Materials Selection for Petroleum Refineries and Gathering Facilities

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Preface

The purpose of this book is to enable engineers with limited knowledge of materials selection to benefit from the information the author has gathered in his 40 years in the engineering and construction business and to have in one place information that is scattered throughout various technical articles, committee minutes, engineering office files, and so forth. Since the author has spent his career in the engineering and construction field as a materials engineer with a corrosion and metallurgy background, the information is presented from that point of view. A detailed discussion of refinery processes, safety, reliability, effect of fire, fitness for service, and prediction of deterioration is beyond the scope of this book.

During the five years since the publication of the first edition, coauthored by E.F. Ehmke, a great deal more has been learned about materials of construction for petroleum facilities. Every chapter, appendix, etc., has been reexamined and updated. In addition, the bibliographies have been updated, and specific references have been added.

There have been major changes in sections covering naphthenic acid corrosion, overhead corrosion, alkylation plants, amine units, sensitization of austenitic stainless steels, hydroprocessing unit air cooler corrosion, wet hydrogen sulfide effects, corrosion in gas streams containing hydrogen sulfide/carbon dioxide mixtures, and pitting of stainless steels (including super and duplex). Finally, this edition also includes sections covering flare tips, bending, and deaerator cracking.

As with the first edition, the first part of Chapter 1 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 materials of construction and equipment used in the various petroleum refinery processes and gathering facilities.

The original four appendices also have been updated. As with the previous edition, 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 typical specifications for steel line pipe.

This book is, by necessity, condensed. Because information on materials performance is continually being generated 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 references and bibliographies. The reader also should 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 materials of construction for engineers unfamiliar with the subject. It has been expanded into a course available through Bechtel Corp.

Numerous colleagues contributed valuable suggestions that were incorporated into the book, for which the author is extremely grateful. In particular, the author is indebted to E.F. Ehmke, who was so helpful during the author's early years in materials engineering, and with Chapter 1 in the first edition. Most recently, the author is indebted to the Chevron materials engineers at CRTC, with whom he has had the privilege of enhancing his experience while working with them. Special thanks go to Jo Gutzeit, Keith Lewis, and Robert D. Merrick, who supplied numerous excellent comments that were incorporated and make a much better presentation.

Finally, the author is indebted to his wife, Barbara, for her constant support and suggestions.

R.A. White, Ph.D

Contents

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Petroleum Refining Processes, Petroleum Corrosion, Crude Oil Fractionation Units, Utilities

OVERVIEW

1.1 Refinery Processes

Common refinery processes are:

Distillation - Atmospheric and vacuum distillation of crude oil and downstream conversion unit distillation that separates molecules by their boiling points.

Hydrotreating - A catalytic reaction of distillate fractions with hydrogen at elevated pressures and temperatures primarily used to desulfurize the feed. The products are hydrogen sulfide and hydrocarbon; organic nitrogen compounds react to form ammonia and hydrocarbon while 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 occurs.

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, lower boiling-point products.

- **Thermal cracking** - The most prevalent thermal processes are visbreaking and coking, both of which are applied to residuum.(2) Visbreaking is a mild thermal cracking; coking is a severe thermal cracking.
- **Fluid Catalytic Cracking (FCC)** - 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(3) 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, also are produced.

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(1) Naphtha often is confused with naphthene. Naphthenes are cyclic hydrocarbon compounds, whereas, naphtha is defined as a hydrocarbon mixture with a boiling point from 50°C to 200°C (120°F to 400°F).

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

(3) See section 2.1, no. 2 for definition of olefin.

- **Hydrocracking** - Distillates heavier than diesel are catalytically cracked at high pressure and elevated temperature 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 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 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.

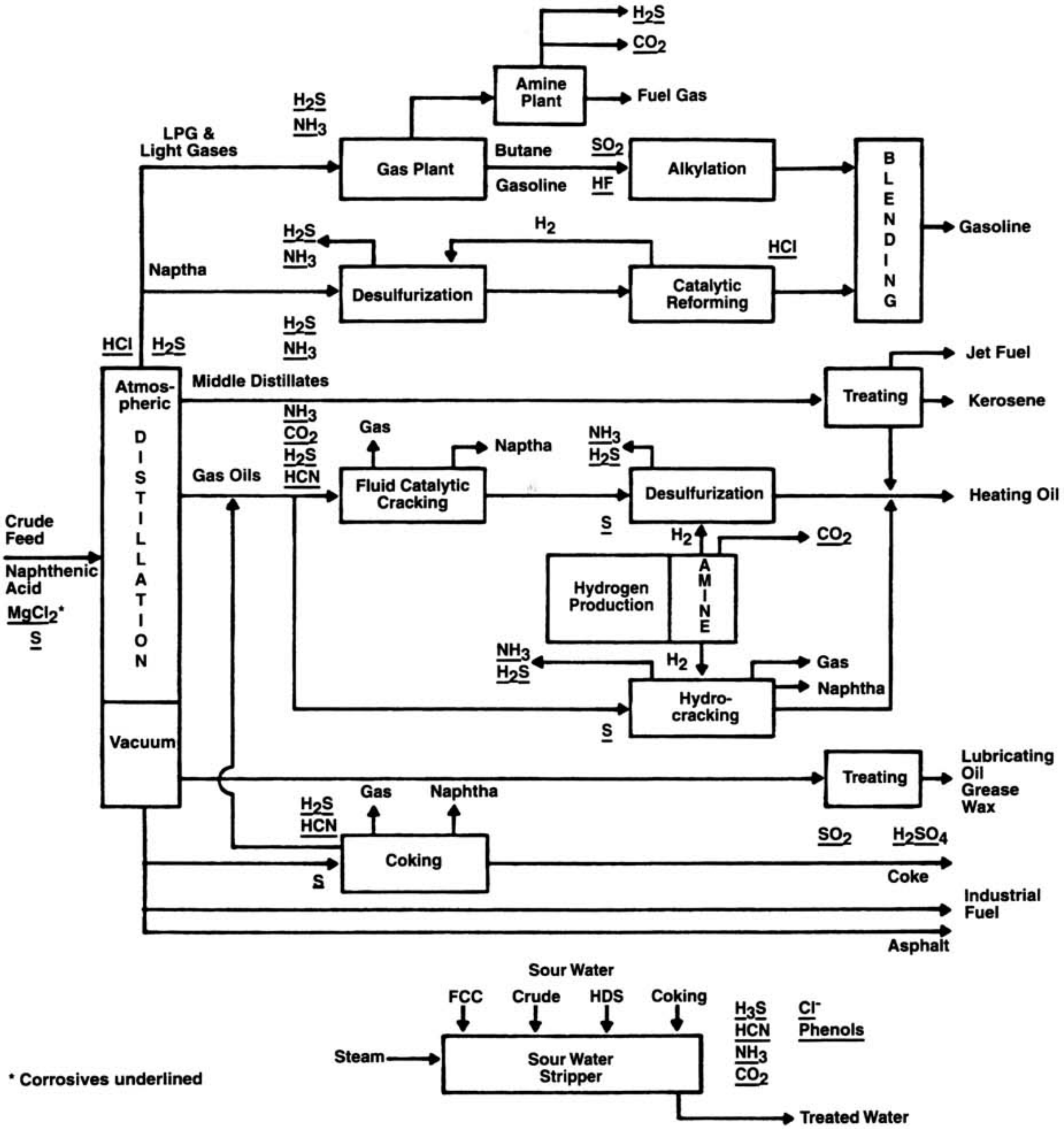
Supporting Processes - The primary support process units are:

1. Amine unit - Light gases are brought into contact with amine to absorb hydrogen sulfide and/or carbon dioxide. The amine is regenerated by removing hydrogen sulfide and/or carbon dioxide, which is then fed to a sulfur plant.
2. Sulfur plant - Acid gas (hydrogen sulfide, sulfur dioxide, and carbon dioxide) is fed to a sulfur plant, where the hydrogen sulfide is converted to elemental sulfur by partial oxidation with air.
3. 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.
4. Hydrogen plant - Natural gas (or refinery gas) and steam catalytically react at high temperature to form carbon dioxide and hydrogen. The carbon dioxide is removed by absorption, and the hydrogen is used in hydroprocessing units.

Figure 1.1 is a simplified block flow diagram for a refinery processing a high sulfur crude oil to obtain a large number of products.[1] The crude oil is fractionated in an atmospheric distillation unit at about 345 kPaa (50 psia) at temperatures up to about 370°C (700°F). Naphtha and lighter components are produced at the top of the column (overhead products). The kerosene, diesel, and light gas-oil 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 runs at about 10 kPaa (1.45 psia) and at temperatures up to about 415°C (775°F).

The boiling ranges of the products generally are:

Light ends:	butane and lighter
Light gasoline:	C_5 to 82°C (180°F)
Heavy naphtha:	82-177°C (180-350°F)
Kerosene:	177-260°C (350-500°F)
Diesel:	260-343°C(500-650°F)
Light gas-oil (atmospheric column):	343-370°C (650-700°F)
Light gas-oil (vacuum column):	370-455°C (700-850°F)
Heavy gas-oil:	455-565°C (850-1,050°F)
Residuum:	565°C (1,050°F) plus



* Corrosives underlined

Figure 1.1 - Simplified refinery process flow diagram.[1]
(Reprinted with permission from *The Role of Stainless Steels in Petroleum Refining*, April 1977, American Iron and Steel Institute, Washington, DC)

Butane and lighter gases from the atmospheric crude oil distillation unit, hydrotreaters, catalytic reformers, and hydrocrackers are fed to a gas plant to recover C_3 and C_4 compounds. 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) 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 (HDS). 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 a 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 residuum 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 residuum can be fed to a visbreaker for viscosity reduction. Alternatively, the vacuum residuum 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. FCC, fluid cokers, delayed cokers, sour water strippers, and sulfur plants are covered in Chapter 2. Desulfurizers, reformers, hydrocrackers, and flue gas are discussed in Chapter 3. Hydrogen plants, methanol plants, ammonia plants, and gas treating are discussed in Chapter 4. Underground piping, pipelines, production gathering equipment, and tankage associated with the refinery industry are covered in Chapter 5. 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.

1.2 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, and so forth 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 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.

The corrosion allowances given in Appendix A are the product of maximum anticipated corrosion rate and the design lives listed in Appendix A. Corrosion allowances are given in millimeters. The typical corrosion allowances used in the metric system (e.g., 1.5 mm, 3 mm, etc.) are not numerically equal to the typical corrosion allowances used in English units (e.g., 1/16 inch, 1/8 inch, etc.). However, they are roughly equivalent. Often temperatures (e.g., 150°C [300°F]) also are only approximately equal, because it usually is more convenient to use round numbers in each system.

It must be recognized that corrosion is not uniform, and the equipment may be exposed to unanticipated corrosives. Therefore, in order to have the least expensive equipment consistent with good engineering practice, it is recognized that some areas may require repair during the design life. Although it is often more economical to have a minimum first-cost for equipment – consistent with avoiding premature plant shutdowns – then to use maintenance dollars to obtain the total design life, safety and reliability also must be taken into account when selecting materials of construction.

A corrosion allowance of 1.5 mm (1/16-inch) is the generally accepted minimum for carbon and low alloy steel equipment(4)(5)(6) consistent with the minimum first-cost approach. Because material normally is purchased in standard wall thickness, e.g., specifying a 1.5 mm (1/16-inch) minimum corrosion allowance for carbon and low alloy steel usually results in an actual corrosion allowance closer to 3 mm (1/8-in.), because the actual corrosion allowance is the wall thickness minus that calculated for pressure.

Both clad and weld overlay are used interchangeably to indicate materials of construction. The choice between roll bond clad, weld overlay, and explosive bond clad basically is a matter of economics. Roll bond cladding usually is economical when the calculated thickness of the high alloy material is in the order of 13 mm (0.5 in.) or greater. As the cost of high alloy material increases, the thickness where roll bond cladding becomes economical decreases. When the backing plate thickness exceeds 51 mm to 64 mm (2 in. to 2.5 in.), weld overlay and explosive bonding become more attractive. Explosive bonding often is economical for thick backing plates, such as those used for tubesheets.

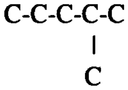
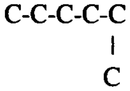
There are, however, some additional considerations. The backing material for roll bond clad plate is heat treated after the cladding operation. This can be detrimental to high alloy cladding that form undesirable phases at the temperatures required to heat treat the backing material.[2] Thus, weld overlay or explosive bond clad might be more desirable for these materials. Note, however, there have been some lack of bond problems reported with explosive bonded materials when the backing plate was too thin, e.g., 9.5 mm (3/8 in.).

Materials selection for centrifugal pumps is contained in API 610, Appendices G and H.[3] Minimum requirements for fired heaters are contained in API 560. Both NACE International Group Committee T-8 on Refinery Industry Corrosion and the API Corrosion Committee publish minutes of their semiannual meetings. A computer software database of the 1959 to 1994 T-8 minutes is available from NACE International.[4]

2. CRUDE UNITS

2.1 Crude Oil

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

1. Paraffin series	C_nH_{2n+2}	Saturated (-ane suffix) e.g., hexane
2. Olefin or ethylene	C_nH_{2n}	Unsaturated (double bond; -ene suffix) e.g., ethylene
3. Naphthenes	C_nH_{2n}	Saturated, ring compound, e.g., cyclohexane
4. Aromatic	C_nH_{2n-6}	Benzene series
5. Diolefin	C_nH_{2n-2}	Two double bonds
6. Cyclic series	C_nH_{2n-2}	C_nH_{2n-8}, etc. -uncommon
7. Paraffin isomers	 $\text{C-C-C-}\underset{\underset{\text{C}}{\mid}}{\text{C}}\text{-C}$	 $\text{C-C-C-C-}\underset{\underset{\text{C}}{\mid}}{\text{C}}$

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(4) For an internally lined and externally painted equipment, a zero corrosion allowance is often used. For SS and high alloy material, 0.5 mm (1/32 -in.) is usually a minimum if some corrosion is expected. Where no corrosion is expected on SS or high alloy material, zero corrosion allowance is sometimes specified.

(5) Heat exchanger tubes are a special case. They are normally specified as a particular gauge, e.g., 12-gauge, 14-gauge, etc. This usually results in an adequate amount of corrosion allowance for the typical five-year life assumed for exchanger tubes. This is because exchanger tubes normally are only 19 mm to 25 mm (0.75 in. to 1 in.) in diameter; thus, the wall thickness required for pressure usually is very small. However, when the gauge is specified, the wall thickness required for pressure must be determined by the designer to make sure the thickness is adequate for pressure plus some nominal corrosion allowance. This is particularly important if there is a high differential pressure across the tubes and the unit must operate with loss of pressure on either side. Alternatively, some users specify small corrosion allowances ranging from 0.25 mm to 1.5 mm (0.01 in. to 0.065 in.)

(6) The minimum corrosion allowance for pressure containing parts in TEMA (Tubular Exchangers Manufacturing Association) Class R heat exchangers is 3.0 mm (1/8 in.).

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

Constituent	Volume %
Heavy oil (approximately C_{35})	29
Asphalt (approximately C_{50})	2
Wax (approximately C_{40})	2
Paint thinner (approximately C_{10} - C_{12})	12
Kerosene/jet fuel (approximately C_{12} - C_{16})	12
Gasoline (C_7 - C_{11})	31
Miscellaneous hydrocarbon impurities	12
Salt, water, sulfur, and nitrogen compounds	Trace

2.2 Corrosive Constituents in Oil

The constituents in oil that cause corrosion are sulfur compounds, saltwater, inorganic and organic chlorides, inorganic and organic acids, and organic nitrogen compounds (which form cyanides). The sulfur compounds found in crude oil are shown in Figure 1.2.[5] As can be seen from the tabulation, a wide variety of sulfur compounds may be present in crude oil. A crude oil containing more than 0.0014 m^3 (0.05 ft^3) of dissolved hydrogen sulfide per 378 liters (100 gal.) of oil is called sour. However, a crude oil containing less than 0.014 m^3 (0.5 ft^3) of hydrogen sulfide per 378 L (100 gal.) of oil is not corrosive to steel in petroleum processing equipment.

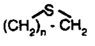
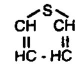
Type		Formula	Found In Crude Oil	 Straight-Run Products	 Cracked Products
Elemental Sulfur		S	Yes	Yes	Yes
Hydrogen Sulfide		H_2S	Yes	Yes	Yes
Mercaptans					
	Aliphatic	RSH	Yes	Yes	Yes
	Aromatic	RSH	Yes	Yes	Yes
	Naphthenic	RSH	No	No	No
Sulfides					
	Aliphatic	R-S-R	Yes	Yes	Yes
	Aromatic	R-S-R	No	No	No
	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.[5]

(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)

The types of organic sulfur compounds shown in the first column in Figure 1.2 thermally decompose during processing to constituents, such as hydrogen sulfide and mercaptans. If sufficient quantities of organic sulfur compounds (above about 0.2 wt% to 0.3 wt% sulfur) are present, the crude oil is corrosive to carbon and low alloy steels at temperatures above about 232°C to 288°C (450°F to 550°F) and up to 455°C (850°F). Above 455°C (850°F), corrosion rates drop if coking occurs on the walls; otherwise, the corrosion rates continue to increase. It is important to note that the wt% sulfur limit is for crude oil, not cracked products. As can be seen in Figure 1.2, a number of sulfur compounds remain in cracked products in addition to H_2S. Foroulis has shown that the aliphatic and aromatic mercaptans and the aliphatic sulfides and disulfides that remain in cracked products are very corrosive.[10] (Conversely, the thiophenes do not decompose, hence, are not corrosive.) These compounds are corrosive in ppm quantities at elevated temperatures as discussed in Chapter 3, Section 2.7.

Chromium steels, e.g., 1-1/4 Cr-1/2 Mo, are required in naphthalene above 370°C (700°F) even when the sulfur is below 0.2 wt%. This is because the decomposition of naphthalene to undesirable products is catalyzed by carbon steel above 370°C (700°F).

Assays of crude oil 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 oil increases. Fire flooding, 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 if naphthenic acid corrosion will be a problem. The increase in crude oil specific gravity makes the determination of the total acid number more difficult and more subject to error.

The total acid number (TAN), or neutralization number, of crude oil is determined by titration with KOH, as described in ASTM D974-95 ("Standard for Test Method for Acid and Base Number by Color-Indicator Titration" [British Standard 2634]) or D664-95 ("Test Method for Acid Number of Petroleum Products by Potentiometric Titration" [British Standard 4457)] for *neutralization value*. This value is expressed in milligrams of KOH required to neutralize the acid constituents present in one gram of sample. Although the TAN is only an indicator of the presence of naphthenic acids in crude oils (because other organic acids also contribute to the total acid number), a TAN exceeding 1.5 to 1.8 (mg KOH/g) indicates the presence of a sufficient amount of naphthenic acids to be corrosive. However, attack has been reported in turbulent areas where the velocity exceeds 30 m/s (100 ft/s) when the TAN exceeds 0.3. The situation is further complicated because the light naphthenic acids are more corrosive than the heavy naphthenic acids.

Crude oils from Venezuela and California often contain naphthenic acids.(7) Naphthenic acids become corrosive to carbon steel above about 200°C (400°F), although attack has been seen as low as 170°C (340°F) in turbulent areas. Crude oils with a TAN in excess of 0.5 mg KOH/g cause serious corrosion problems in the vacuum column flash zone because naphthenic acids tend to concentrate in the heavier constituents,(8) (because the lighter hydrocarbons are vaporized in the atmospheric unit) which are sent to the vacuum column.

Naphthenic acid corrosion problems have been reported in the low sulfur Asian crude oils with neutralization numbers below 0.5. This is because very high TANs are found in fractions within a very narrow boiling point range. Conversely, in high sulfur crude oils naphthenic acids appear to be less of a factor in corrosion. For example, to date there has been a notable lack of naphthenic acid attack reported in high sulfur (2.9% to 4.3% S) Northern Alberta, Canada recovered bitumens with TANs from 0.75 to 2.8. The lack of attack may be because the liberated H_2S reacts with the iron naphthenates to form a protective iron sulfide scale, or that the naphthenic acids are destroyed by initial processing, such as hydrotreating.(9)

Recently, a test (limited to carbon steel) has been developed to try to distinguish between corrosion controlled by sulfidation and corrosion controlled by naphthenic acid. In this test, the ratio of the corrosion rate in mils/y to the weight of corrosion product in mg/cm^2 is used to define which mechanism is controlling. A ratio of less than 10 indicates sulfidation is controlling. A ratio of 100 or greater indicates naphthenic acid corrosion is controlling. Between these two limits is mixed control.(10)

Inorganic chlorides (e.g., hydrogen chloride) usually collect in the tops of columns and in equipment connected to the tops of columns. This results in mild to serious corrosion. Conversely, organic chlorides tend to stay with the residuum stream and cause problems downstream. When organic nitrogen compounds in the feed exceed 0.05 wt% (500 parts per million [ppm]), cyanides and ammonia are formed in units downstream of the crude unit, e.g., cokers and catalytic crackers. Only ammonia is formed in hydroprocessing units. These compounds collect in the aqueous phases and cause corrosion of certain materials.

If air (oxygen) gets into equipment during operation it also can cause corrosion and fouling problems in

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(7) Naphthenic acids also have been reported in some Far East, African, Russian, Gulf Coast, Indian North Sea, and Canadian crudes.

(8) Primarily vacuum (heavy) gas oil.

(9) It is well established that naphthenic acids are destroyed in hydrotreater reactors.

(10) In essence, all that is being done is to say if almost all of the metal loss from corrosion can be accounted for in the (iron sulfide) scale then sulfidation is controlling. Conversely, if a great deal of the metal loss cannot be accounted for in the scale, then naphthenic acid is controlling.

hydrocarbon streams that contain water. Therefore, care should be exercised to minimize air getting into equipment from leakage in seals, air in-leakage in vacuum columns, etc. Corrosion problems in the aqueous phases are discussed in the following section on overhead systems, in the Chapter 2 section on characteristics of sour water, and in the Chapter 3 section on coolers.

2.3 Corrosion in Crude Units

2.3.1 Overview

Figure 1.3 shows a simplified flow diagram and process description of a crude oil distillation unit.[1] The crude oil is first desalted to minimize formation of hydrochloric acid in waters condensed from the top of the fractionator columns and to minimize salt deposits in the preheat section. As the crude oil is heated above 232°C to 288°C (450°F to 550°F), depending on the wt% sulfur,(11) corrosion begins to occur due to breakdown of sulfur compounds. Condensing water containing hydrogen sulfide and hydrogen chloride 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 vapor velocities and flashing. The cycle of corrosion above 232°C to 288°C (450°F to 550°F) and in the condensing water in the overhead system is repeated in the other two columns as the bottoms from the preceding column are further distilled.

2.3.2 Overhead Systems

Figure 1.3 shows a single-drum overhead system. Double-drum systems also are used. The difference between the two systems is the reflux temperature at the top of the tower. In the single drum system, total

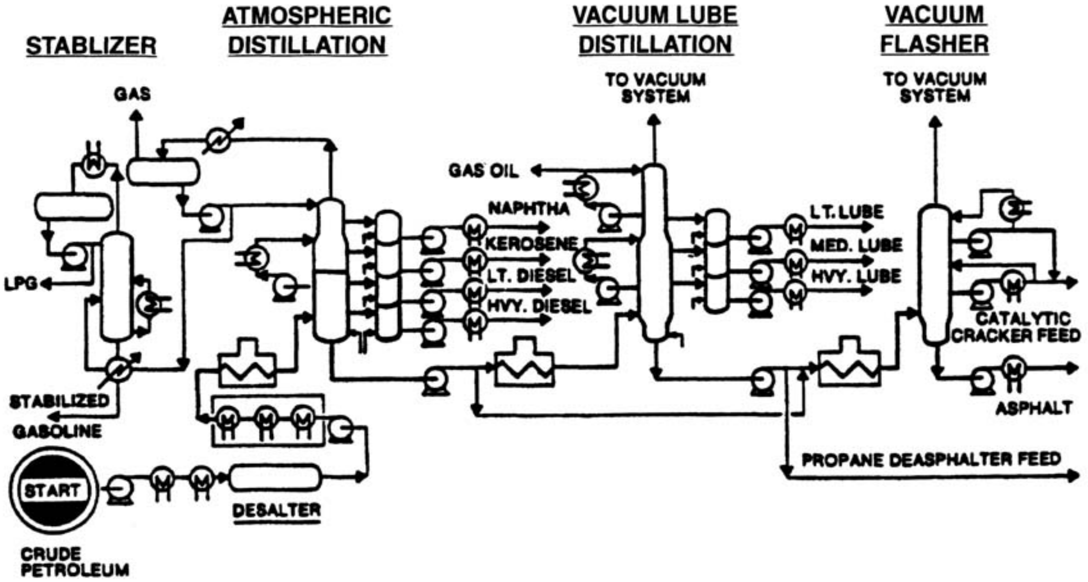

Figure 1.3 - Crude distillation, three stages.[1]
(Reprinted with permission from *The Role of Stainless Steels in Petroleum Refining*, April 1977, American Iron and Steel Institute, Washington, DC)

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(11) In general, the higher the sulfur content, the lower the temperature where corrosion begins to be a problem. However, as shown in Figure 1.13, it is the sulfur release characteristics that determine at what temperature corrosion begins to be a problem.

liquid condensation occurs in the overhead condensers. The reflux will be cool and 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. If direct addition of the cold reflux will cause condensation on the trays, measures such as spray distribution of the reflux or raising the tower top temperatures should be taken to prevent this. Addition of neutralizing amines to the reflux to neutralize the acid should not be done because this results in column tray corrosion from the formation of amine hydrochloride salts. Some refiners recommend limiting the vapor velocity in the overhead lines to 15 m/s (50 ft/s); however, 37 m/s to 43 m/s (120 ft/s to 140 ft/s) is more common. The vapor velocity is limited to 7.5 m/s (25 ft/s) in the presence of water (two-phase flow).

The initial corrosion control system used in a crude unit is a desalter. Modern desalters accomplish separation of oil and water electrostatically. The internals used to accomplish electrostatic separation normally are of a propriety design. The vessel itself usually is carbon steel. Some refiners specify that the bottom be cement-lined; however, most refiners specify only a heavy corrosion allowance to protect against corrosion from the saltwater that collects on the bottom of the vessel. The payout on a desalter is difficult to establish. Desalters normally are used when the salt content of the crude oil exceeds 76 ppm (20 lbs per 1,000 barrels [ptb]).(12) When high reliability of the unit is desired, crude oils with salt contents of 30 ppm to 38 ppm (8 ptb to 10 ptb) are desalted. Some refiners now feel that a desalter should be used regardless of the salt content. The goal in desalting is 3.8 ppm (1 ptb) or less in the effluent crude oil. This results in 50 ppm or less of HCl in the overhead water. 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 (BS&W) as well as any brines in the crude oil that result from lack of settling in the oil field, saltwater from tankers, and emulsified salt brine in the crude oil. Additives are used to help break the emulsion after the crude oil is heated to about 120°C to 135°C (250°F to 275°F) depending on the viscosity of the crude oil. Wash water, preheated by the effluent water, helps to dissolve the salts from the crude oil. Although mixing the water and crude oil is important, some systems are not designed to accommodate this procedure. For example, some systems are not designed for the 207 kPa (30 psi) pressure drop required across the mixing valve.

Removal of salts from crude oil is important to avoid corrosion and plugging of the overhead system. Plugging is caused by the formation of salts, e.g., ammonium chloride, from the reaction of neutralizers and HCl. Saltwater in crude oil usually is similar to ocean water. Sodium chloride is thermodynamically stable; however, magnesium and calcium chlorides thermally decompose at relatively low temperatures.(13) The decomposition reaction converts about 90% of the $MgCl_2$ and about 15% of the $CaCl_2$ to metal oxides and hydrochloric acid in the presence of water vapor (hydrolysis). The hydrolysis takes place in the vapor phase as the crude oil is heated to be fed to the atmospheric and vacuum towers. Since the hydrolysis takes place in the vapor phase at temperatures below the temperature where HCl causes a significant acceleration of corrosion in the crude oil environment, corrosion from the HCl does not occur until it dissolves in the condensing water in the top of the towers. Desalting to 3.8 ppm (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. Adding sufficient water to quench through the dew point before the first exchanger will minimize the hydrochloric acid concentration.

One way to reduce the amount of HCl is caustic injection after the desalter. The injection amount is guided by the amount of salt in the overhead condensate. The amount of caustic added usually is limited to 10 ppm (2.6 ptb). Caustic normally is not added when the products of the crude unit will be fed to hydrotreaters or fluid catalytic crackers because it may deactivate the catalyst. Fluid cokers will foul from premature coking if more than 19 ppm (5 ptb) of caustic is used. 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

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(12) The exception is when the specific gravity of the crude oil is the same as that of the water. Although there are some recent developments which may allow desalting in this situation, in the past it has not been possible to desalt when there was not a significant difference in the specific gravity of the crude oil and that of water.

(13) Magnesium chloride thermally decomposes at around 120°C (250°F).

required to avoid problems with a caustic injection system:

1. Use an injection quill(14) designed to avoid caustic embrittlement at the injection point.
2. Inject the caustic into a slipstream of crude.
3. Put the crude oil on the tube side of preheat exchangers. This will prevent the caustic from concentrating in pockets around baffles and floating heads.
4. Avoid overfeeding. Overfeeding caustic, poor mixing, or using a caustic that is too strong causes furnace tube coking, fouling of crude oil preheat exchangers, and caustic embrittlement.

Caustic injection is used to convert magnesium chloride to sodium chloride since sodium chloride does not readily hydrolyze 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 hydrolyzes, 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, fluid catalytic crackers, 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, which contains hydrogen chloride, ammonia, and hydrogen sulfide. Corrosion rates can be severe if the chloride content is high. For this reason, alloy 400 (UNS N04400) has been used as a crude tower lining and as a tray material. Alloy 400 is resistant to these waters under 120°C (250°F); however, corrosion will occur if the H_2S or NH_3 levels are too high. Alloy 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. Recent experience indicates 6 Mo super SS (UNS N08367) has worked in overhead systems where alloy 400 has failed. Alloy C276 (UNS N10276) also has been used where alloy 400 has failed.

Corrosion protection in a single-drum system has been achieved by neutralizing the water condensate to a pH of 5.5 to 6.5 and using a filming amine inhibitor. More recently, some refiners have concluded that proper neutralizing is all that is required. Neutralizers used are ammonia and neutralizing amines. There are pros and cons associated with each neutralizer. Control of pH with ammonia is difficult unless aqueous ammonia is used because of the strong effect hydrogen chloride or ammonia have on condensate pH if too little or too much ammonia is used. With neutralizing amines it is easier to control the pH over a wide range of amine concentrations. However, neutralizing amines are soluble in both water and hydrocarbon.

If the amine chloride concentration is high, the amine chloride will return to the fractionator and cause chloride corrosion. High amine chloride concentrations can occur if there is insufficient water to quench through the dew point before the first exchanger or in a dual reflux system when the system is designed to condense water in the second reflux drum. Neutralizers known to form hydrochloride salts include MEA and morpholine. Fortunately, some neutralizing amines that do not form high temperature salts are now commercially available.

Ammonia or neutralizing amines are injected in the fractionator overhead line so they can react with the HCl both before and after the dew point of hydrochloric acid in solution is reached. Severe localized corrosion can occur at injection points if injection is not done properly. Drip injection of concentrated inhibitor can result in a sludge layer of concentrated inhibitor on the bottom of a pipe. This inhibitor sludge layer can cause dissolution of the protective scale on the inside of the pipe at temperatures in excess of 121°C (250°F). A catastrophic fire, resulting in an entire unit being destroyed, was caused by erosion-corrosion in an area where scale was removed by drip inhibitor injection. Tests revealed corrosion rates of 0.5 mm/y to 1 mm/y

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(14) UNS N10276 is used for the quill and the injection line by some refiners.

(20 mils/y to 40 mils/y) at 177°C (350°F). To minimize corrosion problems at injection points, the following are recommended:

1. Use quills to inject neutralizers or inhibitors, particularly for temperatures above 121°C (250°F).
2. Do not inject concentrated neutralizers or inhibitors, i.e., dilute them with water and a slip stream of naphtha before injection.
3. Inject water through spray nozzles pointed downstream.
4. Locate injection points well ahead of any bends.
5. Periodically inspect injection points (API Standard RP570, "Piping Inspection Code; Inspection, Repair, Alteration and Rerating of In-Service Piping Conditions" recommends every three years).

Often, however, neutralization is not accomplished, and severe corrosion from hydrochloric acid still occurs at the dew point. This is because the first drops of condensate have a very low pH (e.g., pH 1 to 2) even if the pH of the total condensate is alkaline, e.g., pH 8. The pH is controlled at the overhead receiver water draw because dew point pH measurement is not feasible. Continuous monitoring of the pH and the chloride concentration is preferred to make sure overhead corrosion control is maintained. 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 oil or another stream condenses only hydrocarbon in the first drum. This hydrocarbon, usually called heavy naphtha, is a hot reflux that controls the tower top temperature. As mentioned previously, neither ammonia nor neutralizing amines should be used in this system because these amine chloride salts can be carried back to the column in the reflux and cause severe corrosion.

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 (approximately 38°C [100°F]) required for gas and gasoline separation. Corrosion can occur in these condensers; therefore, the same corrosion controls used in a single-drum system should 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 saltwater cooling, the use of titanium (UNS R50400) tubes is economical since carbon steel cannot be used. Titanium is also cost competitive with SS, alloy 400 (UNS N04400), brasses, and copper-nickel alloys in fresh (treated) water.

If ammonium chloride forms and plugs the hot areas, pitting of titanium, as well as SS, alloy 400, brasses, and copper-nickel alloys can occur. This has been reported for both air coolers and water coolers. Brasses such as admiralty brass (UNS C44300) have been used successfully where water side velocities are controlled to under 2.4 m/s (8 ft/s) and ammonia is not high enough to corrode or crack the brass (pH below 7.2).

Note that admiralty (UNS C44300) can crack in the presence of air, e.g., during downtime, if ammonium chloride is present. Copper-nickel alloys are much more resistant to ammonia but will corrode if the hydrogen sulfide content is high. Duplex SS, such as UNS S31500 and UNS S32205, 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 very careful control is exercised on cooling water chemistry.

Figures 1.4 to 1.10 apply to carbon steel overhead systems.[6-11] Figure 1.4 [6] 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 1.5.[7] The chloride concentration at 0°C to 120°C (32°F to 250°F) can be estimated from Figure 1.6[6] if the hydrogen chloride and water vapor partial pressures are known. Once the pH of the overhead has been estimated, or measured under pressure, the corrosion rate can be estimated from Figure 1.7.[8]

Figure 1.8 shows how the corrosion rate on carbon steel increases as the temperature decreases.[9] The increase in solubility of corrosive gases with decreasing temperature more than offsets the slowing of corrosion processes as a result of the temperature decrease.

Figure 1.9 [10] 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 1.7.[8]

Figure 1.10 [11] is a good example of how metal loss is reduced by desalting to remove chlorides. However, using the two corrosion rates shown can be misleading. Fouling is very important to heat transfer, unit throughput, and tube bundle life. For example, after desalting, a 0.08 mm/y (3.2 mpy)

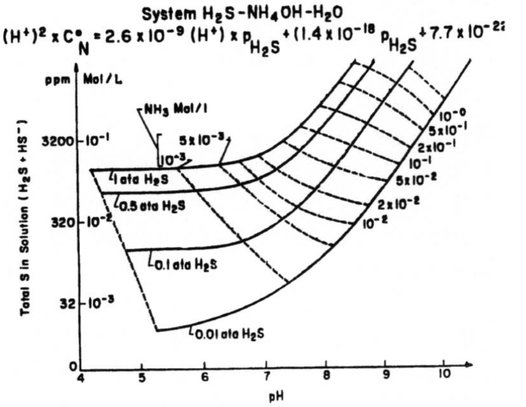


Figure 1.4 - Total S in solution vs pH.[6]
(Reprinted with permission from "Crude Unit Overhead Corrosion," *Hydrocarbon Processing*, May 1972, Gulf Publishing Co., Houston, TX)

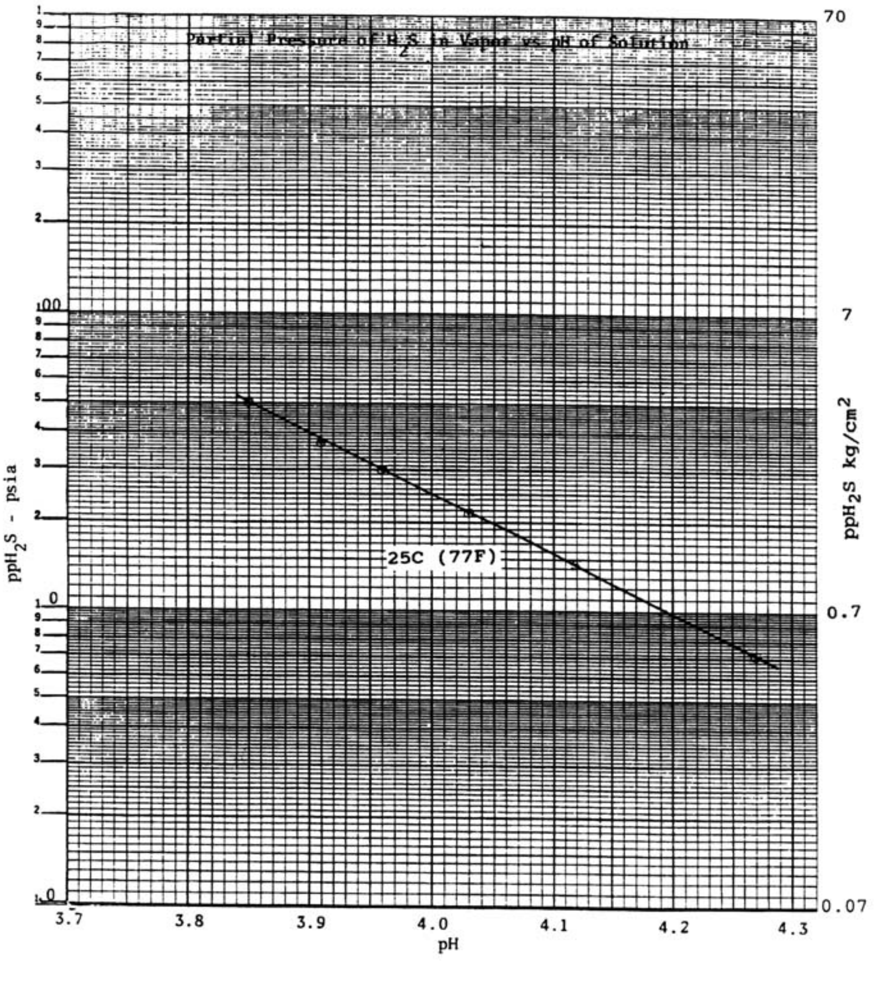
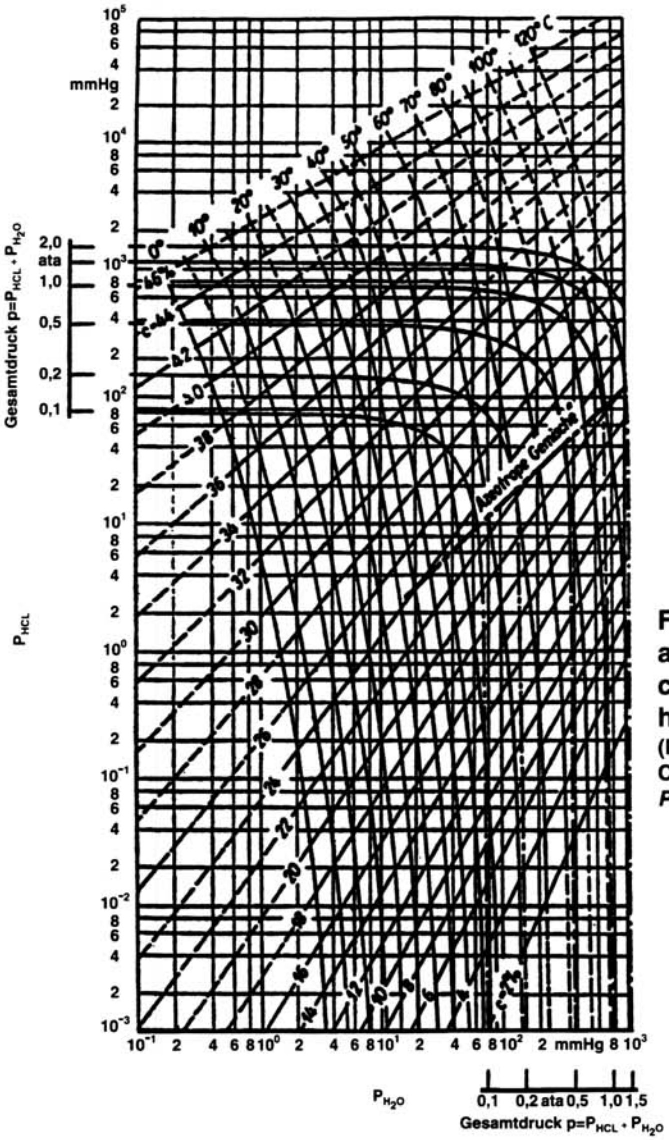


Figure 1.5 - Solubility of H_2S in water. Partial pressure of H_2S in vapor vs pH of solution.[7]
(Reprinted with permission from *Handbook of Chemistry*, 6th Edition, 1979, McGraw-Hill Publishing Co., New York, NY)



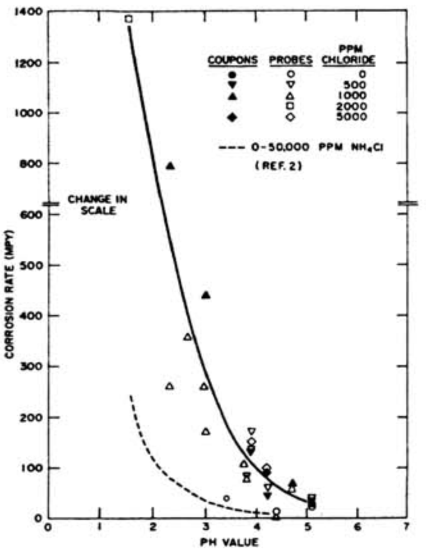


Figure 1.7 - (above) Corrosion of steel in aqueous sulfide solutions. Note the acid corrosion region because of an excess of hydrogen ions at pH values below 4.5.[8] **(Reprinted from "Corrosion of Steel by Sulfides and Cyanides in Refinery Condensate Water,"** ***Materials Protection*****, December 1968)**

Figure 1.6 - (above left) HCl and H_2O partial pressures over HCl depending on temper-ature, total pressure, and acid concentration.[6] **(Reprinted with permission from "Crude Unit Overhead Corrosion,"** ***Hydrocarbon Processing,*** **May 1972, Gulf Publishing Co., Houston, TX)**

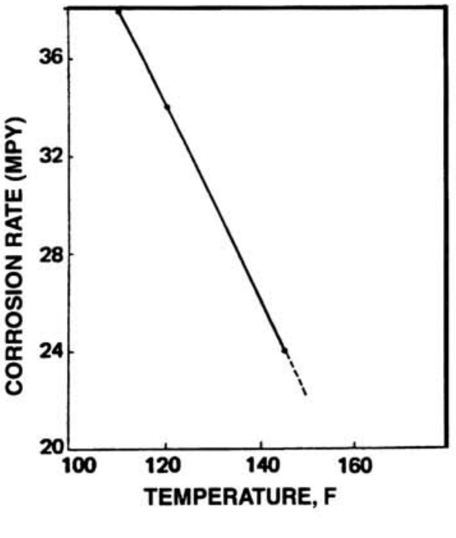


Figure 1.8 - (left) Corrosion rate of steel vs temperature of atmospheric tower sour condensate water.[9]
(Reprinted with permission from "Determination of Refinery Corrosion Rates Using the Pair Technique," ***Materials Protection,*** **June 1969.**

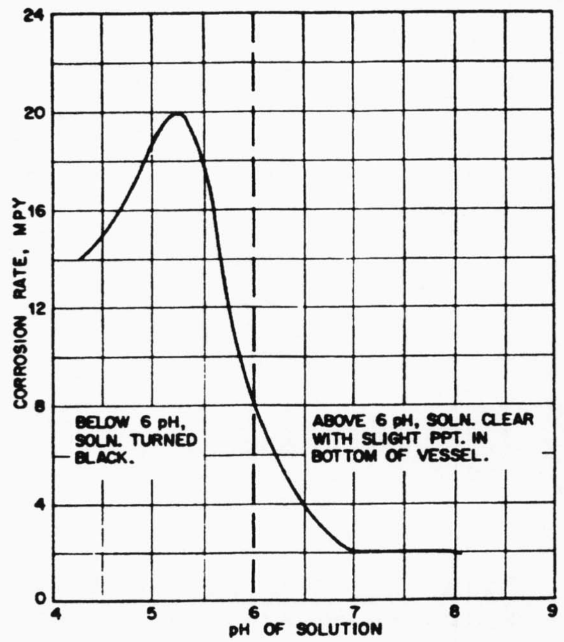


Figure 1.9 - Effect of pH on corrosion rate of iron in solution of the same H_2S activity.[10]

(Reprinted from "Corrosion of Refinery Equipment by Aqueous Hydrogen Sulfide," *Corrosion* 4, 1959)

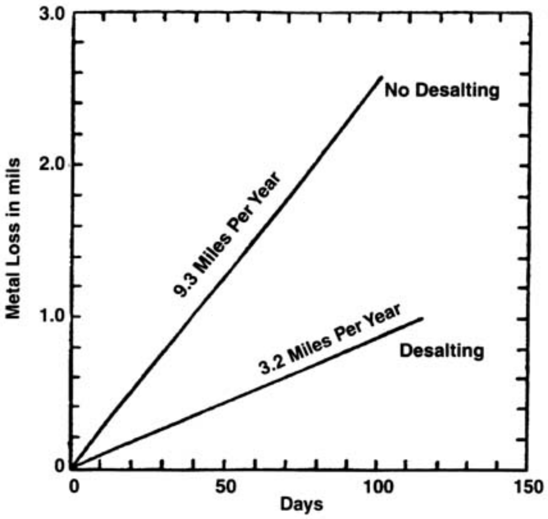


Figure 1.10 - Corrosion rates of steel in a crude unit secondary tower overhead. Desalting produced drastic reduction in corrosion rates.[11]

(Reprinted from "Crude Oil Desalting to Reduce Refinery Corrosion Problems," *Materials Protection*, May 1962)

corrosion rate predicts that a 2.1 mm (0.083 in.) wall tube will last 25 years (providing wall is not reduced below the containing capacity of the tube).

