not practical to electric weld.

[c] Limited by welding at and below this thickness.

## TABLE 5.2
## Typical Cathodic Protection Current Density Ranges

| Coating | Bare Surface Area Expected over 20 y Design Life (percent) | Range of Current Density Requirements ($ma/ft^2$) |
|---|---|---|
| A. Shop Applied | | |
| Fusion-Bonded Epoxy | 2 | 0.02 to 0.2 |
| Polyethylene Extruded | 2 | 0.02 to 0.2 |
| Coal-tar | 3 | 0.03 to 0.3 |
| Asphalt | 3 | 0.03 to 0.3 |
| Bituminous | 3 | 0.03 to 0.3 |
| Mastics | 3 | 0.03 to 0.3 |
| Tapes | 5 | 0.05 to 0.5 |
| B. Field Applied | | |
| Coal-tar | 6 | 0.06 to 0.6 |
| Asphalt | 6 | 0.06 to 0.6 |
| Bituminous Mastics | 6 | 0.06 to 0.6 |
| Tapes | 10 | 0.1 to 1 |
| C. None (bare pipes) | 100 | 1.0 to 10 |



General Description
UOE pipe is made from plate. After being subjected to automatic ultrasonic inspection, each plate is trimmed and beveled on the side edges and then transferred to a U-ing press where it is formed into a U-shape. It is subsequently formed into a round shell on an O-ing press. The straight seam is submerged arc welded from both the inside and outside. Mechanical expansion turns the pipe into an exactly round, straight section. Each length of pipe is hydrostatically tested before final inspection. The defect-free quality of Kawasaki UOE pipe is assured by both advanced inspection equipment, including full-length weld automatic ultrasonic tester (AUT), and qualified inspection personnel with wide experience.

Figure 5.1 UOE Pipe[1]

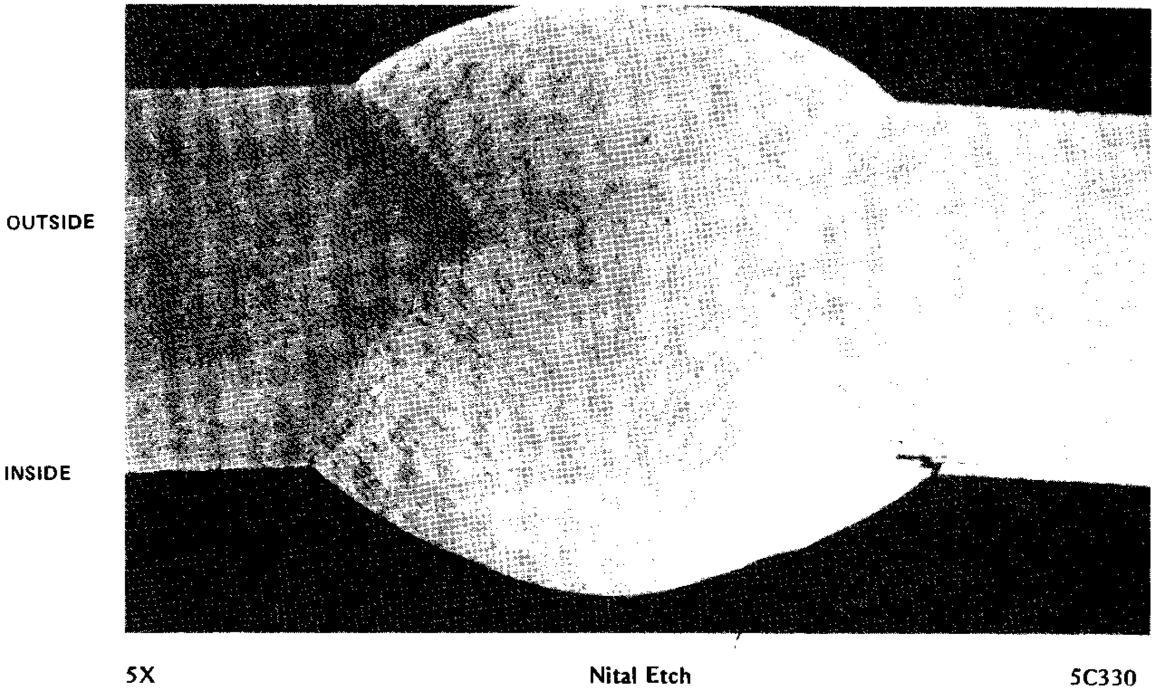
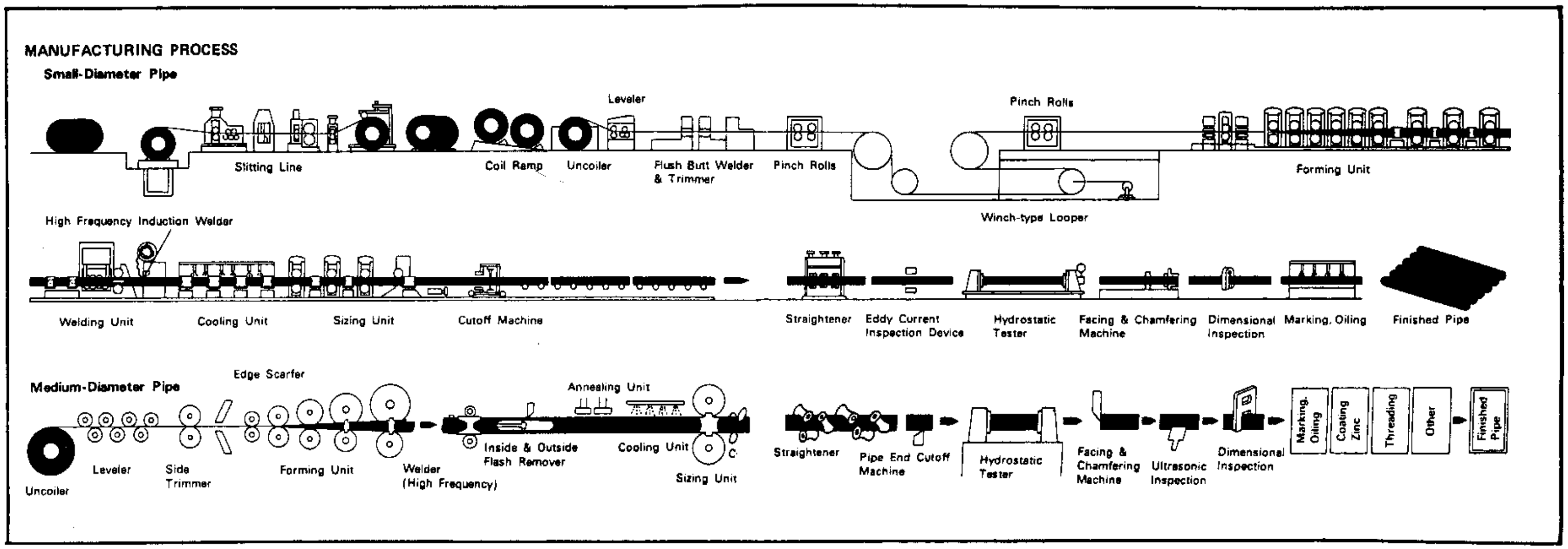


Figure 5.2 Toe cracks in the HAZ of a DSA weld[2]



General Description
Electric resistance weld pipe is made from strip in coil form. After being uncoiled, flat strip is progressively rounded as it passes through a series of vertical and horizontal forming rolls before welding. Small-diameter pipe is welded by the high frequency induction method and medium-diameter pipe by the high frequency electric resistance method. Continuously welded pipe is cut to the specified lengths by a flying cutoff machine, and each length goes through straightening, hydrostatic and inspection equipment before it becomes a finished product with the desired diameter.

Figure 5.3 Electric Resistance Weld Pipe[1]

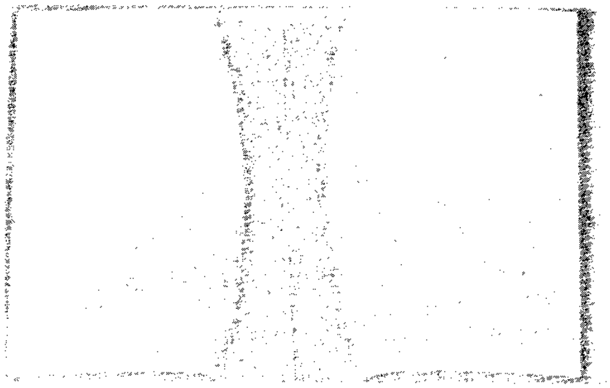


Figure 5.4 High frequency weld[2]

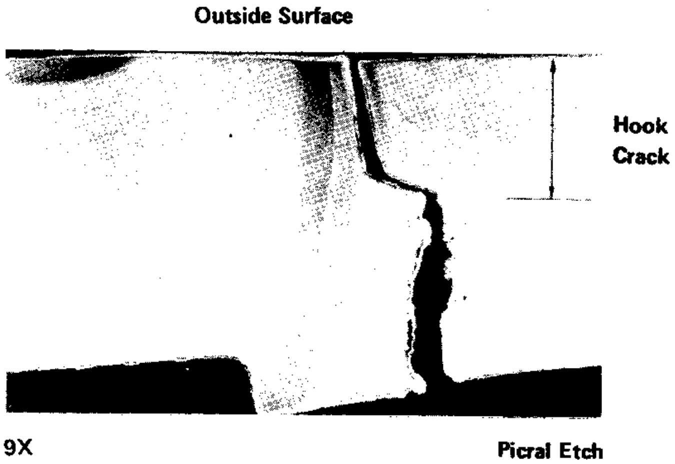


Figure 5.5 Appearance of a hook crack in ERW weld[2]

Figure 5.6 Through wall penetrators in ERW weld[3]

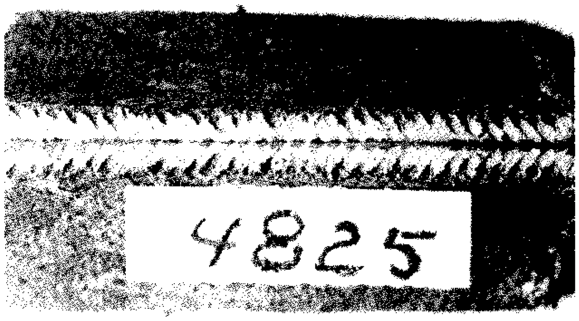
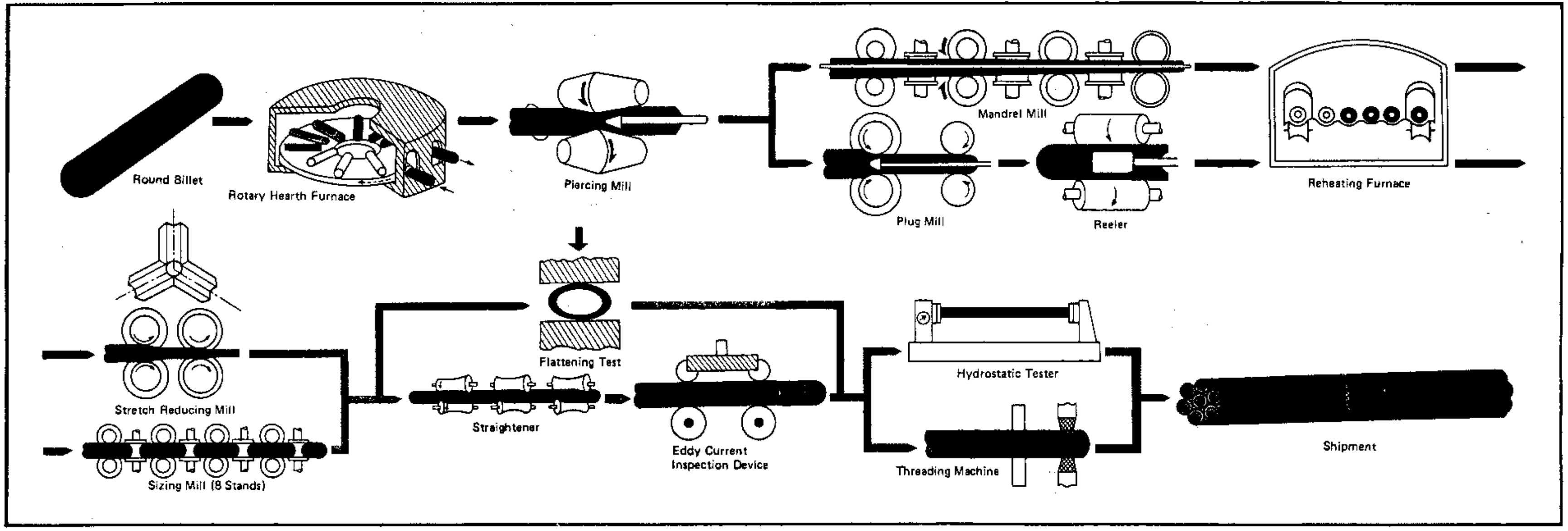


Figure 5.7 Stitch weld (intermittent fusion) in ERW weld[4]



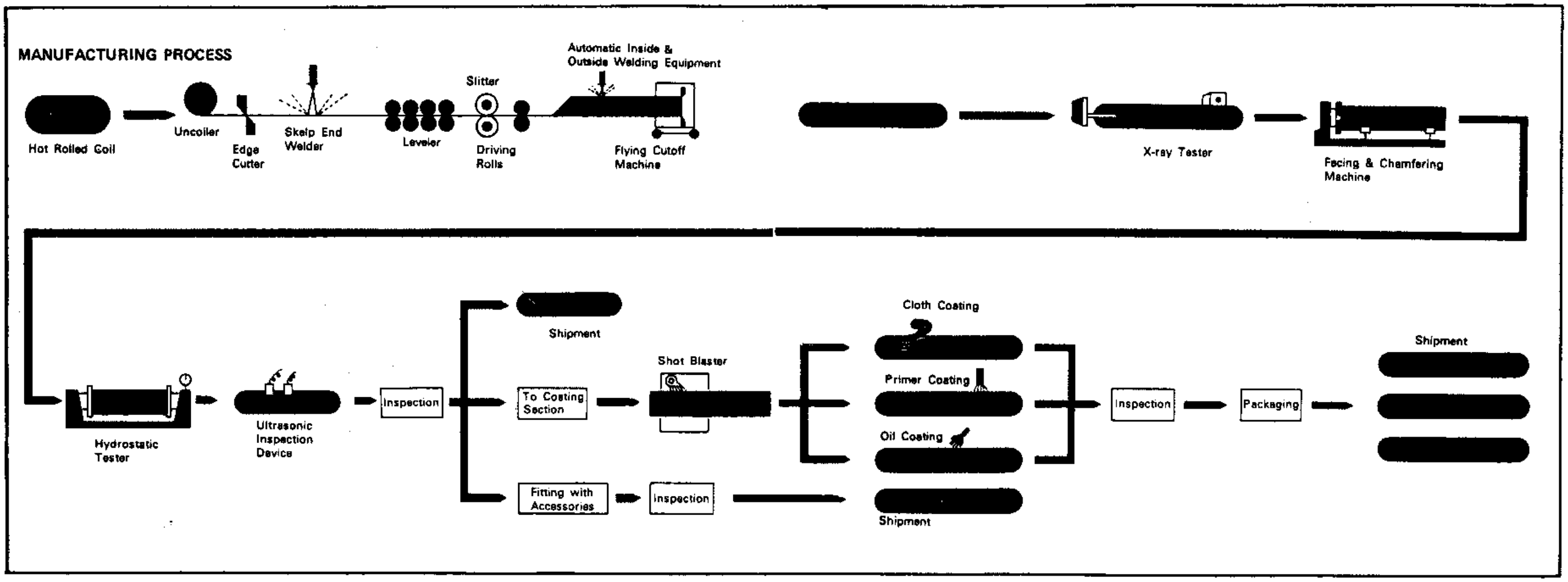
### General Description

Seamless pipe and tubes are produced either by the mandrel mill or the plug rolling mill process. The former process is used for producing small-diameter pipe and the latter for medium-diameter pipe. On either type of mill, each heated billet is peirced through its center on a piercing mill. The pierced billet then moves on to a mandrel or plug rolling mill where it is rolled with a mandrel bar or plug inserted in it. After withdrawal of the mandrel or the plug, the rolled shell is reheated before being processed on a stretch reducing mill or a sizing mill where the desired OD and wall thickness are obtained.

Besides there hot rolled pipe and tubes, Kawasaki Steel also produces cold drawn pipe tubes for use where closer dimensional tolerances are required.

To ensure consistently high quality, the company conducts thorough testing and inspection, using advanced equipment including eddy current, ultrasonic and magna flux devices.

Figure 5.8 Seamless Pipe[1]



General Description
Spiral weld pipe is made from strip in coil form. After the strip is uncoiled, it proceeds to a trimmer and then to forming rolls that shape it into spiral form. The spiral seam is submerged arc welded automatically and continuously—first on the bottom of the rotating pipe from the inside, then on the top from the outside. The welded pipe is cut to the specified lengths by a flying cutoff machine. X-ray and ultrasonic inspection ensures consistently high quality spiral weld pipe.