However, experience reveals that the scale formed is about seven times the volume of metal loss, and the bundle would be completely plugged in four years, assuming 4.8 mm (3/16 in.) ligaments on the tubesheet. Square pitch bundles can be mechanically cleaned, but triangular pitch bundles cannot. Unless chemical cleaning can be done, triangular pitch bundles must be retubed once they are plugged.

The 0.24 mm/y (9.3 mpy) corrosion rate (before desalting) predicts a nine-year life. However, the bundle would be completely plugged with scale in one to four years. In both cases an inhibitor must be used to reduce the corrosion rate and keep the tubes clean.

2.3.3 Corrosion of Equipment and Piping

After the crude oil passes through the desalter in the crude unit, it goes into the crude oil heater. Here, the sulfur compounds are partially thermally decomposed. As mentioned previously, when the sulfur in the crude oil exceeds about 0.2 wt% to 0.3 wt%, corrosion of carbon steel becomes excessive at elevated temperatures. 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 1.11.[12] The corrosion data in Figure 1.11 is from an API survey modified by Gutzeit. Gutzeit modified the data to take into account the fact that survey rates are higher than average by as much as a factor of 2.5. Gutzeit added a sulfur content correction chart (Figure 1.12).[12]

When using the data in Figures 1.11 and 1.12 for furnace tubes, the temperature used should be that of the inside furnace tube film. The reason the original rates were high is because the results of the survey reflect the experience of refiners who have had problems (refiners with problems are the ones with the most data) and the fact that furnace tube data (where high velocities are encountered) are included.

In general, fired heater tubes and piping are made of 5 Cr-1/2 Mo steel for sulfur-bearing crude oils when the temperature exceeds about 288°C (550°F). Where sulfur is present, but in amounts less than 0.2 wt% to 0.3 wt%, silicon-killed steels have shown superior corrosion resistance to semi-killed steels. In addition, silicon-killed steel has shown better corrosion resistance than semi-killed steel to high sulfur crude oils in the 232°C to 288°C (450°F to 550°F) range. Above 399°C (750°F), 9 Cr-1 Mo is used in high sulfur hydrocarbons to minimize corrosion.

The temperature where excessive corrosion of carbon steel occurs is a function of the characteristics of the sulfur compounds in crude oil. This temperature can be estimated by measuring the amount of hydrogen sulfide evolved as a function of temperature (Figure 1.13).[13] The amount of hydrogen sulfide evolved vs temperature varies widely, and there is no relationship to the wt% sulfur.

Figure 1.14[13] shows a correlation between the amount of hydrogen sulfide evolved and temperature to corrosion rates of carbon steel furnace tubes. Since hydrogen sulfide release data are rarely available, materials selection usually is based on wt% sulfur even though the correlation with corrosion rates is only very general. Recent studies indicate that direct reaction of the organic sulfur compound with the metal surface is the predominant mechanism of high-temperature sulfidation.

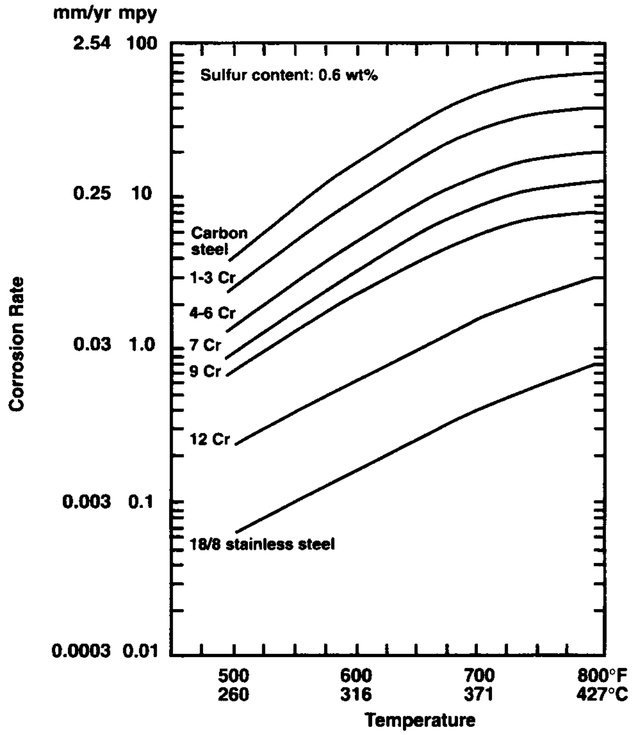


Figure 1.11 - Average corrosion rates of high temperature sulfur corrosion in a hydrogen free environment as compiled from 1961 API questionnaire data from industry-desulfurizing processes and published or reported data-nondesulfurizing processes.[12] (Reprinted from J. Gutzeit, "High Temperature Sulfidic Corrosion of Steels," in *Process Industries Corrosion-Theory and Practice,* 1986)

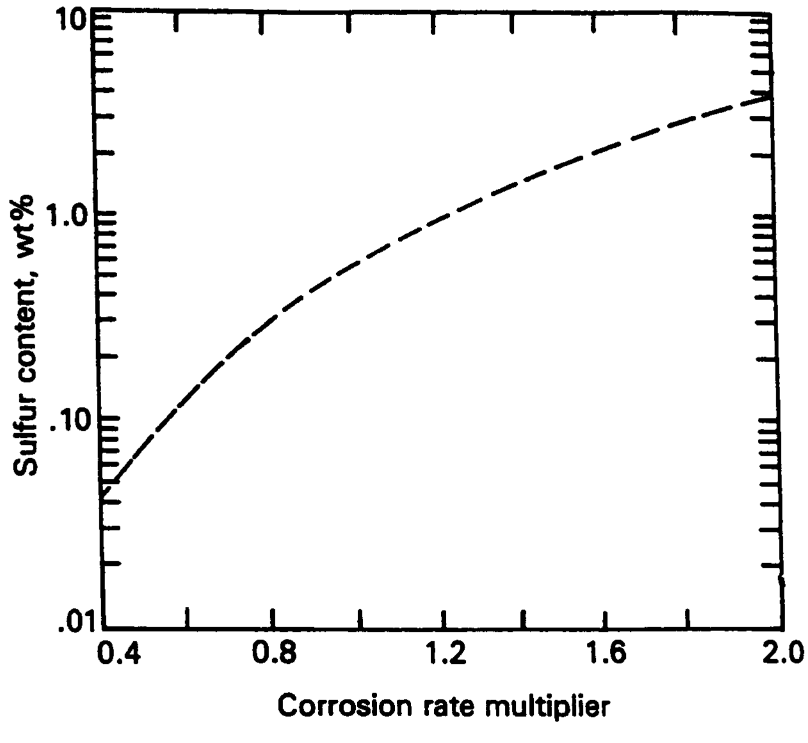


Figure 1.12 - Comparison of sulfur levels vs carbon steel corr-osion rates.[12] (Reprinted from J. Gutzeit, "High Temperature Sulfidic Corrosion of Steels," in *Process Industries Corrosion-Theory and Practice,* 1986)

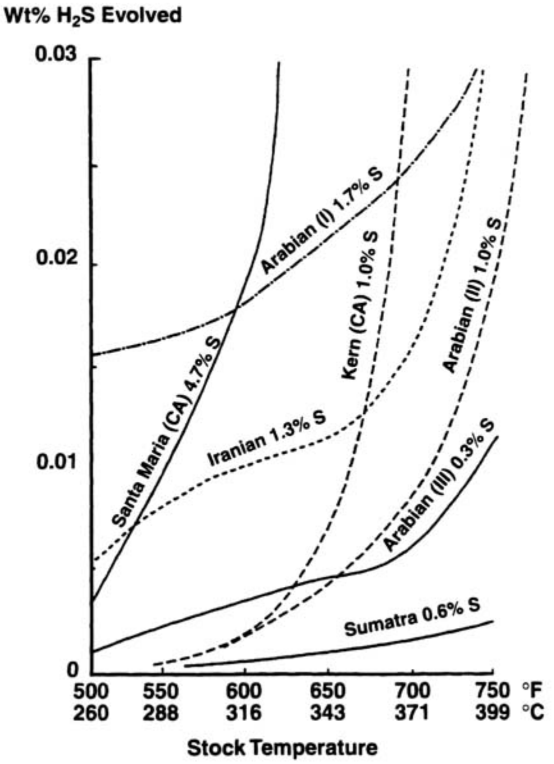


Figure 1.13 - Hydrogen sulfide release from crudes.[13]

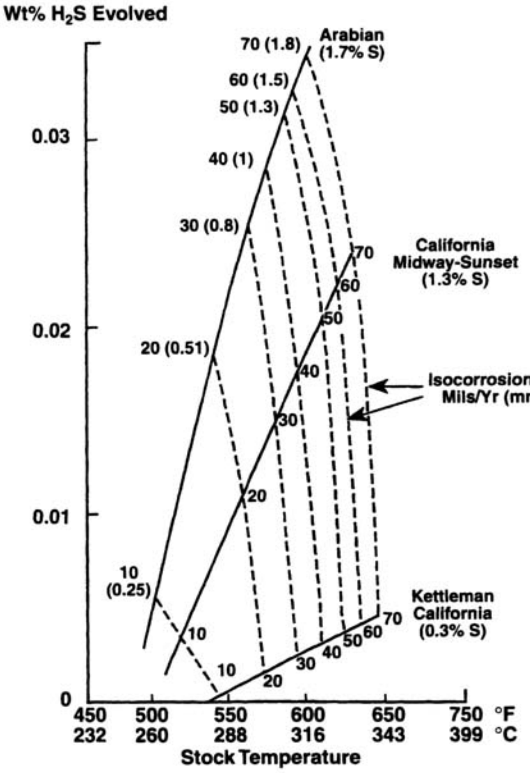


Figure 1.14 - Corrosion of carbon steel furnaces tubes.[13]

The 5 Cr-1/2 Mo alloy commonly used in furnace tubes corrodes at a measurable rate; the design life usually is 5 to 10 y. Even though metal temperatures are higher than the process temperature in furnace tubes, corrosion rates are always reported as a function of the process temperature. Therefore, furnace tubes tend to corrode at higher rates than piping for the same process temperature. Conversely, exchanger tubes corrode at a lower rate than piping when the process fluid is being cooled. Exchangers that have the cooling medium on the shell side often corrode in the tube rolls, where the metal is at the hot stream temperature. Flow velocity also plays a part since the high velocities often encountered in furnace tubes and piping tend to accelerate corrosion.

Columns in crude units are usually clad with 12 Cr above about 288°C (550°F). Some refiners use clad above 232°C (450°F) to minimize maintenance and fouling from corrosion products. The 12 Cr cladding is essentially immune to attack and is used because the design life of columns (which are expensive to replace) usually is 20 years. Pressure retaining parts of 12 Cr usually are limited to 343°C (650°F) to avoid problems resulting from 475°C (885°F) embrittlement.(15) As mentioned previously, the majority of attack occurs in the flash zone, where the feed enters the column and partially flashes to vapor.

When naphthenic acids are present in sufficient quantities (see previous discussion), alloys with 0-12% chromium, as well as 304/304L (UNS S30400/S30403), 321 (UNS S32100) and 347 (UNS S34700) are severely attacked. Conversely, molybdenum-bearing austenitic SS, e.g., 316/316L (UNS S31600/S31603), 317/317L (UNS S31700/S31703), etc., exhibit resistance to naphthenic acid attack. Where hardfacing is necessary, Stellite 6 (UNS R30006)(16) has been used successfully.

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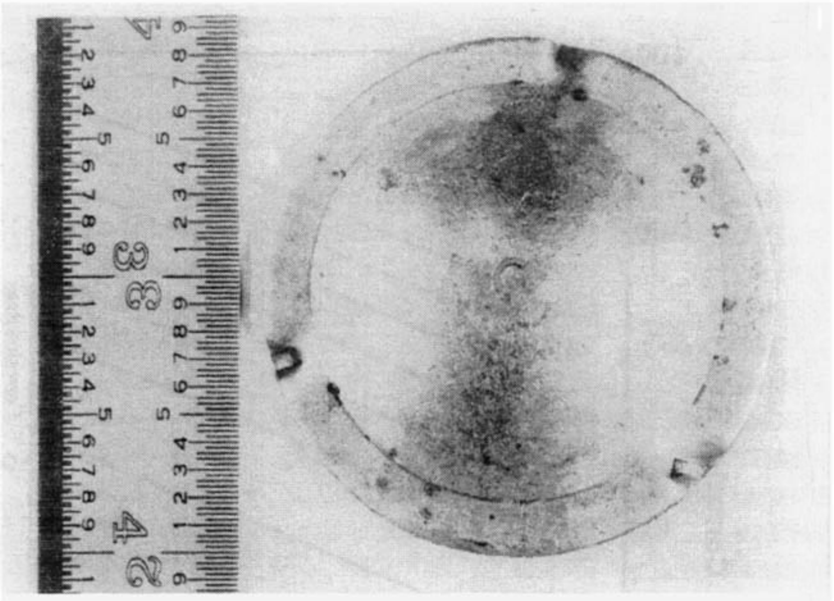
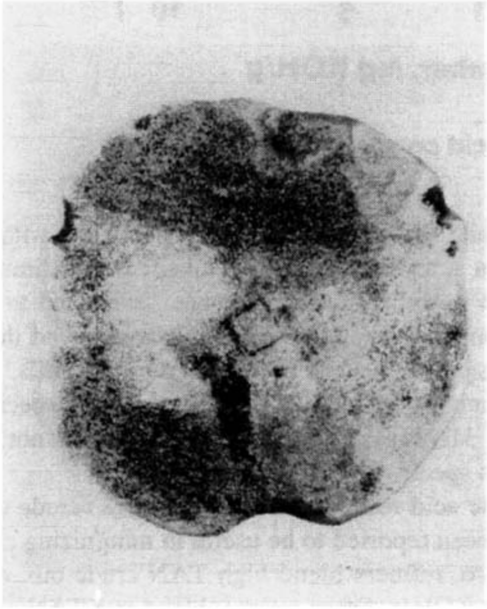
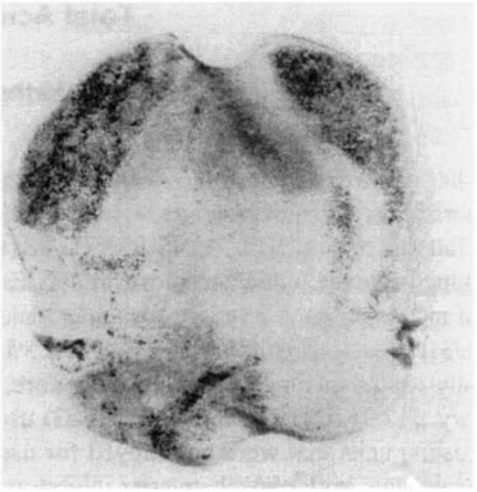
(15) Loss of room temperature toughness due to precipitation of a chromium rich phase in the 370°C to 510°C (700°F to 950°F) range.

(16) 1 C, 4.5 W, 28 Cr, 55 Co.



Type 316 stainless steel





Type 410 stainless steel (left and above right)

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

Figure 1.15 shows the severe attack that occurred on 12 Cr while 316 SS suffered no attack in naphthenic acid service.

Figure 1.16 shows data compiled on the corrosion rate of carbon steel in naphthenic acid containing oils as a function of temperature.[14] In vacuum processing of reduced crude oil (the bottoms from a crude unit), the most severe corrosion often occurs at approximately 288°C (550°F). The reason is that the naphthenic acids tend to concentrate in those fluids with true boiling points in the 370°C to 425°C (700°F to 800°F) range, and the effect of a vacuum (in the vacuum column) is to reduce the boiling point 110°C to 160°C (200°F to 300°F).

Naphthenic acid attack can be minimized by limiting the velocities to 60 m/s (200 ft/s) maximum; however, the velocity limit of 40 m/s (130 ft/s) is preferred. Percent vaporization also is a factor. Some refiners limit vaporization to 60% to minimize corrosion; however, corrosion of 316/316L SS (UNS S31600/

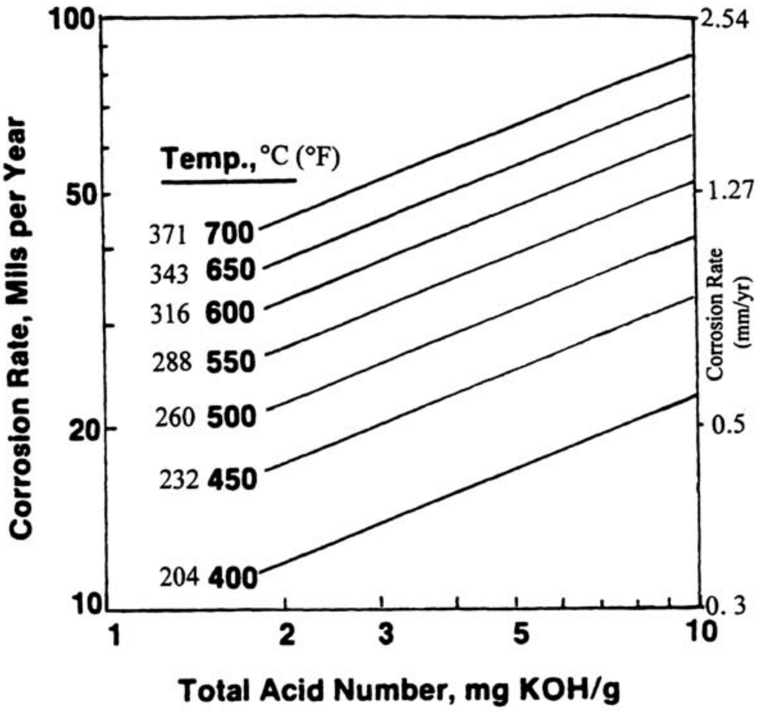


Figure 1.16 - Naphethenic acid corrosion of carbon steel.[14]

S31603) has occurred in vacuum unit transfer lines containing a high naphthenic acid content with 15% to 40% vaporization. To minimize attack, both vaporization and velocity should be kept at a minimum.

The failures of 316/316L (UNS S31600/S31603) in naphthenic acid have been attributed to modern steel-making practices, which result in molybdenum contents very close to 2%. It is believed that 2.5% minimum molybdenum is required for naphthenic acid service, at least for California crude oils.(17) However, 316/316L (UNS S31600/S31603) with 2.5% minimum molybdenum usually requires a special order and usually results in long deliveries. Therefore, when 316/316L (UNS S31600/S31603) is not deemed satisfactory, 317/317L (UNS S31700/S31703) usually is specified.

In existing units that were not alloyed for naphthenic acid resistance but now process crude oils containing naphthenic acid, phosphate ester inhibitors have been reported to be useful in minimizing corrosion until suitable replacement material can be installed. Also, refiners blend high TAN crude oils with low TAN crude oils to keep the TAN of a feed below 1.5 mg KOH/g. Often refiners blend to a TAN of 0.5 mg to 1.0 mg KOH/g.

When SS piping must be welded to a clad vessel, even small diameter (<51 mm [2 in.]) nozzles usually are required to be clad or weld overlaid to avoid a dissimilar weld in the vessel. This is because of the high stresses imposed (at service temperatures above about 232°C [450°F]) by the dissimilar thermal expansion and because the hard fusion line in the dissimilar weld can sulfide stress crack in the presence of H_2S (See Section 6.1 in Chapter 2).

Where dissimilar welds are required, e.g., for 12 Cr clad restoration, 309 SS (UNS S30900) filler metal commonly is used for dissimilar welds for service temperatures below 425°C (800°F), and high nickel [65 Ni-15 Cr-Fe] filler metal is used for dissimilar welds for service temperatures above 425°C (800°F). For service temperatures above 399°C (750°F), the high nickel filler metal should be protected from high sulfur environments except in delayed cokers, where severe corrosion has not been a problem because the coke on

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(17) One refiner has reported that currently produced 316/316L (UNS S31600/S31603) is satisfactory for Venezuelan crude oils containing naphthenic acid.

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the walls acts as a barrier to further corrosion.

In general, sidecut stripper columns corrode much less than the main fractionators for the same temperature. The corrosive sulfur compounds tend to move to the bottom of the main fractionator with the liquid, and the hydrogen sulfide moves to the overhead of the main fractionator. Sidecut strippers usually are not clad until the process temperature exceeds 343°C (650°F). Sometimes, the heavy gas-oil sidecut contains naphthenic acid, which can cause enough corrosion for iron to enter the fluid catalytic cracker unit feed.

Vacuum and visbreaker columns should be treated separately from atmospheric columns. The inlet line from the charge furnace and the inlet area of the tower usually corrode at the highest rate. The overhead 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 can be quite severe in vacuum and visbreaker towers. As discussed above, crude oils with total acid numbers over 1.5 mg to1.8 mg KOH/g require 316 or 316L SS (UNS S31600, S31603) or higher alloys, such as 317 or 317L SS (UNS S31700/S31703) and 904L (UNS N08904). Matching weld filler metal must be used. In one case, a 310 SS (UNS S31000) weld filler metal was used on 316L SS (UNS S31603) lining. While the strip lining was not attacked, the weld was dissolved in one year.

Heat exchangers are treated in a manner similar to columns, i.e., solid 5 Cr-1/2 Mo(18) or 12 Cr clad shells and channels and 5 Cr-1/2 Mo tubes usually are used above 288°C (550°F). 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). In recent years plate heat exchangers have been used increasingly in lieu of the conventional shell and tube exchangers because of superior heat transfer efficiency, compactness, and lower weight. Because the plate sections are very thin, they usually utilize more corrosion-resistant alloys than are used for tubes in conventional shell and tube exchangers. The disadvantages of plate and frame exchangers are that the flow passageways are so narrow they are conducive to fouling, the gasket sealing required around each edge makes them susceptible to crevice corrosion, and thin cold-formed parts are susceptible to stress corrosion cracking.[15]

The wear parts of pumps and valves usually are highly alloyed because of the close tolerances required. Valves with 12 Cr trim (seat and stem) usually are used for all temperatures except in naphthenic acid service where all parts must be 316L as a minimum. Pump impellers (and often the pump case as well) are 12 Cr for temperatures above 288°C (550°F) except in naphthenic acid service where 316 or 316L (UNS S31600, S31603) is required for service temperatures above 232°C (450°F).

Corrosion in dead legs of piping can be a serious problem because of accumulation of water or thermal decomposition of trapped material which forms corrosive compounds. Therefore, dead legs should be eliminated wherever possible.

3. UTILITIES

3.1 Cooling Water

For materials selection, cooling water normally is categorized as either freshwater or salt water. Freshwater may come from lakes, rivers, or wells. Well water often contains corrosion-causing bacteria, which accelerate corrosion of carbon steel (and cast iron) and pitting of many alloys, including SS.

The corrosion rate of carbon steel in both freshwater and salt water is a function of the oxygen content (in the 4 pH to 10 pH range) and temperature. The corrosion rate of carbon steel, being an electrochemical rather than a chemical reaction, doubles approximately every 33°C (60°F) in a closed system. The oxygen solubility decreases with increasing temperature in an open system; therefore, the increased carbon steel corrosion rate due to a rise in temperature is partially offset by the decreased oxygen solubility.

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(18) The notch toughness of 5 Cr-1/2 Mo can be below that required by ASME Section VIII, particularly in heavy sections. Therefore, 12 Cr clad may be a better choice if notch toughness is a concern.

3.2 Corrosion in Freshwater

A cooling water system can be further categorized 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 about 5 ppm) in the water indicates that corrosive bacteria may be present. Although microbiologically influenced corrosion (MIC) is not a problem when the velocity exceeds 1 m/s (3 ft/s) there are always dead zones in a piping system. Therefore, when corrosive bacteria are present, chlorination or other biocide treatment is imperative. In addition to adding a biocide, raising the pH to 10.5 (minimum) or boiling the water for 15 minutes is an effective method of preventing MIC. The latter two methods would be practical only for hydrostatic test water.

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 (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 both scaling and corrosion. There are several indices for determining whether 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 $CaCO_3$)(19) in ppm or mg/L,
- Total alkalinity (as $CaCO_3$) in ppm or mg/L,
- 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. 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 half of the carbonate ion. If the pH is greater than the pH_s(20) value, scale will form and the corrosion rate will decrease (Langelier Index positive). If the pH is less than the pH_s value, the water tends to be corrosive (Langelier Index negative). As mentioned previously, most cooling systems are designed so the water chemistry is such that both scaling and corrosion are a minimum, i.e., Langelier Index is zero.

Figure 1.17 is a chart that can be used in lieu of calculations to determine a Langelier Index value.[16] The index should be used with caution as recent studies indicate a poor correlation between the Langelier Index and the corrosivity of waters.

The corrosion rates of carbon steel and cast iron in freshwaters 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 freshwaters, the total penetration rate (uniform plus pitting) is in the order of 0.25 mm/y (10 mpy) for carbon steel and cast iron at room temperature. Since most waters are treated to prevent scaling by adjusting the pH to equal the pH_s value (saturation index equal to zero), a 0.25 mm/y (10 mpy) average penetration rate often is used as a design basis for fully oxygenated water systems.

Erosion-corrosion has been reported in water slurry lines containing as little as 0.5% fines. The primary

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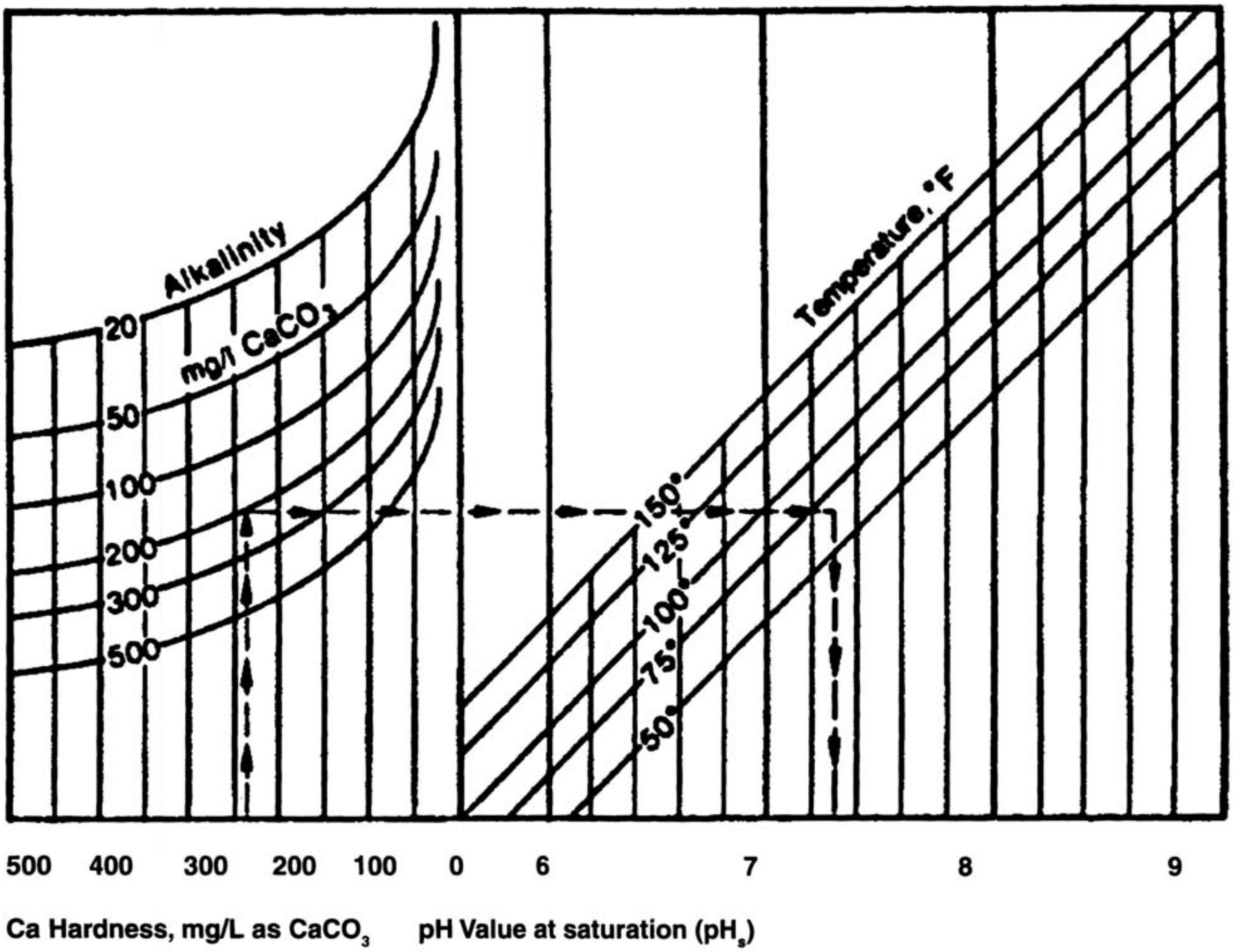
(19) Also called calcium hardness. Total hardness is the sum of the calcium and magnesium hardness (as $CaCO_3$).

(20) Calculated pH of calcium carbonate saturation.



Example:
Raw water Calcium = 240 mg/L
Alkalinity = 190 mg/L
pH = 6.8
Temperature = 70°F
From chart: pH_s = 7.3
Langelier Index = 6.8 - 7.3 = -0.5

Figure 1.17 - Determination of pHs and Langelier Index.[16]
(Reprinted with permission from *The Nalco Water Handbook*, 1979, McGraw-Hill Publishing Co., New York, NY).

areas of concern in slurry lines are where high pressure drop occurs, e.g., control valves. Stellite 6$^{\text{TM}}$ (UNS R30006) trim and, in severe conditions, ceramic lining are used in valves in slurry service. Carbon steel pipe usually is satisfactory provided the velocity is kept below 1 m/s (3 ft/s).

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

$^{\text{TM}}$ Trademark

$V = K_1 t^{-K_2}$
where V = the average corrosion rate in $g/m^2 \times d$(21)
t = time in hours
K_1 = 0.5
K_2 = 0.5

For example, this equation predicts that the corrosion rate after 20 years will be half the rate after five years.

The average corrosion rate of cast iron is only slightly lower (about 20%) than that of carbon steel. But often it appears that cast iron corrodes at a much lower rate than carbon steel. The reasons for this are (1) cast iron is produced in much thicker sections than carbon steel so it has a large corrosion allowance built into the wall. Since the corrosion rate decreases with time, double the corrosion allowance, e.g., 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. (22) 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 completely corroded (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 4-10 pH range at room temperature. If the oxygen is less than 1 ppm, the penetration rate in carbon steel or cast iron will be less than 0.025 mm/y (1 mpy) 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 so difficult and expensive that some refiners prefer to use copper alloy tubes instead. Even with treated water, pitting of carbon steel tubes can occur. The pitting results in tubercle formation which, in turn, impedes flow and increases waterside pressure drop. The restricted flow causes the water temperature to increase which, in turn, increases the corrosion rate. The choice between carbon steel and copper alloy tubes is significantly affected by the relative cost and corrosiveness of the process fluid being cooled. 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 coatings or more corrosion-resistant material is required. Organic coatings usually require repair in 5 to 10 years. In addition, they require flanged connections. Although effective in preventing atmospheric corrosion, zinc coatings on steel (galvanized steel) extend the life of carbon steel only one to three years in water service.

Copper-based alloys generally have penetration (general corrosion plus pitting) rates in the order of 0.025 mm/y (1 mpy) in freshwater in the neutral pH range around room temperature. Therefore, the life of copper-based alloys depends on factors such as erosion, dealloying, under-deposit pitting, and the presence of aggressive species. For example, the pH from ammonia should not exceed 7.2 for admiralty brass, and sulfide should not exceed 0.007 mg/L for copper-nickels.

The erosion resistance of copper base alloys can be related directly to velocity. The velocity limits for common copper base alloy condenser tubes are shown in Table 1.1.[17] The velocity limit is roughly proportional to the strength of the alloy; i.e., copper is the weakest material and has the poorest erosion resistance, whereas 70 Cu-30 Ni (UNS C71500) is one of the strongest alloys and has the best erosion resistance. Usually the cost of pumping limits the cooling water bulk velocities to around 1.5 m/s (5 ft/s); however velocity can be higher in localized areas due to turbulence, etc.

Dealloying is the preferential attack of the less noble metal (i.e., zinc in brasses, aluminum in aluminum bronze, and nickel in copper-nickel alloys), which can lead to unexpected failures because significant metal loss is not apparent by visual inspection. The extent of dealloying depends on the specific conditions. For

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(21) Grams per square meter per day. Multiplying this number by 1.83 (for carbon steel) gives the corrosion rate in mils per year.

(22) Formerly called graphitization but now called graphitic corrosion to avoid confusion with the high temperature formation of graphite in steel that is called graphitization.

Table 1.1
Behavior of Copper Alloy Condenser Tubes Under Velocity Conditions[24]

UNS NUMBER	COMMON NAME	CLEAN SEAWATER	GOOD FRESHWATER
C12200	copper (phosphorus deoxidized)	good up to 0.9 m/s (3 ft/s)	good up to 1.2 m/s (4 ft/s)
C23000	red brass	good up to 1.2 m/s (4 ft/s)	good up to 1.5 m/s (5 ft/s)
C44300	admiralty brass	good up to 1.8 m/s (6 ft/s)	good up to 2.7 m/s (9 ft/s)
C68700	aluminum brass	good up to 2.7 m/s (9 ft/s)	good up to 3.4 m/s (11 ft/s)
C60800	aluminum bronze	good up to 2.4 m/s (8 ft/s)	good up to 3.4 m/s (11 ft/s)
C70600	90-10 copper nickel	good up to 2.4 m/s (8 ft/s)	good up to 3.4 m/s (11 ft/s)
C71500	70-30 copper nickel	good up to 4.6 m/s (15 ft/s)	good up to 4.6+ m/s (15+ ft/s)

example, loss of the zinc-rich phase in brasses is favored by a high dissolved salt content, high free carbon dioxide, 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. Inhibited admiralty brass, UNS C44300, C44400, and C44500 should be used to minimize dealloying. These 30% zinc alloys are 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, UNS C44300 alloy remains the most popular and the most available 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, high salt contents, and particularly crevices. Dealloying of aluminum bronze can be a problem in castings and weld metal with aluminum contents in excess of 8.0%, and the problem can be severe when the aluminum content exceeds 9.1%. Two approaches, temper annealing and nickel additions, are used to minimize this problem in susceptible alloys. Temper annealing consists of heating to 677°C (1,250°F) and holding for six hours (followed by rapid cooling) after casting or welding. Temper annealing has not been effective in preventing dealloying in crevices where the aluminum content exceeds 8.5%. Nickel aluminum bronze alloys are resistant to dealloying if given a temper anneal heat treatment provided the iron is equal to or less than the nickel content and the aluminum content is less than 9.1%. The European practice is to use nickel additions when the aluminum content exceeds 8.0%. The aluminum content in these nickel-aluminum bronzes is limited to 8.5% plus half the nickel content.

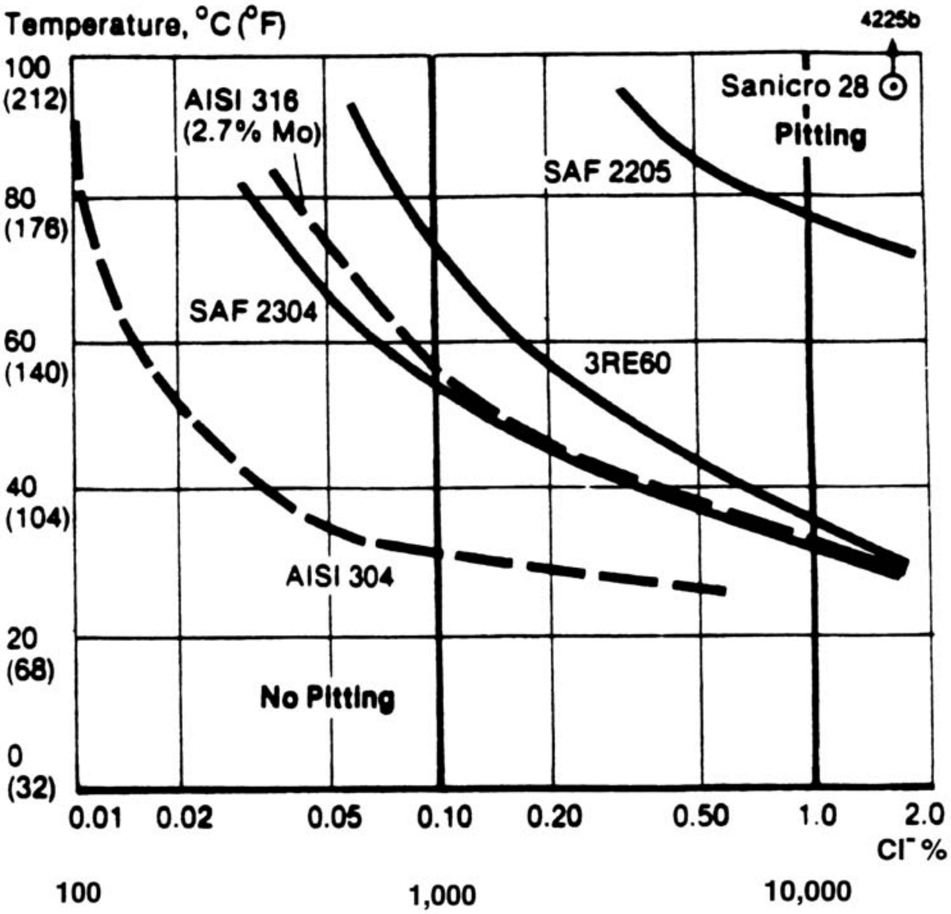

Figure 1.18 - CPT (Critical Pitting Temperatures) of different grades in neutral aqueous chloride solutions. Potential = +300 mV SCE.[18]

Austenitic SS also is used in freshwater. However, because of cost, its use is limited mainly to applications where copper-zinc alloys are unsuitable, as in tubes in which the process side is incompatible with copper-based alloys. To avoid pitting, 304 SS (UNS S30400) and 316 SS (UNS S31600) normally are limited to services where the chloride ion concentration is a maximum of 200 ppm and 1,000 ppm, respectively, provided the pH is above 6 and the temperature is below 60°C (140°F). The relative pitting and crevice corrosion resistance of SS alloys can be approximated by the equation:

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

The higher the PRE the more resistant the material. If the PRE is greater than 45, no crevice corrosion attack will occur in ambient temperature seawater. Theoretically, pitting will not occur (regardless of the chloride ion concentration) if the temperature is limited to 5°C plus seven times the molybdenum content. Thus, for a 2 % molybdenum alloy (e.g., 316 SS [UNS S31600]) the limit would be 5 + 7(2) = 19°C. This critical pitting temperature (CPT) also can be measured in the laboratory. The CPT for typical austenitic and duplex SS, as a function of chloride ion concentration, is shown in Figure 1.18.[18] If the material is good in a critical crevice corrosion test done in accordance with ASTM Standard G48-92 ("Standard Test Methods for Pitting and Crevice Corrosion Resistance of Stainless Steels and Related Alloys by Use of Ferric Chloride Solution"), Method B, it will be good for higher service temperatures than that indicated by the PRE. The temperature should be limited to 60°C (140°F) in the neutral pH range to avoid stress corrosion cracking of 304/304L (UNS S30400/S30403) and 316/316L (UNS S31600/S31603). Above 60°C (140°F), in the absence of concentration mechanisms such as local boiling or crevices, failure is a function of chloride ion concentration, alloy content, and temperature, as indicated in Figure 1.19.[18] When prolonged heating in the sensitizing range of 425°C to 815°C (800°F to 1,500°F) is involved, the stabilized grades of austenitic SS should be used to avoid intergranular corrosion. When only welding is involved, the low carbon grades of austenitic SS can be used to avoid intergranular corrosion.

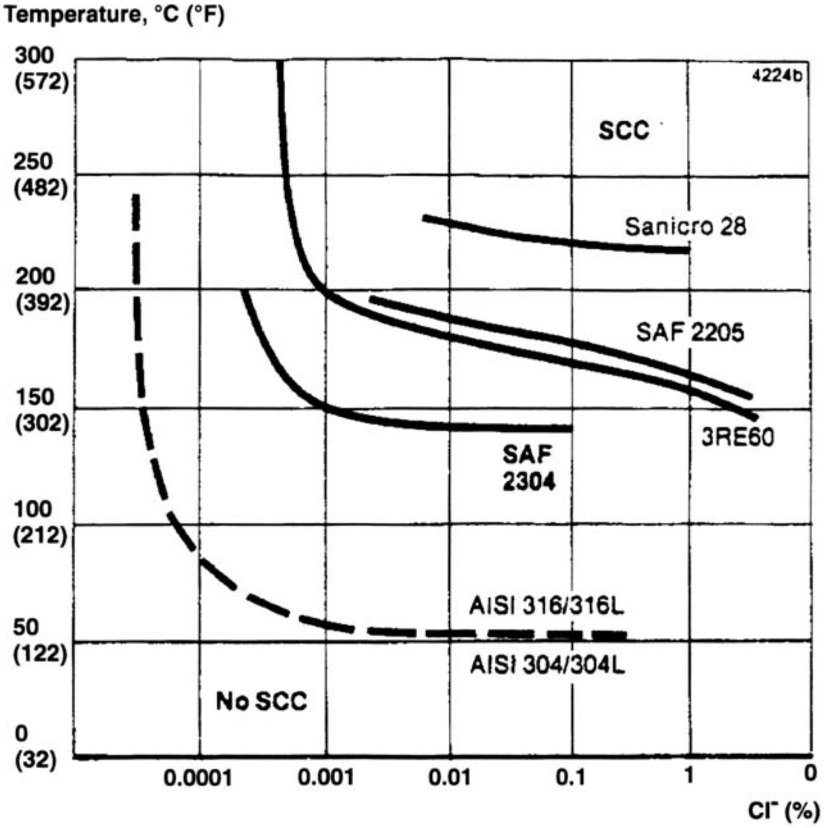

Figure 1.19 - A compilation of practical experience and laboratory test data of different stainless steels in neutral aerated aqueous chloride environments.[18]

3.3 Corrosion in Salt Waters

Salt waters commonly are limited to once-through systems because it is usually not economical to treat salt water to minimize scale and corrosion. Corrosion of metals in saltwater is similar to that of metals in freshwater (dealloying, pitting, etc., occur) except the penetration rates in salt water are higher. For example, carbon steel has an average penetration rate of about 0.64 mm/y (25 mpy) in fully oxygenated seawater vs an average penetration rate of about 0.25 mm/y (10 mpy) in freshwater. The only practical means of reducing corrosion to the point where bare carbon steel can be used are deaeration and the addition of an oxygen scavenger to ensure oxygen is less than 20 ppb. The penetration rate of carbon steel in deaerated saltwater is in the order of 0.076 mm/y (3 mpy) at pH 6.5 or greater. The corrosion rate increases rapidly as the pH is reduced below 6.5 as indicated in Figure 1.20.[19] 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 4.6 m/s (15 ft/s).

Corrosion of materials in seawater also can be affected by chlorination, which is necessary to prevent fouling and the resulting under-deposit corrosion. Shock chlorination (18 ppm to 20 ppm Cl_2) is reported to increase the corrosion of admiralty brass to 1 mm/y (40 mpy) at 48°C (118°F). Even the residual chlorine used to treat seawater in offshore structures (0.5 to 1.0 vs the normal 0.1 ppm Cl_2) can cause pitting and crevice corrosion of super SS particularly as temperature increases. The 6 MoSS are the most resistant to attack from residual chlorine.[20] However, crevice corrosion has been reported in one unit operating at 35°C (95°F). In addition, galvanic corrosion of 6 MoSS has been reported due to graphite gaskets.

Although admiralty brass (UNS C44300) has been used for exchanger tubes in seawater, copper-nickel and aluminum bronze alloys perform somewhat better. The cost of titanium tubes often can be justified when life expectancy is taken into account. Copper-nickel alloys, particularly UNS C70600 (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. The severity of sulfide corrosion increases with increasing velocity.[21] Where the salt water in petroleum streams contains sulfides, admiralty brass (UNS C44300) and, to a lesser extent, aluminum bronze alloys perform better than the copper-nickel alloys. Aluminum bronze alloys have performed satisfactorily in waters containing up to 25 ppm to 30 ppm hydrogen sulfide.

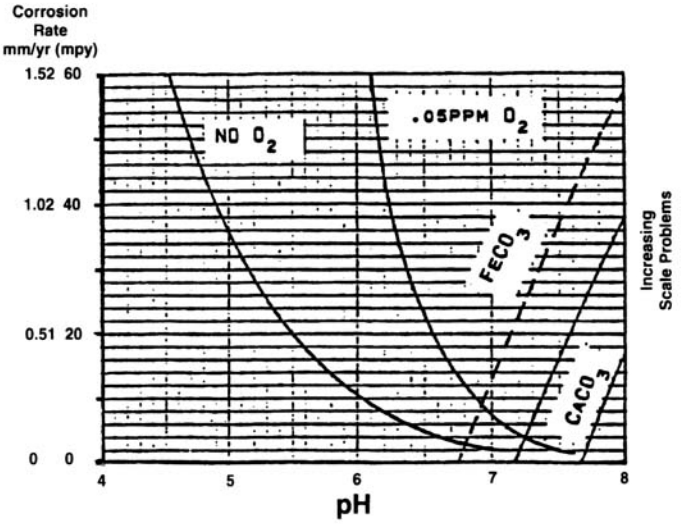

Figure 1.20 - Summary of pH effects on the seawater injection system.[19]

They are not satisfactory at high concentrations (e.g., an 8% aluminum bronze specimen disintegrated in a visbreaker reflux line). Titanium (UNS R50400) is resistant to sulfides but is subject to embrittlement from hydriding above 80°C (176°F) and above 70°C (160°F) in the presence of hydrogen. Hydriding is greatest when the pH is less than 3 or greater than 12. In addition, corrosion from salt plugs has occurred when the velocity in titanium tubes was below 0.9 m/s (3 ft/s).

Theoretically, austenitic SS can be used in salt water as long as the velocity exceeds 0.9 m/s (3 ft/s). Experience has shown that stagnant conditions will always occur in a salt water system, resulting in rapid pitting (average penetration rates are in the order of 1.8 mm/y [70 mpy]). For this reason, the use of austenitic SS in seawater usually is limited to thick pump parts. The new super stainless steels, which are high in molybdenum and resistant to seawater attack, are being used more frequently in cases in which seawater attacks from both sides. Some of the super SS are fully austenitic; some are ferritic, while others are a mixture of austenite and ferrite (duplex stainless steels). Currently, most of the super stainless steels are best known by their suppliers designations, e.g., Sandvik SAF 2205 (UNS S32205) (2% Mo) and Allegheny Ludlum AL-6XN (UNS N08367) (6 % Mo).

In general, duplex SS such as UNS S32205 are limited to less than about 38°C (100°F) in seawater. Therefore, the 6% molybdenum SS or ferritics, such as UNS S44660 (27 Cr, 4 Mo, 1.5 Ni), usually are used for the warm (23) water applications or where high reliability is imperative. A recent failure of 6 MoSS in brackish water has emphasized that the metal temperature must not exceed the critical crevice corrosion temperature, which is 60°C (140°F). See Figure 1.19[18] for the stress corrosion cracking resistance of austenitic and duplex SS as a function of temperature and % chlorides. See Figure 3.18 for the resistance of SS and nickel alloys to localized corrosion (pitting and crevice corrosion) as a function of chloride ion concentration and pH.

The ratio of austenite to ferrite in duplex SS should be 50:50 ± 10% for maximum corrosion resistance. In addition, the nitrogen should be specified to be 0.14% to 0.2%. The amount of sigma phase that can form in wrought duplex SS can be estimated as:

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

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(23) Ferritic SS can be hydrogen embrittled by cathodic protection systems if the potentials are not carefully controlled. For example, UNS S44660 can be embrittled if the temperature is above 45°C (114°F) and the potential is more electronegative than -0.800 volt.

The corrosion resistance of duplex SS can be destroyed (thus requiring annealing) by excessive heat input during welding, e.g., excessive weld repair. Therefore, welding procedure qualifications should include a corrosion test that demonstrates the corrosion rate will be less than 10 mdd in a modified ASTM G48 test (25°C [78°F] for 24 hours). Delayed cracking (up to five weeks after welding) has been reported in high ferrite duplex SS welds made with inadequately dried coated electrodes.

Reinforced (by glass fiber) thermosetting resin pipe (RTRP), commonly known as fiber (glass) reinforced plastic (FRP), is an excellent choice for salt water service provided the temperature limits (usually 82°C to 93°C [180°F to 200°F]) and pressure limits (usually 1.03 MPa [150 psi]) are not exceeded. The manufacturers should be consulted for the limits on their materials for specific wall thicknesses and diameters. Note that closely spaced supports are required for above-ground installations, and ultraviolet degradation inhibitors are required for outdoor exposure. Fire-retardant additives also can be used to minimize the concern about fire resistance.

3.4 Corrosion Inhibition

Corrosion can be prevented by adding inhibitors as well as by using resistant alloys. As previously mentioned, the addition of oxygen scavengers, such as sodium sulfite, is an effective method of inhibiting corrosion. Oxygen scavengers change the environment and, therefore, are not truly inhibitors. In general, inhibitors form a film on the surface that changes (polarizes) the electrochemical potential so the corrosion current is greatly reduced. Corrosion inhibitors can be either cathodic, anodic or a mixture of the two. There are also organic inhibitors that provide a barrier film and thus act in a manner similar to cathodic inhibitors.

Cathodic inhibitors reduce corrosion by rapidly polarizing the cathode. Examples of cathodic inhibitors are salts of zinc, magnesium, and calcium. In waters where calcium carbonate precipitates (as discussed above), a protective film is formed on the surface.

The anodic inhibitors reduce corrosion by rapidly polarizing the anodes. 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.

For cooling water, the six basic systems are: acid chromate/zinc, alkaline chromate/zinc, alkaline zinc, stabilized phosphate, all-organic, and molybdate. A nitrate-borate (800 ppm to 1,200 ppm nitrate) mixture has proven effective in closed-loop cooling systems. All have limitations on their effectiveness based on pH, dissolved solids, and hardness of the water. See Puckorius for the unique problems of water treatment requirements for reuse water.[22]

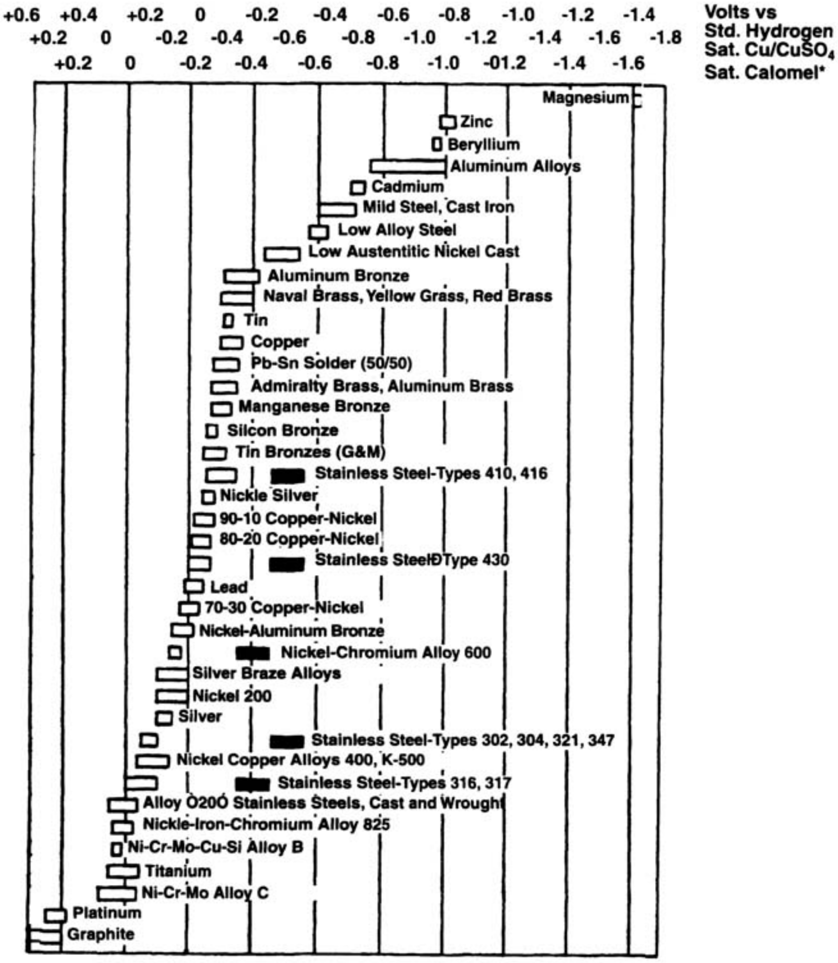
Chromates are one of the most effective classes of inhibitors, but their uses are now limited to closed systems because chromium is highly toxic to aquatic life. As little as 0.05 ppm hexavalent chromium can be lethal to some aquatic life.

For an inhibitor to be effective, it must be able to form a film on the surface of the metal to be protected. Therefore, inhibitors usually are ineffective in high velocity and turbulent areas. When velocities exceed 4.5 m/s (15 ft/s), the inhibitor supplier should be consulted to ensure that the specific inhibitor will be effective. Other factors influencing the effectiveness of inhibitors are the anion concentration and the temperature. At concentrations in the order of 10,000 ppm, some anions (e.g., sulfate) interfere with the inhibitor film formation. A temperature limit of 175°C (350°F) has been reported for the effectiveness of filming amine inhibitors used in water containing oil wells. Again, the supplier should be consulted for the specific limitation of a particular inhibitor.

3.5 Galvanic Corrosion

When two dissimilar metals come into contact in an environment that contains liquid water or moisture, 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 (Figure 1.21).[23] The more noble or corrosion-resistant materials are cathodes that are protected from corrosion when coupled with any material that exhibits a potential above it. The anode, which will corrode, will be a material that appears above with a more electronegative potential. Note that SS may exhibit one of two potentials depending on whether the surface is in the active or passive condition. It is important to recognize that the galvanic series in Figure 1.21[23] applies only to seawater and only in the temperature range indicated.

Furthermore, the severity of corrosion depends on the relative areas as shown in Table 1.2. For example, one would expect severe attack of carbon steel when coupled to the more noble 18 Cr-8 Ni SS in seawater; however, this combination works well provided the area of carbon steel anode is much greater than that of the 18 Cr-8 Ni SS cathode, e.g., SS bolts in carbon steel plates. Conversely, rapid failure of the carbon steel occurs if a small area of carbon steel is coupled to a large area of 18 Cr-8 Ni SS cathode, e.g., carbon steel bolts in stainless steel plates.



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 new -0.5 volts.

* Also Ag/AgCl in 20 Ω-cm seawater.

Figure 1.21 - Corrosion potentials in flowing seawater (2.5 m/s to 4 m/ s [8 ft/s to 13 ft/s] temperature range 10°C to 27°C(50°F to 80°F).[23]

Table 1.2

General Guide to Corrosion Rate "Acceleration" Factors (Coupled Corrosion Rate/Uncoupled Corrosion Rate) in Static Seawater[24]

Material corroding (A)	Uncoupled corrosion rate, mm/y	Cathode member *of couple (C)	Acceleration factor* CA area ratio 10	1	0-1
Aluminum 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	(60)	(5)	(1)
		Monels			
		Inconel 625			
		stainless steels	15	2	1
		titanium			
		copper alloys	5	2	1
Monel 400/K500 alloys	0-02	carbon	(30)	(4)	(1)
		Inconel 625			
		stainless steels	6	2	1
		titanium			
Stainless steels	0-001	Inconel 625	(6)	(2)	(1)
Inconel 625	<0-001	titanium, carbon	....	1	....

• In flowing seawater (1-2 m s^{-1}), factors for aluminum alloys could be 10 times higher. The corrosion rate of uncoupled aluminum alloy is the same in flowing and static seawater. Available evidence indicates that factors for materials other than aluminum alloys will be the same in flowing and static seawater, relative to the uncoupled corrosion rates in flowing and static seawater, respectively. Uncoupled corrosion rates in flowing seawater are: low alloy steels, Ni-Resist 0.10-0.15 mm/y, copper alloys 0.01-0.05 mm/y, Monels 0.002 mm/y.

* Factors in parenthesis have been derived on the basis of a limited amount of evidence.

As mentioned above, the environment has a significant effect on whether galvanic corrosion will be a problem. For example, carbon steel will corrode rapidly if equal or larger areas of alloy 400 (UNS N04400) are coupled with it in seawater. Conversely, carbon steel is compatible with alloy 400 (UNS N04400) in concentrated caustic solutions. Even freshwater can be sufficiently different from seawater that some 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 50°C (120°F), regardless of area ratio because the rapid polarization of the cathodic metal greatly reduces the galvanic current.

Another example of the effect of polarization is coupling 18 Cr-8 Ni SS to UNS C71500 (70 Cu-30 Ni) in water saturated with carbon dioxide at 68°C (155°F). UNS C71500 was anodic to 18 Cr-8 Ni SS for six hours after coupling. At 24 hours the 18 Cr-8 Ni 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 that for near-equal areas in aqueous environments the corrosion rate of the anodic member will double. As can be seen in Table 1.2,[24] the acceleration factor varies with the area ratio.

Coupling of dissimilar metals in the atmosphere also may result in galvanic corrosion. Figure 1.22 [25] 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% to 60%.

Figure 1.22 correctly indicates that galvanized steel is compatible with the 300 series SS if not exposed within two miles of a body of salt water.[25] However, galvanized steel should *never* be welded to 300 series SS, 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 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 does occur under some conditions.

3.6 Materials Selection for Cooling Water

Table A-15 of Appendix A contains a materials selection for aerated freshwater systems. As indicated in Note 27 of Appendix A and mentioned previously, in freshwater systems admiralty brass (UNS C44300) should be limited to a pH of 7.2 maximum from ammonia and copper-nickel alloys and should not be used in waters containing more sulfides than 0.007 mg/L. The process inlet side temperature for admiralty (UNS C44300) usually is limited to about 177°C (350°F) for cooling service. Aluminum bronze or copper-nickel alloys often are used when the process inlet temperature is 177°C to 232°C (350°F to 450°F). In addition, codes such as ASME Section VIII have temperature limitations for these materials. Aluminum bronze alloys have a somewhat higher tolerance for hydrogen sulfide than copper-nickel alloys. It is best to check with the materials supplier to determine which material is best suited to the specific conditions in the cooler.

The materials selection in Table A-15 also is satisfactory for seawater except that pump cases and impellers should be a suitable duplex SS or nickel-aluminum bronze alloy (properly heat treated). Neoprene-lined water boxes should be considered. For piping, fiber-reinforced plastic (up to 1,035 kPag [150 psig] operating pressure) and neoprene-lined steel also should be considered. Titanium (UNS R50400) and 6 MoSS tubes should be considered where low maintenance is required or the cost can be justified by life expectancy.

3.7 Steam and Condensate

Pure dry steam is not corrosive to carbon steel up to about 540°C (1,000°F). Above this temperature the oxidation rate in air and steam increases rapidly. Normally, a minimum alloy content of 1-1/4 Cr-1/2 Mo is used above 455°C (850°F) to avoid graphitization. Oxidation of 1-1/4 Cr-1/2 Mo is not a problem until about 590°C (1,100°F). From 590°C to 650°C (1,100°F to 1,200°F), 2-1/4 Cr-l Mo is satisfactory, although 18 Cr-8 Ni SS has been used above 590°C (1,100°F). Stress corrosion cracking of 18 Cr-8 Ni SS has occurred in crevices, e.g., connections welded to elbows for thermowelds have failed with solids carry-over in the steam. For this reason 2-1/4 Cr-l Mo alloy is preferred in the 590°C to 650°C (1,100°F to 1,200°F) range except in large-diameter, high-pressure systems where alloy T91 (vanadium modified 9 Cr-1 Mo steel) sometimes is more economical because of significantly higher strength.

When austenitic stainless steels are used above 540°C (1,000°F), 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 loss of creep ductility, as well as the loss in strength due to fine grains from recrystallization. Cold forming also can be detrimental to carbon steel heater tubes. For example, very small defects on the outside of cold bends in boiler tubes have propagated to failure in creep at temperatures as low as 320°C (600°F).

Problems with steam can occur in let-down valves due to erosion-corrosion. To prevent attack, hard facing, e.g., Stellite 6™ (UNS R30006 commonly is used when the pressure drop exceeds 1,035 kPa to 1,380 kPa [150 psi to 200 psi]). In addition, 1-1/4 Cr - 1/2 Mo or 2-1/4 Cr - 1 Mo is used for 4 diameters downstream. This limit can be raised to 3,450 kPa (500 psi) for clean, dry steam. Erosion-corrosion also occurs in wet steam. Resistance to wet steam is enhanced by increasing both the metal hardness and chromium content. The product pvx (25) exceeding 2.14 x 10^3 in metric units (1 x 10^5 in English units) has been used as an approximation to estimate if carbon steel would be satisfactory in wet steam. More recently, computer

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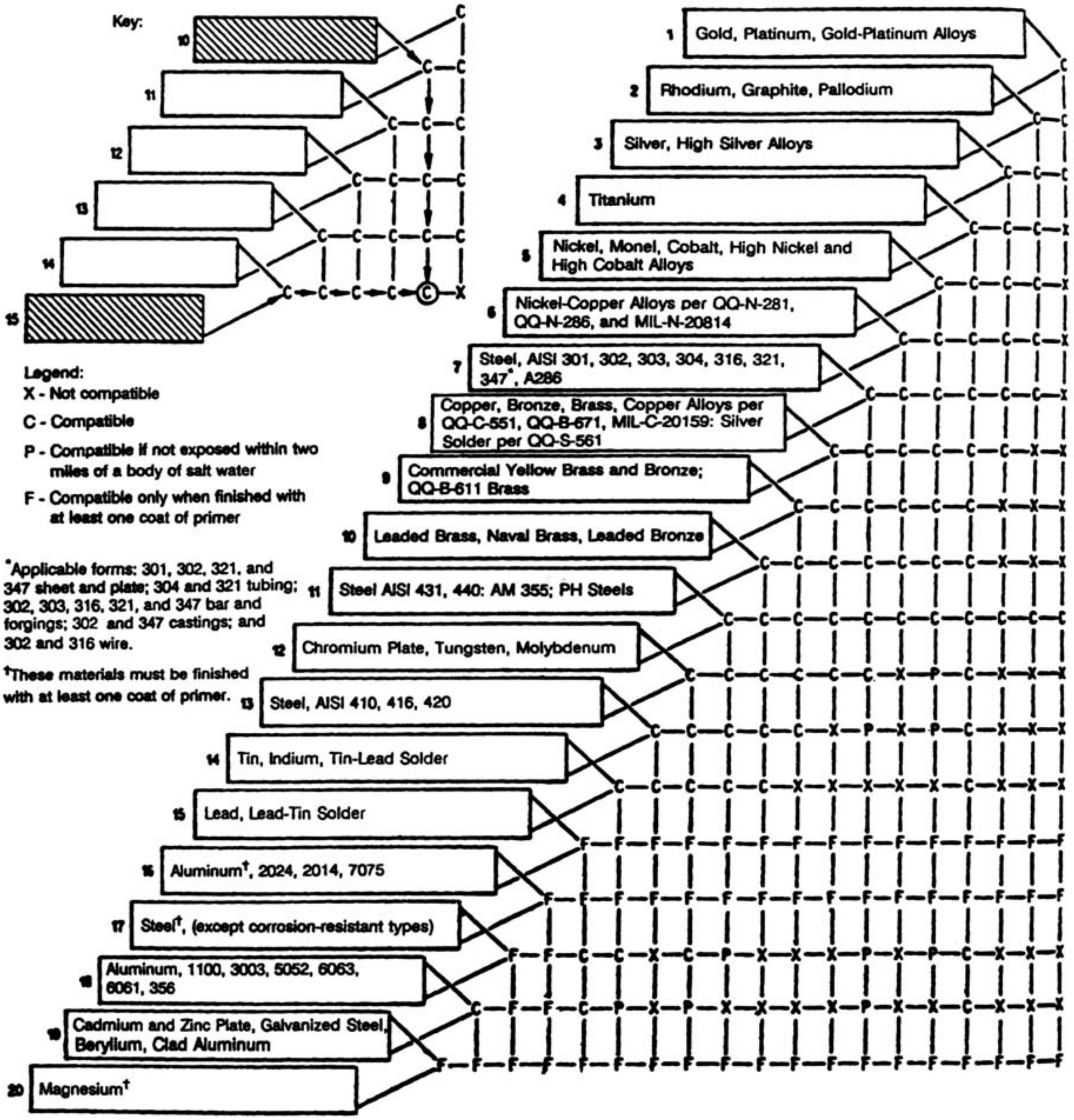
(25) The pressure in kg/cm^2 (psi), the velocity in m/sec (ft/sec), and wetness (% water).



C
C—C
C—C—C
C—C—C—X
C—C—C—C—X
C—C—C—C—C—X
C—C—C—C—C—C—X
C—C—C—C—C—C—X—X
C—C—C—C—C—C—X—X—X
C—C—C—C—C—C—C—X—X—X
C—C—C—C—C—C—C—C—C—C—C
C—C—C—C—C—C—X—P—C—X—X—X
C—C—C—C—C—X—P—X—P—C—X—X—X
C—C—C—C—C—X—X—X—X—X—C—X—X—X
F—F—F—F—F—F—F—F—F—F—F—F—F—F—F
F—F—F—F—F—F—F—F—F—F—F—F—F—F—F—F
F—F—C—C—X—C—P—X—X—X—P—X—P—C—X—X—X
C—F—F—C—P—X—P—X—X—X—X—P—X—X—C—X—X—X
F—F—F—F—F—F—F—F—F—F—F—F—F—F—F—F—F—F—F

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.

Figure 1.22 - Atmospheric compatibility of metals.[25]
(Reprinted with permission from "How to Minimize Galvanic Corrosion," *Machine Design*, May 9 1963)

programs based on the effect of a significant number of parameters and operating experience have been developed to estimate the erosion-corrosion rate in wet steam.

The effect of small amounts of copper in steel on erosion resistance is controversial. Some tests indicate a benefit while others show no effect on wet steam erosion resistance. Huijbretgs used 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.[26] He reported that no failures occurred when R was greater than 1.0. Usually either 1-1/4 Cr-1/2 Mo or 2-1/4 Cr-1 Mo is used for lines containing wet steam or feedwater when erosion-corrosion is anticipated. The 2-1/4 Cr-1 Mo alloy has shown no attack when pvx exceeds 2.14 x 10^3 in metric units (1 x 10^5 in English units). The pH of the water also is a factor; increasing the pH from 8 to 9 can decrease the erosion-corrosion loss by a factor from 2 to 10. To maximize erosion-corrosion resistance, the pH of boiler feedwater should be controlled to a 9.3 minimum.

Boiler feedwater (BFW) also can cause erosion-corrosion in carbon steel pumps when the temperature exceeds approximately 100°C (200°F). Impellers of 12 Cr are normally used above 100°C to 120°C (200°F to 250°F) in BFW pumps to avoid erosion-corrosion. Carbon steel cases have been used above 120°C (250°F), but 5 Cr-1/2 Mo or 12 Cr are preferred. BFW is treated primarily to prevent corrosion from condensate rather than from steam. BFW deaerators work either by a combination of thermal and mechanical means to drive off oxygen or chemically by adding oxygen scavengers, such as catalyzed sodium sulfite or hydrazine. Hydrazine is preferred for high pressure (> 6.89 MPag [1,000 psig]) boilers. 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 indicated that admiralty brass (UNS C44300) is satisfactory if the ammonia content does not exceed 10 ppm, admiralty brass (UNS C44300) tubes failed in an ammonia plant surface condenser designed to hold ammonia to 10 ppm maximum. The copper alloy that has the best resistance to the ammonia and carbon dioxide found in the air removal section of surface condensers is 70 Cu-30 Ni (UNS C71500).

Serious corrosion fatigue cracking has been reported in a large number of deaerator vessels. Cracks often are so tight and filled with scale that they can penetrate throughwall before they are detected. Therefore, wet fluorescent magnetic particle examination (the only way they can be found) is required to avoid catastrophic failure. Most users are now specifying at least 10% radiography and postweld heat treatment for new vessels. New units also are designed to minimize localized stress and internal stress raisers. In some cases, welds are ground to further minimize stress raisers. NACE International Standard RP0590, "Recommended Practices for Prevention, Detection, and Correction of Deaerator Cracking," contains further details on prevention, detection, and correction of deaerator cracking.

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 also can 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 hours from solids carryover.

Clean condensate, free of solids and gases, is relatively non-corrosive and can be handled in carbon steel with a minimal corrosion allowance. When oxygen is present above about 100 ppb in steam condensate, 18 Cr - 8 Ni SS is required. However, low carbon or stabilized SS is required because sensitized 304 (UNS S30400) or 316 (UNS S31600) can fail from intergranular stress corrosion cracking at temperatures above about 110°C (200°F).

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2

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

1. INTRODUCTION

The equipment used in fluid coking and fluid catalytic cracking (FCC) is similar. A catalyst is circulated in a FCC unit, whereas the coke produced in a fluid coker circulates, providing heat and a particle on which coke from cracking of the hydrocarbon can form. 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 done to convert them to branched chain compounds that increase the octane of gasoline. The feed to fluid catalytic crackers are gas-oil distillate (Figure 2.1) or residuum. For delayed cokers and fluid cokers, the feed is residuum.

2. FLUID COKING AND FLUID CATALYTIC CRACKING

In fluid catalytic cracking (Figure 2.1),[1] the feed, often from the vacuum column, is mixed with the hot catalyst, which carries the feed up to the reactor. The reactor operates at about 480°C to 540°C (900 to 1,000°F). The pressure in an FCC unit is 276 kPa to 345 kPa (40 psi to 50 psi). The cracking of the large hydrocarbon molecules takes place in the riser and the reactor. The cracked products flow out of 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. Counter-current steam removes vapors from the FCC catalyst

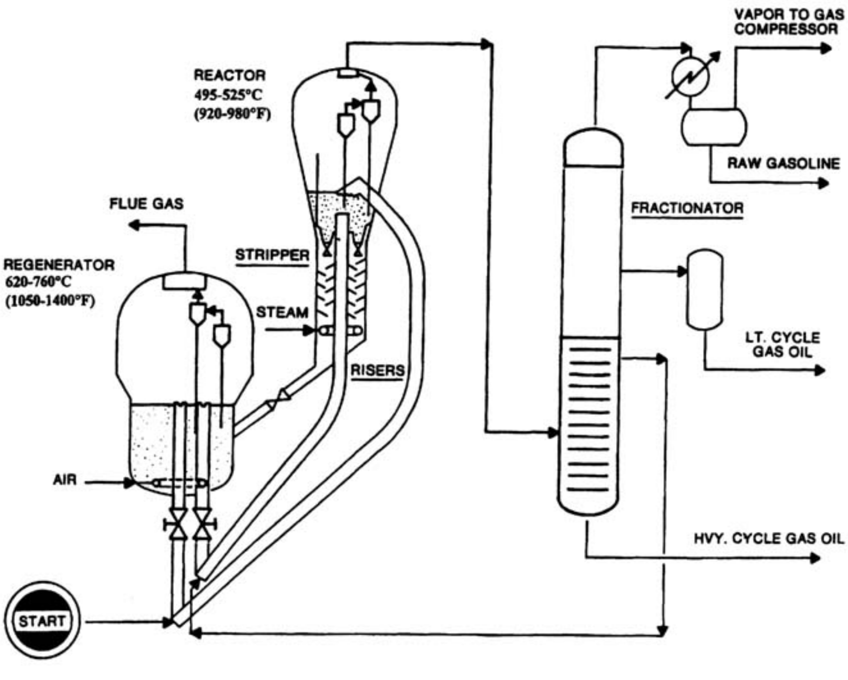

Figure 2.1 - Fluid catalytic cracking.[1]
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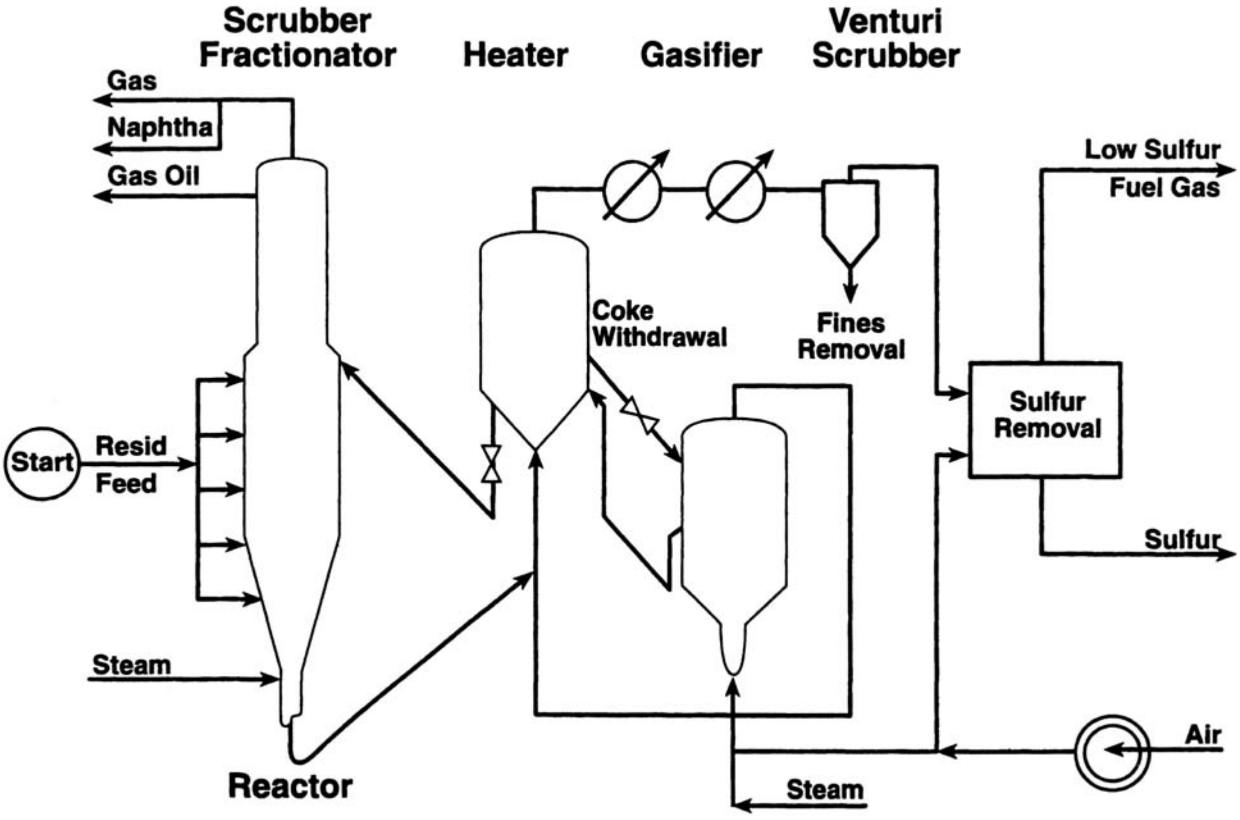

Figure 2.2 - Fluid coking.[2]
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before it flows to the regenerator. In the regenerator, the catalyst is regenerated by the burning of the coke at about 650°C to 760°C (1,200°F to 1,400°F). Entrained catalyst is again removed from the gases before the gases leave the top of the vessel. The hot regenerated catalyst passes out of the bottom of the regenerator where it again is combined with fresh feed plus some recycle from the fractionator.

In fluid coking (Figure 2.2),[2] the reactor also operates at about 480°C to 540°C (900°F to 1,000°F), but the pressure is 172 kPaa to 240 kPaa [25 psia to 35 psia]). The residuum 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 (coke laden catalyst in an FCC) 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.

2.1 Reactors and Regenerator (Burner or Heater) Vessels

The mechanical designs of fluid coker and fluid catalytic cracker reactors and regenerators (called burners or heaters in fluid cokers) are essentially the same. These vessels are often 7.6 m to 9.2 m (25ft to 30 ft) in diameter and 24.5 m to 30.5 m (80ft to 100 ft) high. Walls are usually made of 12.5 mm to 25 mm (0.5 in. to 1 in.) thick carbon steel with refractory lining. The refractory lining is in 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 (temperatures in the regenerators often reach 705°C [1,300°F]) held on by Y-anchors (Nelson-studs) on the wall. A 12 Cr hexmesh (similar to walkway grating) is then attached to the studs, and an erosion-resistant

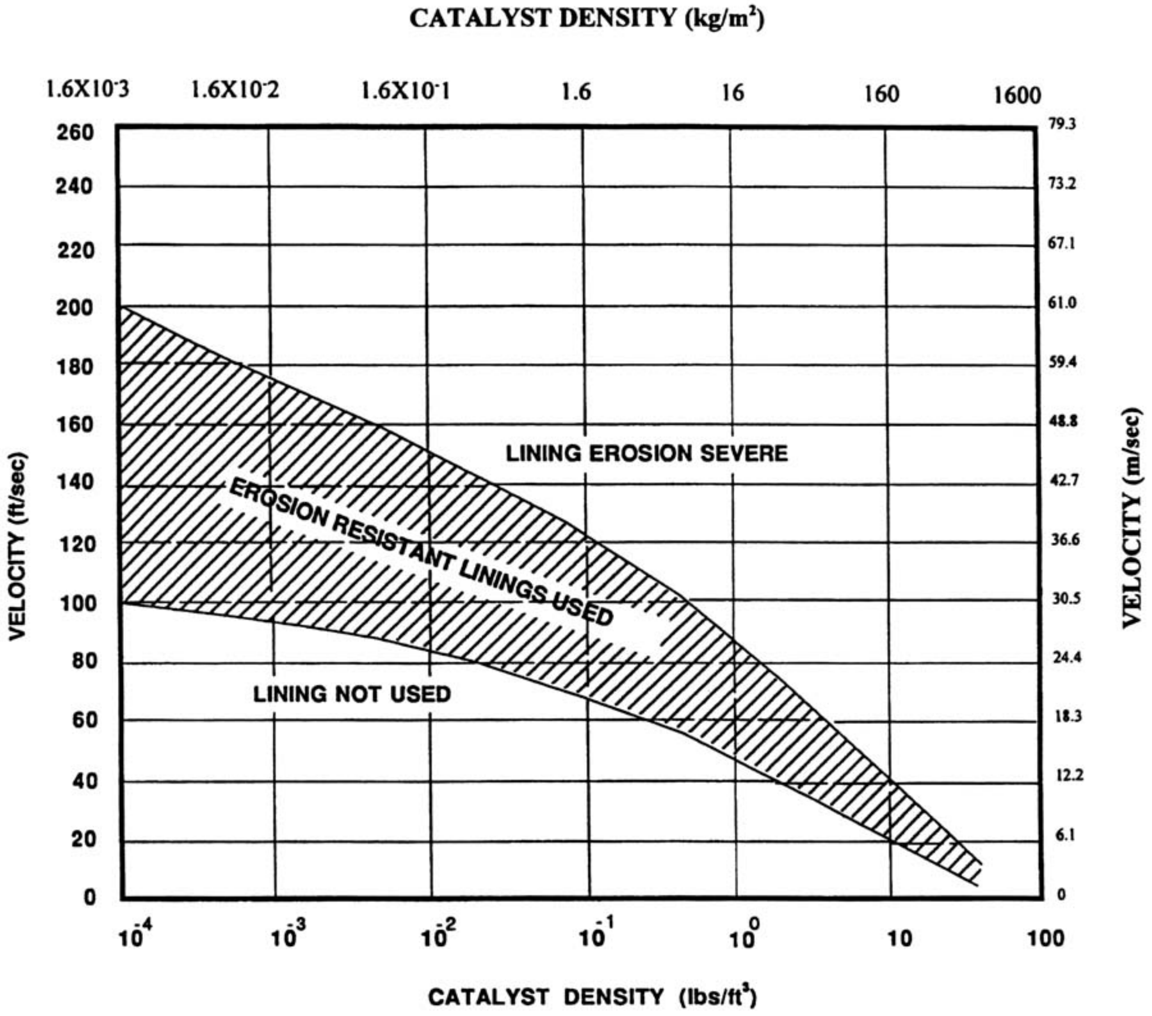

Figure 2.3 - Use of erosion-resistant linings in fluid catalytic cracking units as function of catalyst density and velocity.[3]

refractory is applied over the mesh. Erosion-resistant linings are required because of the fluid catalyst circulating in the system. The extent of the erosion problem is a function of velocity and catalyst density (Figure 2.3).[3]

For the newer high-temperature units, SS fiber-reinforced refractory linings are used because the thermal expansion of the hexmesh refractory support is sufficient to cause cracking problems in the refractory lining. 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 454°C (850°F) to avoid loss of strength due to long-term graphitization. Graphitization is the formation of graphite (free carbon) in steel by the decay of iron carbide.

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

The cyclones in both types of units are lined with erosion-resistant refractory. The cyclones in the reactors usually are made of carbon steel, or C-1/2 Mo; the cyclones in the regenerators are made of either 2-1/4 Cr-1 Mo, 304H (UNS S30409) or 321H (UNS S32109). Oxidation resistance and creep strength, rather than sulfur attack, govern the selection of the cyclone material.

The fluid cracker and coker vessels are often field-erected because of their large size. This means they must be hydrostatically tested for the first time in the field; this poses the risk of brittle fracture. Figures 2.4 to 2.6 show a brittle fracture of a fluid coker burner vessel.[4] Figure 2.4 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 2.5. This gives an impression of the effect the failure had in the immediate area. Figure 2.6 shows the numerous paths the cracks took on the bottom head where the brittle fracture originated. The incident occurred February 17, 1956, in the Avon, California refinery during construction of a fluid coker unit. The vessel, 11 m (36 ft) in diameter by 23 m (75 ft) high, was made from 16 mm (5/8 in) thick A285C (UNS K02801) steel. It failed in the knuckle (ASME head) to skirt attachment during hydrotesting when the ambient temperature was 7°C to 10°C (45°F to 50°F). Since this failure, most designers have used only ellipsoidal or hemispherical heads. They require a minimum temperature, typically 27°C (80°F), for hydrostatic tests of field-erected vessels.

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

2.2 Associated Equipment

Type 304H SS (UNS S30409) commonly is used for the small high-temperature lines around the reactor and regenerator. Intergranular stress corrosion cracking (IGSCC) from polythionic acid(1) has been a severe problem in these lines during shutdown. Presently, a nitrogen and ammonia purge is introduced at 93°C (200°F) above the dew point during cooldown to prevent attack. Expansion bellows in the regenerated catalyst standpipe have been subject to failure. Alloy 625 (UNS N06625) has failed due to loss of ductility

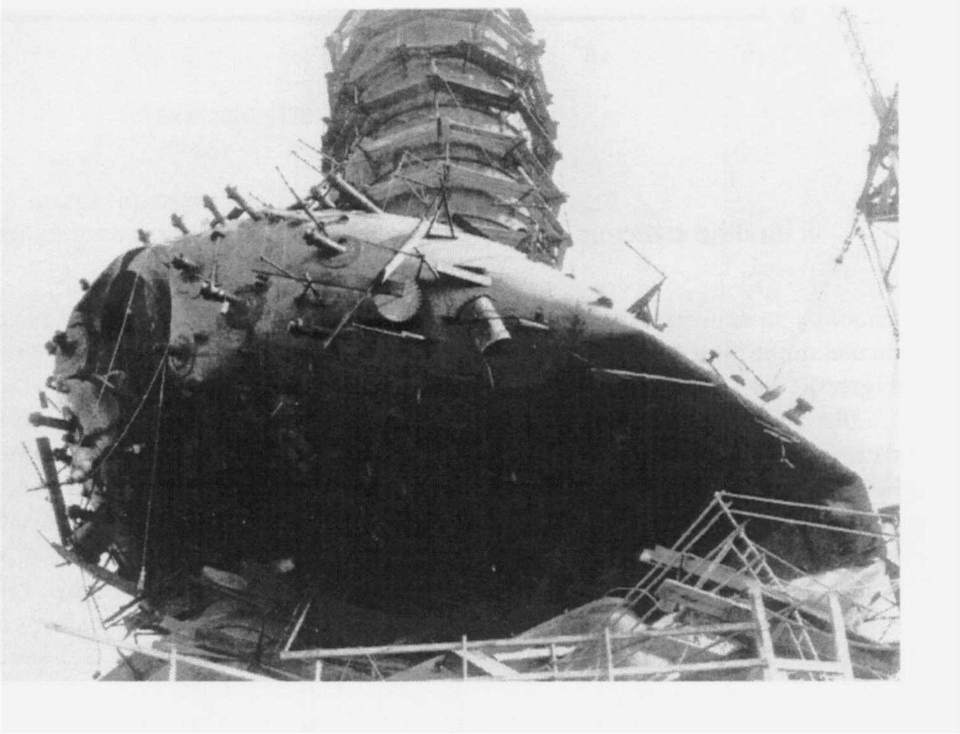

Figure 2.4 - Front view of collapsed vessel. Test closure for vapor line opening in top center of top head at upper left.[4]
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(1) Polythionic acid ($H_2S_xO_6$) or sulfurous acid (H_2SO_3) is formed by the reaction of the iron sulfide scale, water, and oxygen.