Figure 5.9 Helical Seam Pipe[1]

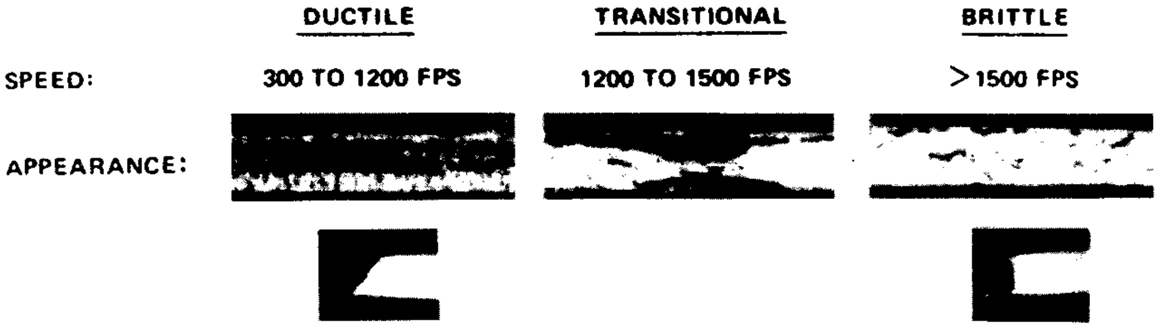


Figure 5.14 Fracture characteristics observed from line pipe through the transition temperature[2]

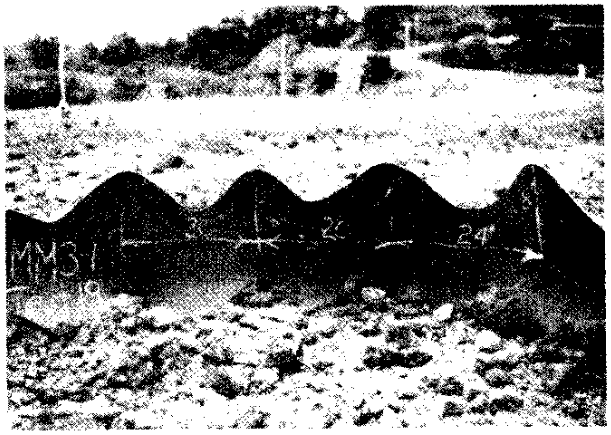


Figure 5.15 Sinusoidal brittle fracture[2]

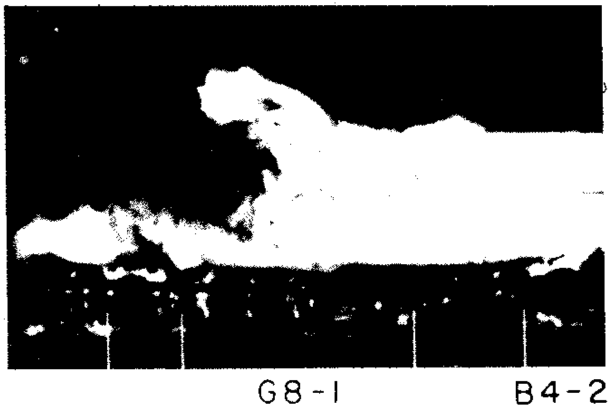


Figure 5.16 Photograph of brittle fracture from high speed movie (3,000 frames/sec)[2]

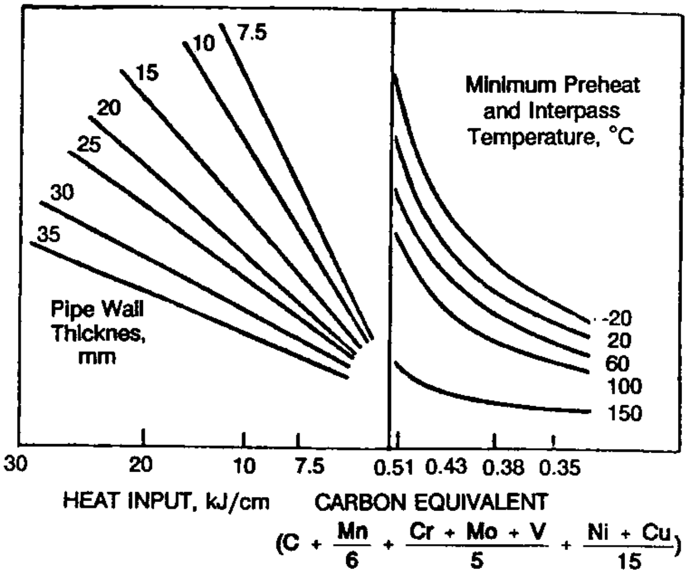


Figure 5.10 The permissible maximum carbon equivalent for butt welds in line pipe using cellulosic (EXX10) electrodes based on minimum preheat and interpass temperature, pipe wall thickness, and heat input.[5]

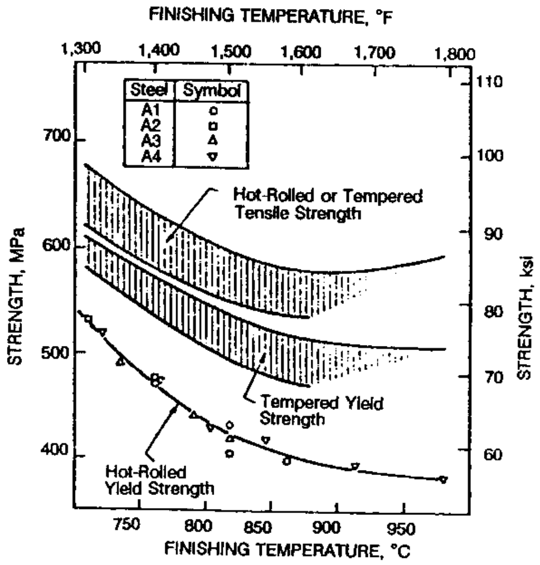


Figure 5.11 Effect of finishing temperature and tempering on the strength of steels A1 to A4.[4]

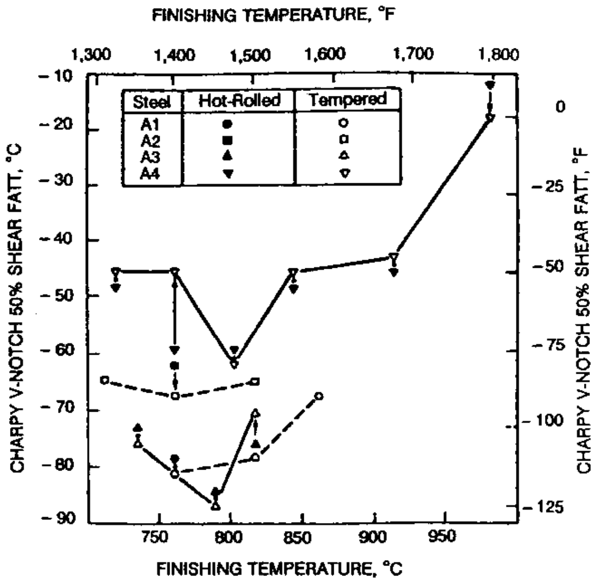


Figure 5.12 How finishing temperature affects the Charpy V-notch 50% shear fracture-appearance- transition temperature (FATT) of steels A1 to A4.[5]

Figure 5.13 Long distance rupturing of pipe tested with gas[11]

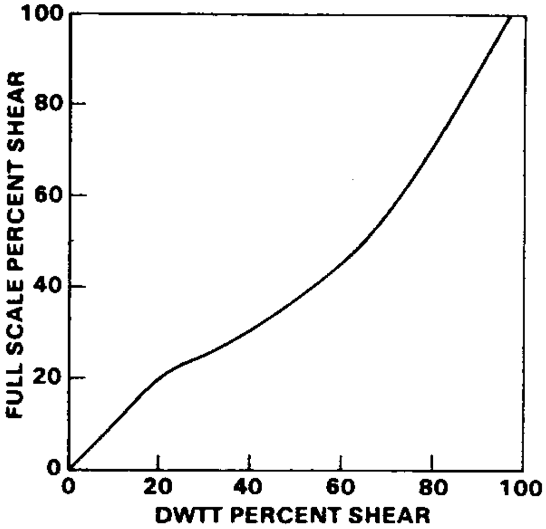


Figure 5.17 Relationship between DWTT percent shear and full-scale pipe percent shear of the fracture surface[2]

Figure 5.18 Photograph of ductile fracture from high speed movie (3,000 frames/sec)[2]

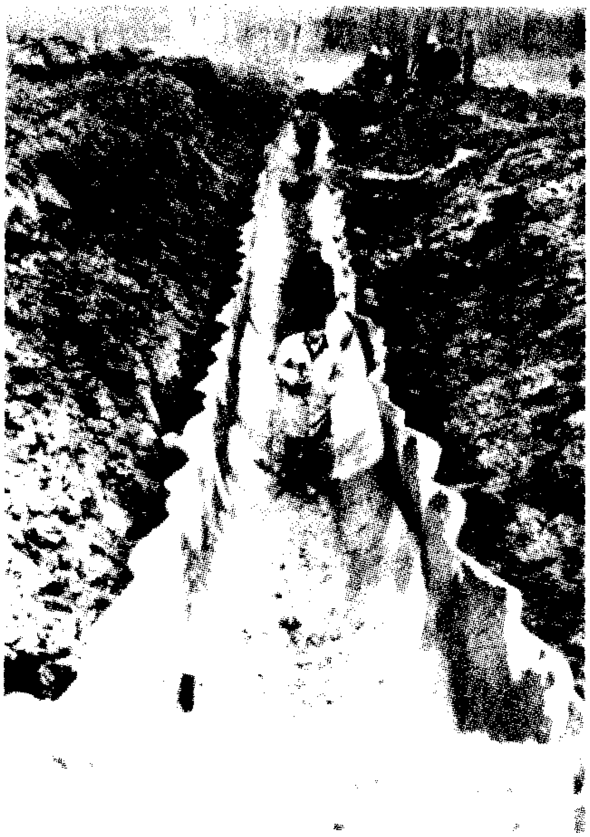
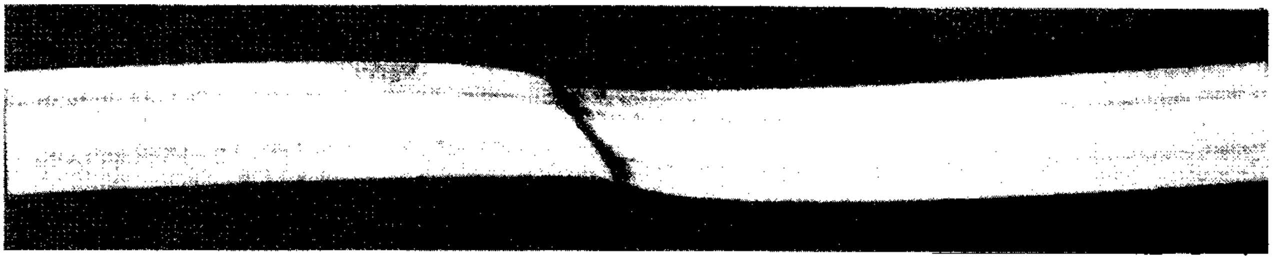


Figure 5.19 Ductile fracture of large diameter line pipe showing scalloped fracture edges[2]

"Propogating" Shear 23226



"Tearing" Shear 23506

Figure 5.20 Section across two types of ductile fracture[2]

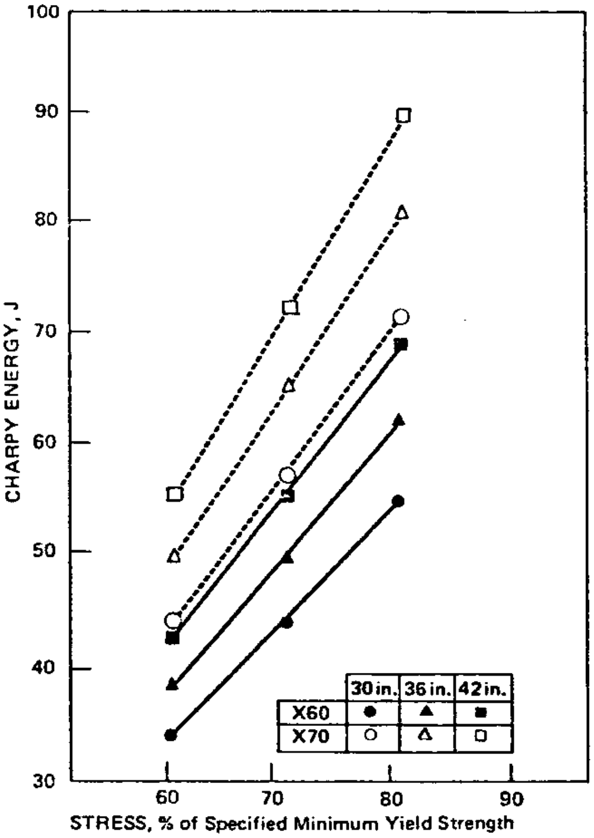


Figure 5.21 The Charpy V-notch energy needed to produce fracture arrest (after Maxey).[5]

The Charpy V-notch absorbed energy is most commonly used to specify a material's resistance to propagating ductile failure. In general, higher absorbed energies are required for higher operating stress levels and pipes having larger diameters, higher strengths, and heavier wall thicknesses. Maxey[5] has proposed that for certain pipe geometries, yield strengths, and stress levels, the Charpy energy required to provide fracture arrest is given by the following formula:

$$C_v = 0.0873\sigma_H^2(Rt)^{\frac{1}{3}} A_c$$

where $C_v$ = minimum Charpy V-notch energy that will produce fracture arrest. (ft./lbs.)

$\sigma_H$ = operating stress level (ksi)

R = pipe radius (in.)

t = pipe thickness (in.)

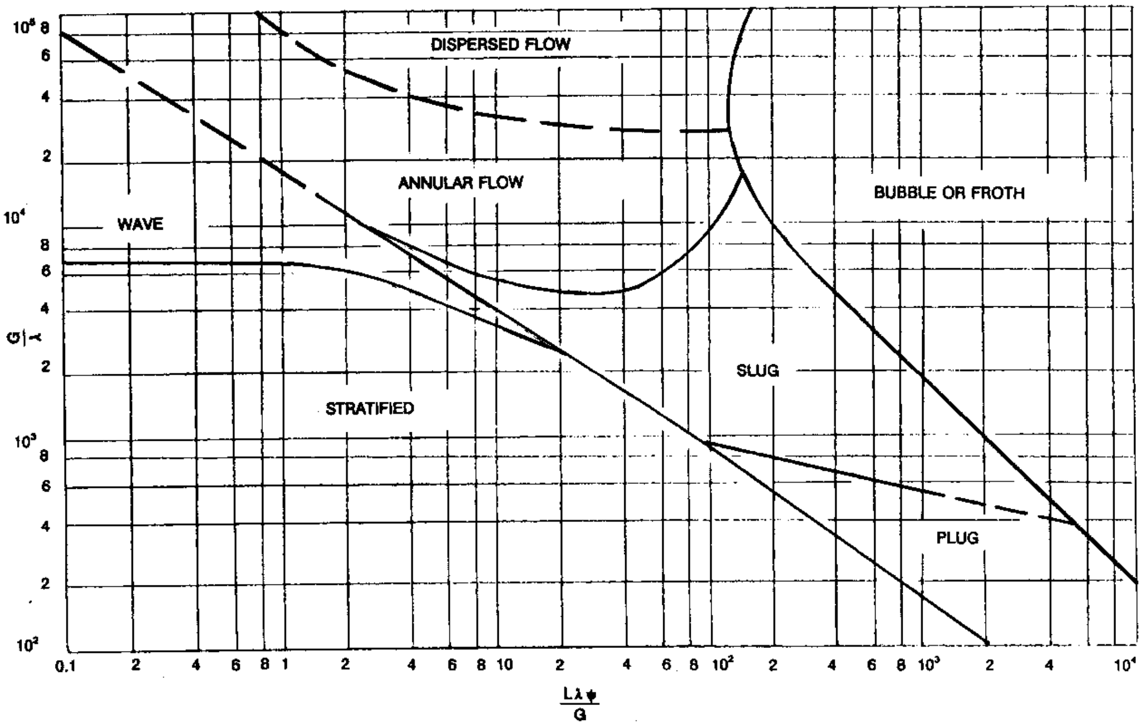


Figure 5.22 Gas/liquid phase flow[8]

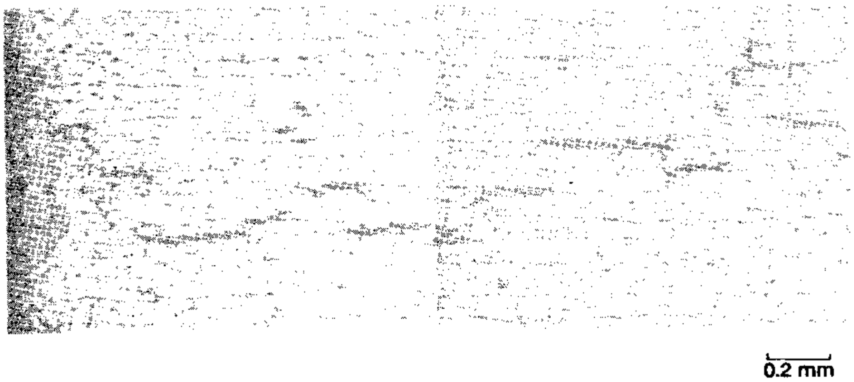


Figure 5.23 Optical micrograph of HIC penetrating the examined surface (x-z) in the specimen[7]

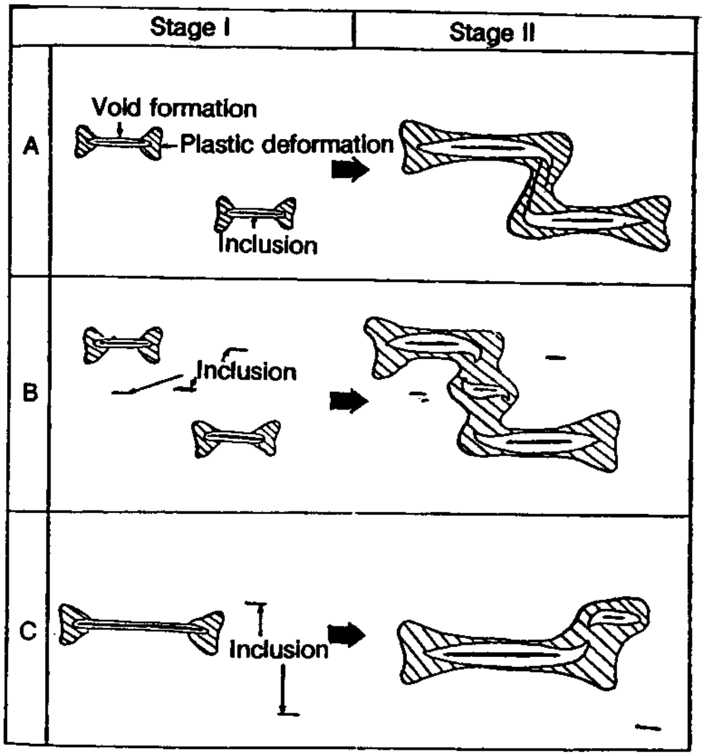


Figure 5.24 Schematic representation of step-wise cracking process.[7]
Creation site of a small crack is indicated by inclusion, for example.
(A) The case of direct joining which could occur at close distance.
(B) Creation of small cracks by the interaction of two main cracks which could occur at long distance. Joining between main crack and a small crack takes place by the way of (A).
(C) Creation of small crack in front of main crack.
Step-wise crack could grow by repeating this process.