Figure 2.5 - Heat fragments directly below collapsed shell.[4]

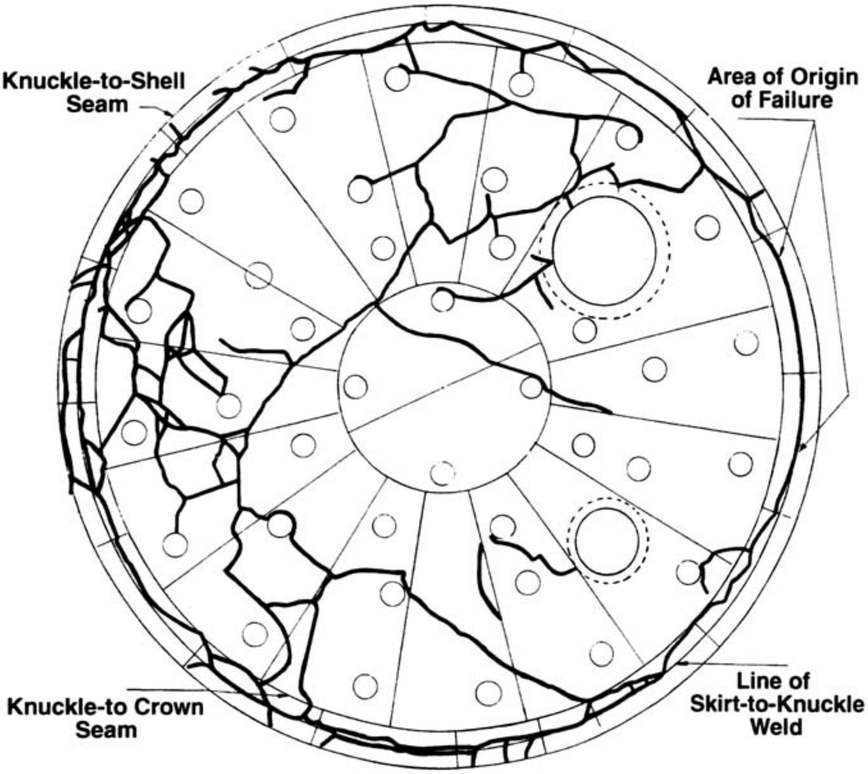

Figure 2.6 - Layout of failed bottom head showing 34-piece construction and brittle fracture lines.[4]
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from an aging reaction that occurs in the 595°C to 815°C (1,100°F to 1,500°F) range. Alloy 801 (UNS N08801), which is titanium-stabilized for resistance to intergranular attack, undergoes a severe loss of ductility above 480°C (900°F). Alloy 800 (UNS N08800) has been used, though it is not immune to all failures (e.g., intergranular attack). Inconel™ 625LCF(2) (UNS N06625), which has improved fatigue resistance and somewhat better resistance to embrittlement, is a popular choice for bellows material. Some refiners use insulation around the bellows to keep the temperature below 538°C (1,000°F) to minimize the risk of embrittlement. Regardless of the alloy used for expansion bellows, the material should be solution-annealed after it is formed, and careful attention to installation procedure details is imperative to minimize failure. It has been recommended to use floating bellows supports when the operating temperature will exceed 540°C (1,000°F). In addition, the metal temperature should be kept above the dew point by use of insulation, etc., to avoid corrosion failures.

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

3. DELAYED COKING

In delayed coking (Figure 2.7),[1] 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, which operates at about 480°C (900°F) and 345 kPaa (50 psia).

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

1. Stripping the coke with steam,
2. Quenching with water, gradually filling the drum,
3. Draining,
4. Opening heads,
5. Cutting the coke with a 22,000 kPag (3,200 psig) 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.

3.1 Coke Drum Materials

Because of the thermal cycling experienced by the coke drums, thermal fatigue is a problem. There is some indication from recent work that controlling the initial quench rate may greatly reduce the thermal fatigue problem. The use of C-1/2 Mo 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

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(2) LCF indicates the alloy is modified for improved fatigue resistance.

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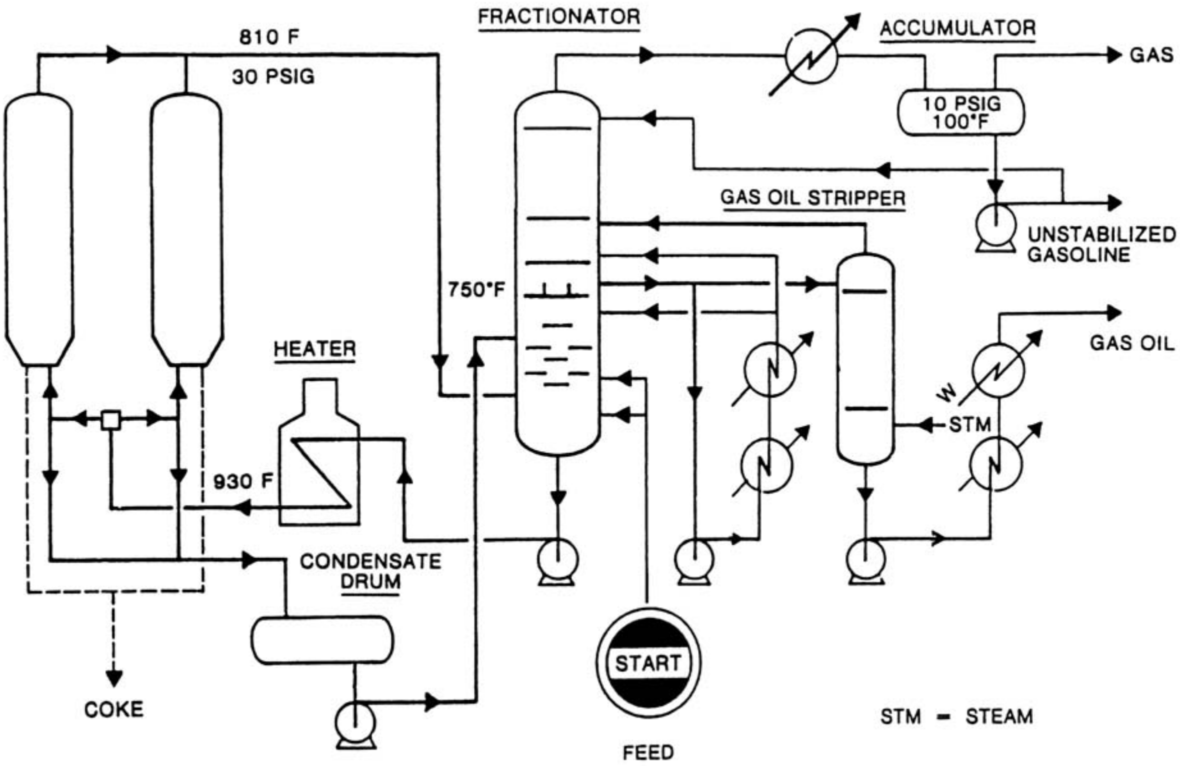

Figure 2.7 - Delayed coking.[1]

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toughness of C-1/2 Mo. Although toughness does not affect fatigue crack growth (fatigue crack growth is a ductile fracture process), brittle fracture will occur in fewer thermal cycles in a low-toughness steel than in a high-toughness steel. This is because high toughness steel can tolerate a larger fatigue crack than a low-toughness material.

Since C-1/2 Mo plate is supplied in the as-rolled condition in the thickness normally used for coke drums (about 25 mm [1 in.] thick), the toughness is usually poor. To obtain improved toughness at minimal cost, one should specify that the C-1/2 Mo be made to fine-grain practice. Many users also specify normalizing, which significantly increases toughness. Most coke drums have been made of 1 Cr-1/2 Mo materials for about the past 15 years because of the controversy over C-1/2 Mo and the higher allowable stress of 1 Cr-1/2 Mo. After the proper toughness requirements are specified, e.g., 20J at -18°C (15 ft-lbs at 0°F) for C-1/2 Mo, the ultimate choice of material should be based on cost.

Delayed cokers usually are clad with 12 Cr to avoid high-temperature sulfur attack. For cladding, type 410S SS (UNS S41008) is preferred over 405 SS (UNS S40500) because the higher chromium in 405 SS causes problems with forming and with 475°C (885°F) embrittlement (discussed in Chapter 1).

Type 309 SS (UNS S30900) normally is used for clad restoration on 12 Cr clad vessels. However, severe cracking has occurred when 309 SS (UNS S30900) was used for clad restoration on coke drums. This is because of the thermal cycling of materials with the large differences in coefficients of thermal expansion, namely the 309 SS (UNS S30900) weld metal , the 12 Cr clad, and the low-alloy steel backing. High nickel (65 Ni-15 Cr-Fe) filler metal performs significantly better than 309 SS (UNS S30900) for clad restoration in coke drums because of the lower coefficient of thermal expansion, and the coke protects the 65 Ni-15 Cr-Fe filler metal from accelerated sulfur attack. Some refiners grind both the inside (clad restoration) and outside (base metal welds) to minimize stress raisers that accelerate thermal fatigue. It is important to note that coke drums are the *only* high-temperature sulfur-containing environment in which the 65 Ni-15 Cr-Fe alloy materials normally are used.

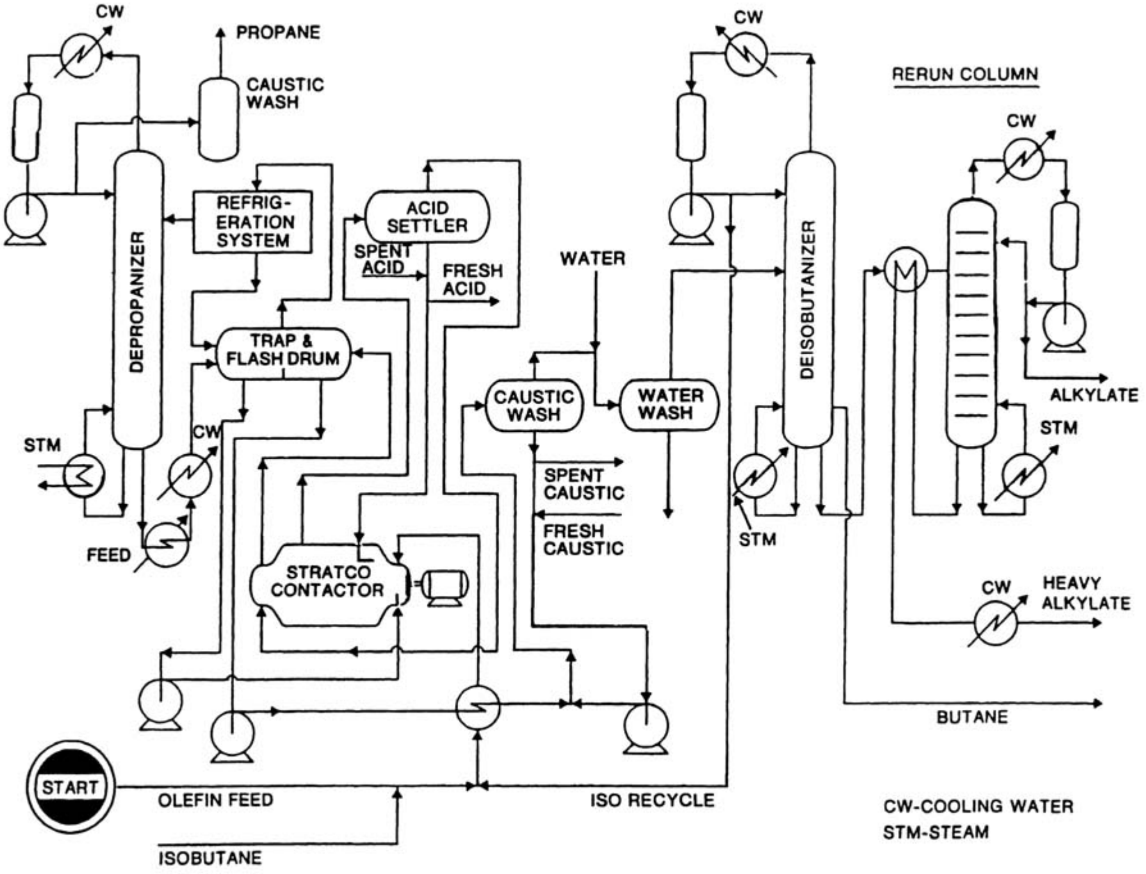

Figure 2.8 - Sulfuric acid alkylation.[1]
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Although there have been reports of good performance of 65 Ni-15 Cr-Fe filler metal in coker fractionators up to 400°C (750°F), presumably because of protection by the coke that occurs in coke drums, severe sulfidation has occurred in a crude fractionation tower when 65 Ni-15 Cr-Fe type electrodes were used above 288°C (550°F). Furthermore, 65 Ni-15 Cr-Fe filler metal is more expensive and more prone to weld cracking than 309 SS (UNS S30900), normally used except in coke drums.

4. ALKYLATION PLANTS

4.1 Sulfuric Acid Alkylation

In sulfuric acid (effluent refrigeration) alkylation (Figure 2.8),[1] the feed and the recycle sulfuric acid are charged to the contactor. The reaction takes place at about 4°C to 10°C (40°F to 50°F) at 345 kPaa (50 psia) 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 the alkylate 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 about 80%; however, most operators require 89% minimum. Since corrosion of carbon steel in concentrated sulfuric acid is accelerated over 50°C (120°F), electrical heat tracing, rather than steam tracing, is used to prevent freezing in cold climates.

Most refiners specify that the acid piping be sloped so it is self-draining. If the velocity exceeds 0.6 m/

s to 0.9 m/s (2-3 ft/s) for carbon steel, alloy 20 (UNS N08020) is used. Although 316L (UNS S31603) can be used up to 1.2 m/sec (4 ft/sec) without accelerated erosion-corrosion, the use of alloy 20 (UNS N08020) is much more common. Where erosion-corrosion is a problem on alloy 20, e.g., on mixers, alloy C276 (UNS N10276) or Stellite™ 21 (UNS R30021 [0.25 C, 27 Cr, 5 Mo, 2.8 Ni, 65 Co]) hard facing is used. Small valves (less than 152 mm [6 in.] in diameter) usually are made of alloy 20 (UNS N08020), and larger valves are made of steel with alloy 20 trim (stem and seats).

Significant corrosion has been reported in dead legs and socket welds in sulfuric acid systems; therefore, these should be avoided. In addition, hydrogen grooving has occurred on the upper portions of horizontal tanks, manways, nozzles, and piping on surfaces exposed to liquid sulfuric acid. The grooving is the result of hydrogen from the corrosion reaction non-uniformly disrupting the protective iron sulfate film. The phenomenon can be prevented by maintaining a minimum velocity of 0.3 m/s (1 ft/s) or by use of 316L (UNS S31603) or alloy 20 (UNS N08020). For more information on hydrogen grooving, see Brubaker and Tatnall.[5]

When proper treatment of the effluent of the reaction section is not maintained, fouling and corrosion from SO_2 combining with water in the overhead can occur. A pH below 6 in the water from the accumulator boot indicates corrosion is occurring. Steel cases and high silicon cast iron impellers often are used for pumps; however, they only last five to ten years. Critical pumps often are made of alloy 20 (UNS N08020) (cast equivalent, ASTM A351 Grade CN-7M). For additional information on materials for handling and storage of concentrated sulfuric acid at ambient temperatures, see NACE Standard RP0391, "Materials for Handling Storage of Concentrated (90% to 100%) Sulfuric Acid at Ambient Temperatures."

4.2 Hydrofluoric Acid Alkylation

The feed to a hydrofluoric acid alkylation unit is desiccant-dried, then sent to the combined reactor settler (Figure 2.9).[2] The reaction takes place at 32°C to 38°C (90°F to 100°F) at 1,725 kPaa (250 psia) 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 to 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

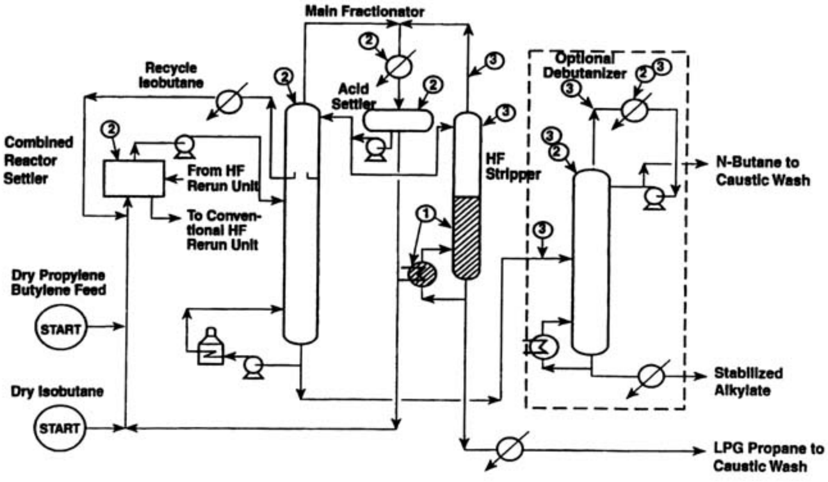

Figure 2.9 - Typical hydrofluoric acid alkylation unit.[2] (Reprinted with permission of Gulf Publishing Co., Houston, TX)

NOTES:

1. Shaded areas are where Monel™ 400 is used.
2. Hydrogen blistering or cracking has occurred
3. Corrosion reported.

often is 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 70% to 80%. The locations where hydrogen blistering, cracking, or corrosion has been reported, as well as where alloy 400 (UNS N04400) is required, are shown in Figure 2.9.[1] It is important to thoroughly dry equipment after a shutdown to avoid corrosion caused by pockets of water left in the equipment diluting the acid so it is corrosive to carbon steel. Drying is aided by specifying that the acid piping be sloped so it is self-draining. It has been reported that limiting the sum of the copper, nickel, and chromium residual elements to 0.02% maximum will minimize corrosion of carbon steel.[6] However, galvanic corrosion problems have been reported in this low residual element carbon steel when it is coupled to weld metal or base metal containing high quantities of residual elements.

For small diameter piping, screwed connections with PTFE tape are preferred over socket or seal-welded threaded connections to avoid crevice corrosion. Hydrogen embrittlement of high strength steels has been a problem; steels of tensile strengths exceeding a specified minimum of 414 MPa (60 ksi) and hardnesses over 200 Brinell usually are avoided. Limiting the arsenic in the fresh acid to 25 ppm often is done to minimize the potential for hydrogen embrittlement. Flange bolts may be ASTM A193 B7, although B7M is preferred; but valve bonnet bolts should be ASTM A193 B7M or alloy 400 (UNS N04400) because of leakage. Alloy K-500 (UNS N05500) bolts have failed where the hardness exceeded HRC 30. Alloy 400 (UNS N04400) spiral wound gaskets filled with PTFE or graphite with PTFE inner rings usually are specified. Where corrosion of flange faces has occurred, alloy 400 (UNS N04400) overlay usually is specified for repair. Weld slag on the surface of carbon steel welds has been reported to cause accelerated attack. Therefore, whenever possible, slag-free processes such as gas-tungsten arc should be used. Alternatively, special care should be taken to ensure slag is removed.

In higher temperature areas (e.g., the acid reboiler and the bottom of the acid regenerator), alloy 400 (UNS N04400) is used. Butt-welded construction is preferred even in small diameter piping to avoid crevice corrosion. Alloy 400 (UNS N04400) 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 solid alloy 400 (UNS N04400). Valves are carbon steel with alloy 400 trim and PTFE packing. Spot chemical testing of alloy 400 usually is specified because it is easily confused with austenitic SS. For additional information on materials for handling hydrofluoric acid, see NACE Publication 5A171, "Materials for Receiving, Handling, and Storing Hydrofluoric Acid."

5. FRACTIONATION

After the reactions have taken place 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 1 (i.e., carbon steel below 288°C to 315°C [550°F to 600°F] and 5 Cr-1/2 Mo piping, and 12 Cr clad vessels above). Because the temperatures in coker fired heaters are higher than in crude units, furnace tubes and furnace transfer lines in delayed cokers usually are 9 Cr-1 Mo.

6. SOUR WATER AND SOUR WATER STRIPPERS

6.1 Characteristics of Sour Water

Coking and catalytic cracking produce cyanides and hydrogen sulfide in the water condensed in these processes. Very little water is produced in the alkylation process. The traces of acid from the alkylation units as well as cyanides (greater than 20 ppm) from coking and catalytic cracking cause corrosion problems in the tops of columns, in the overhead lines, and in the drums where the aqueous phase condenses. Cyanides are very active if the pH is in the alkaline range. Cyanides accelerate corrosion by converting normally protective iron sulfide films into soluble ferrocyanide complexes. Alkaline conditions usually occur because the nitrogen in the streams that produces the cyanide also produces ammonia.

The corrosion problems caused by these produced waters are hydrogen blistering(3) and sulfide stress cracking (SSC)(4) in carbon steel and pitting and stress corrosion cracking of admiralty (UNS C44300) exchanger tubes. The blisters in carbon steel 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 deethanizer columns in fluid catalytic cracker 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[7] (to react with and remove cyanides), and inhibitors have been used to avoid blistering. However, polysulfide additions have caused fouling and accelerated corrosion in stagnant areas and may increase the likelihood of carbonate cracking in FCC overheads. Therefore, polysulfide additions are only used when other control methods are not effective. 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 SSC becomes a problem when the partial pressure

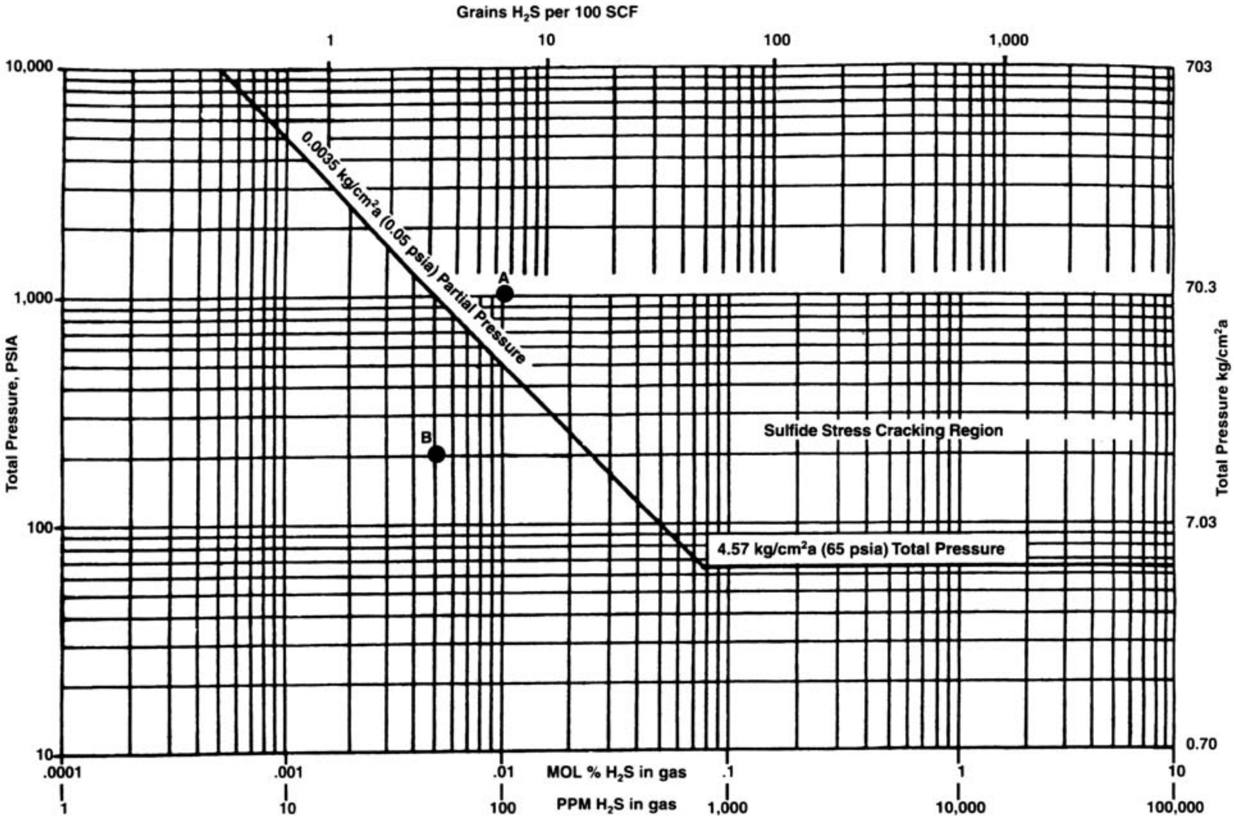

Figure 2.10 - Sour gas systems.[8]

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(3) The formation of blisters on or below the metal surface from excessive internal hydrogen pressure.

(4) Brittle fracture by cracking under the combined action of tensile stress and corrosion in the presence of water and hydrogen sulfide. Sometimes referred to as hydrogen sulfide cracking.

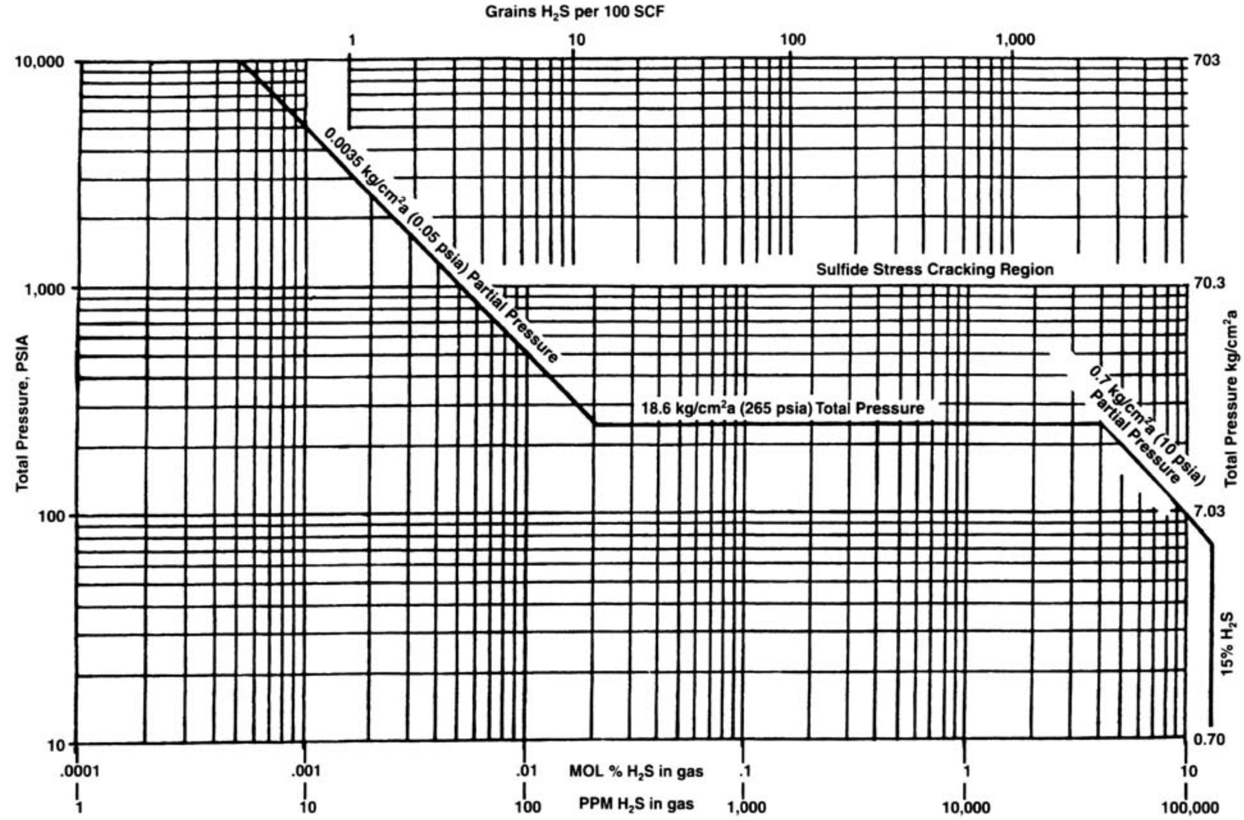

Figure 2.11 - Sour multiphase system.[8]

of hydrogen sulfide exceeds 0.35 kPaa (0.05 psia) and the total pressure exceeds 450 kPaa (65 psia). Typical refinery practice takes into account only the partial pressure, or the ppm of H_2S, i.e., not the total pressure, when determining the potential for SSC. Figures 2.10 and 2.11[8] can be used to predict where SSC will occur as a function of total system pressure vs hydrogen sulfide concentration. McIntyre and Boah have suggested a more conservative definition of sour service in which they ignore total pressure as a criterion, then define sour service as a function of the pH of the water phase and the H_2S partial pressure as follows:[9]

pp H_2S > 0.3 kPaa (0.05 psia) if the water phase pH > 4.0
pp H_2S > 0.05 kPaa (0.008 psia) if the water phase pH < 4.0

However, this approach is controversial.[10]

In refineries, 50 ppm H_2S in the fluid often is used as a basis for defining sour water. When more than 500 ppm of organic acids are present, corrosion of carbon steel becomes excessive and 316L SS (UNS S31603) is required. Oil present in the system tends to inhibit SSC; therefore, limits for the SSC region in the total system pressure vs hydrogen sulfide concentration are somewhat different than those where oil is absent. The limits for sour oil and multiphase systems are shown in Figure 2.11.[8]

To avoid SSC, the hardness of carbon steels should be limited to 200 Brinell, and the hardness of low alloy steels should be limited to about 235 Brinell. See Chapter 5, Section 6, for limits on cold bends in wet H_2S service. For more detailed requirements on materials resistant to SSC, see NACE Standards MR0175 ("Sulfide Stress Cracking Resistant Metallic Material for Oil Field Equipment") and RP0472 (5) ("Methods

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(5) API Standard RP-942 has been discontinued because it covered the same topic as NACE Standard RP0472.

and Controls to Prevent In-Service Cracking of Carbon Steel welds in P-1 materials in corrosive Petroleum Refining Environments"), and NACE Publication 8X194. NACE Standard RP0296 contains guidelines for detection, repair, and mitigation of cracking in wet H_2S (SSC) in existing vessels. NACE Publication 8X194 summarizes current thinking on requirements for pressure vessels in wet H_2S service in refineries. RP0472 is limited to welds in carbon steel equipment in refinery service. It requires a maximum of 200 Brinell for carbon steel welds, whereas MR0175, based on oil and gas field experience, requires a maximum of HRC 22 (HB 241) for carbon steel. MR0175 also has requirements for other materials used in H_2S service. The difference in hardness requirements for carbon steel may have arisen because submerged arc and other automatic welding processes commonly are used for refinery equipment, whereas most carbon steel oil and gas field equipment is welded by the manual metal-arc process, which tends to deposit softer welds than do automatic welding processes. MR0175 is specified for refinery equipment, such as valve trim, springs, and internal bolting. For example, floating head bolting is required to be ASTM A193 B7M, where B7 normally would be used when water and H_2S are present.

Under certain conditions, steels with hardnesses lower than 200 Brinell will crack in H_2S service. Cracking has been reported in low-temperature separators in hydrocrackers and hydrodesulfurizers, in fluid catalytic cracker and fluid coker overhead equipment, and in amine H_2S absorbers. Refiners are now specifying PWHT in these services. This phenomenon is referred to as hydrogen-induced cracking (HIC) or stress-oriented hydrogen-induced cracking (SOHIC). HIC is similar to blistering, except that after the blisters are formed, they join up to form internal fissures parallel to the metal surface. SOHIC is the growth of HIC cracks due to the influence of applied or residual stress. It is believed that PWHT reduces potential for HIC and SOHIC by reducing the driving stress for crack propagation and by increasing the resistance to crack propagation by increasing the notch toughness. See Chapter 5, Section 8.2, for additional discussion of HIC.

In addition to PWHT, some steel companies are suggesting limiting sulfur in steel to 0.001% to minimize failures. Niobium-vanadium steels are used so the high strength can be maintained without the need for high carbon. Conversely, there have been SSC problems with steels of normal carbon contents containing microalloying elements. PWHT at 635°C (1,175°F) minimum is required to lower the heat-affected zone hardness below 248 HVN when the Nb + V is greater than 0.01%. In addition, the effect of PWHT on both hardness and residual stress should be verified for Nb-V steels. For example, Nb-V steel that had been PWHT'd at 593°C (1,100°F) minimum failed in amine service due to stress corrosion cracking. Subsequent laboratory tests revealed that relief of significant residual stress did not occur until the PWHT temperature reached a minimum of 676°C (1,250°F).

Calcium treating the steel and limiting the oxygen to less than 10 ppm have been suggested as ways to minimize HIC and SOHIC. Recent experience indicates calcium treatment may be detrimental to HIC resistance and that so called "HIC-resistant steels" have poorer resistance to SOHIC than steels not made to HIC-

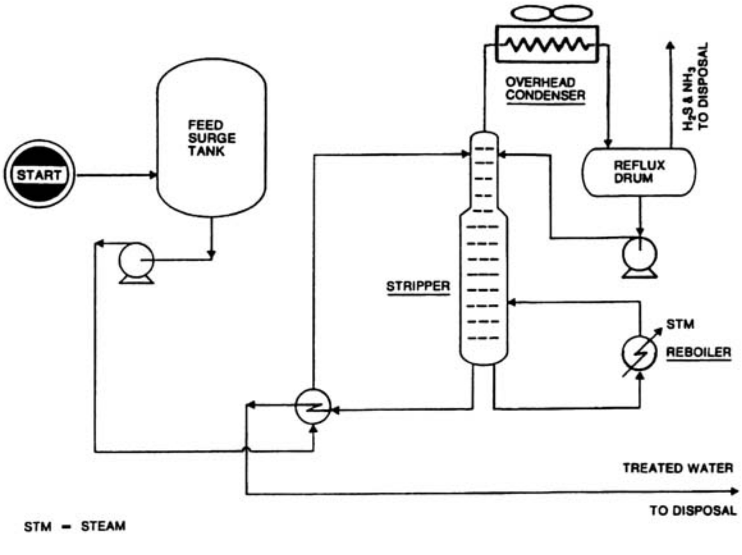

Figure 2.12 - Sour water stripper (non-acidified).[1]
(Reprinted with permission of the American Iron and Steel Institute)

resistant requirements.[11] Furthermore, HIC cracking has been reported in electroslag remelted steel, which is essentially inclusion free. Thus, at this writing the jury is still out on whether the additional cost for so called "HIC-resistant steels" can be justified.

SSC also has been reported in the narrow fusion line between carbon or low alloy steel dissimilar weld when it is welded with an austenitic electrode and not post-weld heat-treated. Hardnesses in the fusion zone have been found to be in the 300 to 400 Brinell range in the as-welded condition.

6.2 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 non-acidified condensing sour water stripper is shown in Figure 2.12.[1] 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 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.

6.3 Corrosion in Sour Water Strippers

The main corrosion problems in a non-acidified condensing sour water stripper occur in the overhead system. Exchanger tubes and headers in the overhead condenser often are titanium. Grade 2 (UNS R50400) is used for tubes and Grade 3 (UNS R50550) for headers. It usually is not possible to electrically isolate the titanium from dissimilar metal (i.e., carbon steel, SS, etc.) piping by insulating flanges. Therefore, there is a potential for embrittlement from hydriding of the titanium when the metal temperature is in excess of 80°C (176°F). For this reason, titanium headers often are specified when titanium tubes are used. Should any hydriding occur, it will be primarily in the thicker headers, thus giving more time to be discovered during the recommended periodic inspection for hydriding.

In low pH environments at temperatures above 110°C (225°F), the high strength Grade 12 (UNS R53400) offers somewhat better resistance to corrosion in tight crevices and under deposits. However, Grade 12 (UNS R53400) is more susceptible to hydriding than Grade 2 (UNS R50400). The line from the condenser to the reflux drum often is 316L SS (UNS S31603), and the reflux drum often is clad with 316L (UNS S31603). The reflux pump often is alloy 20 (UNS N08020). In very corrosive waters, such as those containing phenols or large quantities of salts, alloy C276 (UNS N10276) is used. The velocity in carbon steel piping is limited to 6 m/s (20 ft/s) in two-phase flow and 15 m/s (50 ft/s) in vapor lines. Carbon steel towers have been satisfactory in most units where the overhead is kept above 80°C (180°F). Two API surveys (API Publications 944 and 950) concluded that the location and severity of corrosion vary with the type of unit, as follows: [12,13]

- Acidified: severe corrosion in the feed section, bottom section, and stripper tower,
- Non-acidified condensing: severe corrosion and erosion-corrosion in the overhead section,
- Non-acidified, non-condensing: negligible corrosion.

7. SULFUR PLANTS

7.1 Process

Sulfur is quite versatile; for example, it can be used as an agricultural insecticide or as a raw material for making sulfuric acid. A flow diagram of a typical sulfur plant is shown in Figure 2.13.[2] 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

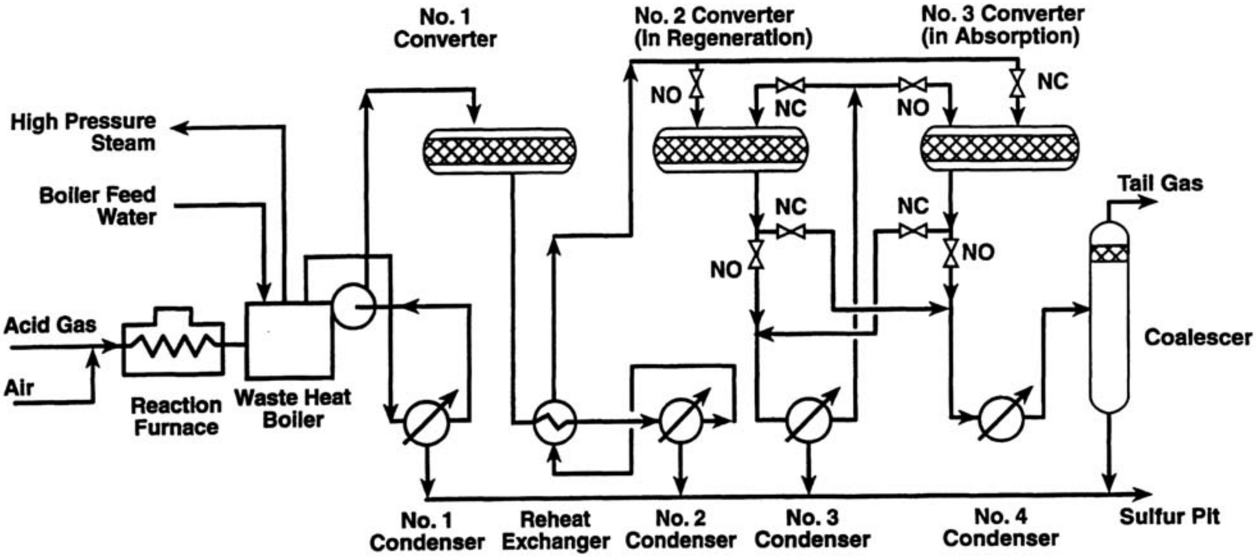

Figure 2.13 - Sulfur plant. [2]

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sulfide is partially burned at about 1,370°C (2,500°F) and 103 kPaa (15 psia) in the reaction furnace to form sulfur dioxide; next the mixture of H_2S and SO_2 is passed through a waste heat boiler then passed over catalyst beds at about 260°C (500°F) and 103 kPaa (15 psia) in the converters. Sulfur is condensed from the effluent of successive converters, then solidified in pits.

7.2 Materials

The effluent from the reaction boiler is handled in 310 SS (UNS S31000) above 425°C (800°F), 321 or 347 SS (UNS S32100 or S34700) above 260°C (500°F), and carbon steel below 260°C (500°F). The acid gas (H_2S, CO_2, and SO_2)are kept above the dew point by, e.g., steam tracing; otherwise, severe corrosion of carbon steel lines will occur. 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 (UNS N08020).

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3

Hydroprocessing, Catalytic Reforming, and Flue Gas

1. INTRODUCTION

Some sulfur compounds are cracked to hydrogen sulfide and removed in the crude unit. The sulfur compounds remaining in the processed crude oil must be removed if the lighter petroleum fractions are to be reformed into products, such as gasoline, etc. Desulfurizing also is necessary (1) to meet the sulfur limits placed on kerosene and diesel products, (2) to prevent the sulfur from "poisoning" catalytic reformer catalyst, and (3) to reduce sulfur dioxide emissions from the fluid catalytic regenerator flue gas.

2. HYDROPROCESSING UNITS

2.1 General

The most common hyroprocessing units are hydrodesulfurizers (Figure 3.1)[1] and hydrocrackers (Figure 3.2).[1] The primary objective in hydrodesulfurizing is to remove sulfur compounds and nitrogen by converting them to H_2S and NH_3, respectively. The amine scrubbing of the recycle gas shown in Figure 3.1 is not always done. In addition, water wash sometimes is recycled from the separator. The hydrocracking process converts gas oils to middle distillates as well as converts sulfur compounds and nitrogen to H_2S and NH_3, respectively. Amine scrubbing of the recycle gas sometimes is done. In addition, water wash sometimes is recycled from the separator. The shell and tube reactor effluent trim coolers shown in both Figures 3.1 and 3.2 are used only occasionally. The feed to hydrodesulfurizers is much heavier material than that is fed to a hydrocracker. In both types of units the feed is first passed to exchangers, where it is heated by the reactor effluent.

The feed next goes to a fired heater then to the reactors at about 370°C to 400°C (700°F to 750°F). The pressures in hydrodesulfurizers normally range from 2,415 kPaa to 13,790 kPaa (350 psia to 2,000 psia); the pressure in the hydrocracker ranges from about 10,340 kPaa to 20,685 kPaa (1,500 psia to 3,000 psia).