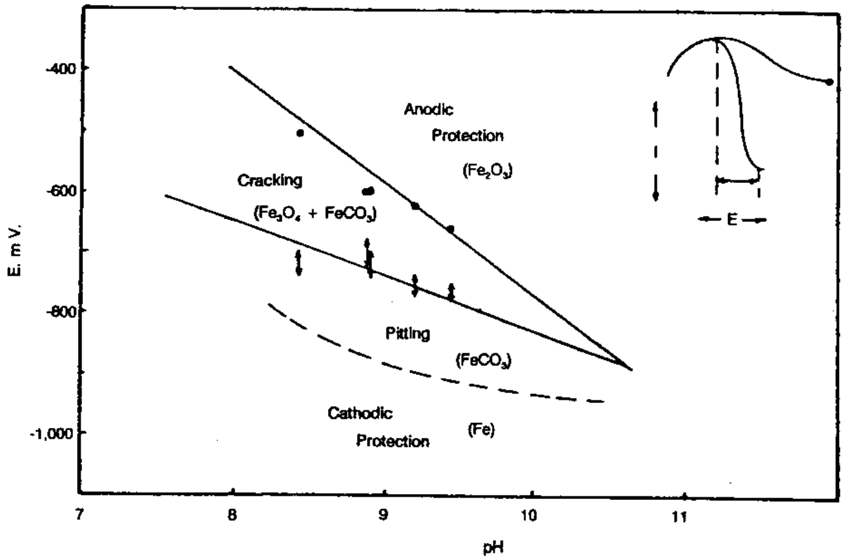


Figure 5.25 Comparison of the results from stress corrosion tests with those from polarization curves at fast and slow potential sweep rates for different carbonate-bicarbonate solutions, indicating the extent to which the experimentally observed cracking range can be predicted from electrochemical measurements.[8]

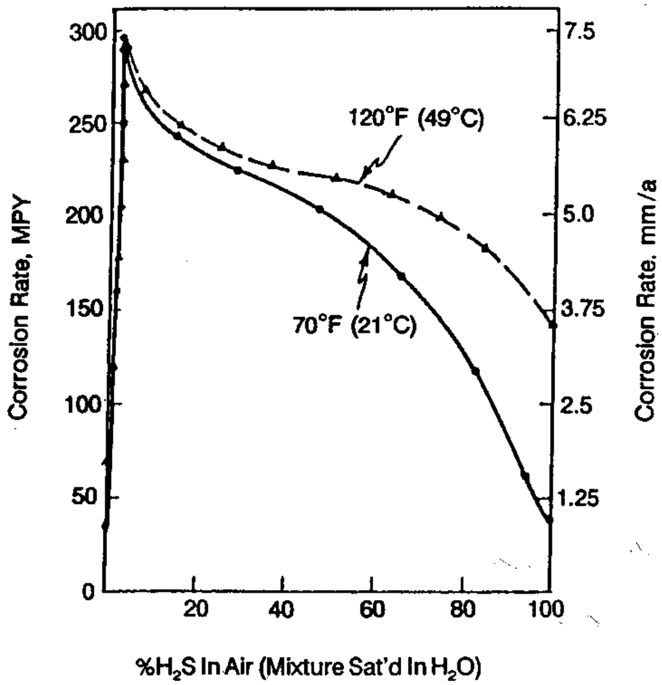


Figure 5.26 Corrosion rate of wet steel in atmospheres containing $H_2S$ mixtures[9]

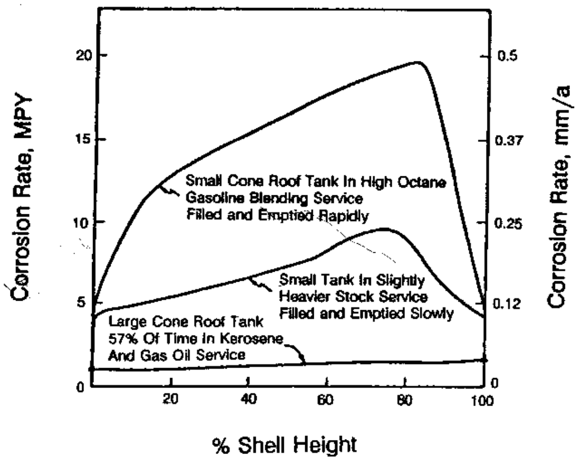


Figure 5.27 Shell corrosion in cone roof storage tanks handling gasoline and heavy distillates[9]

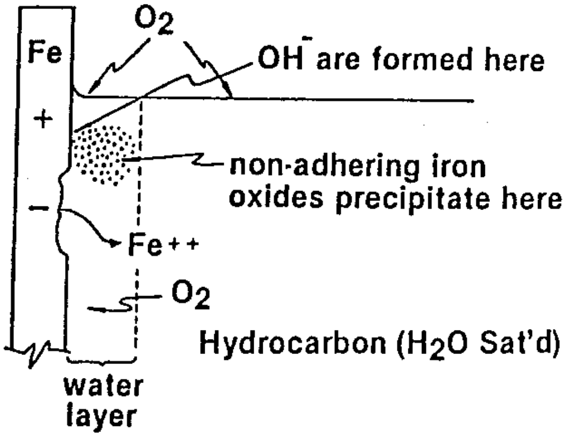


Figure 5.28 Mechanism of shell-side corrosion in gasoline and light-products storage tanks[9]

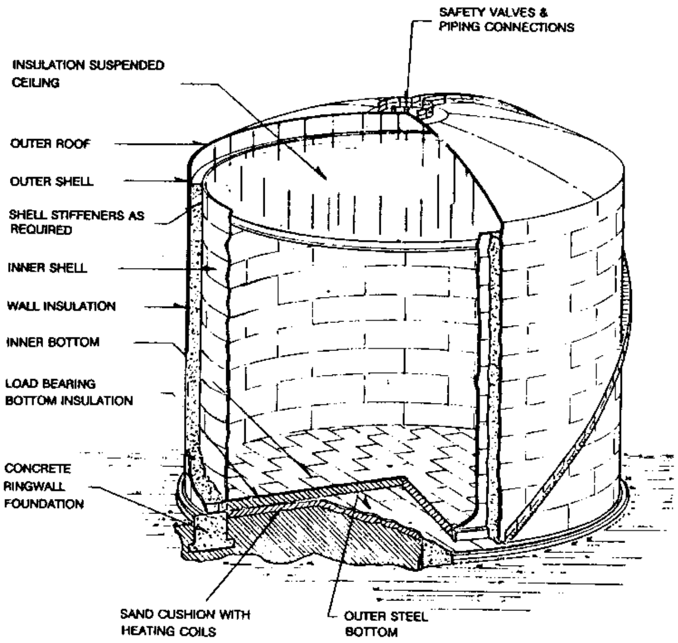


Figure 5.29 Double wall tank for low temperature service[10]

## Appendix
## A

# General Guide for Materials Selection

## SCOPE

This guide covers the following:

- materials and corrosion allowance (CA) for process equipment;
- materials for low-temperature services; and
- materials for wear and abrasion resistance.

## EQUIPMENT DESIGN LIFE

Materials selection is based on the following approximate design lives:

| | |
|---|---|
| large vessels and columns | 25 y |
| small vessels (volume less than 78 $ft^3$ [2.2 $m^3$]) | 10 y |
| exchanger shells and channels | 15 y |
| air coolers | 15 y |
| furnace tubes and supports | 10 y |
| piping, critical and 4 in. (100 mm) or larger | 15 y |
| pumps and valves | 10 y |

## CRITERIA FOR MATERIALS SELECTION

1. Materials selection should be based on design conditions, not operating conditions.

2. Process flow diagrams, stream analyses, contaminant levels, upset conditions, and environmental conditions during shutdowns and start-ups should be evaluated in selecting materials.

3. All materials for process equipment and piping should be identifiable and conform, where necessary, to the requirements of the ASTM(1) or other national standard specifications. Table A-1 contains typical ASTM standard specifications for different product forms in frequent use.

4. When welding is involved, the low-carbon grade stainless steels (304L and 316L) are preferred to the regular grades (304 and 316) except for the use at design temperatures higher than 425°C (800°F).

---

(1) ASTM, Philadelphia, PA.

## TABLE A.1

## Typical ASTM Specifications for Materials

| Material | Plate | Pipe | Tubing | Forgings | Bars | Castings |
|---|---|---|---|---|---|---|
| Cast Iron | | | | | | A48<br>A278 |
| Carbon Steel | A285<br>A515<br>A516 | A53<br>A106<br>A671<br>A672<br>A691 | A161<br>A179<br>A210<br>A214 | A105<br>A181 | A575<br>A576<br>A663<br>A675 | A216 |
| Carbon-½Mo | A204 | A335 | A161<br>A209 | A182 | | A217 |
| 1Cr-½Mo, 1¼Cr-½Mo, & 2¼Cr-1Mo | A387 | A335 | A213 | A182 | | A217 |
| 5Cr-½Mo | A387 | A335 | A213 | A182 | | A217 |
| 12Cr-CA15 | A240 | | A268 | A182 | A479 | A217 |
| Austenitic Stainless 304, 304L, 316, 316L, 321, 347, 310, CF3, CF3M, CF8, CF8C, CF8M | A240 | A312<br>A358 | A213<br>A249 | A182 | A479 | A351 |
| HK40 & HP modified | | | | | | A297 |
| Duplex Stainless 2205 | A240 | A790 | A789 | A182 | A276 | |
| Super Stainless AL6XN | B688 | B675 | B676 | | | |
| Incoloy Alloy 800 | B409 | B407 | B407 | | B408 | |
| Incoloy Alloy 825 | B424 | B423 | B163 | | B425 | |
| Alloy 20 | B463 | B464 | B468 | B462 | B472 | A351 |
| Copper | B152 | B42 | B75<br>B111 | | | |
| Admiralty Brass | | | B111 (Grades B,C,D) | | | |
| Naval Brass | B171 | | | | B124 | |
| 70-30 Cu-Ni | B171 | B467<br>B608 | B111<br>B395 | | | |
| Titanium | B265 | B337 | B338 | B381 | B348 | B367 |
| Monel | B127 | B165 | B163 | | B164 | |
| Inconel 625 | B443 | B444 | B444 | B446 | | |
| Hastelloy C276 | B575 | B622 | B622 | B574 | | A494 |
| Ni Resist | | | | | | A436 |
| Aluminum | B209 | B241 | B234 | B247 | B211 | |

## GENERAL GUIDELINES FOR MATERIALS SELECTION AND CORROSION ALLOWANCES

1. Materials recommendations for the following environments are included in Tables A.2 through A.17:

   - general: hydrocarbon with low-sulfur contents, noncorrosive steam, and water;
   - hydrocarbon plus sulfur greater than 1 wt%;
   - hydrocarbon plus sulfur greater than 0.2 wt% plus naphthenic acid;
   - hydrocarbon plus sulfur between 0.2 and 1.0 wt%;
   - hydrocarbon plus hydrogen;
   - hydrocarbon plus hydrogen and hydrogen sulfide;
   - sour water and desalter water;
   - carbonate;
   - low pressure wet carbon dioxide (regenerator top and overhead);
   - high-pressure wet carbon dioxide;
   - amine;
   - acid gas;
   - liquid sulfur;
   - untreated, aerated water;
   - caustic; and
   - valve trim.

2. The following legend has been used for material designations:

   - CI = cast iron
   - CS = carbon steel
   - 1Cr = 1Cr-½Mo
   - 1¼Cr = 1¼Cr-½Mo
   - 5Cr = 5Cr-½Mo
   - 12Cr = types 405 (UNS S40500), 410 (UNS S41000), 410S (UNS S41008), and CA15
   - 18-8 = types 304 (UNS S30400), 316 (UNS S31600), 321 (UNS S32100), 347 (UNS S34700), and ACI(2) CF3M stainless steel (SS)
   - SS = Austenitic SSs

3. The numerals after a material designation indicate nominal CAs in millimeters (mm) as follows:

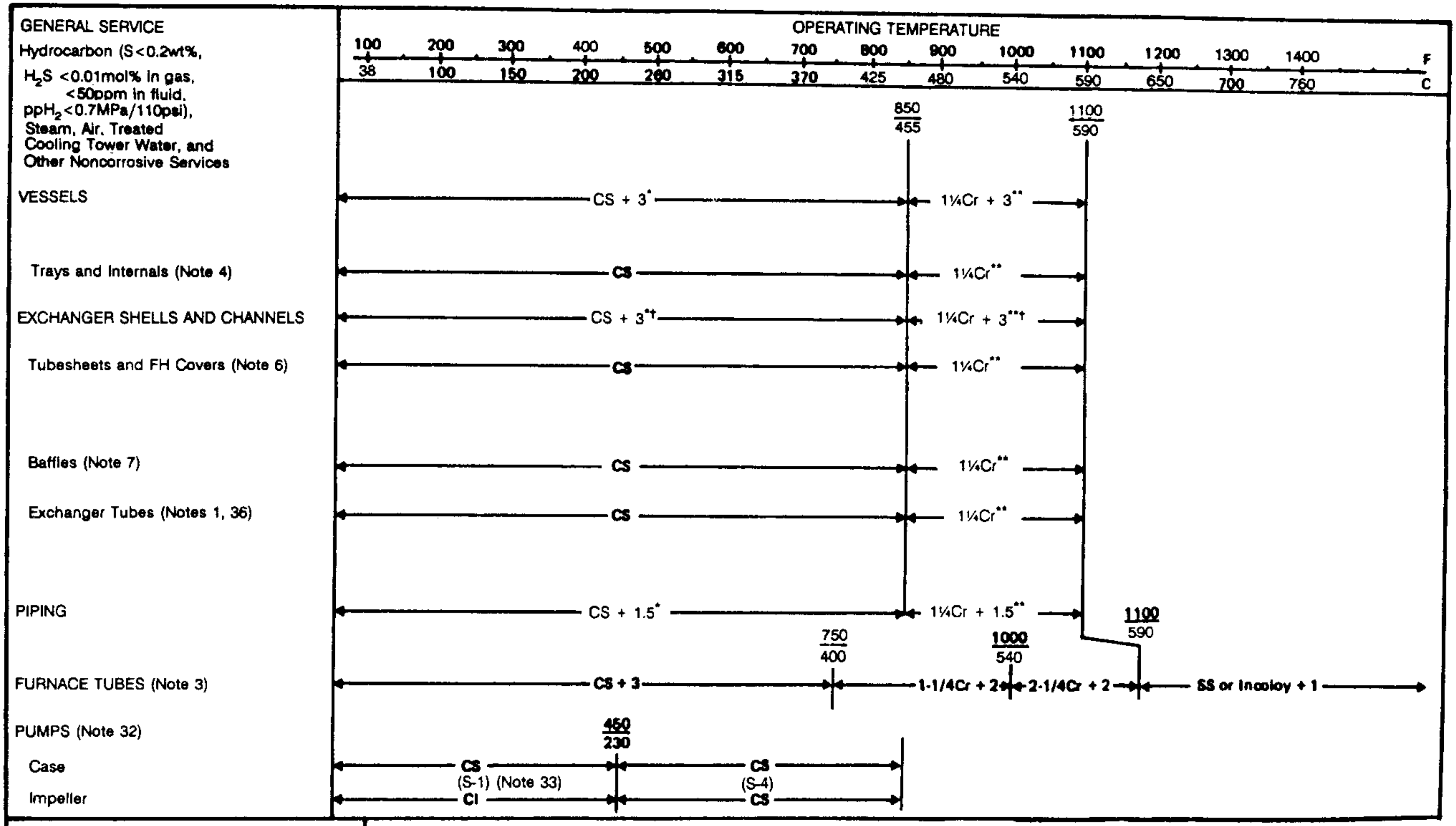
- 1/16 in. (1.5 mm) for piping, unless otherwise specified;
- 1/10 in. (2 mm) for furnace tubes, unless otherwise specified;
- ⅛ in. (3 mm) for TEMA Class R(3) exchangers and sour water piping with hydrogen sulfide partial pressures less than 10 psi (0.07 MPa);
- 3/16 in. (4.5 mm) for sour water vessels and exchangers with hydrogen sulfide partial pressures less than 10 psi (0.07 MPa); and
- ¼ in. (6 mm) for vessels and exchangers with hydrogen sulfide partial pressures greater than 10 psi (0.07 MPa) or carbon dioxide partial pressures less than 4 psi (0.03 MPa).