The sulfur (and 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, the organic nitrogen compounds are converted to ammonia and some hydrogen cyanide (in first-stage hydrocrackers). In hydrodesulfurizers, the reactor effluent is cooled through a series of exchangers, then sent to a high-pressure separator vessel, where the gas is taken off the top to a unit to remove the hydrogen sulfide. The gas, with most of the hydrogen sulfide removed, 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 also is cooled and sent to a high-pressure separator. In

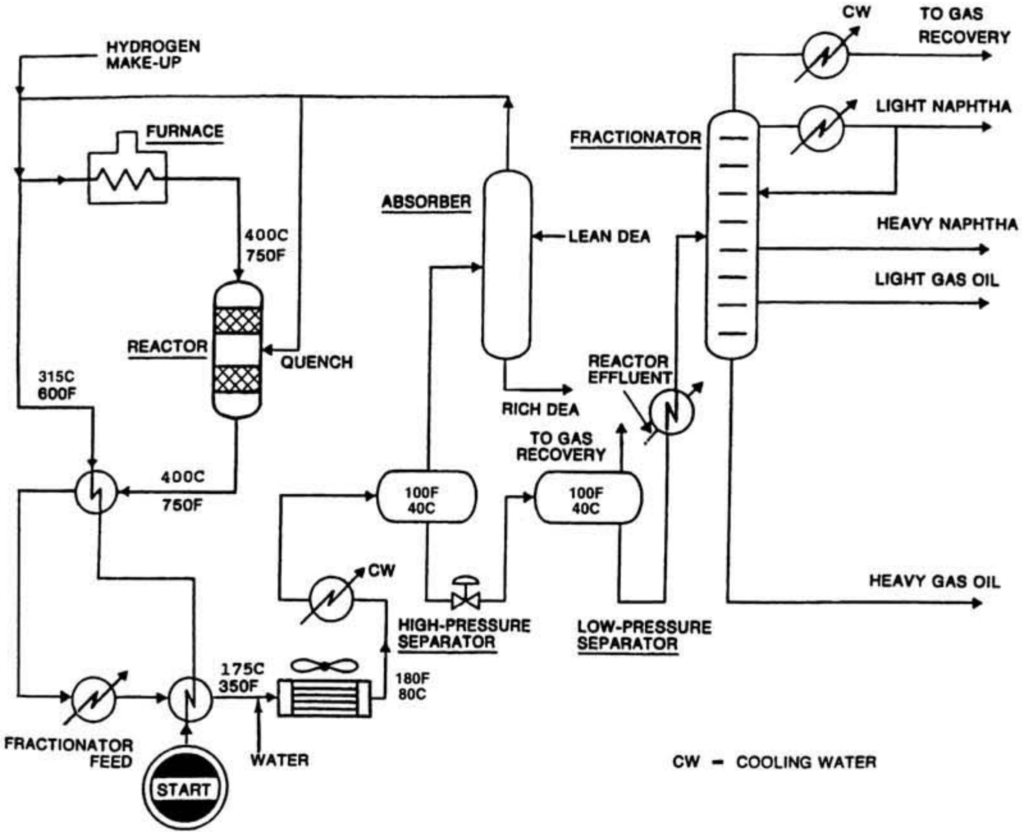


Figure 3.1 - Hydrodesulfurizer.[1]
(Reprinted with permission from "The Role of Stainless Steels in Petroleum Refining," American Iron and Steel Institute, April 1977)

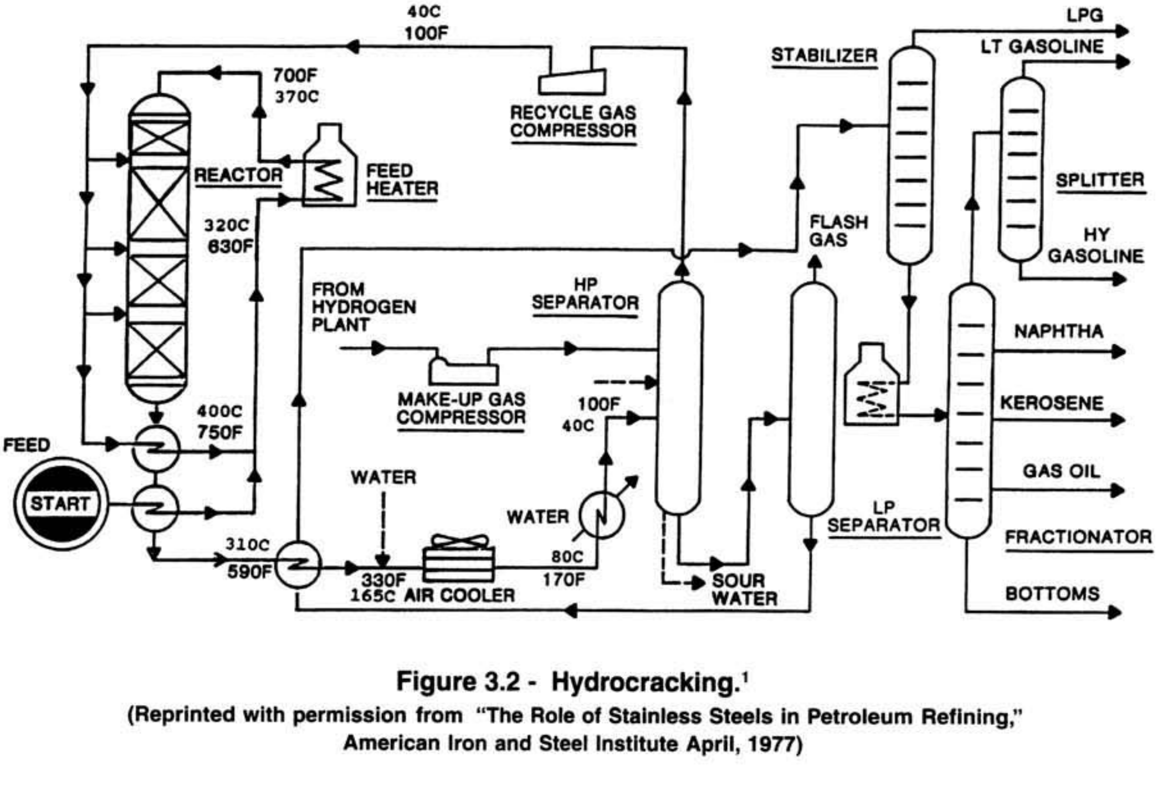


Figure 3.2 - Hydrocracking.[1]
(Reprinted with permission from "The Role of Stainless Steels in Petroleum Refining," American Iron and Steel Institute April, 1977)

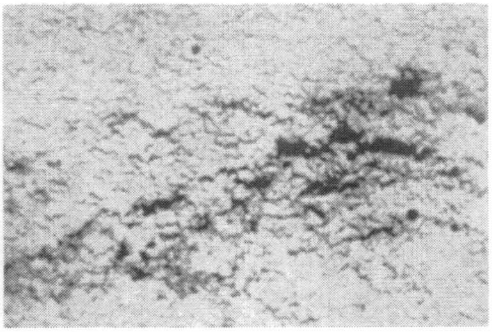


Figure 3.3(b) (left) - Photomicrograph showing fissuring in weld metal. Nital etch, 100X.[2]

Figure 3.3(c) (below) - Photomicrograph showing structure of parent metal.[2]

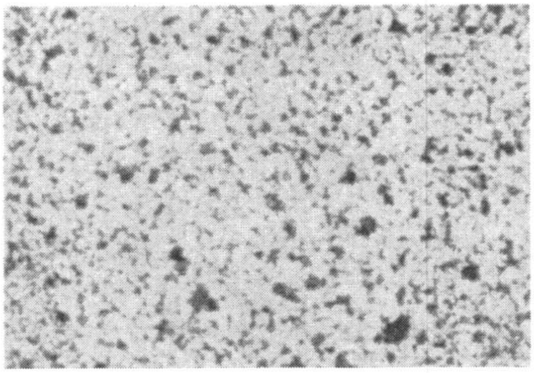


Figure 3.3(a) - (above) Cross section of exchanger. Note cracking in weld metal at right (light colored area) of specimen.[2]

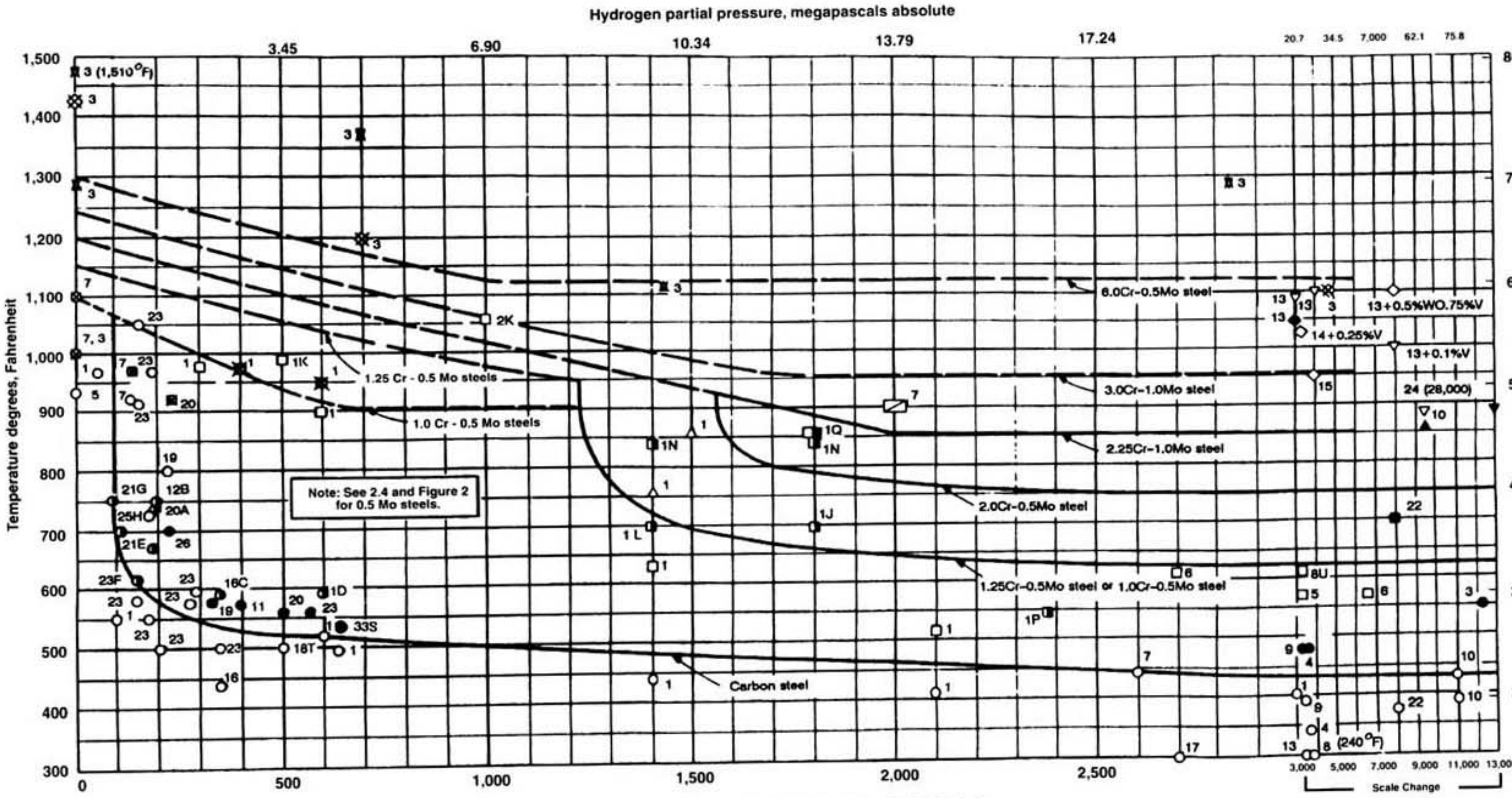
many of the hydrocracking processes, the liquid from the high-pressure separator is then fed to a heater and to a second stage reactor. The effluent from the second stage follows the same scheme as in a hydrodesulfurizer, i.e., exchange cooling, high- and low-pressure separation, then fractionation. The bottom product of the fractionator is 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 4,480 kPaa (650 psia).

2.2 Hydrogen Attack

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, Nb) are present or the microstructure is in the wrong condition from improper heat treatment, the hydrogen that has entered the steel reacts 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 3.3(a).[2] Figures 3.3(b)[2] and 3.3(c)[2] show the microstructures of fissured and unattacked base metal, respectively. Note the absence of the dark (pearlite) constituent in Figure 3.3(b) that is present in Figure 3.3(c). A significant amount of hydrogen attack can occur before the fissures combine to form cracks and before any visible bulging or change in thickness occurs. Thus, this is a very insidious form of attack.

Carbon steel can be used until the temperature exceeds an alloy's limit in API Publication 941.[3] Figure 3.4 (opposite page) shows the temperature vs hydrogen partial pressure limits in API 941 for carbon and alloy steels.[3] Solid lines indicate where internal decarburization and fissuring will occur. Dashed lines indicate where the less harmful surface decarburization will occur.



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	◐	◧	◭	◧	◈	▼

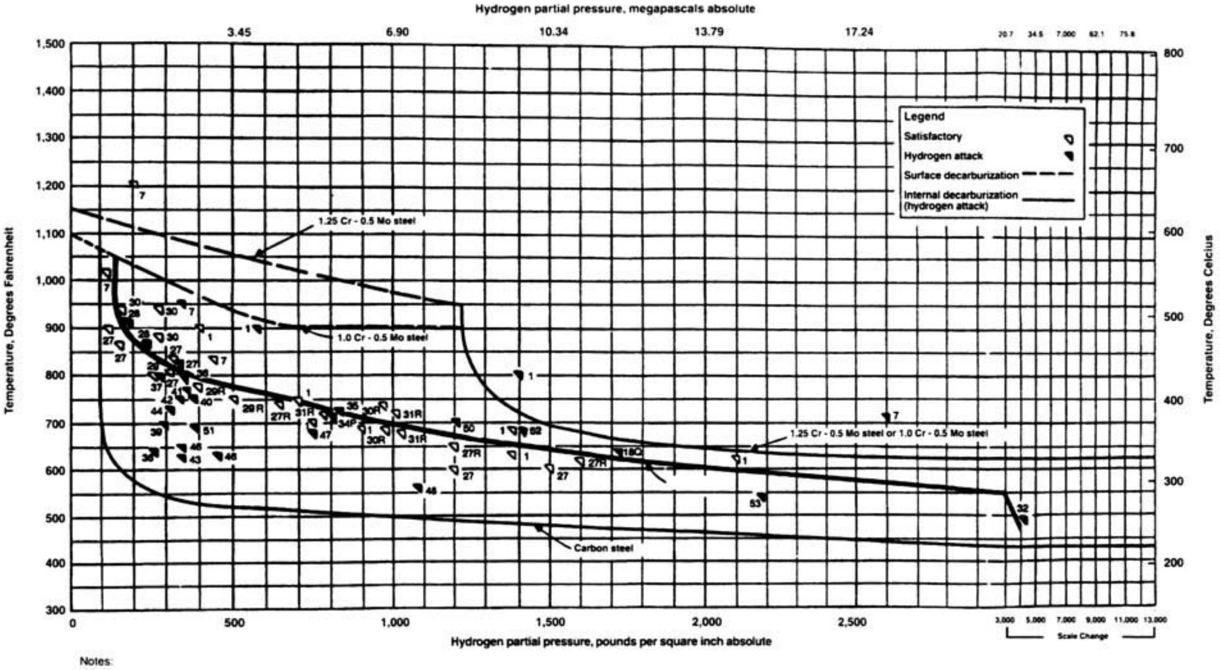
Notes:
1. The limits described by these curves are based on service experience orginally collected by G.A. Nelson and on additional information gathered by or made available to API.
2. Austentitic stainless steels are generally not decarburized in hydrogen at any temperature or hydrogen pressure.
3. The limits described by these curves are based on experience with cast steel as well as annealed and normalized steels.

Figure 3.4 - Operating limits for steels in hydrogen service to avoid decarburization and fissuring.[3]
(Reprinted with permission of the American Petroleum Institute)

API 941 was derived from laboratory work done by Naumann in Germany in the early 1940s.[4] Since then, it has been revised periodically, based on operating experience and test data supplied by various petroleum refining companies. Although the curves originally contained a safety factor on the data, the numerous revisions based on new data have led some companies to apply safety margins, e.g., 30°C (50°F) to the curves. Because API 941 is periodically revised, it is important to verify that the latest revision is used. Because experience with C-1/2 Mo steels (particularly in catalytic reformers) has been poor, API 941 has removed C-1/2 Mo from the design curve and produced a separate "experience" curve for C-1/2 Mo steels (Figure 3.5).[3] API 941 also contains information about three failures of 1-1/4 Cr-1/2 Mo that occurred in zones below the published limits for this material.

Because of the numerous failures of C-1/2 Mo material, most refiners specify a minimum of 1 Cr-1/2 Mo when API 941 indicates that the limits for carbon steel have been exceeded. Research on C-1/2 Mo materials has indicated that some failures can be attributed to the lack of (or improper) heat treatment after forming or welding. Heat treatment should be a minimum of 650°C (1,200°F) to prevent hydrogen attack in C-1/2 Mo steels. Hattori has shown that the onset of hydrogen attack in C-1/2 Mo can be predicted provided one knows the hydrogen partial pressure, the temperature, and the carbide morphology.[5]

When high-pressure hydrogen is to be in contact with metals for only a short period, carbon steel may be used at higher temperatures tean indicated by Figure 3.4.[3] Figure 3.6 gives the permissible times carbon steel may be used as a function of temperature and hydrogen partial pressure.[3] High temperatures can be tolerated for short periods because hydrogen attack has an incubation period. Because hydrogen attack is cumulative, the total anticipated time at temperature for the life of the equipment must be used as a basis for



Notes:

1. References and comments are shown on page 8.
2. Curves for carbon steel, 1.0 Cr - 0.5 Mo steel, and 1.25 Cr - 0.5 Mo 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 0.5 Mo steel curve is the same as the one shown in the third edition of this publication (1983).

Figure 3.5 - Experience with C-0.5 and Mn-0.5 Mo steels in hydrogen service.[3]
(Reprinted with permission of the American Petroleum Institute)

alloy selection. Furthermore, records must be kept to ensure the total cumulative time is not exceeded.

Hydrogen attack has occurred in carbon steel where it was not anticipated. In particular, attack was found in a carbon steel line after 15 year's exposure to a liquid gas oil stream operating at 345°C (650°F). The line was downstream of drums separating hydrogen from the liquid hydrocarbon. The weld that showed hydrogen attack was highly stressed, and there were some upset conditions where exposure to hot hydrogen-rich vapor conditions occurred periodically during the first three years of service. As a result of this and similar problems, API 941 now specifies that "for materials selection purposes, hydrogen dissolved in liquid hydrocarbon should be assumed to exert a vapor pressure equal to the hydrogen partial pressure of the gas with which the liquid is in equilibrium." For example, if the partial pressure of the hydrogen in the gaseous phase in a separator is 140 kg/cm^{2}a (1,991 psia) the materials of construction for the liquid line coming off the bottom of the separator should be selected to resist 140 kg/cm^{2}a (1,991 psia) until the stream reaches the pressure letdown valve.

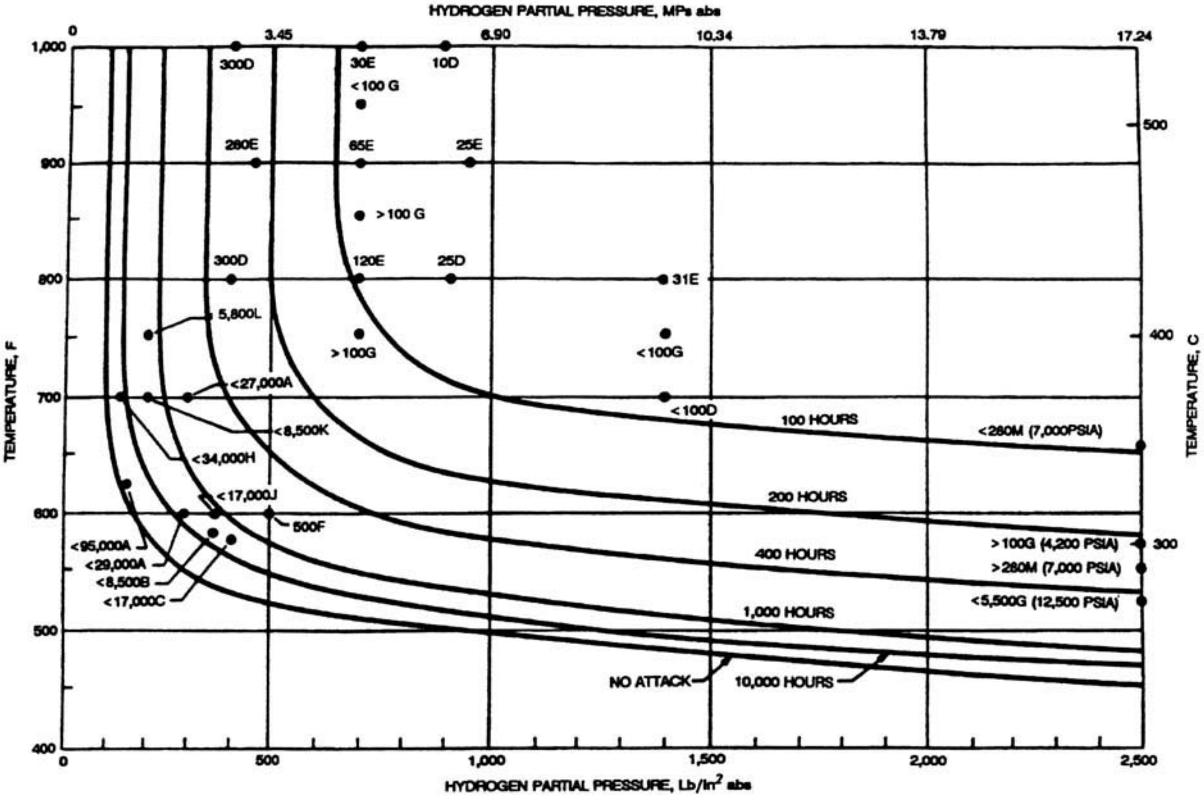


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Figure 3.6 - Time for incipient attack of carbon steel in hydrogen service.[3]
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2.3 Sulfidation by Hydrogen-Hydrogen Sulfide Mixtures

When the temperature exceeds 288°C (550°F) in hydrogen-hydrogen sulfide mixtures, severe corrosion occurs on carbon and low-alloy steels. Corrosion rates of various materials as a function of mole % 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 3.7(j).[6] Although desulfurization takes place 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 any hydrogen enters the process stream, 5 Cr-1/2 Mo and 12 Cr clad steels can be used above 288°C (550°F) provided the feed does not have a lot of free H_2S. When hydrogen is present, 18 Cr-8 Ni SS usually is selected; stabilized grades commonly are used to prevent intergranular attack by polythionic acid during downtime. See Section 2.5 for the discussion of attack by polythionic acid.

The 12 Cr alloy occasionally is used up to 345°C (650°F) when the hydrogen sulfide concentration is less than 1 mol%. Aluminized (diffusion-coated aluminum) carbon and low-alloy steel also display excellent resistance to hydrogen sulfide in these environments; however, attack can occur at breaks in the coatings. Aluminizing also is costly and is subject to damage during mechanical or acid cleaning. Aluminizing is, therefore, usually selected primarily to reduce fouling from scale formation rather than to protect from corrosion.

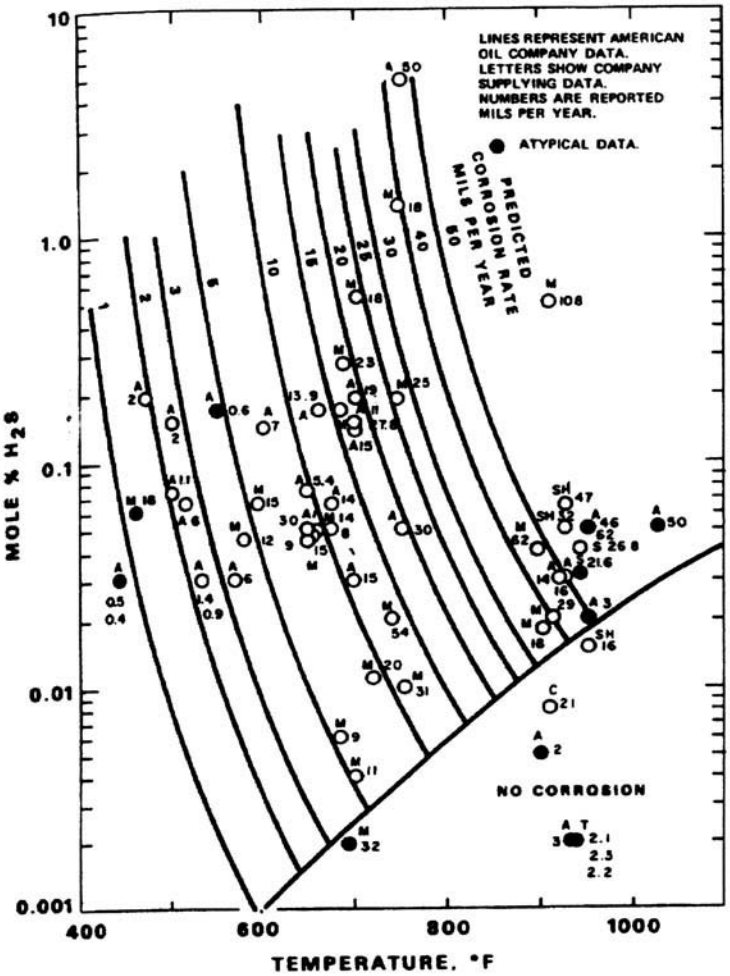

Figure 3.7 - Isocorrosion curves for carbon, low alloy, and stainless steels as a function of mole percent H_2S and temperature.[6]
(Reprinted from "Computer Correlations to Estimate High Temperature Hydrogen Sulfide Corrosion in Refinery Streams," *Materials Protection*, January 1971)

Figure 3.7(a) - Carbon steel, naphtha diluent.[6]

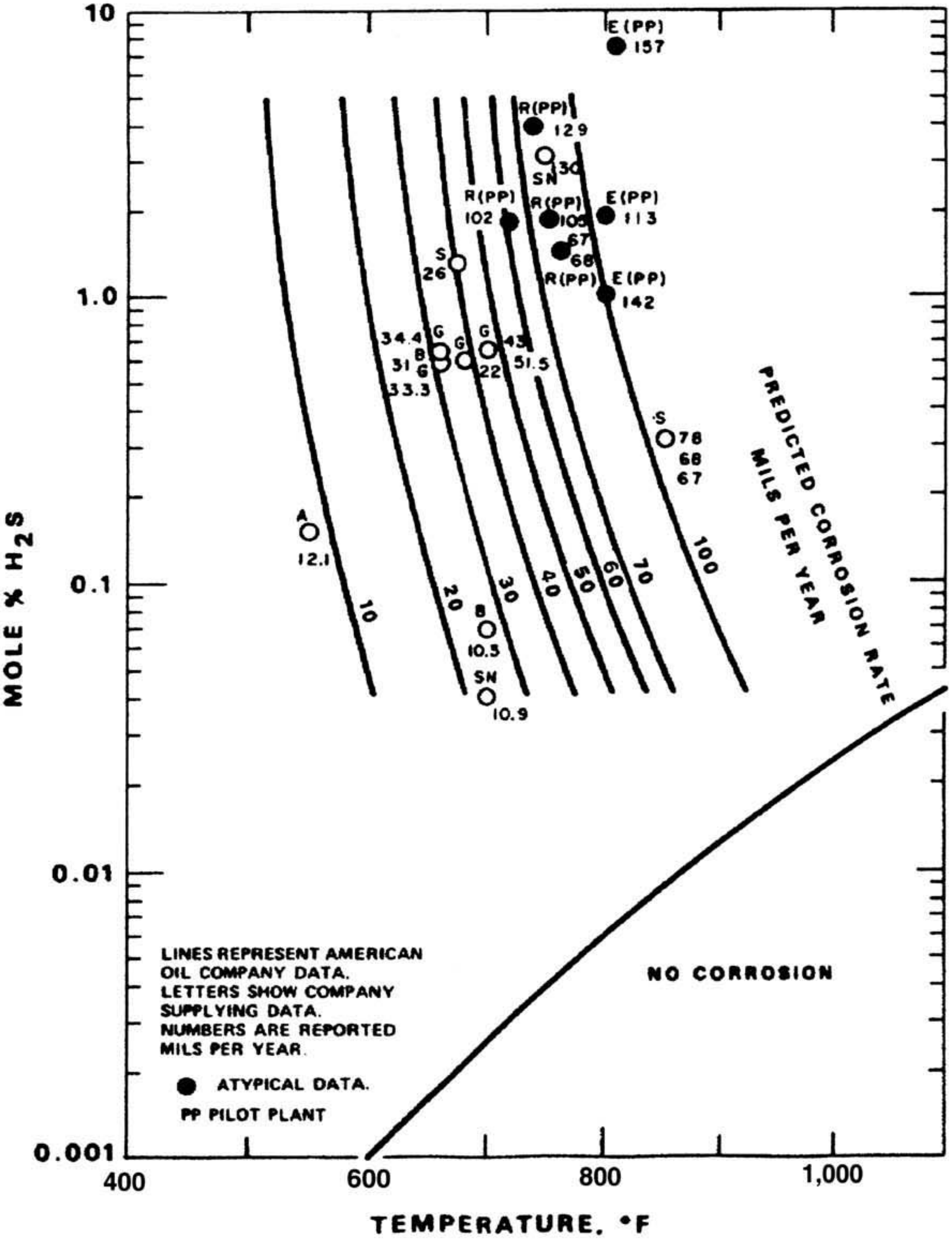

Figure 3.7(b) - Carbon steel, gas oil diluent.[6]

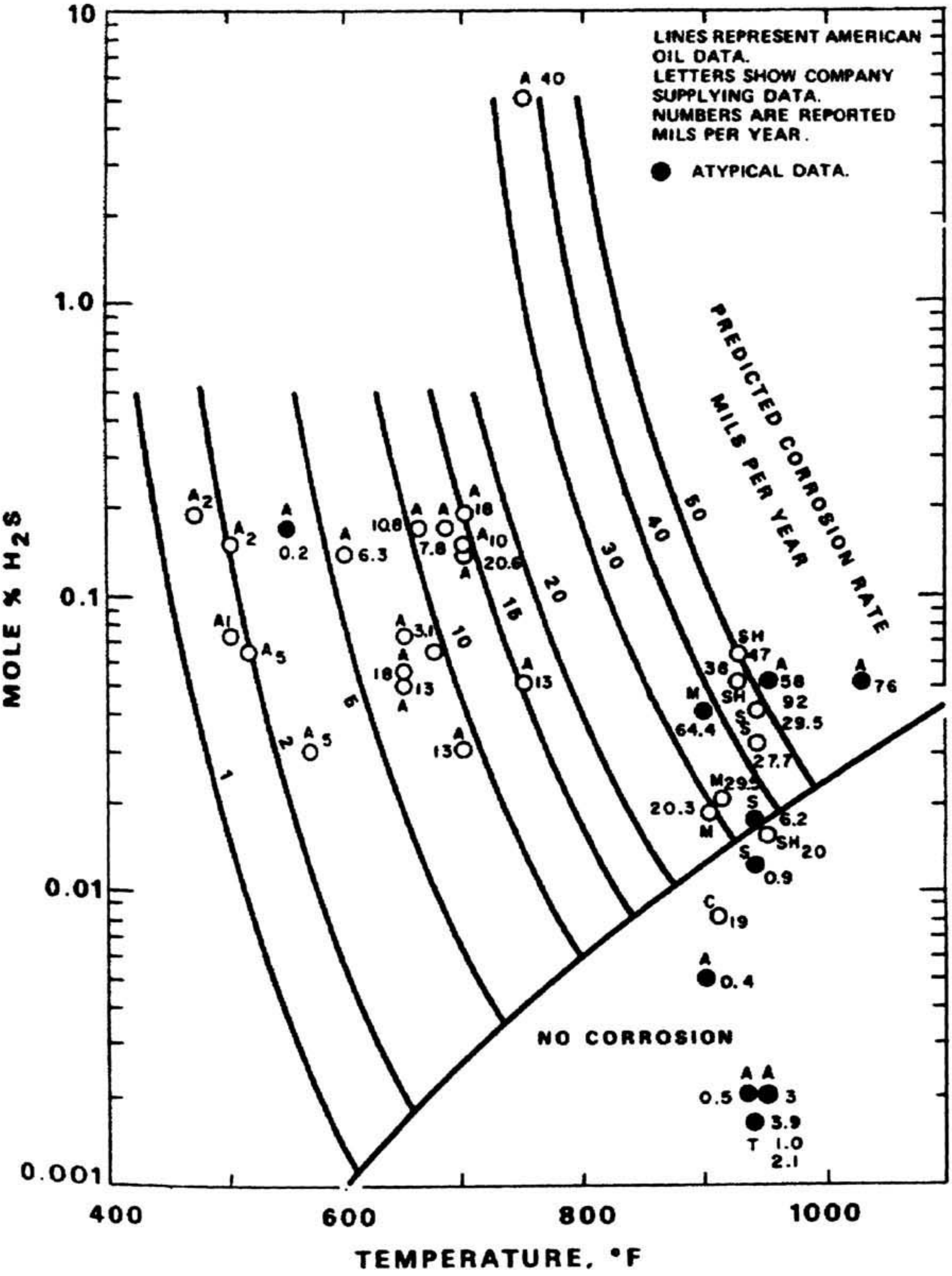

Figure 3.7(c) - 5% Cr steel, naphtha diluent.[6]

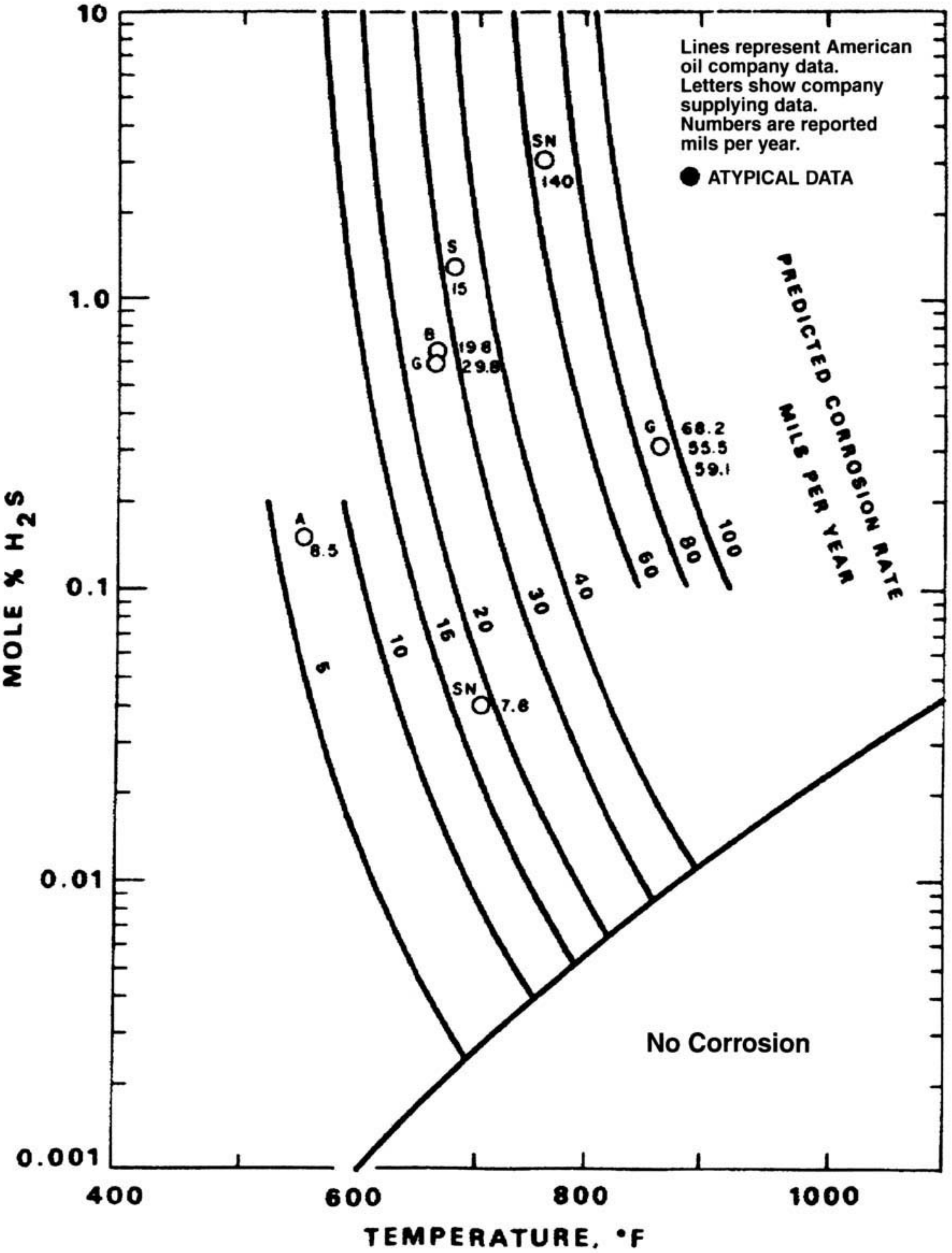

Figure 3.7(d) - 5% Cr steel, gas oil diluent.[6]

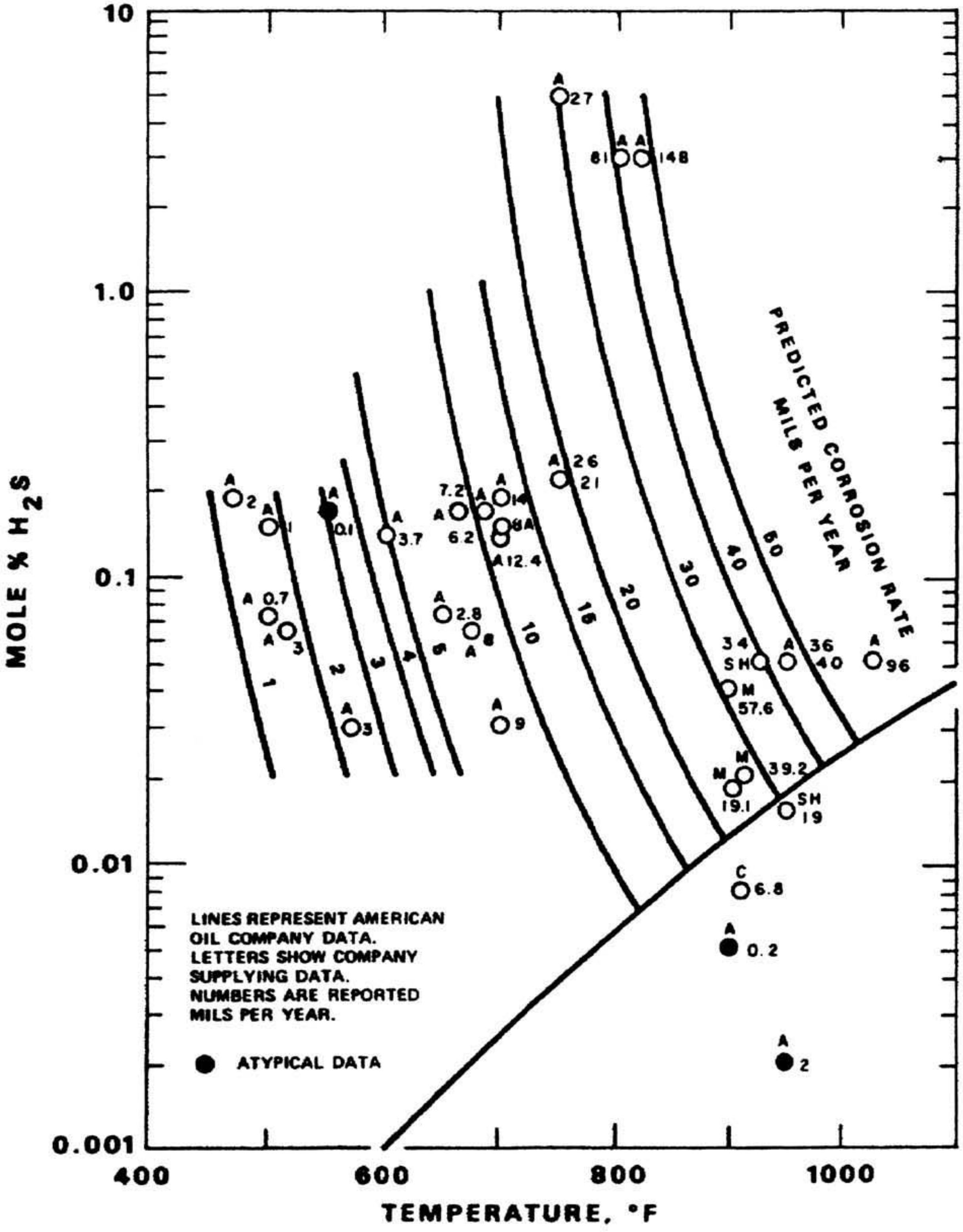

Figure 3.7(e) - 9% Cr steel, naphtha diluent.[6]

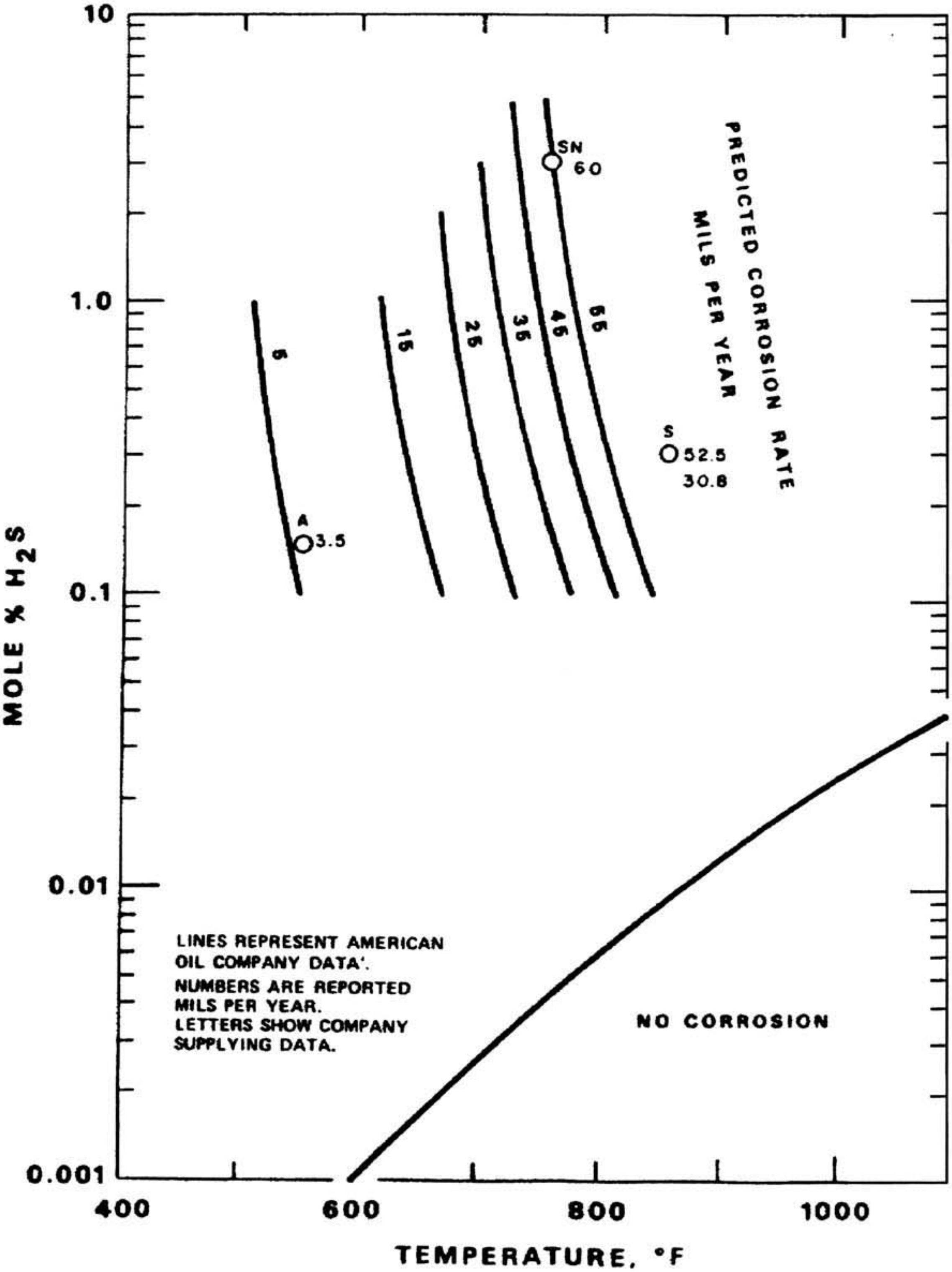

Figure 3.7(f) - 9% Cr steel, naphtha diluent.[6]

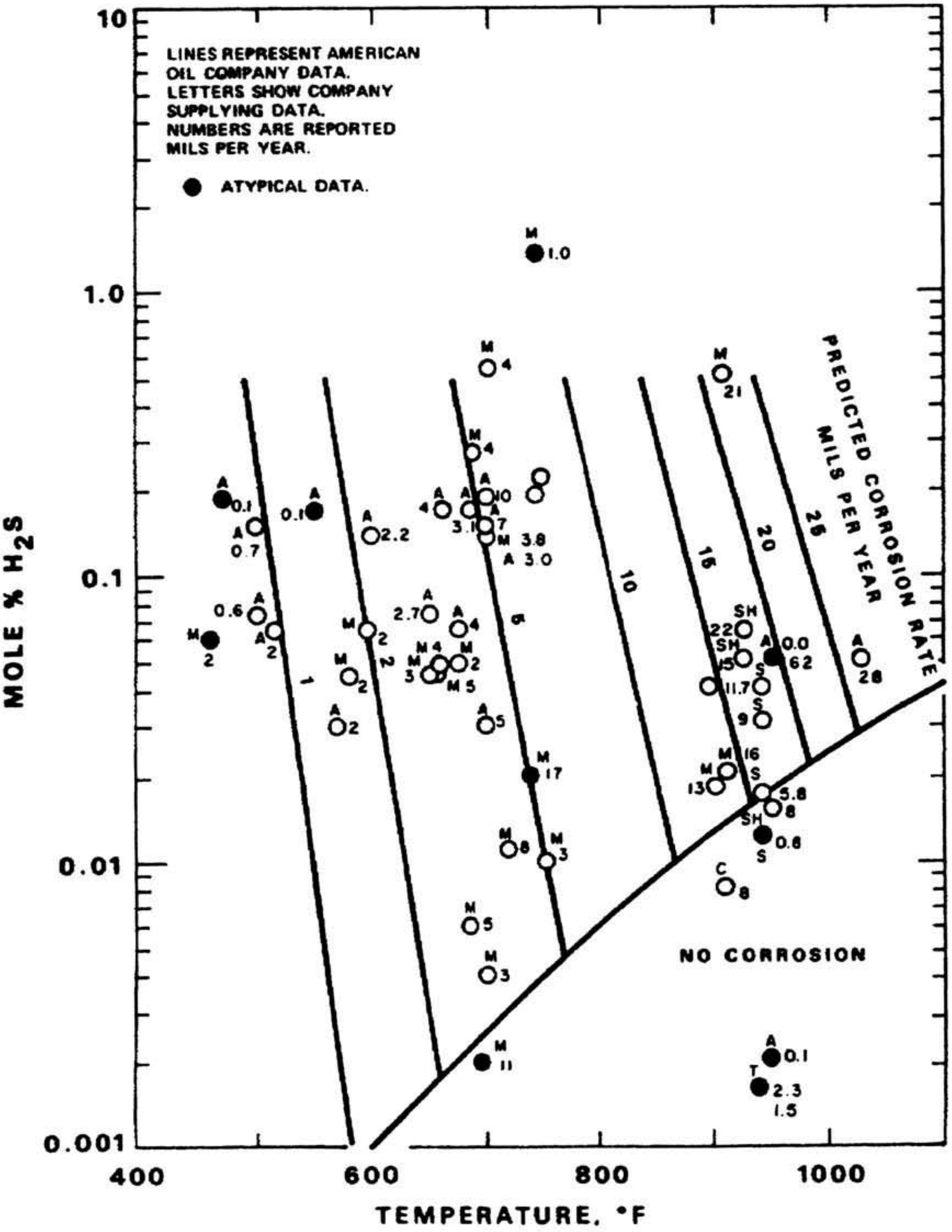

Figure 3.7(g) - Cr stainless steel, naphtha diluent.[6]

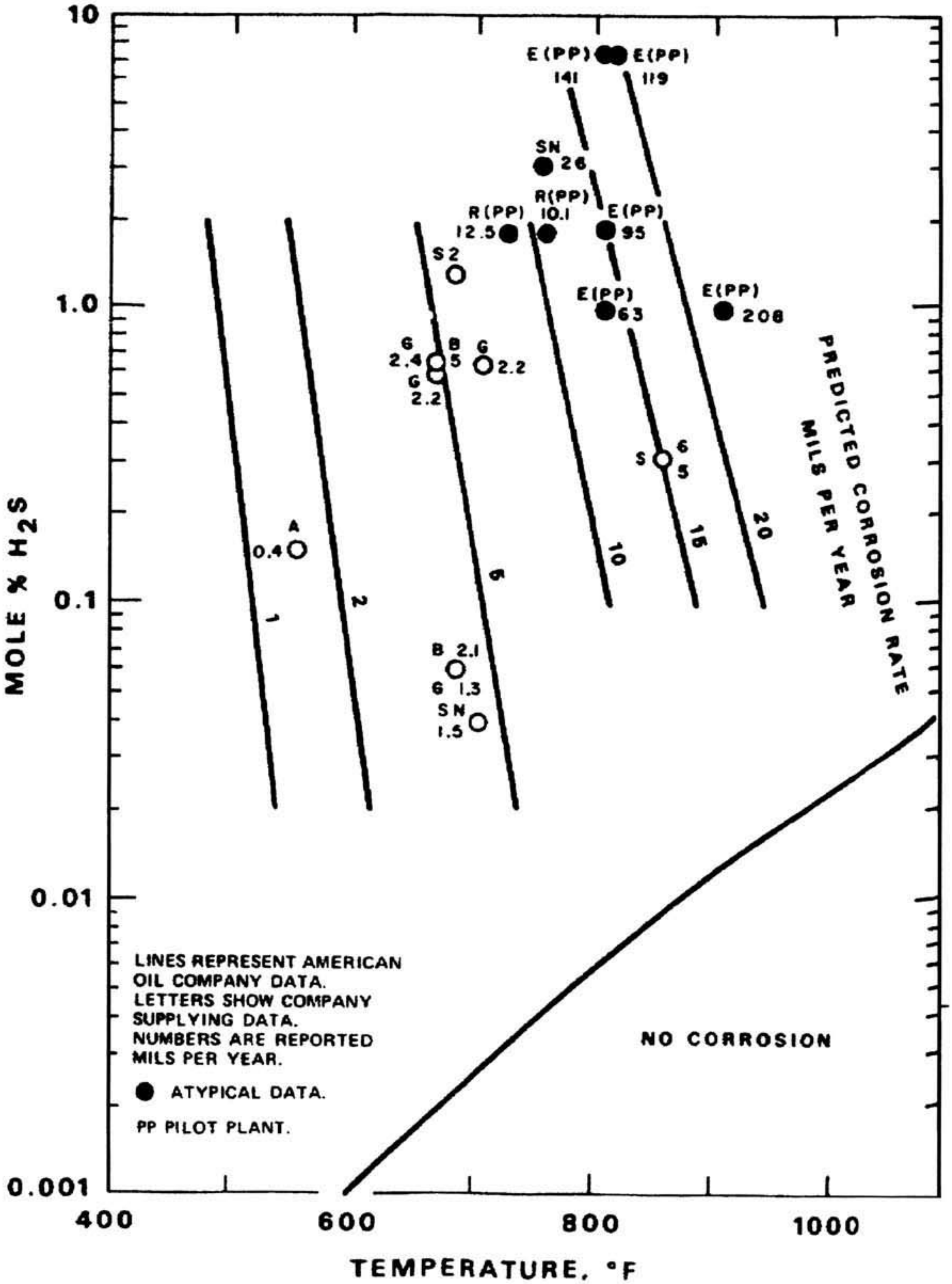

Figure 3.7(h) - 12% Cr stainless steel, gas oil diluent.