---

(2) Alloy Castings Institute, Des Plaines, IL.

(3) Tubular Exchange Manufacturers Association, New York, NY.

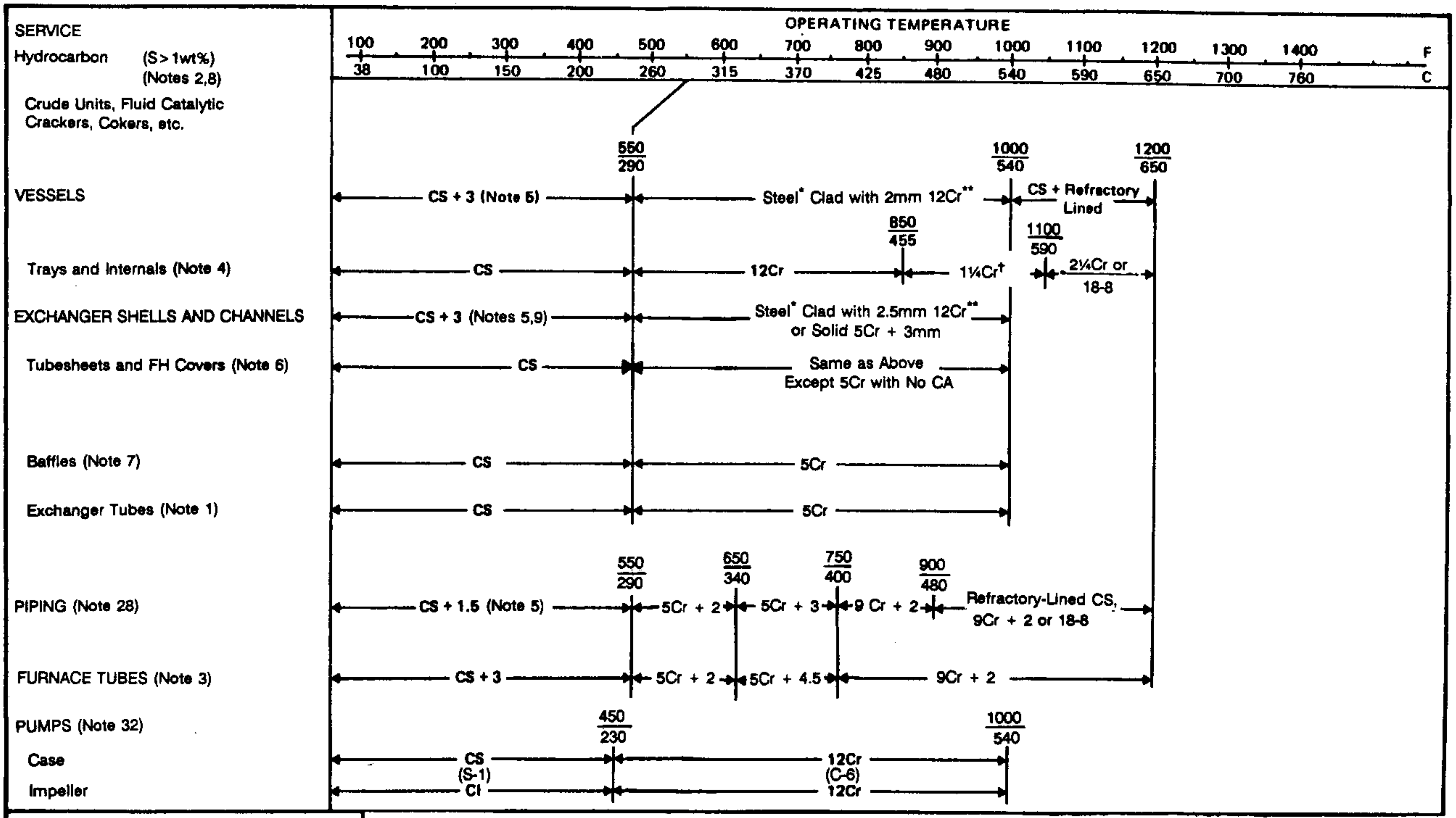
Table A.2



NOTES:

- * See Note 2
- ** See Note 8
- † See Note 9

## Table A.3



| SERVICE<br>Hydrocarbon (S>1wt%) (Notes 2,8)<br>Crude Units, Fluid Catalytic Crackers, Cokers, etc. | OPERATING TEMPERATURE |
|---|---|
| VESSELS | CS + 3 (Note 5) — 550/290 — Steel* Clad with 2mm 12Cr** — 1000/540 — CS + Refractory Lined — 1200/650 |
| Trays and Internals (Note 4) | CS — 550/290 — 12Cr — 850/455 — 1¼Cr† — 1100/590 — 2¼Cr or 18-8 — 1200/650 |
| EXCHANGER SHELLS AND CHANNELS | CS + 3 (Notes 5,9) — 550/290 — Steel* Clad with 2.5mm 12Cr** or Solid 5Cr + 3mm — 1000/540 |
| Tubesheets and FH Covers (Note 6) | CS — 550/290 — Same as Above Except 5Cr with No CA — 1000/540 |
| Baffles (Note 7) | CS — 550/290 — 5Cr — 1000/540 |
| Exchanger Tubes (Note 1) | CS — 550/290 — 5Cr — 1000/540 |
| PIPING (Note 28) | CS + 1.5 (Note 5) — 550/290 — 5Cr + 2 — 650/340 — 5Cr + 3 — 750/400 — 9 Cr + 2 — 900/480 — Refractory-Lined CS, 9Cr + 2 or 18-8 — 1200/650 |
| FURNACE TUBES (Note 3) | CS + 3 — 550/290 — 5Cr + 2 — 650/340 — 5Cr + 4.5 — 750/400 — 9Cr + 2 — 1200/650 |
| PUMPS (Note 32) | |
| Case | CS (S-1) — 450/230 — 12Cr (C-6) — 1000/540 |
| Impeller | CI — 450/230 — 12Cr — 1000/540 |

NOTES:

* See Notes 2, 28
**See Notes 18, 29
†See Note 8

## Table A.4

OPERATING TEMPERATURE

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 100 | 200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 | 1100 | 1200 | 1300 | F |
| 38 | 100 | 150 | 200 | 260 | 315 | 370 | 425 | 480 | 540 | 590 | 650 | 700 | C |

| SERVICE<br>Hydrocarbon (S>0.2wt% + Naphthenic Acid; Notes 2,8,29) | to 450<br>230 | 450<br>230 to 850<br>455 |
|---|---|---|
| VESSELS | CS + 3 (Note 5) | Steel* clad with 2mm 316L** |
| Trays and Internals (Note 4) | CS | 316L** |
| EXCHANGER SHELLS AND CHANNELS | CS + 3 (Notes 5, 9) | Steel* clad with 2mm 316L** |
| Tubesheets and FH Covers (Note 6) | CS | Same as Above |
| Baffles (Note 7) | CS | 316L** |
| Exchanger Tubes (Note 1) | CS | 316L** |
| PIPING | CS + 1.5 (Note 5) | 316** |
| FURNACE TUBES (Note 3) | CS + 3 | 316L** |
| PUMPS (Note 32) | | |
| Case | CS<br>(S-1) | 316**<br>(A-8) |
| Impeller | C1 | 316L** |

NOTES:

* See Note 2

**See Note 29

Table A.5

OPERATING TEMPERATURE

| F | 100 | 200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 | 1100 | 1200 | 1300 | 1400 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 38 | 100 | 150 | 200 | 260 | 315 | 370 | 425 | 480 | 540 | 590 | 650 | 700 | 760 |

| SERVICE<br>Hydrocarbon (0.2<S<1wt%)<br>Crude Units, Fluid Catalytic Crackers, Cokers, etc. | 100/38 – 450/230 | 450/230 – 550/290 | 550/290 – 650/340 | 650/340 – 850/455 |
|---|---|---|---|---|
| VESSELS | CS + 3 (Note 5) | | | CS Clad with 2mm 12Cr** |
| Trays and Internals (Note 4) | CS | | | 12Cr |
| EXCHANGER SHELLS AND CHANNELS | CS + 3 (Notes 5, 9) | | | CS Clad with 2mm 12Cr** or Solid 5Cr + 3 |
| Tubesheets and FH Covers (Note 6) | CS | | | CS Clad with 2mm 12Cr** |
| Baffles (Note 7) | CS | | | 5Cr |
| Exchanger Tubes (Note 1) | CS | | | 5Cr |
| PIPING (Note 28) | CS + 1.5 (Note 5) | | CS + 3 | 5Cr + 2 |
| FURNACE TUBES (Note 3) | CS + 3 | | 5Cr + 2 | |
| PUMPS (Note 32) | | | | |
| Case | CS<br>(S-1) | CS<br>(S-4) | CS<br>(S-6) | 5CR<br>(D-6) |
| Impeller | CI | CS | 12Cr | 12Cr |

NOTES:

**See Notes 18, 28, 29

Table A.6

SERVICE
Hydrocarbon + $H_2S < 0.01$ mol%)
ppH 0.7-3.5MPa (100-500 psi)
If >3.5MPa (500psi), see Note 20

(Noncorrosive)
Hydrogen Plants, Catalytic Reformers, etc.

OPERATING TEMPERATURE

| F | 100 | 200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 | 1100 | 1200 | 1300 | 1400 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 38 | 100 | 150 | 200 | 260 | 315 | 370 | 425 | 480 | 540 | 590 | 650 | 700 | 760 |

| SERVICE | – 500/260 | 500/260 – 700/370 | 700/370 – 850/455 | 850/455 – 1050/565 | 1050/565 – 1650/900 | 1650/900 – 1800/980 |
|---|---|---|---|---|---|---|
| VESSELS | CS + 3 | (Note 20) | 1-1/4Cr + 3, | 1-1/4Cr + 3,<br>18 - 8 + 1 or Ref. lined CS* | 18 - 8 + 1 or Ref. lined CS* | |
| Trays and Internals (Note 4) | CS | (Note 20) | 1-1/4Cr | 1-1/4Cr | 18 - 8 | |
| EXCHANGER SHELLS AND CHANNELS | CS + 3 | (Note 20) | 1-1/4Cr + 3,<br>(Note 9) | 1-1/4Cr + 3,<br>18 - 8 + 1 or Ref. lined CS* | 18 - 8 + 1 or Ref. lined CS* | |
| Tubesheets and FH Covers (Note 6) | CS | (Note 20) | 1-1/4Cr | 1-1/4Cr | 18 - 8 | |
| Baffles (Note 7) | CS | (Note 20) | 1-1/4Cr | 1-1/4Cr | 18 - 8 | |
| Exchanger Tubes (Notes 1) | CS | (Note 20) | 1-1/4Cr | 1-1/4Cr | 18 - 8 or Incoloy 800H | |
| PIPING | CS + 1.5 | (Note 20) | 1-1/4Cr + 1.5 | 1-1/4Cr + 1.5 | Ref. lined CS* or 18 - 8, or Incoloy 800H + 1 | |
| FURNACE TUBES (Notes 3,5) | CS + 3 (– 400/200) | (Note 20) (400/200 – 600/315) | 1-1/4Cr + 2 (600/315 – 1000/540) | 1-1/4Cr + 2 (– 1000/540)<br>2-1/4Cr + 2 (1000/540 – 1050/565) | 18 - 8 or Incoloy 800H + 1, (Note 17) | HP Mod. |
| PUMPS (Note 32) | | | | | | |
| Case | CS (S-1) (– 450/230) | | | | | |
| Impeller | CI (– 450/230) | | | | | |

NOTES:

* See Note 15
Ref. = Refractory

## Table A.7

| SERVICE<br>Hydrocarbon + $H_2$ + $H_2S$<br>pp$H_2$ < 10.34MPa (1550psi)<br>$H_2S$ > 0.01 mol%<br>Hydrodesulfurizers, Hydrocrackers, etc. | OPERATING TEMPERATURE<br>100 F / 38 C → 450/230 | 450/230 → 550/290 | 550/290 → 1000/540 |
|---|---|---|---|
| VESSELS | CS + 3* | •• | 1¼Cr, or 2¼Cr**<br>Clad with 2mm 321 or 347 |
| Trays and Internals (Note 4) | CS* | •• | 321 or 347 |
| EXCHANGER SHELLS AND CHANNELS | CS + 3* | •• | Same as Vessel |
| Tubesheets and FH Covers (Note 6) | CS* | •• | 321 or 347 |
| Baffles (Note 7) | CS* | •• | 321 or 347 |
| Exchanger Tubes (Note 1) | CS* | •• | 321 or 347 (Note 19) |
| PIPING | CS + 1.5 | •• | 321 or 347 + 1.5 |
| FURNACE TUBES (Note 3) | CS + 3 → 350/175 •• | 321 or 347 + 2 | 321 or 347 + 2 |
| PUMPS (Note 32) | | | |
| Case | CS<br>(S-1) | | |
| Impeller | CI | | |

OPERATING TEMPERATURE scale: F 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400; C 38, 100, 150, 200, 260, 315, 370, 425, 480, 540, 590, 650, 700, 760

NOTES:

* See Note 5
**See Note 20

## Table A.8

| SERVICE | OPERATING TEMPERATURE |
|---|---|
| | F: 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 |
| | C: 38 100 150 200 260 315 370 425 480 540 590 650 700 760 |
| Sour Water<br>Desalter Water | 300/150 |
| VESSELS | |
| $ppH_2S$ < 70 kpa (10psi) | CS + 4.5* |
| $ppH_2S$ > 70 kpa (10psi) | CS + 6* |
| Trays and Internals (Note 4) | CS + 3* |
| EXCHANGER SHELLS AND CHANNELS | Same as Vessel |
| Tubesheets and FH Covers (Note 6)<br>Air, H.C., or treated water on the other side | CS + 4.5* |
| Baffles (Note 7) | CS |
| Exchanger Tubes (Note 1) | |
| $ppH_2S$ < 70 kpa (10psi) | CS 10GA min † |
| $ppH_2S$ > 70 kpa (10psi) | CS 10GA min † or 2205 |
| Untreated water otherside | 2205 |
| PIPING | |
| $ppH_2S$ < 70 kpa (10psi) | CS + 3* |
| $ppH_2S$ > 70 kpa (10psi) | CS + 6*,† |
| FURNACE TUBES (Note 3) | |
| PUMPS (Note 32) | |
| Case | CS* (Note 34) |
| Impeller | 18-8 |

NOTES:

* See Note 13

**See Note 24

## Table A.9

| SERVICE | OPERATING TEMPERATURE |
|---|---|
| | F: 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400 |
| | C: 38, 100, 150, 200, 260, 315, 370, 425, 480, 540, 590, 650, 700, 760 |
| Carbonate<br>$CO_2$ Removal (Note 25) | |
| Hydrogen Plant, Gas Treating Plant, etc. | 300<br>150 |
| VESSELS | CS + 3* |
| Trays and Internals (Note 4) | CS* |
| EXCHANGER SHELLS AND CHANNELS | CS + 3* |
| Tubesheets and FH Covers (Note 6) | CS* |
| Baffles (Note 7) | CS* |
| Exchanger Tubes (Note 1) | CS** |
| PIPING | CS + 1.5* |
| FURNACE TUBES (Note 3) | |
| PUMPS (Note 32) | 150<br>65 |
| Case | CS (S-1) \| SS (A-7) |
| Impeller | CI \| SS |

NOTES:

* Notes 10, 12, 21
** Notes 10, 12

## Table A.10

| SERVICE | OPERATING TEMPERATURE |
|---|---|
| Low Pressure Wet $CO_2$<br>pp $CO_2$<0.03MPa/4psi<br>Regenerator Top & Overhead<br>Hydrogen Plant, Gas Treating Plant, etc. | F: 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400<br>C: 38, 100, 150, 200, 260, 315, 370, 425, 480, 540, 590, 650, 700, 760 |
| | Dew Point |
| VESSELS | CS + 6 or 304L* |
| Trays and Internals (Note 4) | 12Cr |
| EXCHANGER SHELLS AND CHANNELS | CS + 6 or 304L* |
| Tubesheets and FH Covers (Note 6) | CS or 304L |
| Baffles (Note 7) | CS or 304L |
| Exchanger Tubes (Note 1) | CS 10GA min or 304<br>(Notes 12, 19) |
| PIPING | |
| Before Condensation | CS + 1 |
| Two Phase Flow | CS + 6* |
| FURNACE TUBES (Note 3) | |
| PUMPS (Note 32) | |
| Case | CS<br>(S-6) |
| Impeller | 12Cr |

NOTES:

* Note 12

## Table A.11

OPERATING TEMPERATURE

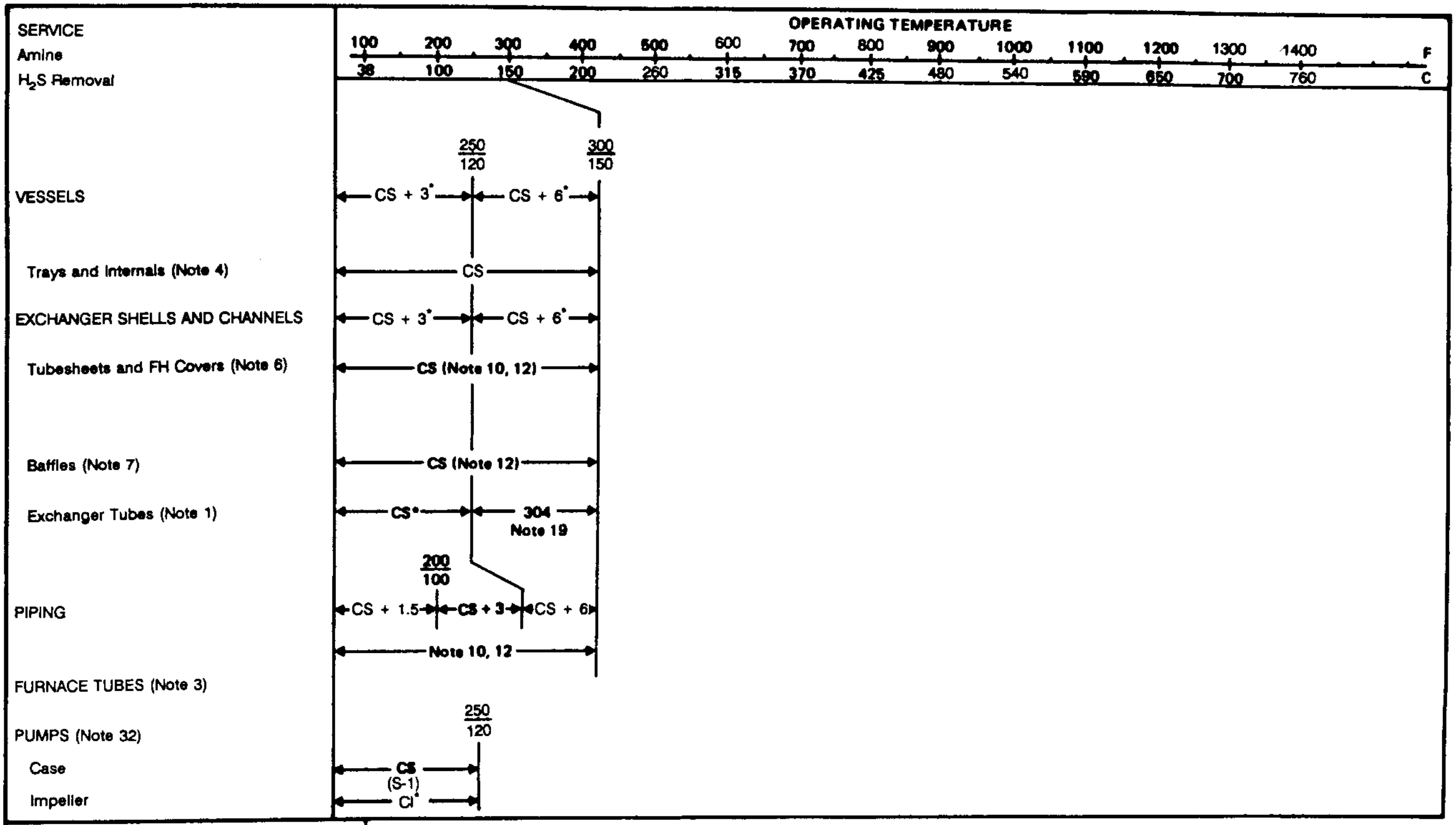
F: 100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400

C: 38 100 150 200 260 315 370 425 480 540 590 650 700 760

| SERVICE | 120<br>50 | Dew Point |
|---|---|---|
| High Pressure<br>Wet $CO_2$ - $H_2$ Mixtures<br>pp $CO_2$>0.03MPa/4psi<br>Hydrogen Plant, Gas Treating Plant, etc. | | |
| VESSELS | CS + 6 | CS Clad with 2mm 304L |
| Trays and Internals (Note 4) | 12Cr or 304L | |
| EXCHANGER SHELLS AND CHANNELS | CS + 6 | CS Clad with 2mm 304L |
| Tubesheets and FH Covers (Note 6) | CS + 6 | **CS Clad with 2mm 304L** |
| Baffles (Note 7) | **CS** | 304 |
| Exchanger Tubes (Note 1) | **10GA CS** | 304 (Note 19) |
| PIPING | **CS + 6** (Note 12) | 304L + 1 |
| FURNACE TUBES (Note 3) | | |
| PUMPS (Note 32) | | |
| Case | **CS** (S-6) | 18-8 (A-7) |
| Impeller | **12Cr** | 18-8 |

NOTES:

Table A.12



SERVICE
Amine
$H_2S$ Removal

OPERATING TEMPERATURE

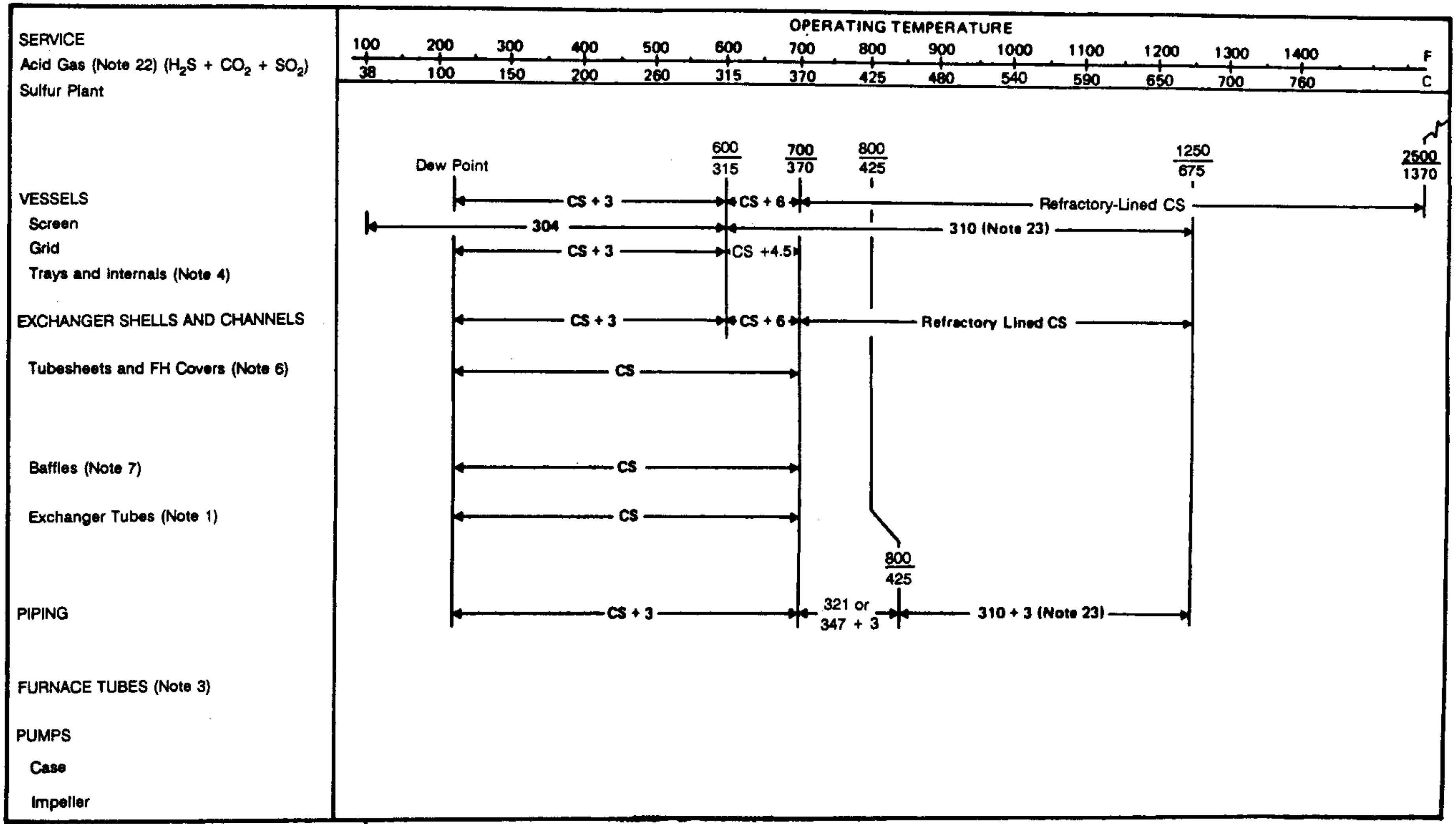
| F | 100 | 200 | 300 | 400 | 500 | 600 | 700 | 800 | 900 | 1000 | 1100 | 1200 | 1300 | 1400 |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C | 38 | 100 | 150 | 200 | 260 | 315 | 370 | 425 | 480 | 540 | 590 | 650 | 700 | 760 |

| | | | |
|---|---|---|---|
| VESSELS | CS + 3* (to 250/120) | | CS + 6* (250/120 to 300/150) |
| Trays and Internals (Note 4) | CS (to 300/150) | | |
| EXCHANGER SHELLS AND CHANNELS | CS + 3* (to 250/120) | | CS + 6* (250/120 to 300/150) |
| Tubesheets and FH Covers (Note 6) | CS (Note 10, 12) (to 300/150) | | |
| Baffles (Note 7) | CS (Note 12) (to 300/150) | | |
| Exchanger Tubes (Note 1) | CS* (to 250/120) | | 304 Note 19 (250/120 to 300/150) |
| PIPING | CS + 1.5 (to 200/100) | CS + 3 (200/100 to 250/120) | CS + 6 (250/120 to 300/150) |
| | Note 10, 12 (to 300/150) | | |
| FURNACE TUBES (Note 3) | | | |
| PUMPS (Note 32) | | | |
| Case | CS (S-1) (to 250/120) | | |
| Impeller | CI* (to 250/120) | | |

NOTES:

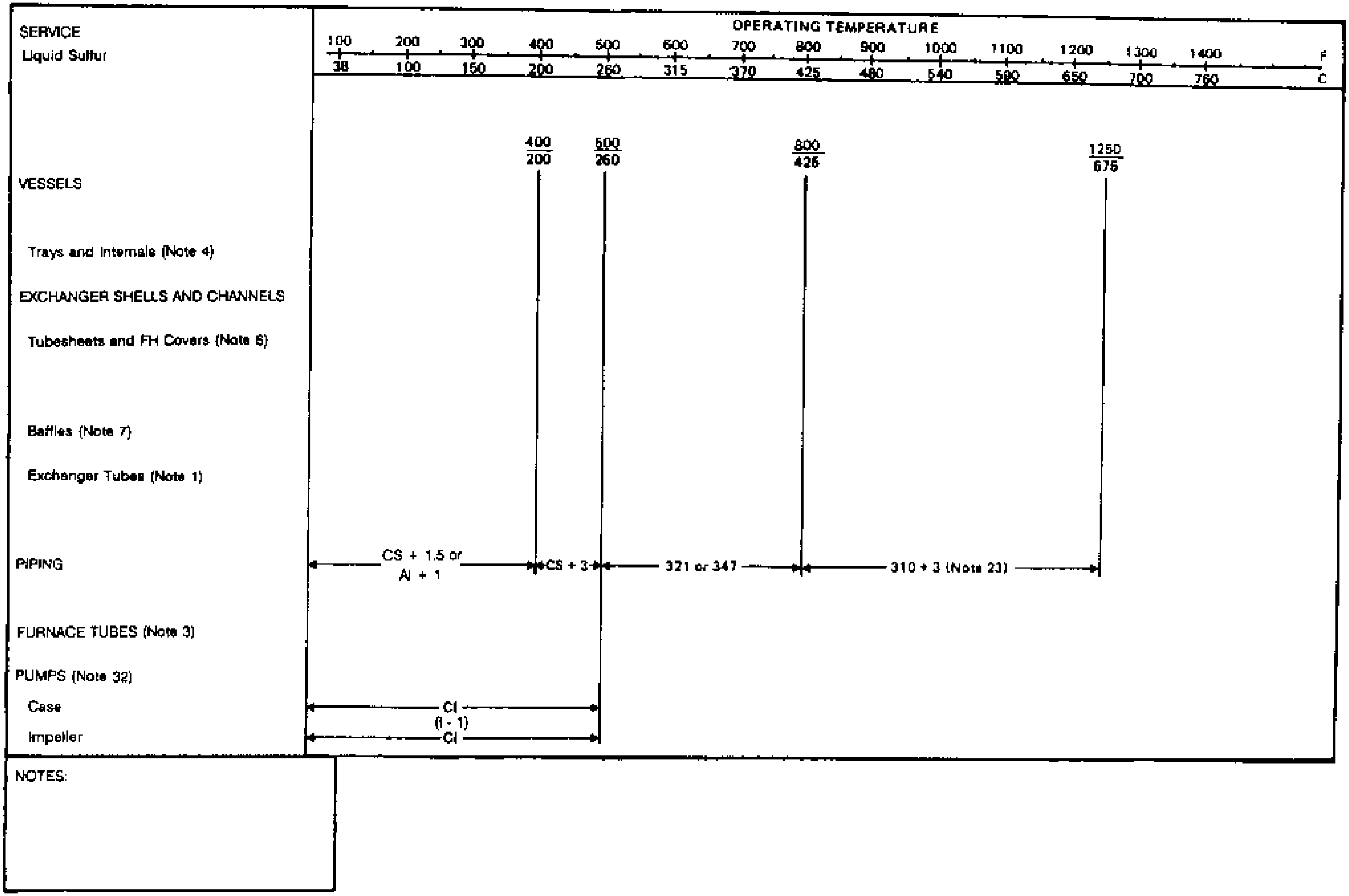
* See Notes 5, 10

Table A.13



NOTES:

## Table A.14


SERVICE
Liquid Sulfur
OPERATING TEMPERATURE
100 200 300 400 500 600 700 800 900 1000 1100 1200 1300 1400 F
38 100 150 200 260 315 370 425 480 540 590 650 700 760 C
400/200
500/260
800/425
1250/675
VESSELS
Trays and Internals (Note 4)
EXCHANGER SHELLS AND CHANNELS
Tubesheets and FH Covers (Note 6)
Baffles (Note 7)
Exchanger Tubes (Note 1)
PIPING
CS + 1.5 or Al + 1
CS + 3
321 or 347
310 + 3 (Note 23)
FURNACE TUBES (Note 3)
PUMPS (Note 32)
Case
CI
(I - 1)
Impeller
CI
NOTES:

### Table A.15

| SERVICE<br>Untreated, Aerated Water | OPERATING TEMPERATURE |
|---|---|
| F | 100, 200, 300, 400, 500, 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400 |
| C | 38, 100, 150, 200, 260, 315, 370, 425, 480, 540, 590, 650, 700, 760 |
| | 300/150 |
| VESSELS | CS + 2mm 90-10 Cu-Ni Clad |
| Trays and Internals (Note 4) | |
| EXCHANGER SHELLS AND CHANNELS | CS + 2mm 90-10 Cu-Ni Clad |
| Tubesheets and FH Covers (Note 6) | Naval Brass or 70-30 Cu-Ni* |
| Baffles (Note 7) | Naval Brass or 70-30 Cu-Ni* |
| Exchanger Tubes (Note 1) | Admiralty Brass or 70-30 Cu-Ni* |
| PIPING | Cement-Lined CS |
| FURNACE TUBES (Note 3) | |
| PUMPS (Note 32) | |
| Case | CI (I-2) |
| Impeller | Al Bronze |

NOTES:

* See Note 27

## Table A.16

| SERVICE<br>Caustic<br>NaOH, KOH | OPERATING TEMPERATURE |  |  |  |  |
|---|---|---|---|---|---|
|  | 10 – 30 wt % |  |  | 50 wt% |  |
|  | 200/100 | 250/125 | 400/200 | 170/75 | 400/200 |
| VESSELS | CS + 1.5* | CS + 6 | Monel + 1.5 | CS + 3* | Monel + 1.5 |
| Trays and Internals (Note 4) | CS* |  | Monel | CS* | Monel |
| EXCHANGER SHELLS AND CHANNELS | CS + 1.5* | CS + 6 | Monel + 1.5 | CS + 3* | Monel + 1.5 |
| Tubesheets and FH Covers (Note 6) | CS* |  | Monel | CS* | Monel |
| Baffles (Note 7) | CS* |  | Monel | CS* | Monel |
| Exchanger Tubes (Note 1) | CS* | Monel |  | CS* | Monel |
| PIPING | CS + 1.5* | CS + 6 (Note 14) | Monel + 1.5 | CS + 3* | Monel + 1.5 |
| FURNACE TUBES (Note 3) |  |  |  |  |  |
| PUMPS (Note 32) |  |  |  |  |  |
| Case | CS (S-1) | Monel (Note 35) |  | CS (S-1) | Monel (Note 35) |
| Impeller | CI* | Monel |  | CI* | Monel |

NOTES:

* See Note 10

## TABLE A.17

## Valve Trim

| Environmental | Valve Trim Material (Note 37) |
|---|---|
| 1. General Service | |
| a) Treated Water | 12 Cr |
| b) Steam $\Delta p$ <150 psi in multiphase flow or <500 psi in single phase flow | 12Cr |
| $\Delta p$ >150 psi in multiphase flow or >500 psi in single phase flow | Stellite 6 |
| 2. Hydrocarbon; Carbonate, Wet $CO_2$, Acid Gas, Liquid Sulfur | |
| a) Carbon and low-alloy steel piping | 12 Cr |
| b) 321 or 347 piping | 18-8 |
| 3. Sour Water; Desalter Water | 18-8 or<br>12 Cr (HRC 22 max) |
| 4. Amine | |
| a) <100°C (200°F) | 12 Cr |
| b) >100°C (200°F) | 18-8 |
| 5. Untreated Water <100°C (200°F) | Bronze |
| 6. Caustic | |
| a) 10-30 wt%, <100°C (200°F) | 12 Cr |
| b) 10-30 wt%, >100°C (200°F), 50 wt% all temperatures | Monel |

## *NOTES FOR TABLES A.2 THROUGH A.17*

1. Thickness of exchanger tubes should be that specified in the exchanger design criteria. CA need not be added.

2. Above 750°F (400°C), use silicon-killed (not aluminum-killed) carbon steel. Above 850°F (450°C), use 1Cr-½Mo or 1¼Cr-½Mo.