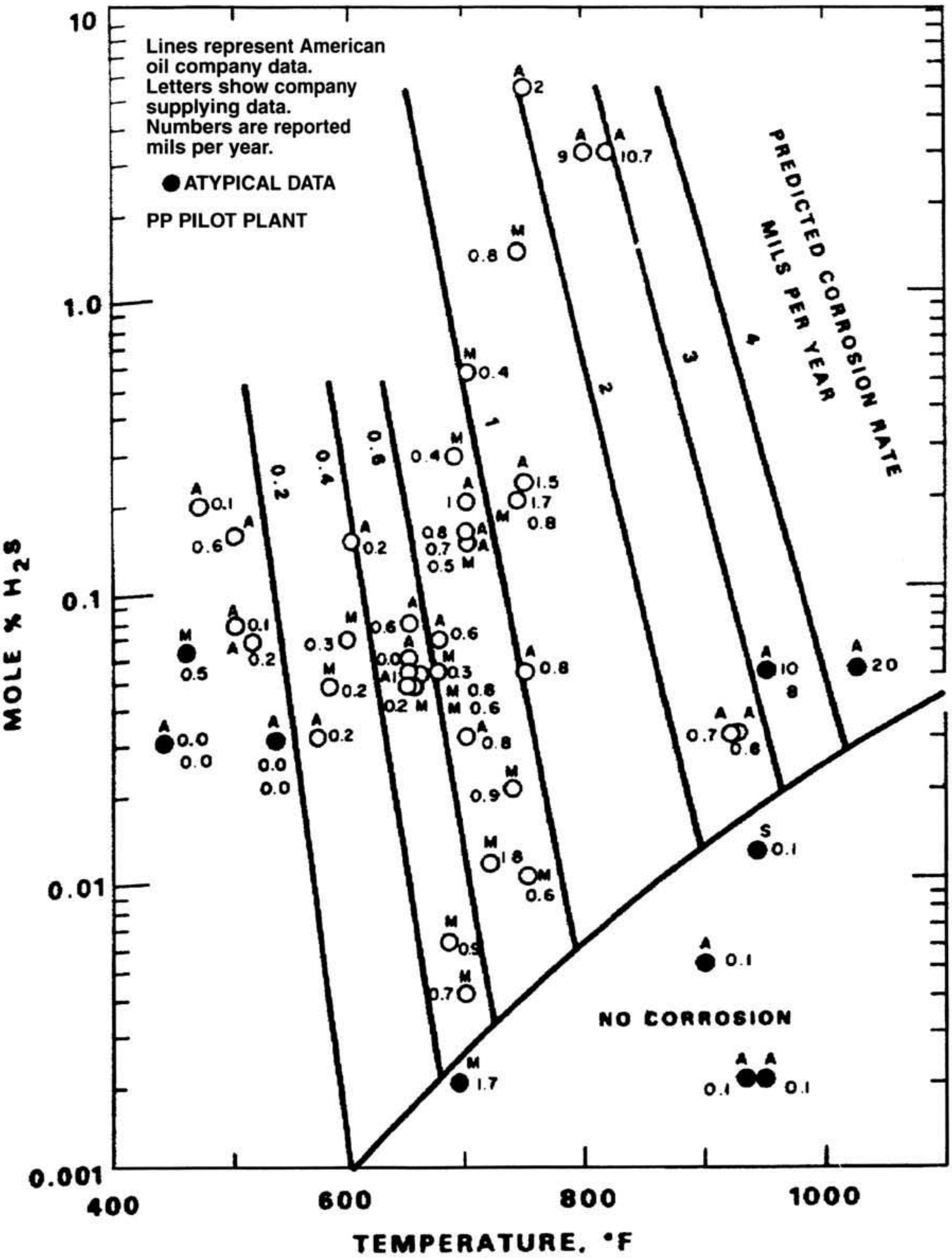

Figure 3.7(i) - 18-8 stainless steel, naphtha diluent.[6]

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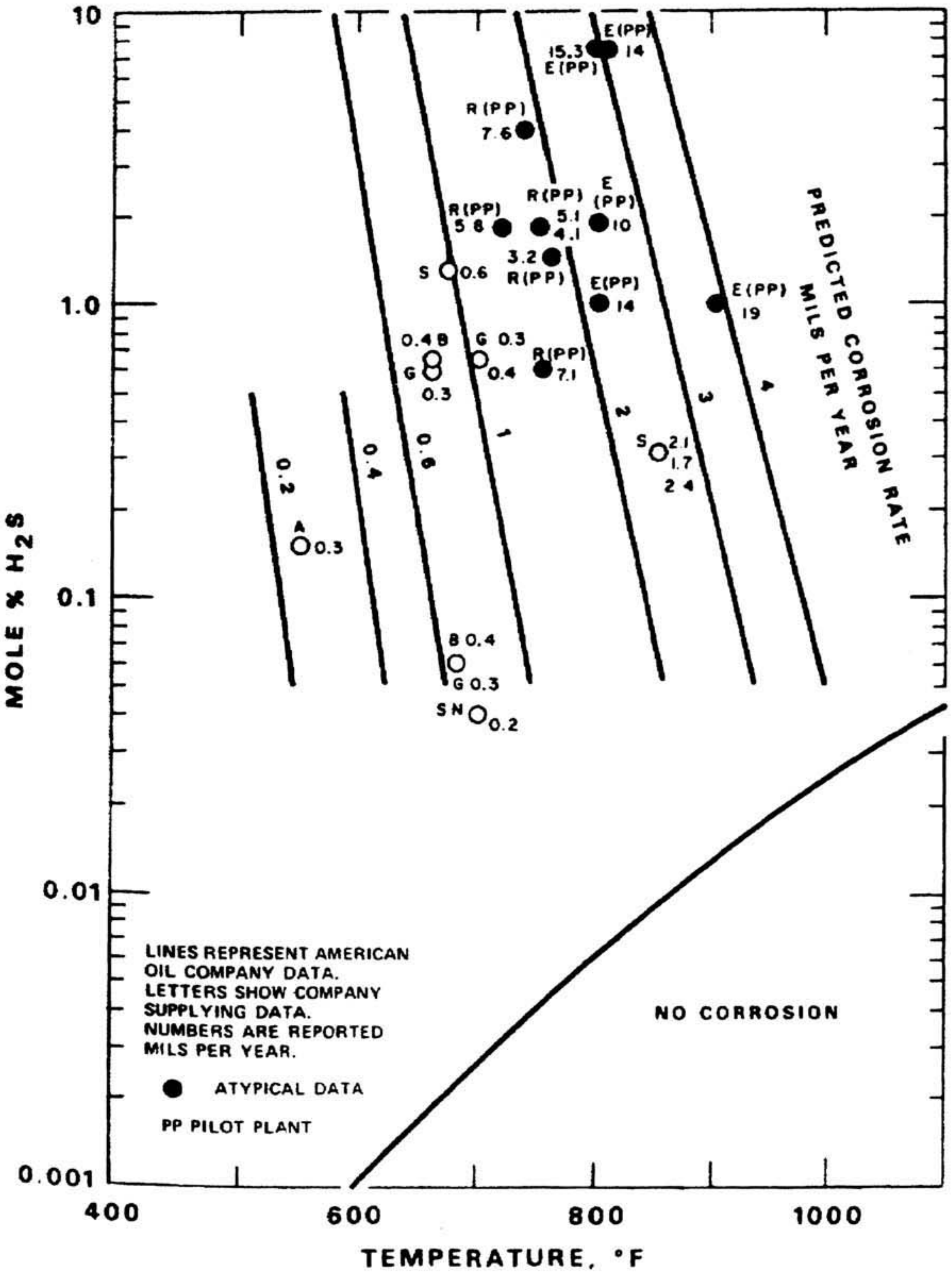

Figure 3.7(j) - 18-8 stainless steel, gas oil diluent.[6]

2.4 Reactors

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

A number of potential problems with reactors exist because of the heavy walls (up to about 254 mm [10 in.] thick) and the high operating temperatures (up to about 455°C [850°F]). The most commonly used low-alloy steel for reactors is 2-1/4 Cr-l Mo. High-strength reactor steels (2-1/4 Cr-1 Mo-V and 3 Cr-1 Mo-V-Ti-B) are covered by ASME Code Cases 2098, 2151, and 1961. The high-strength reactor steels are more resistant to temper embrittlement and hydrogen flaking than conventional Cr-Mo steels. They do have a narrower PWHT window than conventional Cr-Mo steels. A hardness limit of 235 HB currently is being specified. Because of the economic attractiveness and superior properties of the 2-1/4 Cr-1 Mo-V and 3 Cr-1 Mo-V-Ti-B steels, it appears most future reactors will be made of these materials.

Welding of Cr-Mo steels requires both preheat and PWHT. The 2-1/4 Cr-l Mo material usually is quenched and tempered to produce the best combination of strength and toughness possible. The tensile strength is controlled from 517 MPa to 690 MPa (75 ksi to 100 ksi). See the discussion on internal flaking for a discussion of the reason for the 690 MPa (100 ksi) maximum. The total amount of PWHT must be controlled so the strength will not be reduced below the required minimum. The maximum amount of PWHT permitted is estimated by plotting strength vs the tempering parameter $T\ (20 + \log t) \times 10^{-3}$ (see Figure 3.8),[7] where "T" is temperature of the final PWHT in degrees Rankine, and "t" is the total equivalent time in hours at the final PWHT temperature. For example, an intermediate stress relief at 593°C (1,100°F) for six hours is equivalent to 0.09 h at 677°C (1,250°F). Coupons heat treated with the material usually are used to confirm the estimates of the tempering parameter.

If the chromium content of the steel exceeds 1.75%, some users require the preheat to be held until an intermediate PWHT is performed. The intermediate PWHT sometimes is waved if a vendor can show that a hydrogen bakeout at 315°C (600°F) for 1 h will not result in crack formation. Stress relief cracking may occur if the sulfides are not controlled by addition of cerium or zirconium, for example. Steels with greater than 2.5% chromium are resistant to stress relief cracking. An empirical equation has been developed to predict stress relief cracking of steels with less than 2.5 % chromium. Cracking is predicted when ΔG is greater than zero where ΔG is defined as:

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

Other phenomena that may occur during PWHT are sigma phase embrittlement of the 347 SS (UNS S34700) weld overlay, secondary hardening of the base metal, and cracking of internal attachment welds to the shell. Ferrite and sigma phase also are susceptible to hydrogen embrittlement. The detrimental effects of sigma phase (a brittle non-magnetic Fe-Cr compound) are limited by specifying that the overlay have no more than 9% ferrite, which transforms to sigma phase. Ferrite is a magnetic phase which forms on cooling in an otherwise non-magnetic phase called austenite. Its formation depends on alloy content. The 9% limit prevents the formation of a continuous ferrite network, which in turn could transform to a continuous brittle sigma phase network. A minimum ferrite content of 2% is required to avoid weld cracking. However, a minimum of 5% ferrite normally is specified, as this has been shown to be required to prevent intergranular stress corrosion 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 SS alloys.[8] Secondary hardening due to precipitation of a phase during PWHT is minimized by limiting copper to 0.2% in 2-1/4 Cr-l Mo. Nickel sometimes is limited to 0.2% to 0.3% to minimize hardenability and reduce temper embrittlement. Cracking of 347 SS (UNS S34700) fillet welds on internal attachments welded directly to the 347 cladding has been attributed to hydrogen embrittlement of the 347. To avoid the problem, attachments have been made to the low alloy base metal, and the attachment is weld overlaid. The second pass of weld overlay is put on after PWHT.

Long-term potential problems are weld overlay disbondment, temper embrittlement, and internal hydrogen 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, whereas the surfaces of forgings are not because they are machined after forming. Therefore, the machined surfaces of forgings are more hardenable, i.e., more crack-sensitive. Disbonding in forgings (and plate) can be avoided by limiting the carbon on the surface to be overlaid to 0.15% and by using low-carbon SS in the first overlay pass. The resultant overlay should not have more than 0.03% carbon.

The major cause of temper embrittlement[1] is segregation of phos-

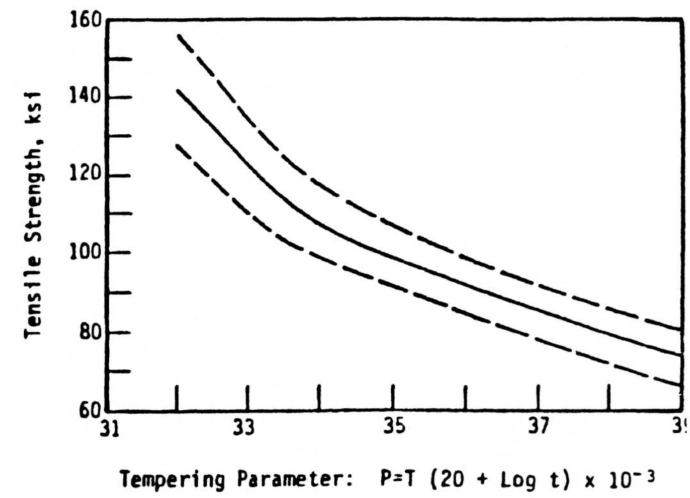

Figure 3.8 - Tempering parameter vs tensile strength for quenched and tempered 1 1/4Cr-1Mo steel.[7]
(Reprinted with permission from "The Use of Quenched and Tempered 2-1/4 Cr-l Mo Steel for Thick Wall Reactor Vessels in Petroleum Refinery Processes: An Interpretive Review of 25 Years of Research and Application," *WRC Bulletin* 275, February 1982, Welding Research Council, New York, NY)

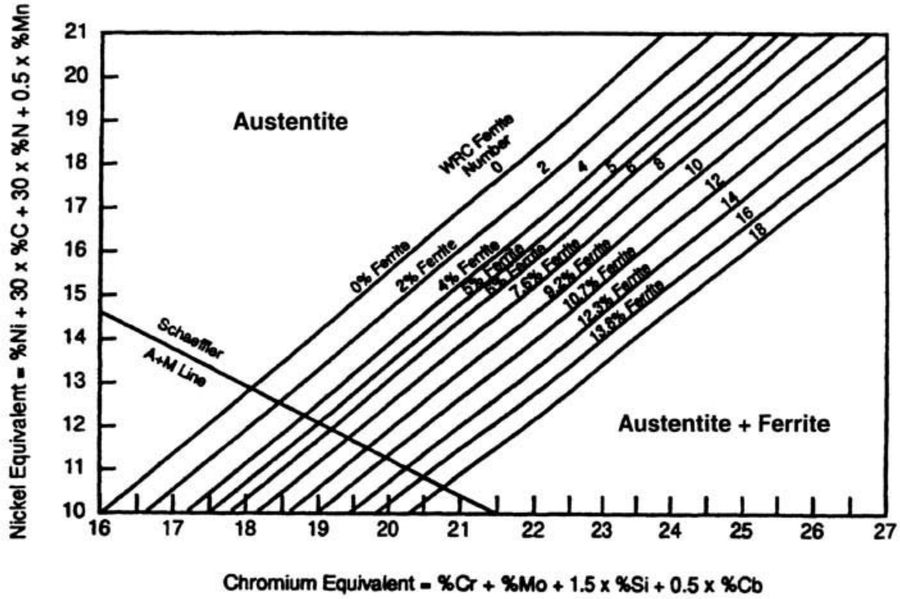

Figure 3.9 - Delta ferrite content of stainless steel weld metals.[8] **(Reprinted with permission from ASME Code Sec-tion III, Division 1, NB, 1983 ed., American Society of Mechanical Engineers, New York, NY)**

Note: The actual nitrogen content is preferred. If this is not available, the following applicable nitrogen value shall be used: GMAW welds-0.08% (except self-shielding flux cored electrode GMAW welds-0.12%); welds of other processes-0.06%.

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(1) Embrittlement of alloy steels caused by holding within or cooling slowly through a temperature range just below the transformation range. It is usually manifested as an upward shift in the ductile to brittle transition temperature.

phorus to the grain boundaries. A common way to minimize temper embrittlement of 2-1/4 Cr - 1 Mo base metal is to limit the "J factor" where J is defined as:

$$J = (Si + Mn) \times (P + Sn) \times 10^4$$

where concentrations are in weight %

For example, the increase in the transition temperature (2) resulting from temper embrittlement is 0°C to 19°C (0°F to 35°F) for a J factor less than 180 while an average of a 42°C (75°F) increase can be expected with a 260 "J" factor. A "J" factor of 100 maximum, and in some cases 80 maximum, can now be obtained from suppliers. More recent studies indicate that limiting the (P + S) to less than 0.01 % is sufficient because Si and Mn only control the rate of embrittlement. The "X" factor has been developed to indicate the potential for temper embrittlement of weld metal where:

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

Concentrations are in parts per million (ppm). An X factor of less than 15 often is specified. Some users specify a step cooling test of 2-1/4 Cr - 1 Mo. Step cooling simulates about half the increase in the ductile-brittle transition that will occur after long-term service. A typical step cooling sequence is:

Heat to 595°C (1,100°F), heating rate above 315°C (600°F) = 55°C (100°F)/h (max.)
Heat at 595°C (1,100°F) for 1 hour, cool at 5.5°C (10°F)/h max. to 540°C (1,000°F)
Heat at 540°C (1,000°F) for 15 hours, cool at 5.5°C (10°F)/ h max. to 525°C (975°F)
Heat at 525°C (975°F) for 24 hours, cool at 5.5°C (10°F)/ h max. to 495°C (925°F)
Heat at 495°C (925°F) for 60 hours, cool at 3°C (5°F)/ h max. to 470°C (875°F)
Heat at 470°C (875°F) for 100 hours, cool at 28°C (50°F)/ h max. to 315°C (600°F)

One advantage of requiring the step cooling approach is that one gets upper shelf notch toughness data, which can be used later for fitness-for-service evaluations.

Temper embrittlement of 2-1/4 Cr-1 Mo can occur at operating temperatures above 343°C (650°F). It can be reversed by heating at 620°C (1,150°F) for two hours per inch of thickness. Embrittlement 1-1/4 Cr - 1/2 Mo can occur at operating temperatures above 399°C (750°F). For example, a 55°C (100°F) increase in transition temperature was reported after eight years at 500°C (930°F). Step cooling will not simulate embrittlement of 1-1/4 Cr - 1/2 Mo because the embrittlement in 1-1/4 Cr - 1/2 Mo is caused by precipitation of carbides in the ferrite phase rather than segregation of impurities to the grain boundaries. Excessive PWHT, e.g., T > 700°C (1,300°F) of 1-1/4 Cr-1/2 Mo, causes coalescence of carbides at grain boundaries, which promotes crack growth and can increase the transition temperature 25°C to 50°C (50°F to 100°F). For this reason some users specify a 675°C (1,250°F) maximum PWHT temperature for 1-1/4 Cr-1/2 Mo. In addition, good through thickness properties are difficult to obtain in 1-1/4 Cr - 1/2 Mo in thickness in excess of 51 mm (2 in.) unless low sulfur (0.010 wt% max.) and sulfide shape control are specified.

Internal hydrogen flaking or cracking, which result when the steel becomes supersaturated in hydrogen, can be avoided by using careful shutdown procedures, including slow cooldown rates after depressurizing the equipment. There is a potential for crack growth during cooldown when the concentration of hydrogen exceeds 3 ppm, the temperature is below 150°C (300°F), and the wall thickness exceeds 150 mm (6 in.). The potential for crack growth is greatly increased in steels when the tensile strength exceeds 690 MPa (100

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(2) The temperature at which the mode of fracture is roughly half ductile and half brittle. It usually is considered the lowest safe operating temperature when the tensile stress exceeds 41.4 MPa (6 ksi).

ksi). 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 (K_{Ic}) in the absence of hydrogen increases significantly with temperature.

Whether there are harmful effects during operation from laminations is controversial; however, most users specify the plate to meet the ultrasonic testing requirements in ASTM 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. A 27°C to 38°C (80°F to 100°F) minimum hydrostatic test temperature often is specified to minimize the possibility of brittle fracture during hydrostatic testing. To minimize the possibility of brittle fracture of heavy wall reactors during startup and shutdown, reduced pressure below 90°C to 150°C (200°F to 300°F) usually is specified. Typical limitations are 25% and 40% of the design pressure for ASME Section VIII, Division 2 and ASME Section VIII, Division 1 vessels, respectively, 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 38°C (100°F).

2.5 Feed-Effluent Exchangers and Piping

Feed-effluent heat exchangers are made of materials similar to those used in the reactors because they are exposed to the same environments. Tubes usually are 321 (UNS S32100) or 347 (UNS S34700) SS, although 304 SS (UNS S30400) has been used where seal welding is not required. Because of thin walls and high stresses on tubes, as well as thermal stress, crevices, etc., there is a potential for both transgranular and intergranular stress corrosion cracking of austenitic SS tubes. Table 3.1 is from a study of stress corrosion cracking failures of austenitic SS.[9] The alloys that failed included 301 (UNS S30100), 303 (UNS S30300), 304 (UNS S30400), 304L (UNS S30403), 309 (UNS S30900), 316 (UNS S31600), 321 (UNS S32100), 347

Table 3.1
Distribution of Cases of Stress Corrosion Cracking Among Various Refinery Units.[9]

Equipment	Failures	Onstream Cracking				Shutdown Cracking				Cracking Service Uncertain			
		Crude Still	Hudrodesulfurizer and Reformer	Chemical	Miscellaneous	Crude Still	Hudrodesulfurizer and Reformer	Chemical	Miscellaneous	Crude Still	Hudrodesulfurizer and Reformer	Chemical	Miscellaneous
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.

(UNS S34700) and alloy 800 (UNS N08800). Intergranular stress corrosion cracking has occurred primarily in 304, although 321 and 347 may fail intergranularly when improper heat treatments are applied, as discussed below in this section.

U-bent austenitic SS tubes are stress relieved at 900°C (1,650°F) or annealed at 980°C (1,800°F) to minimize transgranular stress corrosion cracking. Using resistance coil heating for five seconds on the U-bends is a satisfactory method for relieving stresses in 321 (UNS S32100) and 347 (UNS S34700) SS exchanger tubing. This is not recommended for 304 (UNS S30400), 316 (UNS S31600), etc., SS because a zone that is subject to intergranular stress corrosion cracking is created adjacent to the area in which the bend is heated. U-bends in duplex SS, such as 2205 (UNS S32205), normally are not heat treated unless there is greater than 15% cold work or less than a three diameter bend. When post bend heat treatment of duplex SS is done it should be by the induction heating method at the solution-annealing temperature for one to two minutes. Although induction heating also is used in bending austenitic SS, occasional problems have resulted due to the induction currents causing incipient melting at preexisting cracks in pipe.

Intergranular stress corrosion cracking can occur during downtime as a result of exposure to polythionic acid ($H_2S_xO_6$) or sulfurous acid (H_2SO_3). These corrosives are formed by the reaction of the iron sulfide scale formed in the reducing environment of a hydroprocessing unit with moisture and air. In contrast, the scale formed in crude units usually does not form polythionic acid in the presence of water and oxygen. Some refiners think the use of stabilized grades is sufficient to avoid attack. Others think a stabilizing heat treatment at 900°C (1,650°F) for four hours is required for the stabilized grades when service temperatures exceed 455°C (850°F). For thermal stabilization to be effective, it must be done after all welding has been completed. Still others think that specifying a 1,065°C (1,950°F) maximum annealing temperature will ensure that niobium carbides in 347 (UNS S34700) or titanium carbides in 321 (UNS S32100) will form in lieu of chromium carbides, thus preventing polythionic acid SCC. Type 321 and 347 are used interchangeably by most refiners except in a few instances. When a distinction is made, it usually is based on balancing the significance of the following:

- For service temperature above 455°C to 480°C (850°F to 900°F), where both 321 and 347 can sensitize, 347 has a smaller sensitization envelope on the temperature-time C-curves than 321.
- The allowable stresses for 347 are higher than for 321. This can make a significant difference in the required thickness, thus in the cost of heavy wall equipment.
- Type 321 is more resistant to heat-affected zone cracking than 347. This is most significant for welding sections over about 19 mm (0.75 in.) and for service temperatures in the creep range.

Since failure almost always occurs during downtime, NACE has issued a "Recommended Practice on the Protection of Austenitic Stainless Steels During Downtime." RP0170 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 where a coke deposit was not removed. Where downtime procedures were carefully controlled and tubes and U-bends were properly heat treated, types 321 and 347 SS have given good service.

2.6 Coolers

In desulfurizers and first stage hydrocrackers, the water from the process 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. Wash water sometimes is injected between exchangers, cooling the process fluid to dilute the corrosive constituents and to prevent plugging. Ammonium chloride, which accelerates pitting, begins to condense in the 175°C to 230°C (350°F to 450°F) range. Therefore, there is a potential for ammonium chloride plugging in the exchanger just before the air cooler.

With the advent of high pressure hydrotreating, e.g., hydrocracking, severe corrosion of carbon steel reactor effluent air cooler tubes appeared. This came as a surprise because carbon steel had worked quite well in the lower pressure units. Investigation revealed that the problem was related to velocity, condensa-

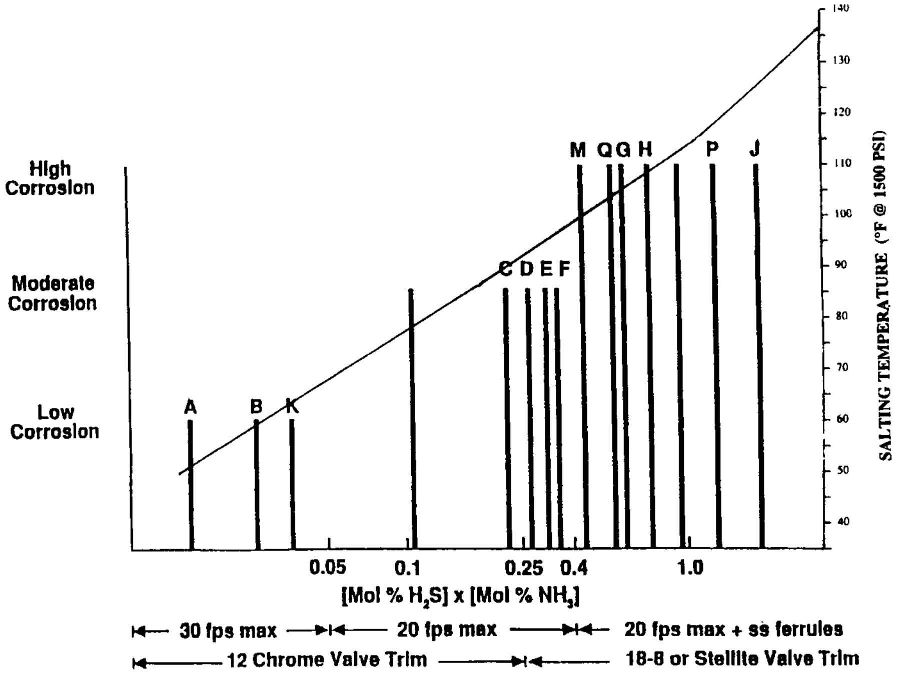

Figure 3.10 - Effect of stock composition on corrosivity for hydrocracker air coolers.[11,12]
(Reprinted with permission of the American Petroleum Institute)

tion temperature of ammonium bisulfide (about 120°C [250°F]), concentration of ammonium bisulfide, and fluid flow regime. Corrosion was found to be particularly severe if velocities exceeded 6 m/s (20 ft/s) and the product of the mol% hydrogen sulfide and the mol% ammonia is high. Above 35% ammonium bisulfide, both carbon steel and 18Cr - 8Ni SS corrode at high rates even under stagnant conditions.[10] In Figure 3.10, the severity of corrosion at different units (designated as A, B, etc.) is plotted against the product of the mol% hydrogen sulfide and the mol% ammonia (based on total stream analysis).[11,12] This indicates the higher the product, the higher the probability of severe corrosion. However, Turner has pointed out that if the H_2S concentration is greater than the NH_3 concentration, the NH_4HS concentration is related only to the NH_3 concentration, not the product.[13] Therefore, the product of the H_2S and NH_3 concentrations is only a rough guide to corrosivity. For this reason, the NH_4HS concentration from the bottom of the separator is used for a design basis. As also can be seen from Figure 3.10, there is a correlation between the temperature where ammonium bisulfide salt forms (salting temperature) and severity of corrosion. Since the salting temperature is lower in the older lower pressure units, the salting temperature was not reached in most cases. The lower salting temperature plus lower concentration of ammonium bisulfide accounts for the absence of a corrosion problem in the older low pressure units.

One of the major causes of failure in many of the high pressure units was that ammonium bisulfide was plugging the cooler tubes, causing significantly increased velocities in the remaining tubes. This has been overcome by water washing and making sure the flow is balanced in all sections of the air coolers and by installing variable pitch fans and louvers. With these modifications, the outlet temperatures of each section of the air cooler can be controlled so they are above the salting temperature and can be maintained close to the same temperature. In addition, it is necessary to use water additions to dilute the ammonium bisulfide and to control the flow regime for two-phase flow (see Chapter 5, Figure 5.22 and the discussion of the flow regimes in the section on Internal Corrosion of Piping). The severity of corrosion is a function of flow regime, being most severe in wave, slug, and dispersed flow and least severe in annular and stratified flow. Conditions close to borderlines between flow regimes should be avoided because the effect on corrosion is unknown in these zones. In most cases, water additions are used to control the flow in the annular region. If this water is not removed, e.g., by a coalescer, corrosion can occur when this water gets into equipment downstream.

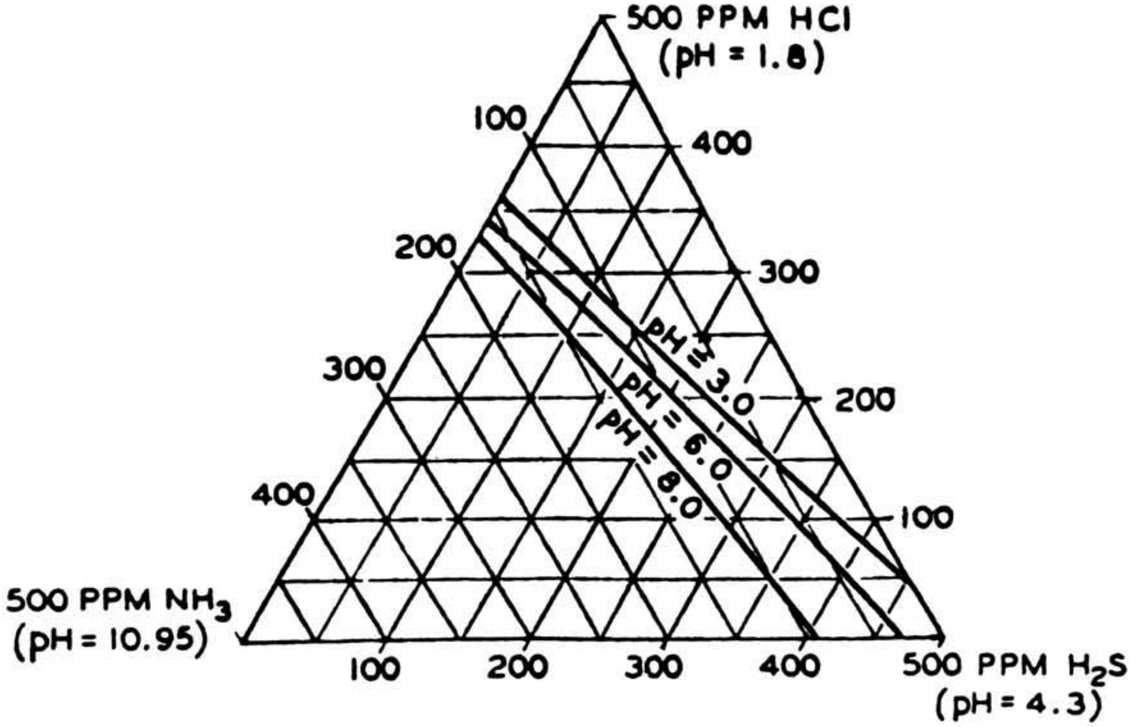

Figure 3.11 - Iso-pH lines for the aqueous HCl-H$_2$S-NH$_3$ system (500 ppm total).[14]

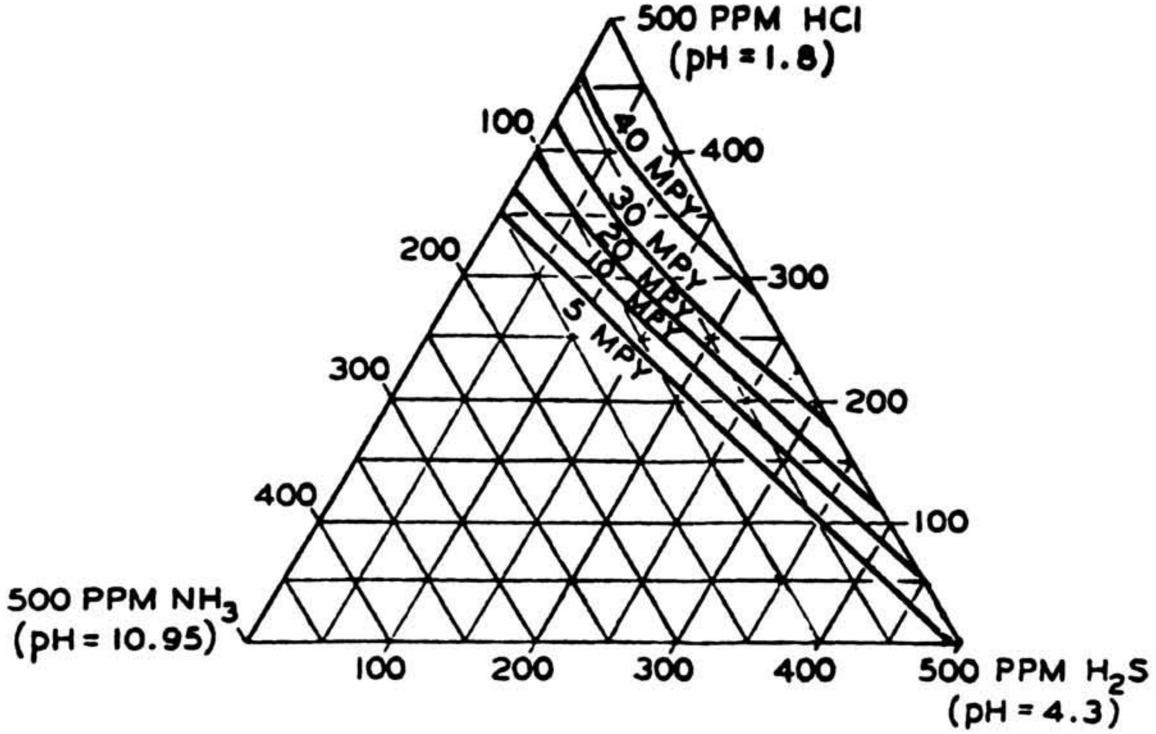

Figure 3.12 - Iso-corrosion lines for carbon steel in aqueous HCl-H$_2$S-NH$_3$ system (500 ppm total; nitrogen atmosphere, room temperature and atmospheric pressure).[14]

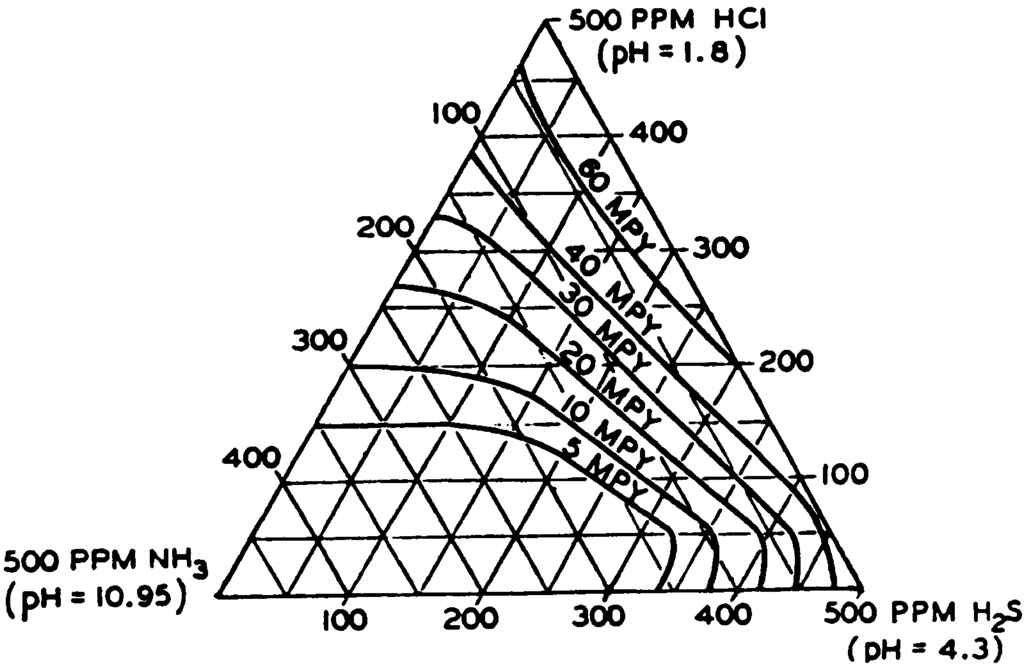

Figure 3.13 - Iso-corrosion lines for carbon steel in aqueous HCl-H_2S-NH_3 system (500 ppm total; air atmosphere, room temperature and atmospheric pressure).[14]

When the ammonium bisulfide concentration in the first separator is below 4%, carbon steel tubes have been used successfully, provided the pH of the water drawoff 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. To make sure the ammonium bisulfide is diluted, there should be 20% to 25% unvaporized water downstream of the water injection point.[13] An ammonium bisulfide concentration of greater than 4% in the separator also is an indicator of potential corrosion problems. Some refiners limit the velocity in all exchangers to 6 m/s (20 ft/s) when the product of the mol% ammonia and the mol% hydrogen sulfide exceeds 0.05 where two-phase flow occurs. In addition, the 6 m/s (20 ft/s) velocity limit is applied when the ammonium bisulfide concentration in equipment and piping exceed 2% regardless of the flow regime. Carbon steel piping with 6 mm (1/4 in.) corrosion allowance has given satisfactory service in streams with ammonium bisulfide concentrations up to 8%. For concentrations greater than 8%, SS resistant to SCC is required. Some refiners require the cold high-pressure separator to be clad with 304L (UNS S30403) or 347 (UNS S34700) when the ammonium bisulfide concentration in the separator water will exceed 8%.

As indicated in Figure 3.10, SS ferrules are required when the product of the mol% H_2S and the mol% NH_3 exceeds 0.4. For ferrules to be effective, they must have at least a 3/1 taper on the end inside the tube. Ferrules should not be installed in units that have been in service because corrosion under the ferrules may result. Where limits for carbon steel are exceeded, alloys such as Alloy 400 (UNS N04400), Alloy 800 (UNS N08800) with 0.05 C max., and Alloy 825 (UNS N08825) have been used. Admiralty brass (UNS C44300) cannot be used because it is rapidly attacked by ammonium bisulfide solutions. Recently, duplex stainless steels, such as ASTM A789 (UNS S32205), have performed well in reactor effluent air cooler tubes.