3. Materials selection for furnace tubes in hydrocarbon plus sulfur services is based on process temperature because the data have been generated on that basis. For all other services, materials selection for furnace tubes is based on the assumption that the metal temperature is 100°F (50°C) higher than the internal fluid temperature. In no case should the outside skin temperature exceed 1,000°F (530°C) for carbon steel, 1,200°F (650°C) for 1¼Cr to 9Cr, and 1,700°F (930°C) for 18-8 SS. When austenitic SS's are specified for temperatures above 1,000°F (530°C), "*H*" grades should be used, and cold forming should be prohibited unless it is followed by solution annealing.

4. CA for trays and materials:

| | Removable | Welded In |
|---|---|---|
| Carbon steel | 1/32 in. (1 mm) | Vessel CA x 1.5 |
| Corrosion-resistant alloys in carbon steel vessel | none | 1/16 in. (1.5 mm) |
| Corrosion-resistant alloys in alloy vessel | none | Vessel CA |

5. For areas where sour water collects, see Table A-8. Where mild corrosion is expected, use carbon steel with ⅛ in. (3 mm) CA on piping.

6. Where not covered by TEMA Class R and material specified for both sides is the same, CA should be 0.75 times the sum of the CAs for each side up to a ¼ in. (6 mm) maximum. Where not covered by TEMA and alloy requirements for two sides are different and a solid alloy tube sheet is used, use CA for higher alloy side as total.

7. Baffles should have a minimum thickness of ¼ in. (6 mm); no other CA.

8. Where 1¼Cr-½Mo is specified, 1Cr-½Mo may also be used. Do not use 1Cr-½Mo in hydrogen service if hydrogen partial pressure is greater than 100 psi (0.7 MPa) above 900°F (480°C). Do not use 1Cr-½Mo in general service above 1,000°F (530°C).

9. A CA of ⅛ in. (3 mm) should be used on carbon steel exchangers since it is standard for TEMA Class R.

10. Stress relieve carbon and chrome steel welds and cold bends in amine service regardless of service temperature. For all concentrations of carbonate solutions and in concentrations of caustic up to 30 percent, stress relieve for service temperatures above 140°F (60°C). For 30 to 50 percent caustic, the service temperature where stress relief is required decreased from 140°F(60°C) to 118°F (48°C). Welded tubing does not require heat treatment in addition to that required by the ASTM specifications. Rolled tube-to-tube sheet joints do not require stress relief.

11. Use 12Cr for valve trays and valves. Sieve trays and stationary bubble cap trays may be made of carbon steel.

12. For control valves and other areas of high-turbulence (velocity 8 ft/s [2.5 m/s]) (i.e. downstream of control valves, rich carbonate inlet of carbonate regenerator, reboiler tube sheet, and baffles), use type 304 SS plus 1/32 in. (1 mm) CA. Do not use miters; long radius elbows are preferred. See piping specifications for other limitations on miters.

13. Hardness of completed carbon and low-alloy steel welds should not exceed 200 Brinell.[4] Valve trim shall be 18Cr-8Ni SS and meet NACE Standard MR0175.[5]

14. Use Monel[6] 400 valve trim for caustic above 200°F (93°C).

15. Metal temperature should not exceed the point at which carbon steel starts to lose its resistance to hydrogen attack.

16. Use 12Cr cases and impellers for main boiler feedwater above 250°F (120°C). Use carbon steel for circulating boiler feedwater.

17. Stress corrosion cracking (SCC) of type 300 (UNS S30000) series SS may result if solid carry-over exceeds 1 ppm.

18. Do not use type 405 SS above 750°F (400°C). When welding is anticipated, use type 410S SS (0.08% carbon maximum) rather than type 410 SS.

19. For U-bends, heat treat the entire 18Cr-8Ni SS tube at 1,850°F (1,000°C) minimum after bending. Use type 321 or type 347 SS only if the U-bends are heat treated.

20. For choice between carbon or alloy steels in hydrogen service, see API[7] Standard 941. The corrosion allowance given in the Table must be applied.

21. See Table A-10 for top of regenerator column and overhead system.

22. Severe corrosion may occur if lines are not kept above the dew point.

23. Welded assemblies must be heat treated at 1,650°F (900°C) for 4 h after completion in order to prevent polythionic acid cracking during downtime.

24. Unless more restrictive velocities are specified, maximum velocity should not exceed 20ft/s (6 m/s) in mixed phase flow.

25. Do not use nickel or cobalt base alloys. (e.g., Inconel[8] 600, Monel 400, Colmonoy[9], etc.). Stellite[10] may be used.

26. Neoprene should not be used if water is contaminated with aromatic hydrocarbons. (No longer used)

27. The choice between brass and copper-nickel alloys is contingent on ammonia content and temperature of process side. Brass should not be used when the pH due to ammonia exceeds 7.2. Copper-nickel alloys should not be used if the sulfides in the water exceed 0.007 mg/L.

---

[4] Trade name.

[5] NACE Standard MR0175, "Sulfide Stress Corrosion Cracking Resistant Metallic Material for Oilfield Equipment," NACE, Houston, TX, latest revision.

[6] Trade name.

[7] American Petroleum Institute, Washington, DC.

[8] Trade name.

[9] Trade name.

[10] Trade name.

28. For lines and equipment handling catalyst, use refractory-lined steel or hard facing on indicated alloy. Hard facing is not required for vertical pipe runs.

29. Use solid 5Cr or 12Cr clad for crudes containing over 1 wt% sulfur above 550°F (290°C) and for crudes containing 0.1 to 1.0 wt% sulfur above 650°F (340°C), unless there is operating experience or hydrogen sulfide evolution data to indicate where the break between carbon steel and alloy should be.

    For naphthenic acid containing hydrocarbons (Table A-4) where the neutralization number of the feed exceeds 2 mg of KOH/g in a crude unit or 0.5 mg of KOH/g in a vacuum unit, use type 316L (UNS S31603) SS (2.5% Mo minimum) above 450°F (23°C) regardless of sulfur content. For castings, 316 (CF8M) with 2.5% Mo minimum may be used provided the ferrite content is 8% minimum.

30. When 18Cr-8Ni SS is specified, any grade may be used; however, unstabilized regular carbon (0.08% carbon maximum) grades are usually not used for operating temperatures above 800°F (425°C). For temperatures below 800°F (425°C), stabilized grades should be used if there is a possibility of intergranular attack during downtime. Types 309 (UNS S30900), 310 (UNS S31000), 316, 321, and 347 SS's should be used with caution for operating temperatures above 1,100°F (600°C) because of the possibility of sigma phase embrittlement.

31. When welding is involved, the low-carbon grade SS's (types 304L (UNS S30403) and 316L) are preferred to the regular grades (types 304 and 316) except for use at design temperatures higher than 800°F (425°C). (No longer used)

32. Designations in parenthesis (e.g., [S-1] are API 610 materials classes).

33. For water service from 250°F (120°C) to 350°F (175°C), use class S-5. For water service over 350°F (175°C) or boiler feed water over 200°F (100°C), use class C-6.

34. Use class S-3, except use 18-8 impellar.

35. See note 6 in Table F-2 of API 610.

36. Experience has shown that carbon steel tubes will only give economical life if water treating and corrosion inhibitors additions are carefully controlled on a continuous basis.

37. When service temperature exceeds 900°F (480°C), check with a materials engineer.

## *GENERAL GUIDELINES FOR MATERIALS SELECTION FOR LOW-TEMPERATURE SERVICES*

1. In this guide, low temperature is defined as any temperature below 135°F (57°C).

2. Materials listed in Table A-18 are selected based on minimum requirements for operation with respect to brittle fracture at indicated temperatures in accordance with the requirements of the following codes:

    - ASME[11] "Boiler and Pressure Vessel Code," Section VIII, Division 1 (UCS-66) and Division 2 (AM 204); and

    - ASME B31.3, Chemical Plant and Petroleum Refinery Piping (323.2).

---

[11] American Society of Mechanical Engineers, New York, NY.

3. The above code requirements are considered the minimum. Additional testing requirements or more stringent requirements than those designated by the codes may be necessary, depending on the specific circumstances.

4. The minimum operating temperature should include cold start ups at low-ambient temperatures where applicable (e.g., mining equipment that normally does not require warm start ups) and upset conditions.

5. Select low-temperature steels for fracture-critical structural members designed for tensile stress levels greater than 6 ksi (40 MPa) and specify a minimum Charpy V-notch impact energy absorption of 20 ft-lb (27 J) for base metal, heat-affected zones (HAZs), and welds when the structures are exposed to low-ambient temperatures. Fracture-critical members are those tension members whose failure would have a significant economic impact.

6. When materials requiring impact testing are used for welding, impact tests should be conducted on the base metal, weld metal, and HAZs.

7. Materials for atmospheric storage tanks should be selected in accordance with API 650.

8. Materials for low-pressure storage tanks should be selected in accordance with API 620, Appendix R.

# TABLE A.18

| MINIMUM DESIGN TEMP. C | MINIMUM DESIGN TEMP. F | PLATES: SHELLS AND HEADS | PLATES: TRAYS | STRUCTURE NONPRESS. | PIPING | TUBING | FORGINGS & FITTINGS | CASTINGS | FASTENERS |
|---|---|---|---|---|---|---|---|---|---|
| 57 | 135 | COMPLY WITH CODES — NO SPECIAL FRACTURE TOUGHNESS REQUIREMENTS | | | | | | | |
| -6 | 20 | APPLICATIONS FOR ASME BOILER AND PRESSURE VESSEL CODE, SECT. VIII DIVISIONS 1 AND 2 FOLLOW FIGURE UCS-66 FOR DIVISION 1 AND FIGURE AM-218.1 FOR DIVISION 2 FOR MAT'L SELECTION AND IMPACT TEST REQUIREMENTS. | ① | A36 OR A283 | API 5L GR B, A53 GR. B, A106 GR. B, OR A671 | NO SPECIAL REQ'MENT | A105 OR A234 ③④ | A216 GRADE WCB ④ | |
| -17 | 0 | | | FOR NON-CRITICAL A36, OTHERWISE SAME AS PLATE OR PIPING ⑮ | A53 GR. B SEAMLESS, A106 GR. B, OR A671 ④<br>A106 GR. B OR A524 ④ | | A105 A234 A727 OR A758 ③④<br>A707 GR. T (ONLY), A727 OR A758 ④ ⑫ | A352 GRADE LCB (NOT IMPACT TESTED) ④ | A193 GRADE B7 A194 GRADE 2H |
| -30 | -20 | PREFERRED MATERIAL: A 516 (ALL GRADES) ②④⑪ ⑭ | SAME AS VESSEL EXCEPT NO SPECIAL REQ'MENTS FOR BOLTED TRAYS <10 GA. | | A333 GR. 6 ④⑭ | A334 GRADE 6 OR A179 ④⑦⑭ | A350 GR. LF1 OR LF2, A420 GR. WPL6, OR A707 GR. L2 (ONLY) ④ | A352 GRADE LCB | A193 GRADE B7 A194 GRADE 2H ⑥ |
| -46 | -50 | FOR ASME SECTION VIII, DIVISIONS 1 & 2 USE A203 OR A537 AS APPLICABLE FOR MAT'LS AND IMPACT TEST REQ'MENTS | SAME AS VESSEL TYPE 304 OR ALUMINUM | SAME AS PLATE OR PIPING | A333 GRADE 7 TO -74 °C/-100 °F | A334 GRADE 3 | A350 GRADE LF3 | A352 GRADE LC1 | A320 GRADE L7 A194 GRADE 4 |
| -60 | -75 | A203 GRADE D ② ⑪ | | | A333 GRADE 3 | | | A352 GRADE LC2 TO -74 °C/-100°F<br>A352 GR. LC3 | |
| -100 | -150 | A553 OR A353 ②⑬⑯ (TO -196 °C/-320°F) | A353 OR A553 TYPE 1 | | A333 GR. 8 ⑯ | A334 GRADE 8 ⑯ | A522 TP 1 A420 [WPL8] ⑯ | A351 GRADE CF8 ⑩ | A320, GR. B8 A194, GR. 8 ANNEALED |
| | | A240 TYPE 304 ⑤ | TYPE 304 | | A312 TP 304 ⑤ | A213 TP 304 ⑤ | A182 GR. F304 ⑤ | | B211 TP 2024-T6 |
| | | B209 AL ALLOY 5083/5456 | ALUMINUM | | B241 [6061] | B234 [6061] | B247/361[6061] | | |
| 200 | -325 | A240 TYPE 304 ⑤⑨ | TYPE 304 ⑤ ⑨ | | A312 ⑤ TP. 304 ⑨ | A213 ⑤ TP. 304 ⑨ | A182, F304 ⑤ ⑨ A403, WP304 | A351 GRADE CF8 ⑤⑨ | SAME AS ABOVE (I.E. GR. 8 OR 2024-T6) ⑧ ⑨ |
| -255 | -425 | B209 AL ALLOY 5083/5456 ⑧ | ALUMINUM ⑧ | | B241 ⑧ ALLOY 6061 | B234 ⑧ ALLOY 6061 | B247/361 ⑧ ALLOY 6061 | | |

NOTE. The numbers in circles correspond to numbered notes on the following pages.

1. Bolted trays: no special requirements

   Welded trays: no special requirements, up to and including ½ in. (12 mm) thick. Same as vessel shell above ½ in. (12 mm) thick.

2. All weld seams in materials requiring impact tests per ASME Section VIII, Divisions 1 and 2, Figures UCS-66 and AM218.1 (regardless of the governing code) should be 100 percent radiographed and magnetic particle inspected.

3. Carbon content for forgings in thicknesses greater than 1 in. (25 mm) should not exceed 0.32%. A105 forgings are not permitted for tubesheets or shell rings per the scope of the materials standard.

4. In general, carbon, low alloy, and high-alloy steels may be used at design metal temperatures down to -50°F (-46°C) without impact testing under the following (exempt) conditions:

| | Applicable Code | Summary of Rules |
|---|---|---|
| a. | ASME Section VIII, Division 1, Paragraphs UCS-66 and UCS-67 (and Figures UCS-66 and UCS-66.1)<br>[*]Note: The MDMT at which impact testing would otherwise be required may be reduced in accordance with Figure UCS-66.1 when the stress in tension is less than the maximum allowable design stress. It may also be reduced 30°F (14.7°C) under UCS-68 if postweld heat treatment is performed when not otherwise required by Code. | Impact tests are not required when the intersection of minimum design metal temperature (MDMT)[*] and nominal material thickness lies on or above the applicable material curve in Figure UCS-66; however, impact testing is mandatory for the following:<br>• all material thicknesses greater than 4 in. (101.6 mm) for welded construction; and<br>• all material thicknesses greater than 6 in. (152.4 mm) for nonwelded materials with a MDMT less than 120°F (49°C).<br>Also exempt from impact tests are the following:<br>• ANSI B16.5 ferritic steel flanges with a MDMT not colder than -20°F (-30°C);<br>• all UCS materials less than 0.098 in. (2.5 mm) thick and UCS nuts, provided such UCS materials are used at MDMTs not colder than -50°F (-46°C); and<br>• all P-No. 1 Group 1 or 2 materials 1 in. (25.4 mm) or less, provided that the vessel is hydrostatically tested, has a MDMT between 650°F (343°C) and -20°F (-30°C), and shock or cyclic loading is not a controlling condition.<br>Note: Welding Procedure Qualification Tests must include weld and HAZ impact tests unless specifically exempted by paragraph UCS-67. |
| b. | ASME Section VIII, Division 2, Paragraph AM-218 (and Figure AM-218.1) | Impact tests are not required when the intersection of MDMT and nominal material thickness lies on or above applicable material curve in Figure AM-218.1; however, impact testing is mandatory for the following:<br>• all material thicknesses greater than 3 in. (76.2 mm) when the MDMT is lower than 120°F (49°C); and |

| | |
|---|---|
| | - all material thicknesses greater than 2 in. (50.8 mm) that have been subjected to accelerated cooling (during heat treatment), when the MDMT is lower than 120°F (49°C).<br>Also exempt from impact tests are materials used in vessels with MDMT not colder than -50°F (-46°C) and design stress intensities not higher than 6,000 psi (41 MPa).<br>The above exemptions do not apply to vessels in lethal service. |
| c. ANSI B31.3, Section 323.2.2 (and Table 323.2.2) | Impact tests are not required when the MDMT is below -20°F (-29°C) but are required at or above -50°F (-46°C), and both the maximum operating pressure does not exceed 25 percent of the maximum allowable design pressure at ambient temperature and the combined longitudinal stress (from pressure, dead weight, and displacement strain) does not exceed 6,000 psi (41 MPa).<br>Note: This exemption is not applicable for Category M (hazardous) fluid service. |

5. Type 304 is listed because it is the least costly of the acceptable materials. Other 300 series SS's may be needed for considerations other than low temperature. For example, low-carbon grades are desirable for seacoast environments to avoid intergranular stress corrosion cracking during the periods when the material is not at cryogenic temperature.

   In general, austenitic SS materials are exempt from impact testing at temperatures of -425°F (-254°C) and higher, with the following exceptions:

| Applicable Code | Summary of Rules |
|---|---|
| a. ASME Section VIII, Division 1, Paragraph UHA-51 | Grades other than 304, 304L, 316, 316L, and 347 are not exempt from impact tests at temperatures of -325°F (-200°C) and higher, if they are materials with allowable contents in excess of 0.10%, are materials in cast form, are materials that have not been solution heat treated, or are materials in the form of weld metal, unless they are otherwise exempted by Paragraph UHA-51. |
| b. ASME Section VIII, Division 2, Paragraph AM-213 | Same exceptions from impact tests as Division 1, except that types 316 and 316L are not in the first category exempt from testing down to -425°F (-254°C). |
| c. ANSI B31.3, Section 323.2.2 (and Table 323.2.2) | Essentially the same exceptions from impact tests as ASME VIII, Division 2, with slight variations. |

6. Impact testing of Grade B7 studs (but not Grade 2H nuts) is required by ASME Section VIII, Division 1 for temperatures below -40°F (-40°C), by ASME VIII, Division 2 for temperatures below -20°F (-30°C), but not by ANSI B31.3 above -50°F (-46°C) if the material is quenched and tempered.

7. Where design temperatures are not lower than -50°F (-46°C), Impact testing is not required on thin materials: less than 0.098 in. (2.5 mm) under ASME VIII, Division 1 and less than 0.099 in. (2.5 mm) under ASME VIII, Division 2 (see Paragraphs UCS-66[d] and AM204.2).

8. Impact tests of aluminum are required only under ASME B31.3 for service below -452°F (-270°C). Notched tensile tests to prove ductility are required for service below -452°F (-270°C) by ASME Section VIII, Division 1.

9. Impact test all forms for service below -425°F (-255°C).

10. Impact tests are required for austenitic SS castings by ASME Section VIII, Division 1 and Division 2, and under ANSI B31.3 for castings in the nonsolution annealed condition.

11. ASTM Specification A20 lists impact properties that are generally achievable using standard mill practice.

12. Material should be specified to be in the normalized condition when used in this temperature range.

13. Transverse Charpy V-notch shall be specified as a supplemental requirement.

14. For postweld heat treatment requirements, see the following:

    a. ASME Section VIII, Division 1, paragraph UCS-56 (c);[12]
    b. ASME Section VIII, Division 2, paragraph AF-402; and
    c. ASME B 31.1, Table 331.1.1.

15. For fracture-critical tension members, Charpy impact test may be required.

16. For use not lower than -320°F (-196°C).

## *GENERAL GUIDELINES FOR MATERIALS SELECTION FOR WEAR AND ABRASION RESISTANCE*

1. Materials selection for wear and abrasion resistance should be based on service performance records. Materials listed below are common materials used for abrasive service:

    - tungsten carbide and sintered carbide compacts;
    - chromium and nickel cast irons (ASTM A532—Class I, Type A; Class III, Type A; etc.);
    - triten OPS-T200X (plate, pipe, and overlay);
    - austenitic cast irons;
    - martensitic steels;
    - abrasion resistant steels;
    - austenitic manganese steels;

---

[12] Reductions in the minimum postweld heat treatment temperature (permitted by Table UCS-56.1) should not be allowed for materials that must meet the fracture toughness requirements of Figure UCS-66. Postweld heat treatment should be considered for pressure vessels with walls 1 in. (25.4 mm) or thicker to minimize the possibility of brittle fracture during hydrostatic test. In some cases, this will allow a 30°F (14.7°C) reduction in impact testing exemption temperature (see ASME VIII, Division 1, UCS-68).

- hardfacing alloys (Lincoln Faceweld No. 12 [$CrC_x$], MG Industries alloy 770 and 790 [AWS 5.21-80 Class EFeCr-Al], Stellite 6 and 21, etc.);

- rubber or polyurethane lining; and

- ceramic lining (basalt, high-density alumina ceramic, mullite-bonded silicon carbide-fused cast) manufactured by Abresist,(13) Basramite or equal.

2. For some components, toughness as well as abrasion resistance is required. For example, ditch teeth should have a minimum Charpy V-notch impact energy of 20 ft-lb (27J) at the design temperature and a minimum hardness of Rockwell C 50.

---

(13) Trade name.

Appendix

# A

## BIBLIOGRAPHY

API Standard 620, "Recommended Rules for Design and Construction of Large, Welded, Low-Pressure Storage Tanks," Appendix R, American Petroleum Institute, Washington, DC, latest revision.

API Standard 650, "Welded Steel Tanks for Oil Storage, Section 2—Materials," American Petroleum Institute, Washington, DC, latest revision.

API Standard 941, "Steel for Hydrogen Service at Elevated Temperature and Pressure in Petroleum Refineries and Petrochemical Plants," American Petroleum Institute, Washington, DC, latest revision.

API Standard 942, "Recommended Practice for Welded, Plain Carbon Steel Refinery Equipment for Environmental Cracking Service," American Petroleum Institute, Washington, DC, latest revision.

ASME Code B31.3, "Chemical Plant and Petroleum Refinery Piping," American Society of Mechanical Engineers, New York, NY.

NACE Standard MR0175, "Sulfide Stress Cracking Resistant Metallic Material for Oil Field Equipment," NACE, Houston, TX, latest revision.

NACE Standard RP0472, "Methods and Controls to Prevent In-Service Cracking of Carbon Steel Welds in (P-1) Corrosive Petroleum Refining Environments," NACE, Houston, TX, latest revision.

**Appendix**

# B

# Rules of Thumb for Materials of Construction for Refineries

1. The effects of temperature in the absence of hydrogen or corrosives in process streams are as follows:

| | |
|---|---|
| Below -150°F (-100°C): | 18Cr-8Ni stainless steel (SS), aluminum or 9 percent nickel steel required |
| Below -50°F (-45°C): | impact-tested low-alloy (nickel) steels required |
| Below -20°F (-29°C): | Most codes require impact tests of carbon steel unless stress below 6,000 psi (41,370 kPa). (See specific code requirements.) |
| Below 60°F (16°C): | brittle fracture of steel over approximately ½ in. (13 mm) thick possible. (See Figure AM218.1 of ASME(14) Section VIII, Division 2 or Figure UCS-66 of ASME Section VIII, Division 1, for specific thickness-temperature relationships.) |
| Above 650°F (345°C): | Do not use 17Cr steel and avoid 12Cr steel because of embrittlement. To avoid graphitization, use silicon-killed carbon steels only (e.g., ASTM(15) A106, ASTM A515). |
| Above 850°F (455°C): | 1Cr minimum is required for continuous service to avoid graphitization; however, furnace tubes usually are limited by oxidation. |
| Above 1,000°F (540°C): | 1¼Cr to 9Cr required to resist oxidation |
| Above 1,200°F (648°C): | 18Cr-8Ni SS is required to resist oxidation; however, embrittlement due to formation of sigma phase possible in some grades. Avoid cold work. |
| Above 1,700°F (930°C): | Use 25Cr-12Ni SS's (limited to nonpressure parts) (e.g., type 309 [UNS S30900] and ACI(16) HH or 25Cr-20Ni; type 310 [UNS S31000] or ACI HK required to resist oxidation). |
| Above 2,000 to 2,200°F (1,095 to 1,205°C): | refractory-lined materials required |

---

(14) American Society of Mechanical Engineers, New York, NY.

(15) ASTM, Philadelphia, PA.

(16) Alloy Castings Institute, Des Plaines, IL.

2. Hydrocarbon + sulfur, hydrogen free (e.g., crude units, cokers):

| | |
|---|---|
| Above 450°F (230°C): | Use type 316L (UNS S31603) SS (2.5% Mo minimum) cladding in vacuum column only when neutralization number exceeds 0.5 mg KOH/gm. Use type 316L SS (2.5% Mo minimum) in the crude column as well when the neutralization number exceeds 2.0 mg KOH/gm. |
| Above 550°F (288°C): | Solid 5Cr or 12Cr clad is required for crudes containing over 1 wt% sulfur in absence of operating experience or hydrogen sulfide evolution data. For all hydrogen sulfide, use 9Cr minimum. |
| Above 650°F (345°C): | Solid 5Cr or 12Cr clad is required for crudes containing 0.1 to 1.0 wt% sulfur in absence of operating experience or hydrogen sulfide evolution data. Consider all steel when sulfur content is below 0.3 wt%. |
| Above 1,000 to 1,100°F (540 to 595°C): | 1Cr is adequate for resistance to corrosion from sulfur containing hydrocarbons when coking occurs on walls. |

3. Hydrocarbon + hydrogen, hydrogen sulfide less than 0.01 mol%:

| | |
|---|---|
| Above 400°F (205°C): | See API[17] Standard 941 for 1Cr, 1¼-½Mo, etc., based on hydrogen partial pressure. Avoid the use of C-½Mo in hydrogen service. Be sure to calculate the hydrogen partial pressure based on gaseous products only. Beware of furnace tubes and exchangers, as API Publication 941 curve is based on metal temperature. |

4. Hydrocarbon + hydrogen + hydrogen sulfide greater than 0.01 mol%:

| | |
|---|---|
| Above 400°F (205°C): | same as Number 3 above |
| Above 550°F (288°C): | Type 321 (UNS S32100) or type 347 (UNS S34700) SS cladding or solid. Consider 12Cr (650°F [345°C] maximum). Avoid type 304 (UNS S30400) and type 316 (UNS S31600) SS's because of intergranular stress corrosion cracking during downtime. Also avoid low-carbon grades of SS's (e.g., type 304L [UNS S30403], type 316L) because they may become susceptible to intergranular attack as a result of exposure to regeneration temperatures and because they have poor high-temperature strength. |

5. Sulfur dioxide/sulfur plants only:

| | |
|---|---|
| Below dew point: | type 304L SS (type 316L or alloy 20 required in many cases) |
| Above 700°F (370°C): | 18Cr-8Ni SS required |
| Above 800°F (425°C): | type 310 SS required (thermally stabilize after welding) |

---

[17] American Petroleum Institute, Washington, DC.

Above 1,200°F (650°C): refractory-lined materials required

6. Monoethanolamine (MEA) and diethanolamine (DEA):

All temperatures: stress relieve carbon steel welds and cold bends

Above 275°F (135°C): type 304 SS exchanger tubes to 285°F (141°C) maximum (based on metal temperature)

7. Potassium carbonate:

Above 140°F (60°C): stress relieve carbon steel. The use of 18Cr-8Ni SS required in reboilers and where turbulence (e.g., velocity) exceeds 8 ft/s (2.4 m/s). Do not use Monel(18) 400, Inconel(19) 600, or Colmonoy(20). Stellite(21) is acceptable.

8. Carbon dioxide in water:

Above 120°F (50°C): Use type 304L SS to dew point when the carbon dioxide partial pressure exceeds 4 psi (28 kPa). Aluminum is acceptable under the following conditions:

- a pH value between 4 and 8;
- no carbonate carry-over;
- copper less than 0.1 ppm and chloride less than 50 ppm; and
- velocity less than 100 ft/s (30 m/s) for mist-free gas; less than 60 ft/s (18 m/s) for up to 5 percent moisture; less than 10 ft/s (3.0 m/s) for gas loaded with condensate.

9. Sulfuric acid alkylation:

Below 100°F (38°C): Carbon steel is good in 70 to 99% $H_2SO_4$ for velocities less than 2 ft/s (0.6 m/s). Use alloy 20 in valves and in high-velocity areas.

10. Hydrogen sulfide:

Below water dew point: When the hydrogen sulfide partial pressure is greater than 0.05 psi (0.34 kPa), cracking of steels and some nonferrous materials can occur when hardness exceeds 235 Brinell(22) (Rockwell C 22) (see NACE Standard

---

(18) Trade name.

(19) Trade name.

(20) Trade name.

(21) Trade name.

(22) Trade name.

MR0175).[23] For carbon steel, the hardness limit should be 200 Brinell (Rockwell B 95) (see NACE Standard RP0472).[24] Avoid use of cement linings or Monel 400 for sour water. See Number 14 for corrosion allowance on carbon steel exposed to sour water.

Above 400°F (205°C): Monel 400 has no tolerance for hydrogen sulfide (gaseous or in aqueous solution).

11. Sodium and potassium hydroxide:

Above 140°F (60°C): Stress relief is required of carbon steel to avoid stress corrosion cracking of solutions containing less than 30% hydroxide.

Above 300°F (150°C): Monel 400 or Nickel 200 is required to resist corrosion (based on metal temperature).

12. Aqueous chlorides:

a. Pitting of 18Cr-8Ni SS in pH 8.3 water

Maximum Chloride Content Without Pitting or Crevice Corrosion, ppm

| Temperature | type 304 | type 316 |
|---|---|---|
| 77°F (25°C) | 180 | 500 |
| 104°F (40°C) | 100 | 220 |
| 140°F (60°C) | 60 | 150 |
| 176°F (80°C) | 40 | 90 |

b. Stress corrosion cracking

Above 120°F (50°C): SCC of 18Cr-8Ni SS is possible; therefore, alternative materials or precautions during shutdown of units containing significant amounts of hydrocarbon are necessary. Solution annealing at 1,800°F (980°C) or stress relieving at 1,650°F (900°C) is required for 18Cr-8Ni SS U-bent exchanger tubes. Type 321 or type 347 SS required when only U-bent portion of exchanger tubes heat treated.

13. Boiler feedwater:

Above 250°F (120°C): Use 12Cr pumps (ACI CA15 or CA6NM).

---

[23] NACE Standard MR0175, "Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment," NACE, Houston, TX, latest revision.

[24] NACE Standard RP0472," Methods and Controls to Prevent In-Service Cracking of Carbon Steel (P-1) Welds in Corrosive Petroleum Refining Environments," NACE, Houston, TX, latest revision.

14. Corrosion allowance on carbon steel:

| | |
|---|---|
| 1/16 in. (1.6 mm): | Use on vessels and piping in noncorrosive service unless otherwise specified. |
| 1/10 in. (2.5 mm): | Use for furnace tubes unless otherwise specified. |
| ⅛ in. (3.2 mm): | Required by many refiners as a minimum on vessels. Use on heat exchangers unless otherwise specified since no money is saved by specifying 1/16 in. (1.6mm) because ⅛ in. (3.2 mm) is a TEMA[25] Standard. Use for sour water piping when the hydrogen sulfide partial pressure exceeds 10 psi (70 kPa). |
| 3/16 in. (4.8 mm): | primarily used for sour water vessels and exchangers where the hydrogen sulfide partial pressure is less than 10 psi (70 kPa) |
| ¼ in. (6.4 mm): | Maximum corrosion allowance. Primarily used for wet carbon dioxide equipment when the carbon dioxide partial pressure is less than 4 psi (30 kPa) and for sour water equipment when the hydrogen sulfide partial pressure exceeds 10 psi (70 kPa). |

---

[25] Tubular Exchange Manufacturers Association, New York, NY.