2.7 Other Corrosion and Material Problems

Corrosion in condensate containing hydrochloric acid, hydrogen sulfide, and ammonia has been a problem in some units. From Figure 3.11, the pH of condensed water can be predicted from the ppm level of hydrochloric acid, hydrogen sulfide, and ammonia at room temperature.[14] Note that the hydrogen sulfide content has little effect on the pH. Figures 3.12 and 3.13 show the effect on corrosion of these constituents without and with air, respectively, at room temperature.[14] As can be seen, the corrosion rate is roughly a

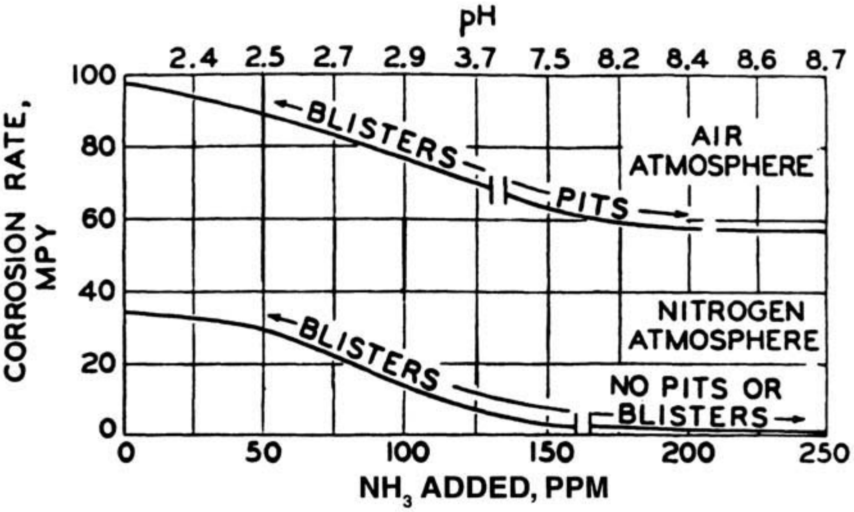

Figure 3.14 - Effect of NH_3 neutralization on corrosion of carbon steel in an aqueous solution containing 400 ppm HCl, 50 ppm H_2S, 50 ppm NH_3 at room temperature, and atmospheric pressure.[14]

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 3.14.[14] Again it can be seen that air (oxygen) greatly accelerates corrosion. A pH greater than 8 must be reached to obtain maximum benefit from ammonia additions.

Figures 3.15 and 3.16 show the effect of ammonia additions on corrosion at 150°C (300°F).[14] When a tenacious oxide film is formed on steel (Figure 3.16),[14] corrosion is much greater than when only a thin iron sulfide film is present. Corrosion control is not maximized until a pH greater than 8 is reached. Corrosion problems also have occurred in effluent separators, compressors, sour water valve trims, expan-

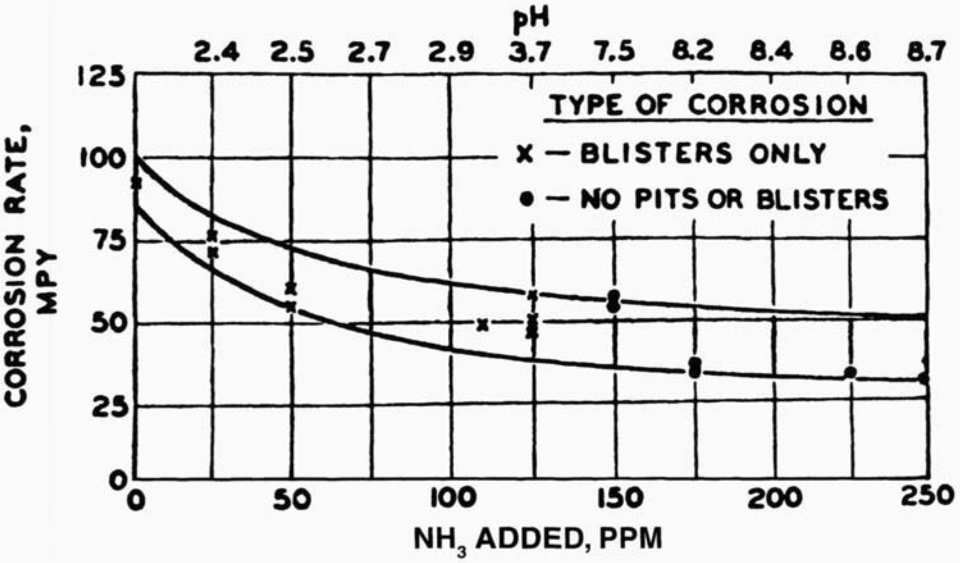

Figure 3.15 - Effect of NH_3 neutralization on corrosion when only a sulfide film formed on the test coupons. Carbon steel coupons were in aqueous HCl-H_2S-NH_3 solutions for 24 hours at 300°F and 625 psi under nitrogen.[14]

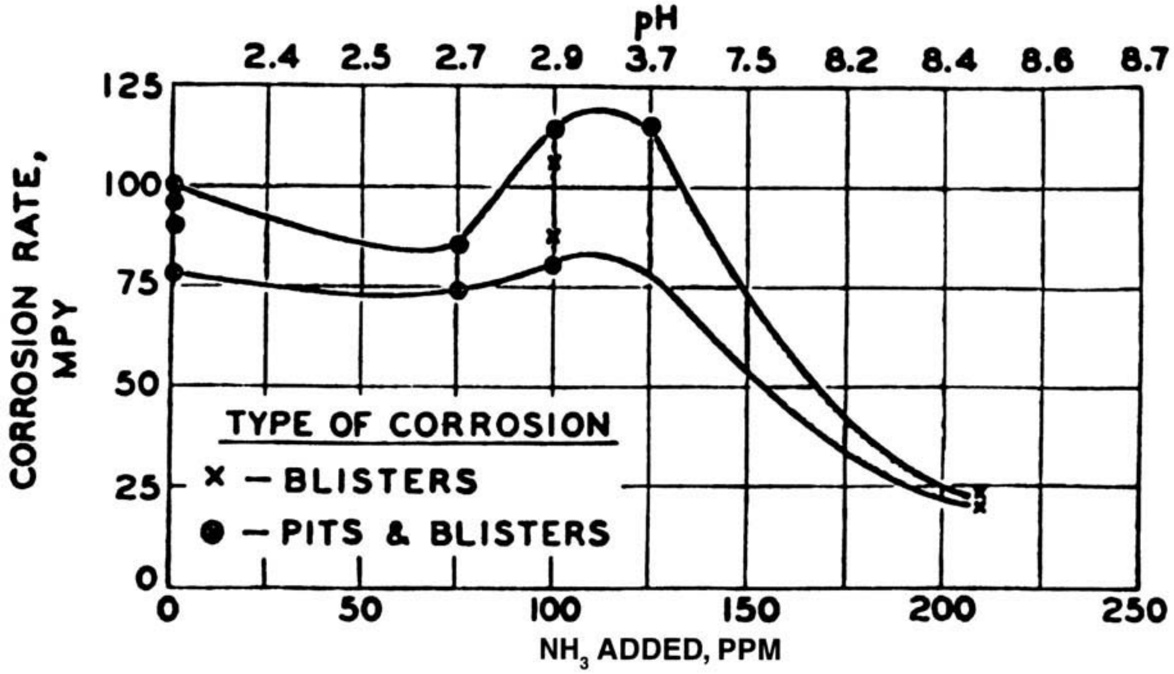

Figure 3.16 - Effect of NH_3 neutralization on corrosion when non-removable oxide film formed on the test coupons. Carbon steel coupons were in aqueous HCl-H_2S-NH_3 solutions for 24 hours at 300ºF and 625 psi under nitrogen.[14]

sion bellows, bolting, and hydrocracker fractionators. Cold high pressure separators have experienced HIC cracking. See Chapter 5, section 8.2, and NACE Publication 8X194 for a discussion of HIC cracking. Either PWHT or 347 (UNS S34700) cladding is used, depending on the potential for HIC cracking in the cold high-pressure separator. AISI 4140 (UNS G41400) compressor impellers have failed from sulfide stress cracking (SSC) in sour gas when the hardness exceeded 235 Brinell. Hardened 12 Cr valve trim also failed from SSC; to prevent this problem, 18 Cr-8 Ni SS trim or other materials complying with MR0175 commonly are used in sour water service. ASTM A193 B7M is used in lieu of B7 for bolting that is exposed to wet H_2S. SSC has not been a significant problem in pumps.

Austenitic SS tubes subject to transgranular chloride stress corrosion cracking should not be used in heat exchangers that generate steam, particularly when the steam is generated on the shell side. Even a few ppm of water in the fluid in an exchanger where the water is evaporated is sufficient to cause failure. This is because the solids concentrate, then cause failure as the water is evaporated. Pitting and stress corrosion cracking of SS tubes from the shell side have occurred in the heat exchanger that exchanges recycle hydrogen and low-pressure separator effluent before it is fed to the fractionator.

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

Above about 104°C (220°F), moisture needed for stress corrosion cracking does not form on the surface in the absence of hygroscopic salts. Stress corrosion cracking 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. Preventative measures are to specify insulation that meets ASTM C795 and to use organic coatings. Both epoxies and silicone coatings have given good results. There is one report that aluminum foil is superior to coatings for preventing atmospheric stress corrosion cracking.

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

Expansion bellows are thin, highly stressed material. They are commonly made of 18 Cr-8 Ni SS; high nickel alloys, such as alloy 400 (UNS N04400); alloy 800 (UNS N08800); and Inconel™ 625LCF(3) (UNS N06625). Some manufacturers claim the fatigue life is enhanced if the bellows are not annealed after forming. Independent studies by the International Nickel Co. and others concluded that all bellows, regardless of alloy, should be annealed after forming.[15]

Materials of construction for the fractionation equipment in a hydrocracker are carbon steel below 288°C (550°F). Although most sulfur is removed, some sulfur compounds still remain. This remaining sulfur is in the form of aliphatic and aromatic mercaptans and aliphatic sulfides and disulfides, as well as H_2S. Severe corrosion of carbon steel and 5 Cr-1/2 Mo fired heater tubes, transfer lines, and heat exchanger tubes has occurred at temperatures above 288°C (550°F), depending on the amount of sulfur (usually reported as H_2S for convenience) in hydrocarbon feed to the fractionator. In one unit, corrosion rates in the order of 2.54 mm/y (100 mils/y) were reported in a fractionator reboiler operating at 343°C (650°F) fluid temperature. The sulfur content in the fluid, reported as H_2S, was estimated to be 30 ppm.

The sulfur content, reported as H_2S in hydrocarbon fractionator feed, can be the residual in the streams from the hydrocracker unit or can come from recycled gas from an amine unit. Passing the hydrocracker effluent through a H_2S stripper prior to feeding it to the fractionator will minimize the corrosion problems above 288°C (550°F), but will not prevent them unless the sulfur content in the fluid, reported as H_2S, is reduced to below 1 ppm. The following have been used for guidelines in selecting materials for hydrocracker fractionator equipment:

	Maximum Temperature [°C (°F)]	
Sulfur Content (reported as H_2S ppm)	**Carbon Steel**	**5 Cr-1/2 Mo**
10	315 (600)	343 (650)
100	300 (575)	330 (625)
1,000	288 (550)	315 (600)

At temperatures above the limits for 5 Cr-1/2 Mo, 18 Cr-8 Ni stainless steels are used for pressure-containing parts, and 12 Cr is used for cladding.

3. CATALYTIC REFORMERS

A typical process flow diagram of a catalytic reformer is shown in Figure 3.17.[1] A modification of catalytic reforming, namely continuously regenerated catalytic reforming (CRCR) shown in Figure 3.18,[16] has become popular recently. In the catalytic reforming processes, desulfurized naphtha is heated in feed-effluent exchangers then passed to a fired heater, where it is heated to 455°C to 540°C (850°F to 1,000°F) at 3,450 kPaa (500 psia) 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, primarily aromatics with some isoparaffins. The reactor effluent is cooled by exchange, then passed to a separator vessel. The gas from the separator is recycled to the reactors. The liquid is fed to a fractionator.

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(3) LCF indicates the alloy is modified for improved fatigue resistance.

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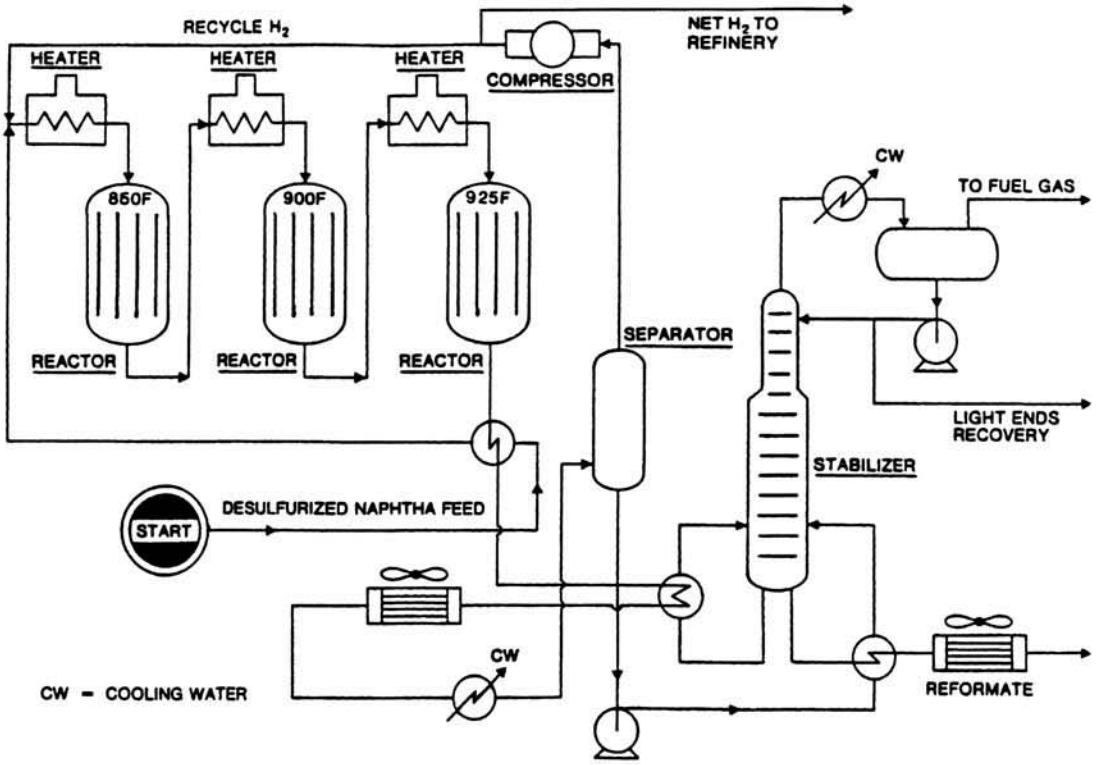
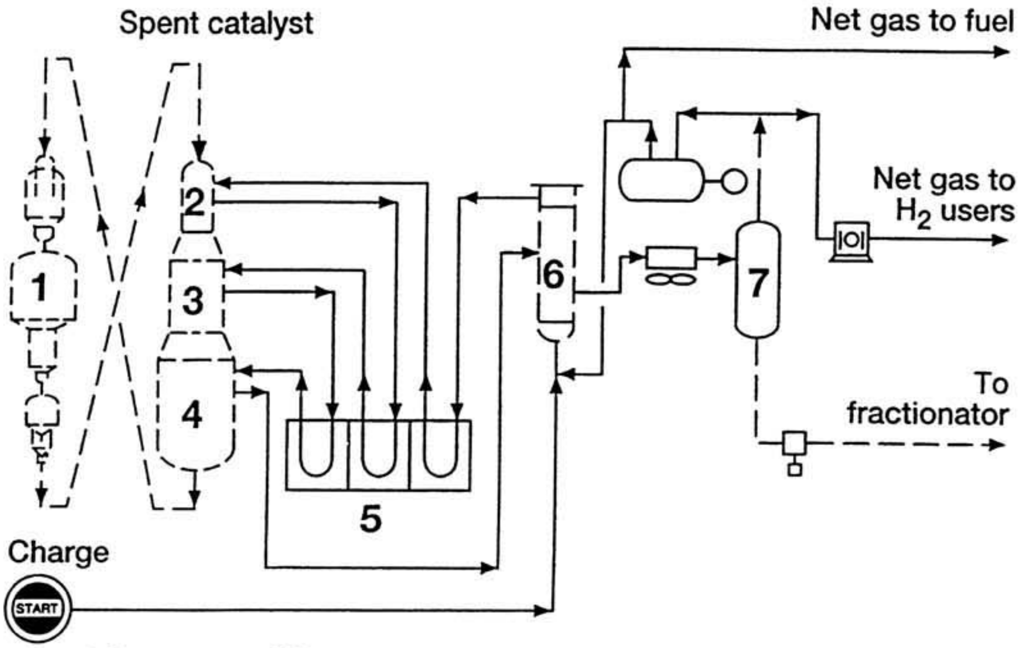


Figure 3.17 - Catalytic reforming.[1]
(Reprinted with permission from "The Role of Stainless Steels in Petroleum Refining," American Iron and Steel Institute, April 1977)



1=Regenerator
2,3,&4=Reactors
5=Heaters
6=Feed/Effluent Exchanger
7=Separator

Figure 3.18 - Continuously regenerated catalytic reforming.[16]
(Reprinted with permission from *Hydrocarbon Processing*, 11, 1996)

Because hydrogen is used in the reforming reaction, materials must be selected according to API 941, except that C-1/2 Mo should not be used (i.e., the minimum alloy for hydrogen service should be 1 Cr-1/2 Mo). As mentioned previously, this is because of C-1/2 Mo failures in catalytic reformers that some refiners have related to the catalytic reformer process regeneration. When selecting fired heater furnace tubes, for example, it is important to select the steel with the hydrogen resistance based on the metal temperature, often 55°C (100°F) greater than the process temperature. There is no hydrogen sulfide in catalytic reformers so SS is not required for sulfidation resistance. Because there is essentially no H_2S in the fluid in the fired heater furnace tubes, there is a potential for metal dusting or carburization. Metal dusting of 2-1/4 Cr - 1 Mo heater tubes has been reported in a CRCR unit at temperatures from 625°C to 675°C (1,150°F to 1,250°F). At slightly higher temperatures, severe carburization of 9 Cr - 1 Mo heater tubes has been found.[17] As a result, the temperature limits of 2-1/4 Cr - 1 Mo and 9 Cr - 1 Mo have been set at 607°C and 635°C (1,125°F and 1,175°F), respectively.

The catalytic reformer reactors normally are refractory-lined steel because the reaction temperatures are about 540°C (1,000°F). Often there is an austenitic SS shroud covering the refractory lining to prevent the process fluids from channeling through the refractory lining rather than 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. Creep cracking in both 1 Cr -1/2 Mo and 1-1/4 Cr - 1/2 Mo nozzles has been reported recently at temperatures in excess of 500°C (930°F). The cause is stress concentration in the low-ductility, coarse-grained weld heat-affected zone. To avoid this problem, some refiners specify 2-1/4 Cr - 1 Mo, while others require 1-1/4 Cr - 1/2 Mo normalized and tempered or other heat treatment to produce annealed properties. In addition, carbon is limited to 0.14% maximum while sulfur and phosphorous are limited to 0.005% when the 1-1/4 Cr-1/2 Mo materials are used.

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. Severe corrosion (e.g., of admiralty [UNS C44300] tubes) can occur during regeneration unless the acid gases are neutralized by an alkaline wash during regeneration.

Chlorides also have been one of the major sources of problems in CRCR units. In particular, problems have been reported in the vent gas scrubber area, the overhead stabilizer and in the light product lines after the fluids are mixed with wet streams.[18] Pitting where moisture is present and fouling in dry areas have been the major problems. Nitrogen contamination in the feed has resulted in the formation of ammonium chloride. Ammonium chloride has caused pitting and fouling in the stabilizer or debutanizer overhead. Low pH excursions and alkaline solids carryover have resulted in pitting and under-deposit pitting, respectively, in vent gas scrubbers. Alloy 600 (UNS N06600), which is used in the overhead of the vet gas scrubber to handle high temperature excursions during venting, also has corroded due to acid chloride condensation. It was reported that alloy 625 (UNS N06625) was resistant under most conditions.

Where condensation can be prevented in equipment operating at high temperature, 321 SS (UNS S32100) and alloy 800 (UNS N08800) have been used. Serious corrosion problems also have occurred downstream in hydrogen or liquefied petroleum gas from catalytic reformers. When mixed with streams from other units that contain free water, the few ppm of hydrochloric acid from the catalytic reformers can dissolve in the free water and cause rapid localized corrosion.[19]

To combat corrosion from the chlorides in the standard catalytic reformer systems during operation, some refiners use alloy 400 (UNS N04400) trim steel valves while others use alloy 20 (UNS N08020) trim. Still others have found that standard 12 Cr 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 stress corrosion cracking of alloy K-500 (UNS N05500), 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 HRC 33) has been used. In addition to the use of alloy 625 (UNS N06625) or alloy C276 (UNS N10276) corrosion preventative measures used in CRCR units include control of the moisture and nitrogen levels in the feed and installing caustic scrubbing on the vent gas hydrogen stream to remove chlorides.

4. 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 540°C (1,000°F). 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 due to the low-melting eutectic that forms around 650°C (1,200°F). As little as 50 ppm of vanadium in the fuel oil may be sufficient to cause the problem.[20] Solutions to this problem are to (l) keep the temperature below 650°C (1,200°F)⁽⁴⁾, (2) design the furnace with soot blowers, (3) keep the excess air to 1-2%, or (4) use a 50 Cr-50 Ni alloy for tube hangers.

If the sulfur in the gas exceeds 23 mg/std m^3 (1 grain/100 std ft^3), 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 200°C [400°F]). The dew point can be estimated from Figure 3.4 of ASME/ANSI STS-1 1986. When the amount of SO_3 is unknown, assume it is 2% of the SO_2 content. In mild concentrations of sulfur oxides, type 316L SS usually performs well below 60°C (140°F) and at somewhat higher temperatures in the absence of chlorides. For flue gas scrubbers that operate below 60°C (140°F), the choice between 316L and the high molybdenum alloys, such as 317LM (UNS S31725), 904L (UNS N08904), alloy 625 (UNS N06625), 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 3.19.[21] For example, at pH 4, 316L could be used up to 60 ppm chlorides; but for 700 ppm chloride at pH 4, 904L would be required.

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

- Refractory-lined carbon steel,
- Organic-coated carbon steel,
- Organic-lined carbon steel,
- Alloy 625 (UNS N06625), clad carbon steel,
- High-alloy strip-lined carbon steel,
- Titanium (either solid or clad on carbon steel).

Maintenance is a problem with 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 1-10 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; alloy 625 (UNS N06625) clad steel usually is 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 also may be a problem in flue gas. Refractory linings, such as AA-22™ and hardfacings, such as Stoody 100 HC,™ often are used where severe erosion occurs. Where milder erosion or alternate wetting and drying is expected (e.g., diesel exhaust stacks), low-alloy steels (e.g., Cor-ten™ UNS K12043) have been used. For continuous operation, low-alloy steels offer no significant advantages over carbon steel, provided the operating temperature is below 455°C (850°F). Stresses (including secondary stresses) on Cor-ten™ should be limited to 55.2 MPa (8 ksi) to avoid downtime cracking due to temper embrittlement. When stresses as high as 55.2 MPa (8 ksi) will be experienced, 1-1/4 Cr - 1/2 Mo should be used in lieu of Cor-ten.™

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(4) Because the corrosivity of fuel ash depends on a complex interaction of vanadium, sodium, chlorine and sulfur, limiting the temperature to as low as 538°C (1,000°F) may be necessary in some cases. See L.D. Paul and R.R. Seeley, "Oil Ash Corrosion - A Review of Utility Boiler Experience," Corrosion 47, 2(1991): p. 152.

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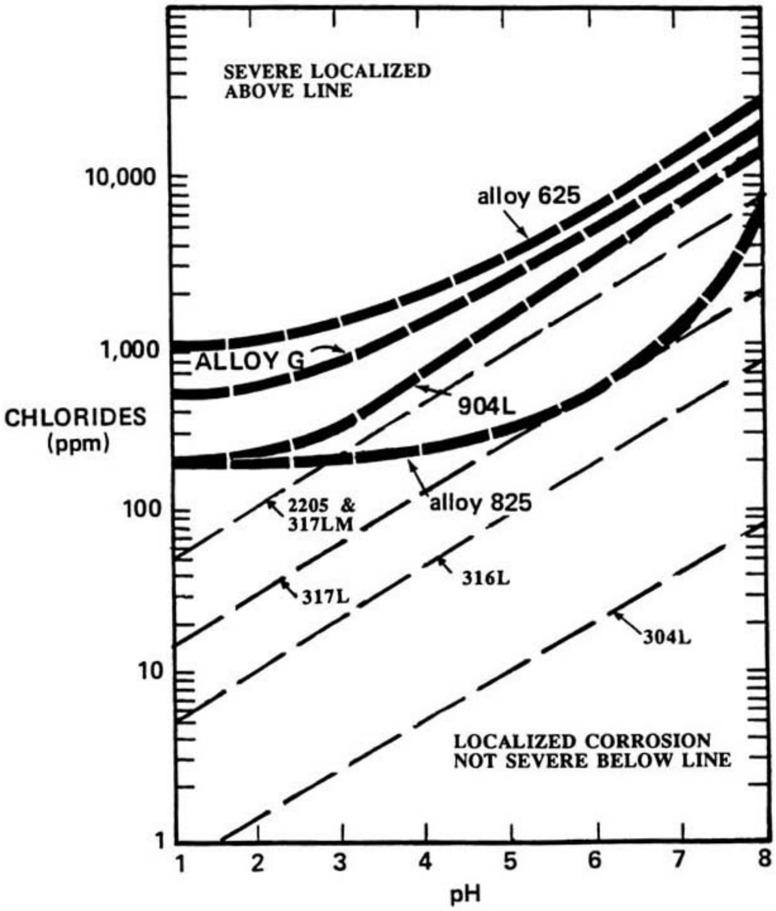

Figure 3.19 - Predicted corrosion behavior of alloys in SO_2 scrubber environments from field tests (125ºF to 160ºF oxidizing).[21]

5. FLARE TIPS

The temperature of flare tips cycle from atmospheric temperature when not operating to temperatures in the order of 1,095°C (2,000°F) during operation. As a result, thermal fatigue cracking is a problem. In addition, intergranular stress corrosion cracking due to the presence of oxides of sulfur and moisture is a problem during downtime. Exposure to a marine environment increases the intergranular stress corrosion cracking problem. Traditionally, flare tips have been made of 309 (UNS S30900) or ACI Type HH (UNS S93503) and 310 (UNS S31000) or ACI Type HK (UNS S94224). Low carbon grades (309S [UNS S30908] and 310S [UNS S31008]) often are specified when the potential for intergranular stress corrosion cracking is high.

Three to five years is not an uncommon life for flare tips because of the above-mentioned problems. Alloy 800 (UNS N08800) and alloy 625 (UNS N06625) have been tried to extend the life. In addition, refractory lined tips have been tried. At best, there has been mixed success with the newer flare tip materials. Alloy 625, and to a lesser extent alloy 800, are subject to high sulfidation rates in flare tips that burn high H_2S (greater than 10%). Refractory lining has fallen off due to the thermal cycling. Because of the potential to plug up the flare line due to refractory falling off, refractory lined flare tips have not been used widely.

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4

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

1. INTRODUCTION

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

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

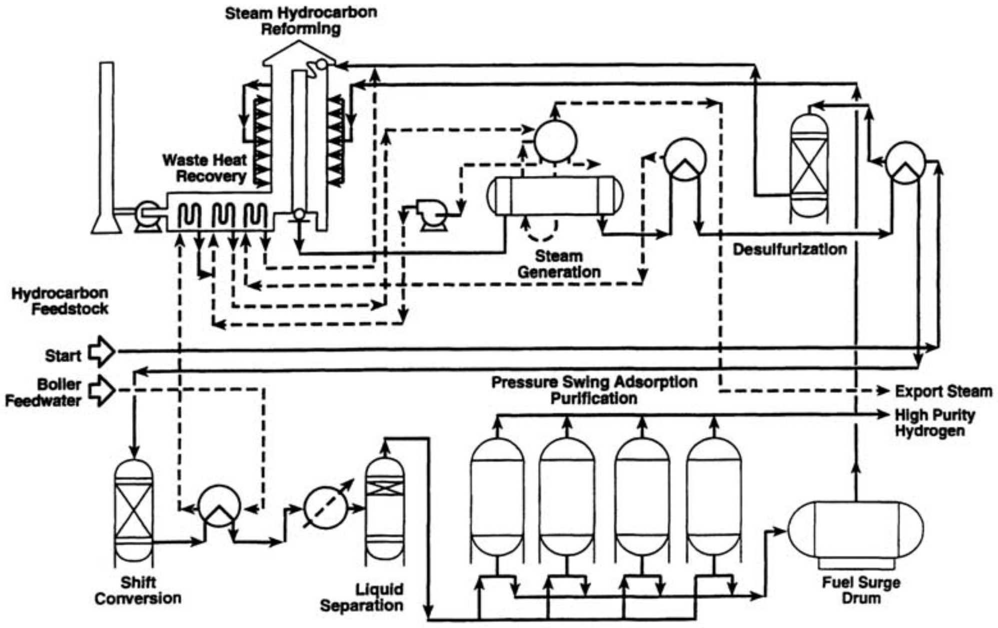

Figure 4.1 - Hydrogen[1]
(Reprinted with permission from "Refinery Process Handbook," *Hydrocarbon Processing*, Houston, TX: Gulf Publishing, September 1968)

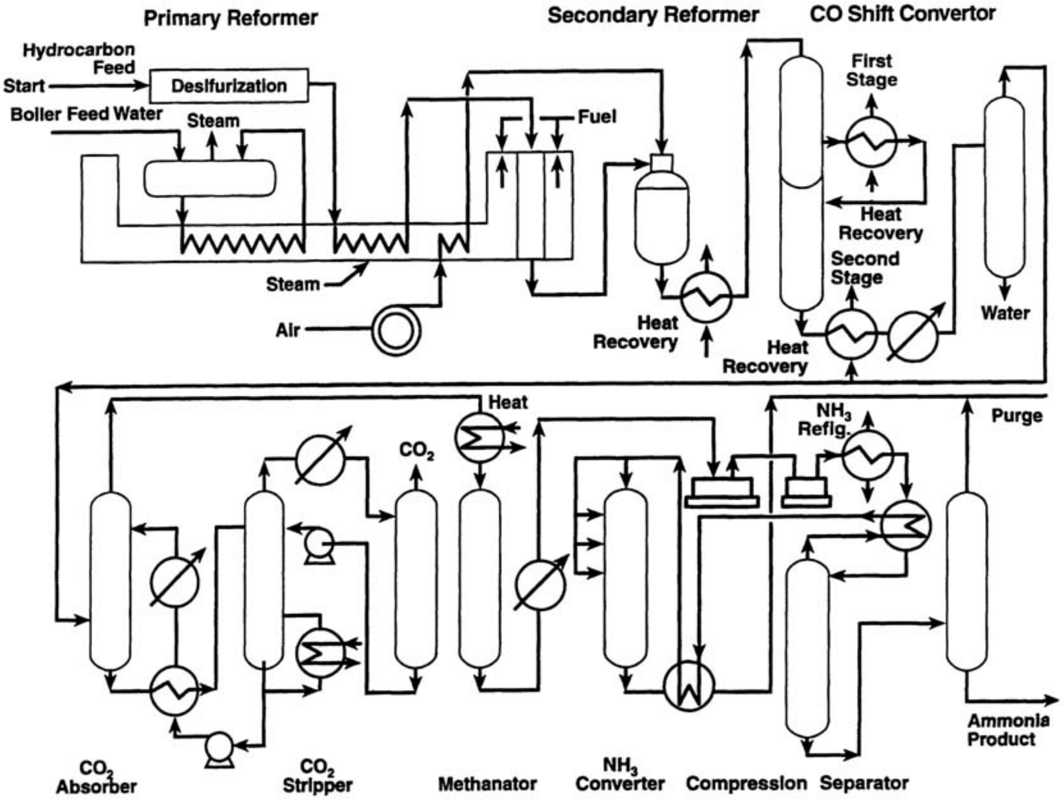

Figure 4.2 - Ammonia.[1]
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In an ammonia plant (Figure 4.2),[1] the synthesis gas from the reformer furnace is fed into a secondary reformer vessel in which air is added through a burner to create outlet vessel temperatures in the order of 980°C (1,800°F). 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. 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 about 20,700 kPaa (3,000 psia). 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),[1] the synthesis gas goes from the reformer furnace to a heat recovery section, where it is cooled to room temperature. The synthesis gas is then compressed from 5,170 kPaa to 10,345 kPaa (750 psia to 1,500 psia) and fed to the converter vessel through preheat exchangers. Methanol is formed as the gas passes over catalyst beds in the converter vessel at 205°C to 315°C (400°F to 600°F). The methanol product is then cooled and fed to separators, then to fractionators to complete the purification.

2. MATERIALS OF CONSTRUCTION

2.1 High-Temperature Front End

The front end section of hydrogen, methanol, and ammonia plants is shown in Figure 4.4.[2] The secondary reformer is used only in an ammonia plant. The feed gas is desulfurized in carbon steel equipment. When

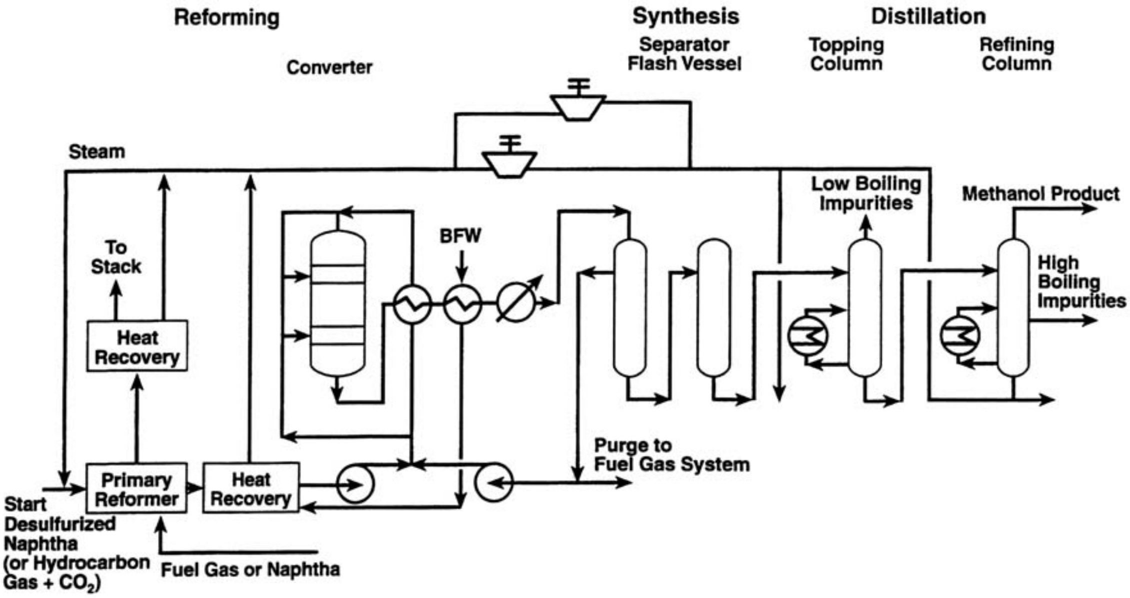

Figure 4.3 - Methanol.[1] (Reprinted with permission from "Refinery Process Handbook," *Hydrocarbon Processing,* Houston, TX: Gulf Publishing, 1968)

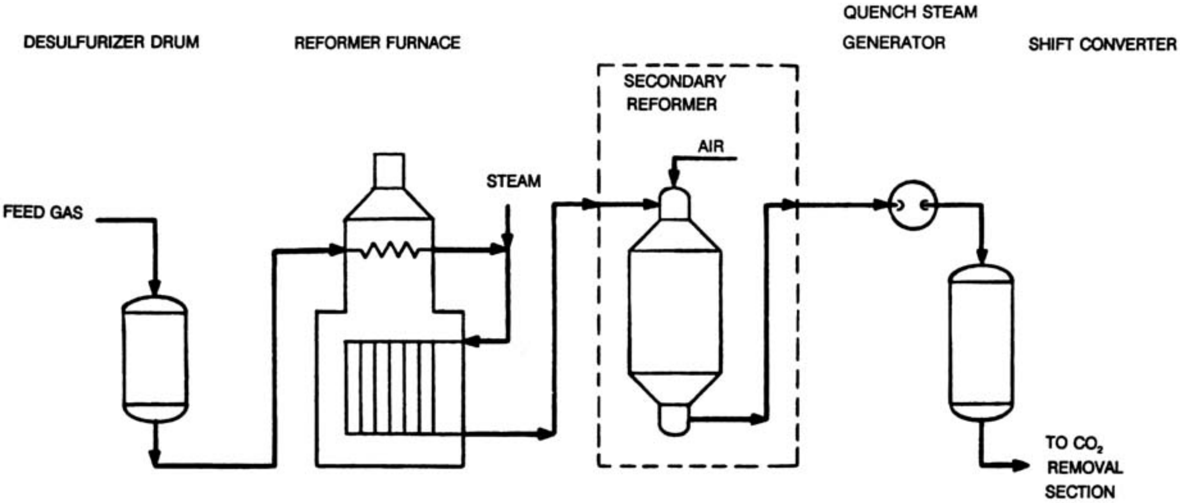

Figure 4.4 - High temperature front end section of reforming plant.[2]

the metal temperature exceeds 425°C to 455°C (800°F to 850°F), 1 Cr-1/2 Mo or 1-1/4 Cr-1/2 Mo is used to avoid long-term deterioration of the mechanical properties by graphitization. Preheat coils in the top of the reformer furnace usually are 2-1/4 Cr - 1 Mo up to 650°C (1,200°F) metal temperature and 304H (UNS S304009) for metal temperatures above 650°C (1,200°F). Caustic stress corrosion cracking from solids can occur in the steam preheat coils if solid carryover is excessive (see Chapter 1, Section 3.7). The inlet connections to the steam methane reformer furnace tubes are either 1-1/4 Cr-1/2 Mo (595°C [1,100°F] maximum) or 2-1/4 Cr-l Mo (650°C [1,200°F] maximum).

The methane (or naphtha) and steam are converted to hydrogen and carbon monoxide along with some carbon dioxide over a nickel catalyst in the HK-40 (UNS J94204) or HP modified, also called CE20N (UNS J92802) primary reformer furnace tubes. CE20N (UNS J92802) has largely replaced HK-40 because of superior stress-to-rupture strength (e.g., 12.55 MPa [1.82 ksi] vs 8.3 MPa [1.2 ksi] at 980°C [1,800°F]). Skin temperatures on these tubes are about 980°C (1,800°F), and the outlet process temperature is about 820°C (1,500°F). Sulfur content in the fuel gas is limited to 2,000 ppm to 3,000 ppm hydrogen sulfide to avoid accelerated oxidation of the outside of the tubes. The tubes are centrifugally cast. They have been used in the as-cast condition which includes about 2.4 mm (3/32 in.) dross and unsoundness on the inside diameter. Currently, most tubes are bored on the inside to remove the dross and unsoundness and machined on the outside. Since the tubes are operating in the range where sigma phase (a brittle Fe-Cr compound) forms, the Cr, Ni, and C are "balanced" to minimize sigma phase embrittlement. The welds must be blasted to remove all residual weld slag; otherwise, the residual weld slag can form a eutectic with the metal oxides, which results in catastrophic oxidation.

The outlets of the primary reformer furnace tubes are connected to either a refractory-lined steel or (occasionally) an alloy 800H (UNS N08810) outlet header with alloy 800H "pigtails." Pigtails are tubes (about 25.4 mm [1 in.] 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 alloy 800 (UNS N08800) pigtails has occurred because of too fine a grain size (smaller in size than ASTM No. 5); however, these problems can be avoided by specifying alloy 800H. Some refiners prefer single-row reformer tubes to minimize the thermal stresses on the pigtails.

For temperatures over 650°C (1,200°F), 65 Ni-15Cr-Fe filler metal, such as INCO82™ (UNS N06082) or INCO A™ (UNS W86133), should be used (although INCO A has a somewhat lower creep strength than INCO 82). Neither INCO 92™ (UNS N07092) nor INCO 182™ (UNS W86182) should be used above 480°C to 510°C (900°F to 950°F), because they embrittle when exposed to high temperatures. In addition, INCO 182 has a significantly lower creep strength than either INCO 82 or INCO A. 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 about 730°C [1,350°F], resulting in rapid deterioration). For the same reason, alloy 600 (UNS N06600), either wrought or cast, should not be used above 730°C (1,350°F) 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 788°C to 980°C (1,450°F to 1,800°F) and usually are made of either alloy 800H (UNS N08810) or refractory-lined carbon steel. Above about 820°C (1,500°F), 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 sometimes can deteriorate due to 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 about 1,090°C (2,000°F) 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 subject to failure if not carefully designed. Quench steam generators have refractory-lined inlet channels and tube sheets. Tubes often are 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 that of the steam. The inlet ends of the tubes are protected from the inlet gas by ferrules, usually 310 SS (UNS S31000) with insulation between the ferrule and the tube. The tube material should be selected according to the maximum anticipated metal temperature and to API 941. The outlet channels usually are made of low-alloy steel selected by using API 941.

2.2 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 and the carbon monoxide to carbon dioxide. Some ammonia is formed in the shift converter when nitrogen is present. Alloy selection is based on API 941 until the synthesis gas is cooled below the dewpoint (usually about 160°C [325°F]). When wet carbon dioxide condenses out of the synthesis gas, severe corrosion of carbon and low alloy steel results, particularly in turbulent areas. Type

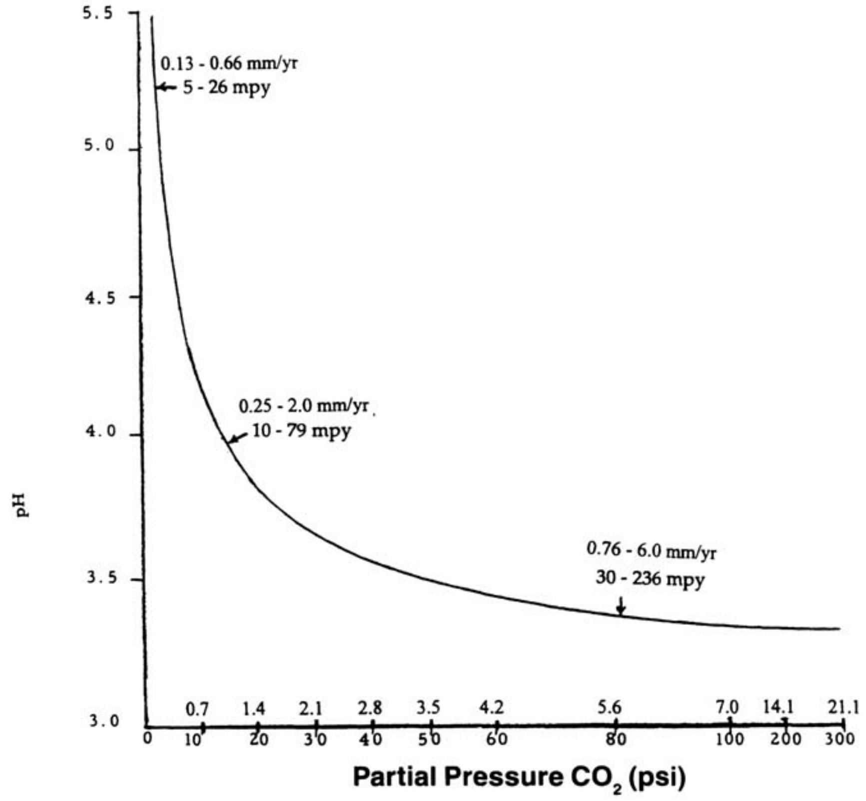

Figure 4.5 - Relationship between pH, carbon dioxide partial pressure, and estimated corrosion rate on carbon steel at 38°C (100°F).[2]

304L SS (UNS S30403) normally is used to resist this attack. Figure 4.5 shows the relationship between pH and carbon dioxide partial pressure.[2] The higher corrosion rates shown are calculated from the deWaard-Lotz equation, which was developed from laboratory data. The lower corrosion rates represent typical values experienced in the field after a corrosion film has formed and steady state conditions exist.

As can be seen in Figure 4.5, the corrosion rate of carbon steel at 38°C (100°F) increases as the carbon dioxide partial pressure increases.[2] For temperatures below 60°C to 70°C (140°F to 160°F), the corrosion rate in wet carbon dioxide is activation-controlled and, therefore, not accelerated by turbulence. Above the 60°C to 70°C (140°F to 160°F) range, the corrosion rate is diffusion-controlled and, therefore, is significantly accelerated by turbulence. The following rates, measured in a two-phase, gas-water system containing carbon dioxide at a partial pressure of 125 kPaa (18 psia), illustrate the effect of turbulence and the effect of alloying elements in reducing corrosion caused by turbulence:

Corrosion Rate (mm/y [mils per year])

Material	Location A - 138°C (280°F)	Location B - 160°C (320°F)
Carbon Steel	1.3 (50)(1)	1.3 (50)(1)
5 Cr	0.3 (11.5)	0.6 (2.2)
12 Cr	0.03 (1.14)	0.02 (0.7)
18 Cr-8 Ni	0.0003 (0.01)	0.0015 (0.06)

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(1) Rates of corrosion probe exceeded 25.4 mm/y (1,000 mpy).