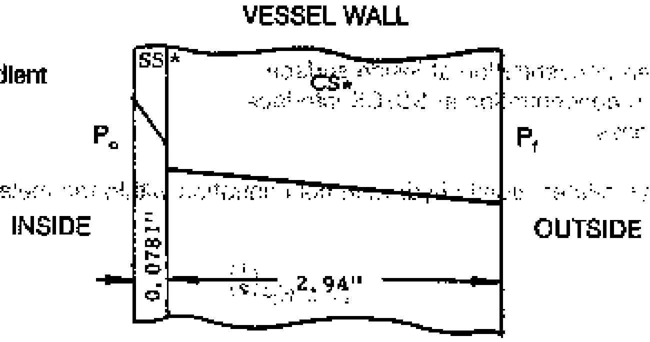
Appendix

# C

# Hydrogen Partial Pressure Calculations

A. **Problem:** Determine the equilibrium hydrogen partial pressure ($P_i$) at the carbon steel (CS) side of the stainless steel (SS)/CS interface in an 18Cr-8Ni SS clad carbon steel vessel, given the following information:

Atomic Hydrogen Concentration Gradient



Temperature: 750°F (400°C)

Partial pressure $H_2$: Inside 475 psia (3,275 kPa) = $P_o$
Outside 0 = $P_f$

Diffusion coefficients:

| | |
|---|---|
| SS | $10^{-9}$ cm²/sec |
| CS | $10^{-4}$ cm²/sec |

B. Theoretical Model

Assumptions:
1. Atomic diffusion limiting transport mechanism
2. Constant temperature through-wall
3. Steady state conditions
4. Hydrogen concentration in carbon steel is solubility limited

Flick's first law of diffusion through a solid (metal)

$$J = -D\frac{\partial C}{\partial X} \qquad \text{(CL.1)}$$

Where J = flow per unit area
D = diffusion coefficient
C = concentration
X = metal thickness

Predicts that at steady

$$\frac{\partial C}{\partial X} = \frac{\Delta C}{\Delta X} = \text{Constant}$$

(CL.2)

then hydrogen flow through the SS clad layer can be expressed as:

$$J_s = -D_s \frac{\Delta C}{\Delta t_s} = -D \frac{C_o - C_i}{t_s}$$

(C.1)

where $C_o$ = hydrogen concentration at inside surface
$C_i$ = hydrogen concentration at SS/CS interface
$t_s$ = SS thickness

However, Sievert's Law relates atomic hydrogen concentration within the metal to partial pressure by:

$$C = KP^{\left(\frac{1}{2}\right)}$$

(C.2)

where K = constant
C = hydrogen concentration
P = pressure (ATM)

Substituting Equation (C.2) into Equation (C.1) yields:

$$J_s = -D_s \frac{K_s(P_o^{\left(\frac{1}{2}\right)} - P_i^{\left(\frac{1}{2}\right)})}{t_s}$$

(C.3)

Similarly for CS backing metal:

$$J_c = -D_c \frac{K_c(P_i^{\left(\frac{1}{2}\right)} - P_1^{\left(\frac{1}{2}\right)}}{t_c}$$

which reduces to:

$$J_c = -D_c \frac{K_c P_I^{\left(\frac{1}{2}\right)}}{t_c}$$

(C.4)

since $P_f = 0$ from initial conditions.

Since flow through CS must equal flow through SS, then:

$$J_s = J_c$$

and, combining Equations (C.3) and (C.4):

$$-D_s \frac{K_s\left(P_o^{\left(\frac{1}{2}\right)} - P_I^{\left(\frac{1}{2}\right)}\right)}{t_s} = -D_c \frac{K_c P_I^{\left(\frac{1}{2}\right)}}{t_c}$$

(C.5)

Rearranging and solving Equation (C.5) for P yields:

$$P_I = \left[\frac{P_o^{\left(\frac{1}{2}\right)}}{1 + \frac{(t_s K_c D_c)}{(t_c K_s D_s)}}\right]^2$$

(C.6)

C. Interface Pressure Calculation

Substituting values given for $P_o$, $t_s$, $t_c$, $D_s$, $D_c$, and calculated for $K_c$ and $K_s$ into Equation (C.6) yields:

$$P_I = \left[\frac{(475)^{\frac{1}{2}}}{1 + \frac{(0.0781)(0.326)(10^{-4})}{(2.94)(3.0)(10^{-6})}}\right]^2$$

<u>$P_I$ = 286 psia</u>

D. Discussion

Results obtained with the theoretical model described above appear to be quite reasonable. An important assumption contained in the model is Assumption 4: *hydrogen concentration in carbon steel is solubility limited*. A necessary result of this assumption is a discontinuity in concentration gradient at the SS/CS interface (illustrated in the figure at the beginning of this Appendix).

Existing literature consistently reports a higher hydrogen solubility in ζ-iron than in α-iron. Therefore, since the crystal structure of the clad vessel wall changes from face-centered cubic (ζ) to body-centered cubic (α) at the SS/CS interface, the predicted discontinuity could be expected.

An alternate model equating interface hydrogen concentration to CS hydrogen concentration (i.e., Equation (C.1) becomes $J_s = D_s (C_o - C_{cs})/t_s$) predicts a pressure greater than seven times the initial hydrogen partial pressure inside the vessel. This result is obviously incorrect. While it is theoretically possible to charge a steel with a hydrogen concentration in excess of the thermodynamic equilibrium solubility, an unusual charging mechanism is required to do so. Since only temperature and pressure are active in this case, only normal thermodynamic equilibrium can exist, and the maximum possible hydrogen concentration is the solubility at given conditions.

In effect, this alternative model averages SS and CS hydrogen concentrations to produce a continuous concentration gradient across the interface. Since the interface concentration is considerably higher in this case than the equilibrium hydrogen concentration (solubility) in CS, the predicted pressure is also higher than equilibrium. Therefore, the solubility of hydrogen in CS at existing conditions becomes a limiting boundary condition, and Assumption 4 is valid.

## E. Calculation of Sievert's Law Constants

1. For carbon steel at a temperature of 750°F(400°C):

$$S = 42.7\, P^{\left(\frac{1}{2}\right)} \exp\left(\frac{-3{,}280}{T}\right)$$

where
S = solubility of hydrogen in ppm
P = pressure in atmospheres
T = temperature in degrees K

For P = 475 psia and T = 750°F(400°C) = 673°K:

$$S = 42.7 \left(\frac{475}{14.7}\right)^{\left(\frac{1}{2}\right)} \exp\left(\frac{-3{,}280}{673}\right)$$

$$S = 1.85 \text{ ppm}$$

Substituting this value into Sievert's Equation (C.2) and solving for K yields:

$$K_c = \frac{C}{P^{\left(\frac{1}{2}\right)}} = \frac{1.8}{\left(\frac{475}{14.7}\right)^{\left(\frac{1}{2}\right)}}$$

$$\underline{K_c = 0.326}$$

2. Stainless steel

Solubility data for type 347 (UNS S34700) SS

| | |
|---|---|
| Temp. | 700°F(371°C) |
| Pressure | 1,500 psia |
| Hydrogen conc. | 30 ppm |

Substituting Into Sievert's Equation (C.2) and solving for K yields:

$$K_s = \frac{C}{P^{\left(\frac{1}{2}\right)}} = \frac{30}{\left(\frac{1,500}{14.7}\right)^{\left(\frac{1}{2}\right)}}$$

$$\underline{K_s = 3.0}$$

Appendix

# D

# Submerged Arc Welded X65 and X70 Line Pipe

## *SCOPE*

Pipe shall be manufactured in accordance with API[25] specification for line pipe, API Standard 5L (List Current Edition). In addition, it shall comply with the provisions and requirements of this specification.

## *MANUFACTURING PROCEDURE*

1. Steel shall be made by the electric furnace or basic oxygen process. Steel shall be fully killed.

2. Pipe shall be made by longitudinally welding cold, preformed plate by the submerged arc welding process, using at least one pass from the inside and at least one pass from the outside, single seam.

3. Pipe may be cold expanded as permitted by API. Cold expansion shall be limited to a maximum of 1.5 percent. The manufacturers shall demonstrate and document in their quality manuals and procedures that expansion does not exceed this amount.

4. Pipe or plate may be heat treated as defined in API 5L, Paragraph 2.4. Details of the heat treatment shall be included in the manufacturing procedure submitted to the buyer.

5. The manufacturer shall perform all fabrication and welding in accordance with an established written procedure. The first production pipe shall be sectioned and tested. Included in the testing shall be the normal physical property and nondestructive testing as well as a microhardness traverse across the weld and heat-affected zone (HAZ). The hardness shall not exceed 280 HV10 at any location. Test results from previous production runs of these grades may be considered to fulfill this requirement if the chemical composition and welding procedure used are substantially the same as proposed for this order.

## *CHEMICAL PROPERTIES*

1. The chemical composition of the pipe shall fall within the following limits on product analyses:

| | Weight Percent |
|---|---|
| Carbon | 0.18 maximum |
| Manganese | 0.8 to 1.5 |
| Silicon | 0.35 maximum |
| Phosphorus | 0.020 maximum |
| Sulfur | 0.010 maximum |
| Columbium (Niobium) | 0.05 maximum |
| Vanadium | 0.08 maximum |
| Columbium + Vanadium | 0.10 maximum |

---

[25] American Petroleum Institute, Washington, DC.

| | Weight Percent |
|---|---|
| Nitrogen | 0.010 maximum |
| Aluminum (total) | 0.04 maximum |
| Aluminum (soluble) | 2 times Nitrogen (minimum) |
| Total of other impurities (Cr, Cu, Ni, etc.) | 0.5 maximum |

2. The manufacturer shall state in the quotation the nominal (aim) chemical composition and steelmaking route for pipe on the order. Intentional alloy additions other than columbium or vanadium will not be permitted without approval of the buyer.

3. The carbon equivalent:

$$C + \frac{Mn}{6} + \frac{Cr + Mo + V}{5} + \frac{Ni + Cu}{15}$$

as determined by product analysis, shall not exceed 0.42.

4. Both heat and product analyses shall be furnished.

5. Analyses shall be taken from each lot of pipe.

## *MECHANICAL PROPERTIES AND FRACTURE TOUGHNESS TEST*

1. Plate and weld tensile properties shall conform with the requirements for the applicable grade as shown in Table 4.1 of API 5L; however, the yield strength shall not exceed 80,000 psi (551,600 kPa) for API X65 and 85,000 psi (586,100 kPa) for API X70 material.

2. Tensile properties shall be measured on one sample per lot of pipe. A lot of pipe is defined as a group of pipe of the same diameter and wall thickness that has been fabricated from the same heat of steel.

3. A set of three Charpy impact test specimens shall be taken from a pipe representing each heat of steel furnished on the order. The samples shall be tested in accordance with Appendix SR-5 of API 5L.

   a. Specimens shall be Charpy V-notch Type A.

   b. Temperature of testing shall be -20°F (-29°C).

   c. To be acceptable, the minimum average of the three tests shall be at least 35 ft-lbs (47.5J) and no individual test shall be fewer than 28 ft-lbs (38J) based on full size (10 mm x 10 mm) specimens. Percent shear area shall also be reported.

   d. If the test results are unacceptable, retests may be performed in accordance with paragraph SR5B.4 of API 5L.

4. Dropweight tear testing on a 20 in. (508 mm) diameter and larger pipe shall be carried out at 32°F (0°C) in accordance with Appendix SR-6 of API 5L; however, 100 percent of the heats shall exhibit 85 percent or more shear fracture area.

## HYDROSTATIC TESTS

1. Each length of pipe shall be given a mill hydrostatic test that will produce in the pipe wall a hoop stress of 95 percent of the minimum specified yield strength. Test pressure shall be maintained for at least 10 seconds.

2. Hydrostatic test gauges shall be calibrated prior to production and at least once a week. Certified dead weight testers shall be used for calibrations. A buyer representative shall witness the calibration of all gauges.

3. The hydrostatic testing records and certificate shall include the pipe numbers.

## DIMENSIONS

1. The pipe shall be furnished in 35 ft (10.7 m) minimum average lengths. The maximum length shall be 45 ft (13.7 m) and the minimum length shall be 19 ft (5.8 m). Not more than 10 percent of the lengths in any shipment shall be less than 26 ft (7.9 m).

2. Jointers shall not be furnished.

3. Pipe diameter, wall thickness, and weights shall be as specified in API 5L, Table 6.2.

4. Pipe ends shall be smoothly beveled to an angle of 30 degrees +5, -0 degrees, up to 5/8 in. (16 mm) thick and 10 degrees for the remaining thickness, measured from a line drawn perpendicular to the axis of the pipe. The root face dimension shall be 1/16 in. (1.5 mm) ± 1/64 in. for 95 percent of the circumference. The remaining 5 percent may vary between 1/32 in. (1 mm) and 3/32 in. (2.5 mm) maximum.

5. Pipe ends shall be machined perpendicular with the longitudinal axis of the pipe. The maximum deviation as measured with a square shall be 1/16 in. (1.5 mm).

## NONDESTRUCTIVE EXAMINATION

1. All plate used for manufacturing pipe shall be ultrasonically examined to detect gross laminations in the plate. Examination shall be in accordance with ASTM(26) A435 or other mill standard technique acceptable to the buyer. Mill procedures shall be submitted to the buyer for permission to proceed prior to production. To be acceptable, lamellar-type defects shall not exceed 4 in. (100 mm) in the longitudinal direction or 1 in. (25 mm) in the transverse direction throughout the body of the plate. The limit along the edges of the plate shall be ¾ in. (19 mm) in any direction.

2. The nondestructive test required by API 5L paragraph 9.1(a) shall be performed for final acceptance after expansion and hydrostatic testing. Any nondestructive examinations performed prior to this shall be for the mills internal quality control and subject to the buyer's mill representative's review.

3. The sensitivity of the ultrasonic examination of the welds shall be calibrated in accordance with paragraph 9.15 of API 5L and the following provisions:

    - The test pipe shall be run at the start of each shift and at other times when requested by the buyer's inspector.

---

(26) ASTM, Philadelphia, PA.

- Calibration shall be performed at the same rate of speed used in production testing.
- Any of the four types of imperfections specified in Paragraph 9.15 of API 5L may be used to calibrate the equipment.

4. Defects found by ultrasonic examination that produce an indication greater than the acceptance limit signal given in Table 9.5 of API 5L shall be investigated further by manual probing and shall be radiographed. Defects that exhibit indications of cracks or lack of penetration shall also be investigated as above.

5. Each end of the longitudinal welds shall be radiographed covering a distance of at least 8 in. (200 mm) after expansion and hydrostatic testing. Radiographic film shall be Kodak[27] Type AA or equivalent, and each film shall contain a 2 percent penetrameter. If the wire type penetrameters are used, the sensitivity shall be 1.5 percent. Penetrameter thickness shall be based on metal thickness.

6. The inside surface of both ends of the weld seam of each pipe shall be examined by the magnetic particle method for a distance of 4 in. (100 mm) in accordance with API 5L paragraph 9.19 through 9.21.

7. All pipe containing injurious defects exceeding the limits of Section 9 of API 5L shall be rejected unless repairs are permitted in accordance with the paragraph on repair of defects of this specification.

8. A written record shall be made of all ultrasonic and radiographic inspection identified to individual pipe lengths and shall be available for review by the buyer's inspector.

9. Residual magnetism shall be measured on the beveled ends of the finished pipe. The maximum permitted residual magnetism shall be 30 gauses.

## *REPAIR OF DEFECTS*

1. Defects not exceeding 8.0 percent of the specified wall thickness may be removed by grinding.

2. No welding repairs shall be made on the parent pipe or plate.

3. Injurious weld defects in excess of 8.0 percent of the specified wall thickness may be repaired by welding on approval of the buyer's inspector; however, cracks in either the original weld or in repair welds shall be unacceptable and may not be repaired.

4. Defects shall be removed completely and the cavity cleaned thoroughly prior to repair welding.

5. The repair welding procedure and operators shall be qualified in accordance with API 5L, Appendix B, in the presence of the buyer's inspector. Manual welding shall be performed using low-hydrogen electrodes. Qualification testing of repair welding procedures shall include Charpy V-notch testing of the weld metal and HAZ. Acceptance criteria shall be the same as specified in the Mechanical Properties and Fracture Toughness Tests section of this specification.

6. No more than three repair welds shall be permitted on any individual pipe and adjacent repairs shall be separated by at least one pipe diameter.

7. All weld repairs shall be xrayed. The film coverage shall extend at least 4 in. (100 mm) beyond the ends of the repair weld.

---

[27] Trade name.

8. Dents in excess of those permitted in paragraph 10.5 of API 5L are unacceptable and shall not be repaired.

9. The manufacturer shall certify that all injurious defects observed during radiographic and ultrasonic inspection have been removed.

## *MARKING*

1. Pipe markings prescribed in API 5L shall be paint-stenciled on the inside of the pipe; however, for pipe with a nominal outside diameter of 12 in. and under, marking may be either on the inside or outside unless otherwise specified on the order. If this identification is lost or obliterated, the length shall be rejected.

2. The joint number, length, and weight shall be paint-stenciled inside one end of the pipe.

3. The length shall be given in feet and tenths of a foot (meters).

4. Color banding for all wall thicknesses may be required. When requested, a stripe approximately 2 in. (51 mm) wide shall be painted on the outside surface around each end of each length of pipe. The exact color code will be specified on the purchase order.

5. Pipe shall be furnished mill coated inside and outside or bare with no lacquer or oil on either the ends or the body of the pipe, except for the necessary markings prescribed above. A light coat of clear lacquer may be sprayed over the stencil area only on bare pipe. If the pipe is coated at the mill, the internal coating shall meet the requirements of API RP 5L2 (list current revision) and the external coating shall meet the requirements of the buyer's specification.

## *END PROTECTORS AND TRANSPORTATION*

Each pipe shall be fitted with bevel protectors to prevent damage during shipment. Pipe that is 14 in. (356 mm) in diameter and larger shall be fitted with metal bevel protectors.

## *TRANSPORTATION*

Pipe shall be loaded for shipment in accordance with API RP 5L1, *Railroad Transportation of Line Pipe*, or API RP 5L5, *Marine Transportation of Line Pipe*, whichever is applicable.

Pipe that travels on board ships shall be stowed below deck unless otherwise authorized by the buyer.

# Index