In ammonia and hydrogen plants, part of the carbon dioxide is removed in the condensate in the knockout pots, which are made of solid or clad 304L SS (UNS S30403) (Figure 4.6).[2] The overhead lines of these knockout pots may be made of carbon steel if no condensation occurs. This is particularly true in ammonia plants where some ammonia formed in the shift converter is present in the stream. In general, the overhead lines of knockout pots used in hydrogen plants are made of 304L SS. The remainder of the carbon dioxide is removed by absorption in a potassium carbonate solution, an amine solution, or in a low temperature PSA™ unit.

Carbonate and PSA™ units are used primarily for carbon dioxide removal. Amine units are used primarily for hydrogen sulfide removal. In refineries, the amine units are primarily used as part of the sulfur recovery system, which consists of a central amine unit, a sour water stripper, and a sulfur plant.

The primary cause of corrosion in amine solutions is degradation products. Although all amines generally are treated the same with respect to materials selection, Dupart has shown that MEA is the most corrosive and MDEA is the least corrosive with DEA in between.[3] This difference in corrosivity is directly related to the amount and type of degradation products formed. Carbon steel is the predominant material of construction for carbonate and amine solution equipment. Corrosion in the overhead lines (hydrogen sulfide or carbon dioxide plus water from the regenerator) is prevented by the addition of corrosion inhibitors. In amine units used in refineries for hydrogen sulfide removal, corrosion in the regenerator (stripper) overhead is caused by ammonium bisulfide, which results from the buildup of ammonia and hydrogen sulfide in the reflux loop when there is insufficient blowdown.

When ammonium bisulfide corrosion on carbon steel is severe, 304L (UNS S30403) or 316L (UNS S31603) often is used as a replacement. Copper and copper-base alloys should be avoided in amine service and are questionable in carbonate service. Nickel or cobalt-base alloys (e.g., alloy 400 [UNS N04400], alloy 600 [UNS N06600], alloy 625 [UNS N06625], etc.) should be avoided in carbonate service. The exception is Stellite™ 6 [UNS R30006]) which has performed well in carbonate service. Alloy 400 should be avoided in amine service if Union Carbide Corp. Amine Guard corrosion inhibitor is used.

In amine units, absorption is typically at 55°C (130°F); in carbonate units, absorption typically is at 93°C (200°F). Absorption pressures typically are 690 kPaa to 2,760 kPaa (100 psia to 400 psia), although units can be designed to handle pressures at about 6,895 kPaa (1,000 psia). Amine and carbonate strippers (regenerators) typically run at 115°C (240°F) and 172 kPaa to 207 kPaa (25 psia to 30 psia). In the past, stress relief of carbon steel welds and cold bends usually was required when the process temperature exceeded 60°C (140°F) in both amine and carbonate solutions. Past practices for amine service varied from requiring stress relief when hydrogen sulfide was present to using 80°C to 93°C (176°F to 200°F) as the process temperature above which stress relief was required.

Russian work and later studies by Parkins and Foroulis revealed that stress corrosion cracking occurs in hot monoethanolamine solutions when the electrochemical potential of the steel surface is more negative than -700 mv vs a silver-silver chloride electrode.[4] The stress corrosion cracking tendency increases with an increase in solution concentration and an increase in temperature. Saturating the hot monoethanolamine solution with hydrogen sulfide makes the potential of the steel more positive (i.e., decreases the tendency for stress corrosion cracking). Conversely, carbon dioxide shifted the potential into the stress corrosion cracking range. Although need to stress relieve carbon steel equipment should be minimized by the inhibiting effect of hydrogen sulfide on amine stress corrosion cracking, there is the offsetting potential for sulfide stress cracking in amine equipment containing hydrogen sulfide as discussed below.

A catastrophic failure in an amine absorber caused many operators to examine their equipment exposed to amine service.[5] The 20-ton absorber exploded, landing 1 km (0.6 mile) away. Seventeen people were killed, and 59 homes within 1 km were damaged. The absorber vessel failure was determined to be caused by SOHIC and hard welds, not amine cracking. However, the examination of equipment in amine service that resulted before the cause finally was determined and revealed that amine stress corrosion cracking existed in many vessels. Cracking was found to be independent of process temperature. Therefore, most operators now

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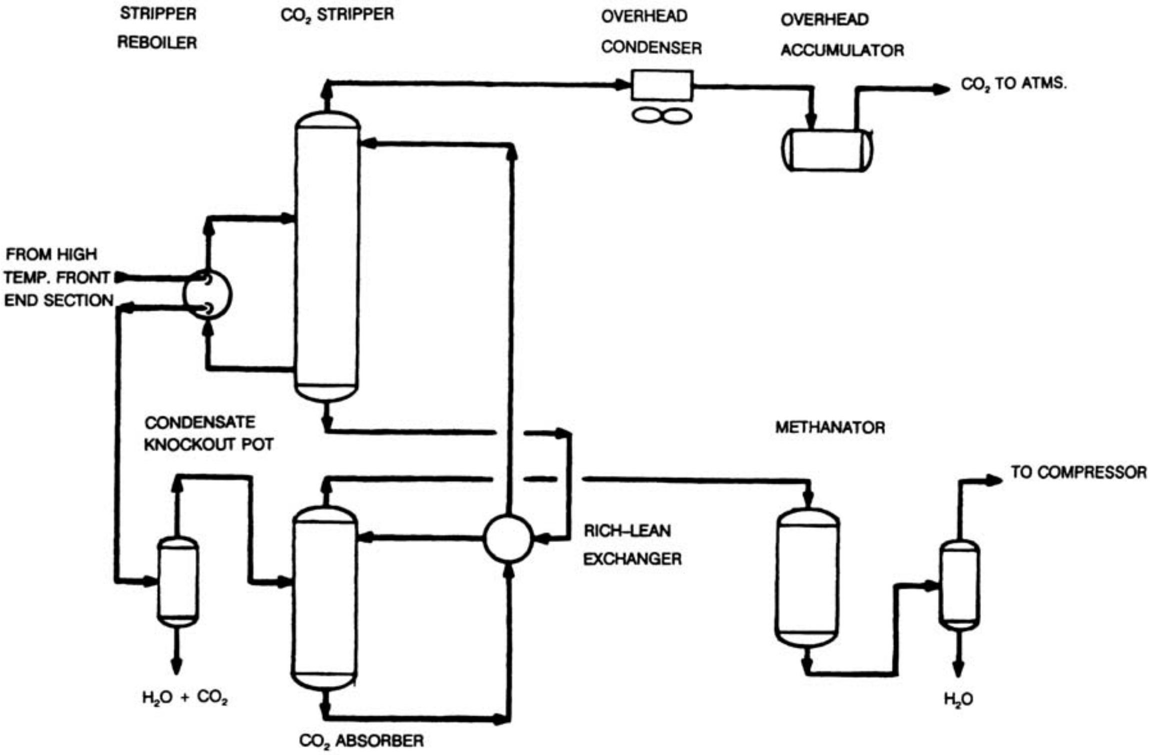

Figure 4.6 - Carbon dioxide removal section of reforming plant.[2]

require stress relief for all equipment exposed to amine solutions regardless of process temperature. An amine solution is defined by API 945 as concentrations of amine over 2 wt%.

A study by Foroulis of stress corrosion cracking (SCC) of carbon steel in potassium carbonate solutions revealed that SSC does not occur in the absence of carbon dioxide but does occur in carbonate/bicarbonate mixtures produced in carbon dioxide absorption.[6] The strong tendency to stress corrode occurs in the -0.85 to -0.55V(SHE) potential range. Use of potassium metavanadate in concentrations greater than 0.5 wt% (as $NaVO_3$) can prevent SCC. Conversely, arsenite inhibitor/activators promote SCC. Oxygen, usually added to maintain the inhibitor in the active (oxidized) state, will minimize the tendency for SCC. Even though proper inhibition theoretically prevents SSC, most operators require stress relief for process temperatures above 60°C (140°F). This is because SSC can occur rapidly if loss of passivity occurs due to loss of inhibitor or overheating.

Typical acid gas loading for amines are as follows:[3]

Amine	wt%	Rich loading (mol/mol)	Total lean loading (mol/mol)
MEA	15 to 20	0.30 to 0.35	0.10 to 0.15
DEA	25 to 30	0.35 to 0.40	0.05 to 0.07
MDEA	50 to 55	0.45 to 0.50	0.004 to 0.010

Threaded connections should be avoided in acid gas amine solution because the turbulence created by the threaded area causes severe erosion-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 2.4 m/s (8 ft/s), 304L SS (UNS S30403) should be used. Reboiler tubes should be made of 304 (UNS S30400) or 316 (UNS S31600). If seal welding is required, 304L (UNS S30403) or 316L (UNS S31603) should be used.

Some operators limit the reboiler steam inlet temperature to 150°C (300°F).

Overheating of carbonates and amines in reboilers has resulted in violent gas evolution from the solution on the shell side leading to severe erosion-corrosion, particularly of carbon steel tube sheets and in the reboiler discharge (vapor) line. Although austenitic stainless steel tubes also have been used in reclaimers, there is at least one reported case of chloride SCC of these tubes. Regenerator overhead condensers often are carbon steel. In older units there often is sufficient amine carryover (at least 0.5%) so that corrosion in the overhead is inhibited. In newer units carryover is minimized and corrosion, when it occurs, is handled by addition of corrosion inhibitors or use of stainless steel tubes.

The PSA™ unit operates at 10°C to 38°C (50 °F to 100°F) and undergoes 14-minute 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.

2.3 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),[2] which requires a startup 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. As mentioned in Chapter 3, section 2.2, because hydrogen attack is cumulative, the total time the material will be at temperature must be used as a basis for alloy selection.

The ammonia reaction takes place in an internal 304 SS (UNS S30400) basket in which the temperature is about 480°C (900°F). Even though the pressure is about 20.7 MPag (3,000 psig), 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. Conversely, when the converter wall is solid alloy or the inner layer of a multilayer vessel is exposed to high temperature, alloy materials are required either for strength, to resist hydrogen attack, or both. The outer layers of a multilayer vessel are vented to the atmosphere so hydrogen attack is not a problem. The outlet connection usually is hot enough to require chrome steel alloys to resist hydrogen attack. Nitriding also should be considered above 400°C (750°F). Using a nitriding allowance (usually 1.5 mm to 3 mm [1/16 in. to 1/8 in.]) is all that is usually required; however, alloy 600 (UNS N06600), which is resistant to nitriding, 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 stress corrosion cracking has occurred in liquid anhydrous ammonia, it has not been a problem in the process plant because no oxygen is introduced until the ammonia gets into the storage equipment. Ammonia is stored at -33°C (-28°F). It used to be thought that this temperature was too low to cause SCC; however, cracking has been observed recently in ammonia storage vessels. Therefore, stress relief of these vessels is being specified. To avoid SCC of carbon steel equipment used for shipment and subsequent storage, at least 0.2 wt% water is required.

2.4 Methonol 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 in the 260°C (500°F) range 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 (page 100) shows corrosion rates of 11 alloys as a function of temperature in the 50-50 carbon dioxide-hydrogen mixtures common in methanol plants.[7] In addition, metal dusting has been reported in the process boiler of a methanol plant. See the following section for a discussion of metal dusting.

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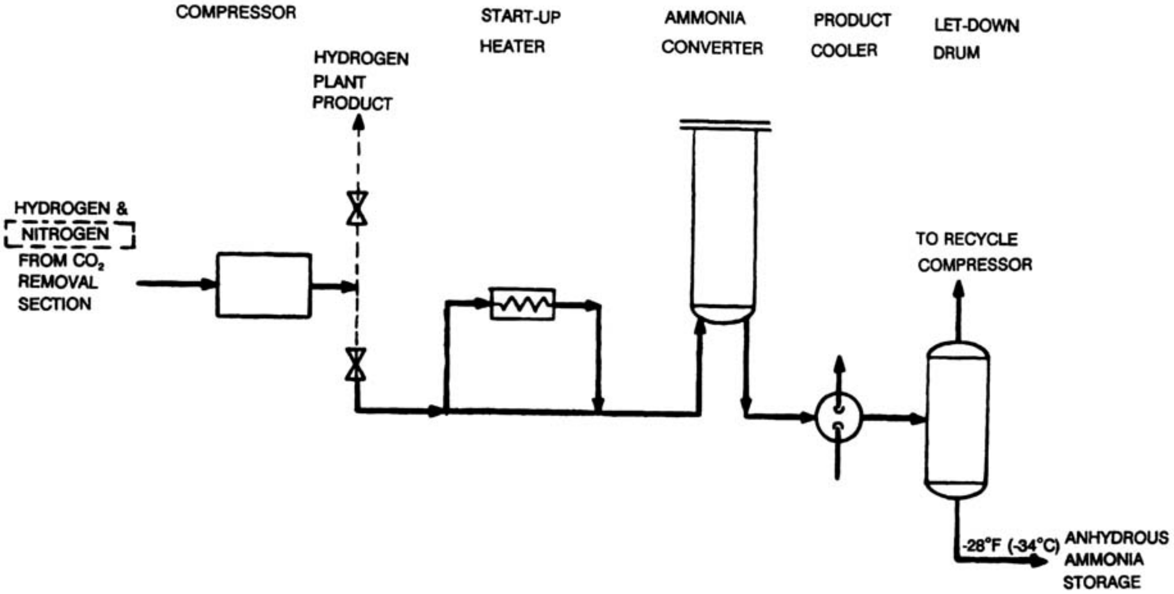


Figure 4.7 - High pressure section of reforming plant.[2]

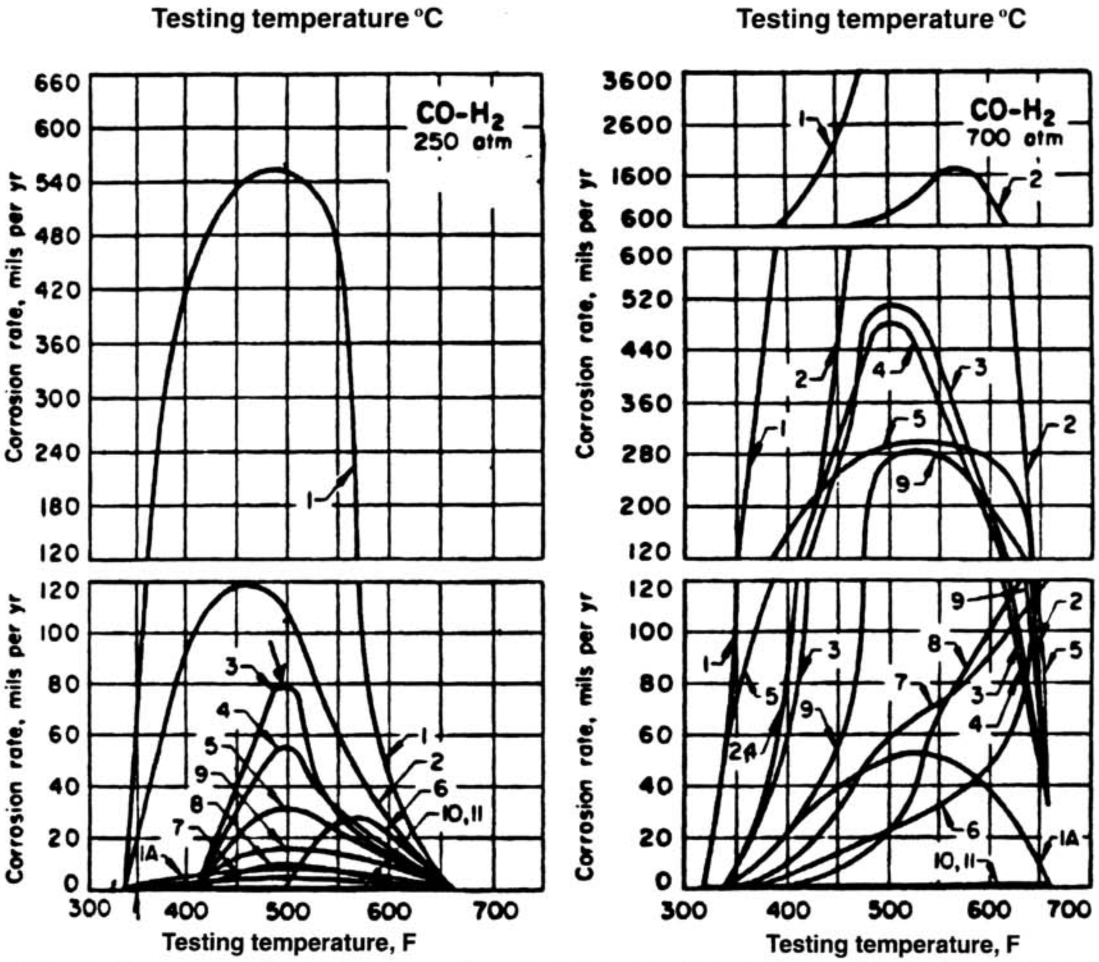
2.5 Other Common Processes

The feed stock in hydrodealkylation units is heated to about 650°C (1,200°F) in a preheat furnace prior to entering the reactor. Above about 590°C (1,100°F) a phenomenon known as 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 wt% to 0.5 wt%) in the form of hydrogen sulfide or mercaptan added to the feed will prevent attack. Aluminizing also has 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 where liquid phosphoric acid exists. At a phosphoric acid concentration of 100%, 304L SS (UNS S30403) is satisfactory to 80°C (120°F), and 316L SS (UNS S31603) is required from 50°C to 107°C (120°F to 225°F).

Phenol is produced by the oxidation of cumene and is followed by cleavage of the oxidation product of phenol and acetone. Solid or clad 304L SS (UNS S30403) is required to resist corrosion in the oxidation vessel, and solid or clad alloy 20 (UNS N08020) often is 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. Conversely, in solvent treating with furfural, some corrosion occurs when the furfural is mixed with water and in the portions where furfural is heated above 215°C (420°F). Where these conditions exist, 304L SS (UNS S30403) is used below 70°C (160°F), and 316L SS (UNS S31603) is used above 70°C (160°F). Where there is a potential for chloride SCC of SS, red brass (UNS C2300), or 70 Cu-30 Ni (UNS C71500), is used at temperatures up to about 93°C (200°F), and alloy 400 (UNS NO4400) is used above. Methyl tertiary butyl ether (MTBE), which is used as an octane enhancer in gasoline, is not corrosive to carbon steel, SS, or aluminum. Conversely, none of the common elastomers, i.e., Viton,™ nitrile, etc., are suitable for MTBE. Some refiners have had success with Kalrez,™ and other proprietary materials. Specially formulated urethanes have been used for vapor seals in storage tanks where PTFE has failed. Viton™ has worked in blends of up to 15% MTBE.



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.[7] (Reprinted with permission from *Metals Handbook*, 8th ed., Vol. 1, Metals Park, OH: ASM)

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5

Underground Piping, Production Gathering Equipment, and Tankage

1. INTRODUCTION

Refinery and production piping usually are designed to ASME B31.3. Atmospheric storage tankage is designed to API 650. Low-pressure tankage is designed to API 620. The design of pipelines containing liquids is covered by ASME B31.4. Guidelines for gas transmission pipeline design are contained in ASME B31.8; however, because of public concern over the large amount of stored energy in gas transmission lines, the U.S. Department of Transportation (DOT) has issued regulations for gas lines (Code of Federal Regulations, Title 49, Part 192). There also are regulations governing liquid lines (Code of Federal Regulations, Title 49, Part 195).

For refineries and production equipment, pipe is purchased to an ASTM or API specification, and very rarely are supplementary requirements added. Supplementary requirements for pipelines almost always are included because pipelines consist of miles of identical material; specifications can thus be tailored to the needs of the job 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 competitive bidding is involved.

2. LINE PIPE

2.1 General

Most line pipe is manufactured by one of four methods:

1. UOE (one pass of submerged arc welding on each side of a long seam),
2. Electric resistance welded long seam,
3. Seamless, or
4. Helical seam (most commonly made using one pass of submerged arc welding on each side).

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

Table 5.1
Minimum Practical Wall Thickness for Thin Wall Pipe

Diameter mm (inches)	Minimum Wall Thickness⁽¹⁾ mm (inches)
58.8 (2.315) (2)	3.2/ 3.9 (0.125/ 0.154)
114 (4.5)	3.9 (0.154)
219 (8.625)	4.0 (0.156) (3)
273 (10.750)	4.8 (0.188)
324 (12.750)	4.8 (0.188)
356 (14)	5.2 (0.203)
406 (16)	5.2 (0.203)
457 (18)	5.6 (0.219) (3)
508 (20)	6.4 (0.250)
610 (24)	6.4 (0.250)
660 (26)	6.4 (0.250)
762 (30)	6.4 (0.250)
813 (32)	7.1 (0.281)
914 (36)	7.9 (0.312)
965 (38)	7.9 (0.312)
1,016 (40)	8.7 (0.344)
1,067 (42)	8.7 (0.344)
1,219 (48)	9.5 (0.375)

2.1.1 UOE Line Pipe

The UOE process for double-submerged arc welded (DSAW) line pipe is schematically shown in Figure 5.1.[1] Plate is prepared then formed into a "U." It is then pressed round into an "O," submerged arc welded and expanded, which is where the "E" comes from. Figure 5.2 shows a typical cross section of a double-submerged arc weld.[2] A minimum of weld passes (in this case, two) is used to maximize production. UOE pipe is available in 406 mm to 1,625 mm (16 in. to 64 in.) diameters. It is the most commonly used pipe, particularly in large diameters, because of its high reliability when the long seam is properly inspected. 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 800 km (500 miles) of test.

2.1.2 Electric Resistance Welded Line Pipe

The process for manufacturing electric resistance welded (ERW) pipe is shown schematically in Figure 5.3.[1] In this process, coils rather than plate are formed, then continuously electric resistance welded. Figure 5.4[2] 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 heat-affected zone; only the light area in the very center is the weld. ERW line pipe is available in 100 mm to 1,220 mm (4 in. to 48 in.) diameters with a 14 mm (0.562 in.) maximum wall thickness. However, it is only cost-competitive in 152

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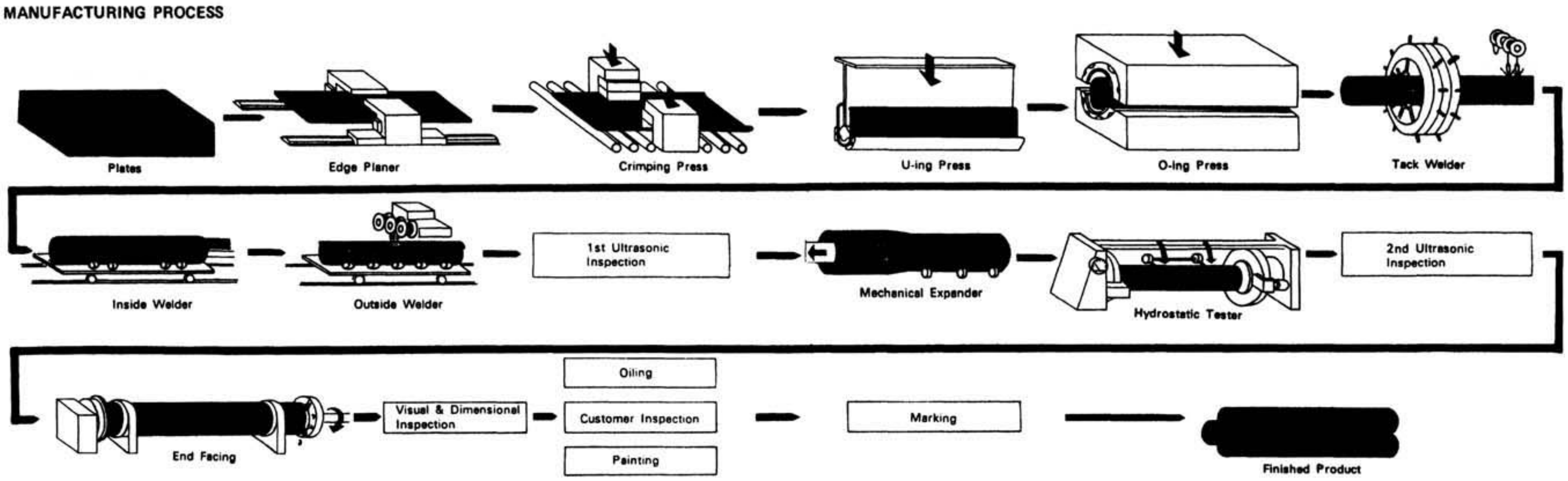
(1) The minimum the mills will offer for submerged arc-welded pipe is 6.4 mm (0.250 in.)

(2) Not practical to electric weld.

(3) Limited by welding at and below this thickness.



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]

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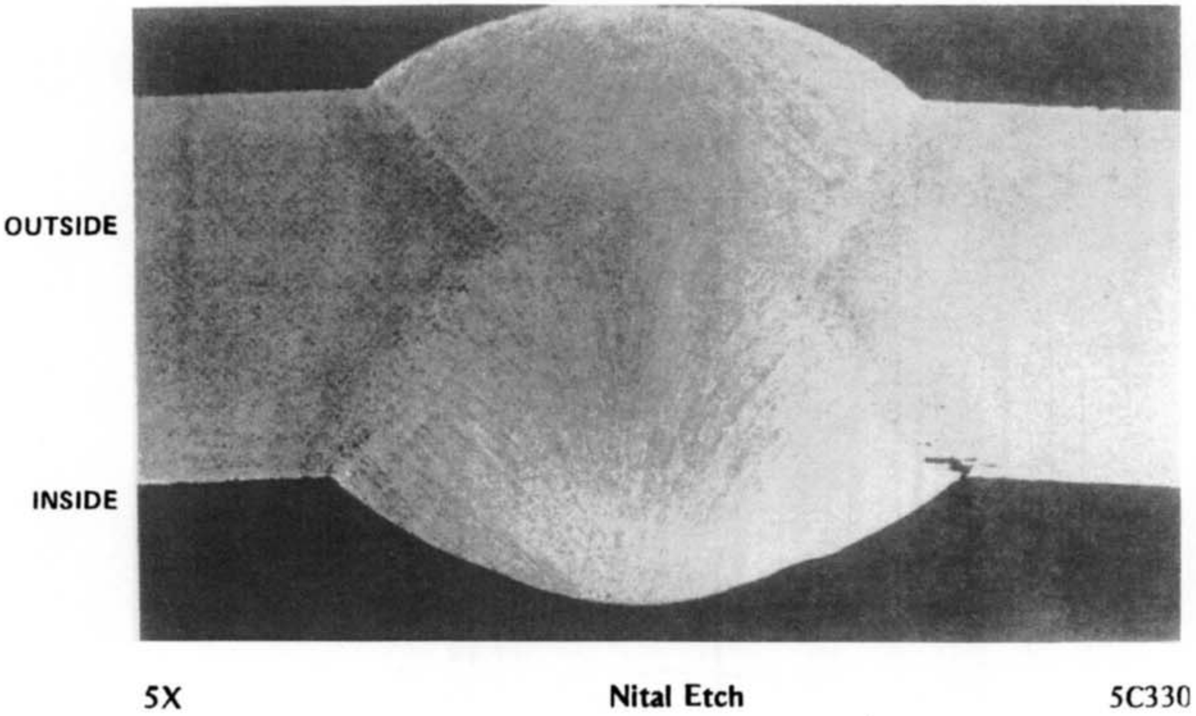

Figure 5.2 - Toe cracks in the HAZ of a DSA weld.[2]
(Reprinted with permission from Sixth Symposium on Line Pipe Research, October 1979. Research sponsored by the Pipeline Research Committee, American Gas Association, Arlington, VA)

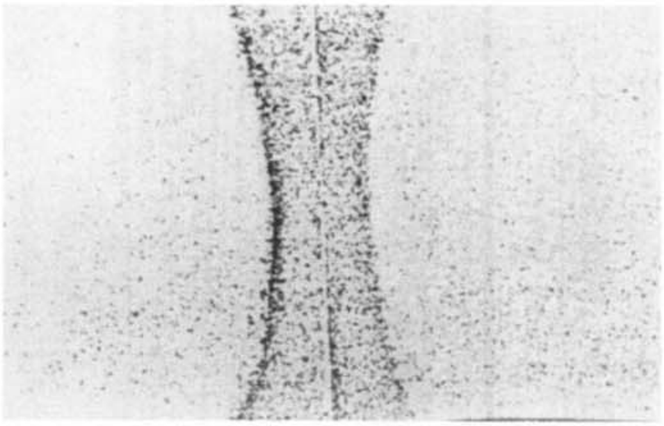

Figure 5.4 - High frequency weld.[2]
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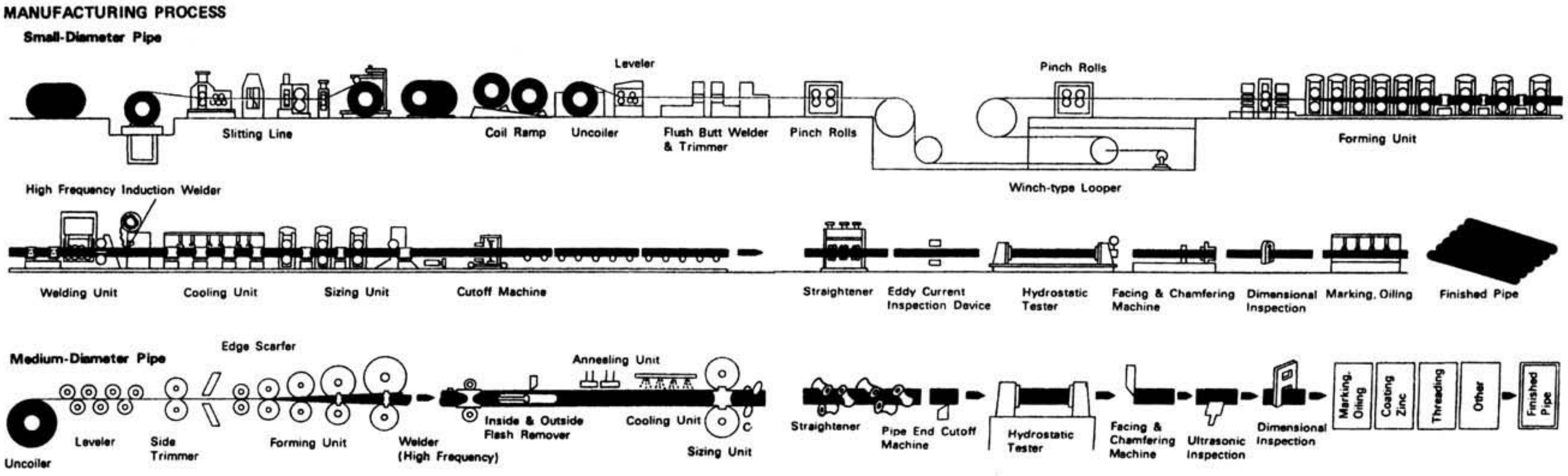

General Description

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]
(Reprinted with permission from Kawasaki Tubular Products, 1978, Kawasaki Steel Corporation, Kobe, Japan)

mm to 660 mm (6 in. to 26 in.) sizes. Although its reliability was low prior to 1970 (hydrostatic test records revealed that about one failure occurred every 16 km [10 miles] of test), it was commonly used because of low cost. With the advent of high frequency ERW, adequate specifications, good mill inspection, and selection of the best suppliers, one can obtain good reliability from ERW pipe. The suppliers who offer a quality product have been able to get gas companies to permit the use of ERW in high pressure gas (9.65 MPag [1,400 psig]) vs the old 1.38 MPag (200 psig) limit. Although the introduction of high frequency welding currents has minimized the defects common to low-frequency, current-welded ERW pipe, they still occur. Therefore, inspection techniques should be stringent enough to make sure the following defects can be identified:

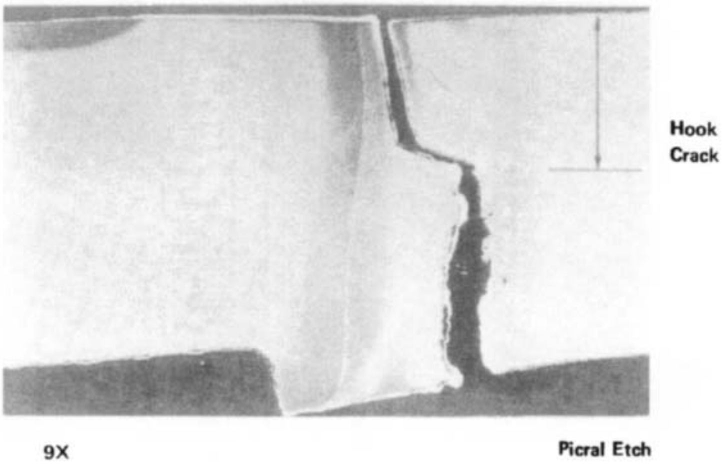

Figure 5.5 - Appearance of a hook crack in ERW weld.[2]
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- Hook cracks - Caused by nonmetallic inclusions at the edge of the material, which follow flow lines of the material as the weld is pushed together during welding (Figure 5.5).[2]
- Penetrators - 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 due to burrs on welding surfaces (Figure 5.6).[3]
- Stitch welds - Intermittent fusion caused by short repetitive variations in the welding heat (Figure 5.7).[4]

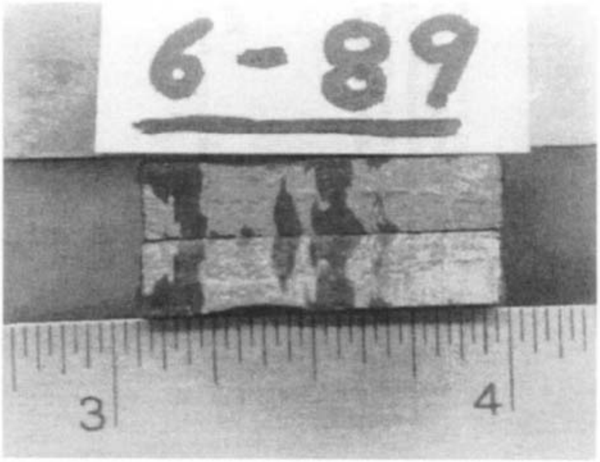


Figure 5.6 - Through wall penetrators in ERW weld.[3]

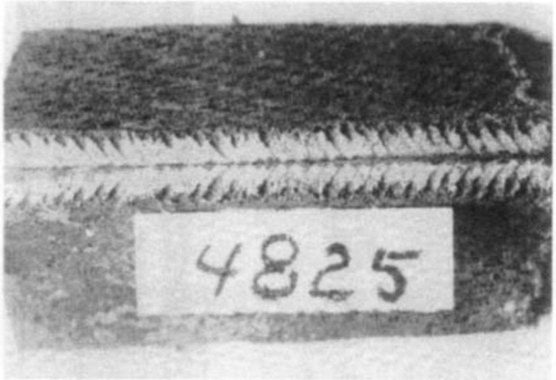
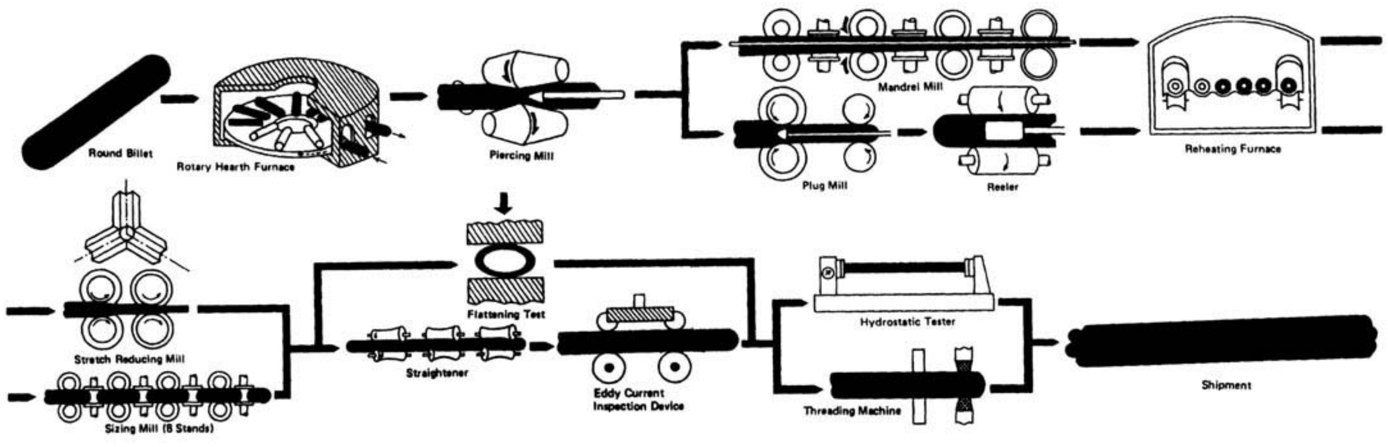


Figure 5.7 - Stitch weld (intermittent fusion) in ERW weld.[4]
(Reprinted with permission from API Bulletin 5TI, "Nondestructive Testing Terminology," 9th ed., May 1987, American Petroleum Institute, Washington, DC)

2.1.3 Seamless Line Pipe

The process for manufacturing seamless line pipe is shown schematically in Figure 5.8.[1] In this process, a heated metal cylinder is pierced then formed into the proper diameter and wall thickness. Seamless pipe is available up through 660 mm (26 in.) diameter, but normally is used only up to 405 mm (16 in.) 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 800 km (500 miles) of test. Some mills produce seamless pipe that has a significantly higher failure rate; it is thus important to ensure adequate quality control.



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 pierced 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 withdrawl 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 the 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]
(Reprinted with permission from Kawasaka Tubular Products, 1978, Kawasaki Steel Corporation, Kobe, Japan)

2.1.4 Helical Seam Line Pipe

The process for manufacturing helical seam line pipe (previously called spiral weld) is schematically shown in Figure 5.9.[1] 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 of the early prejudice against helical seam pipe resulting from unravel failures that occurred many years ago has been overcome. It is available from 152 mm to 2,540 mm (6 in. to 100 in.) diameters, but the smallest diameter commonly used for line pipe is 610 mm (24 in.). Problems sometimes are 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.

2.1.5 Other Pipe Manufacturing Processes

Induction-welded long seam pipe (similar to ERW) normally is used for 50 mm to 100 mm (2 in. to 4 in.) pipe. Continuous (furnace) butt weld pipe is available in 20 mm to 115 mm (0.75 in. to 4.5 in.) pipe; however, it is never used in critical applications because of its very low reliability.

2.2 Specifications for Line Pipe

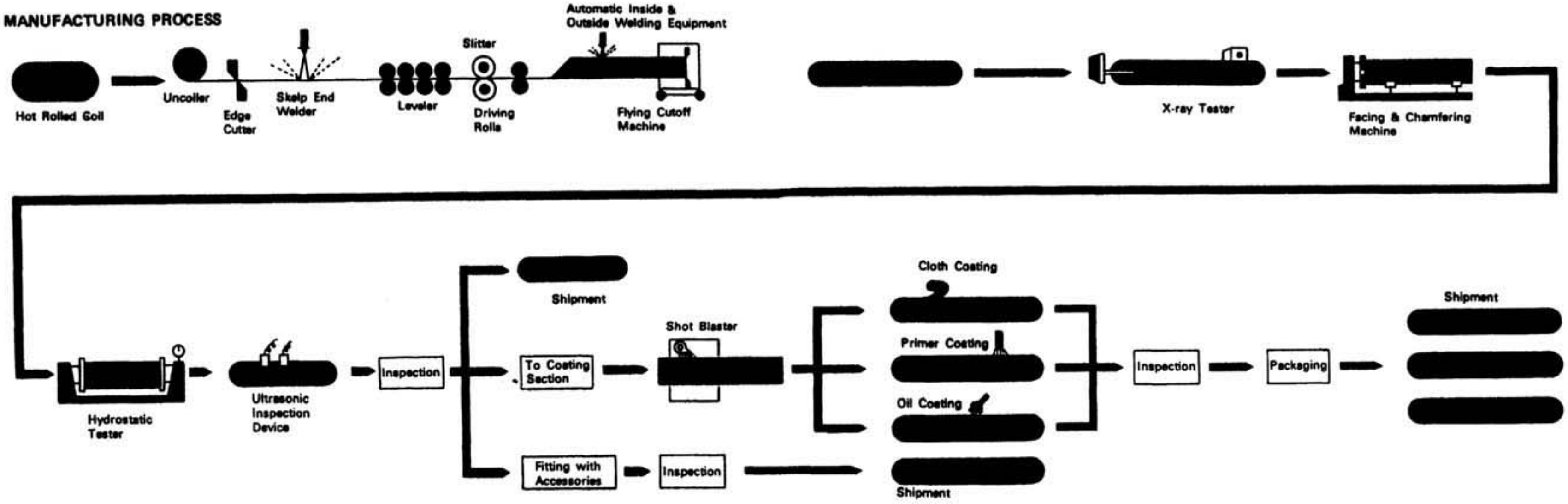
API specification 5L is the principal line pipe specification. It combines the previous API 5L, 5LX, and 5LS. The selection of a grade depends on the strength-to-weight ratio and the pumping costs. ASTM specifications (e.g., A381) often are used for compressor station pipe, particularly for extruded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

- The *low strength grades* in API 5L are A and B. Grade A has a 207 MPa (30 ksi) minimum yield strength, and Grade B has a 241 MPa (35 ksi) 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 X80 grades. The number after the "X" refers to the specified minimum yield strength, i.e., X42 means line pipe with 290 MPa (42 ksi) minimum yield strength. The seamless and welded (ERW, DSAW, and GMA) manufacturing processes are permitted by API 5L. Normally, all grades are 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 also are permitted. In the past 10 to 12 years, 90% of the large-diameter line pipe has been X60 to X70 grades. Recently, Coulson reported on the use of X80.[5] Small amounts of grain-refining alloying additions are used to obtain the desired strength and impact properties of these materials. In general, a minimum preheat (depending on composition and conditions) is required for welding the API X60 and higher-yield strength grades. Matching strength welding electrodes are available for welding the round seams.
- The *helical seam grades* in API 5L range from A to X70. Cold expansion normally is not performed; however, some mills have installed and used expanders successfully.

2.3 Common Supplementary Requirements for Line Pipe

As mentioned previously, specifications to supplement the API requirements normally are written to tailor the line pipe to the specific operating conditions. Appendix D contains two examples of line pipe specifications. Typical requirements are summarized below:

1. Require either vacuum degassing or argon bubbling during steel making to enhance floating of inclusions out of the molten steel. This both improves notch toughness and resistance to hydrogen-induced cracking.
2. Limit cold expansion to 1.5% to avoid degradation of impact properties.



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]
(Reprinted with permission from Kawasaka Tubular Products, 1978, Kawasaki Steel Corporation, Kobe, Japan)

3. Require the hydrostatic test to be at 90% to 100% of the specified minimum yield strength to maximize reliability. Mills often will pay for the pipe that fails in the field even when the pipe is tested at 100% of the specified minimum yield strength.
4. Require radiography of the end of long seams and of all jointer welds (when permitted) per API 1104.
5. Perform ultrasonic examination of long seams at the mill.
6. Require magnetic particle, liquid penetrant, or individual ultrasonic testing of 150 mm (6 in.) of the inside (sometimes the end 150 mm [6 in.] of the outside as well) for X60 and stronger pipe.
7. Prohibit repair of parent pipe after cold expansion because the heat of welding reduces the strength gained from the cold expansion.
8. 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.)
9. When repair is permitted, require radiography for through-wall repairs, magnetic particle examination for other repairs, and re-hydrostatic test for all repaired pipe.
10. Require radiography per API 1104 after forming for skelp welds in helical seam pipe.
11. Require fracture toughness testing based on the design conditions. (See Section 7 in this Chapter).
12. Require residual magnetism to be less than 30 gauss to avoid welding problems.
13. In designing, limit weldolets to 100 mm (4 in.) maximum to minimize stress concentrations and avoid excessive heat input, which destroys the benefits of cold expansion.

3. FITTINGS AND VALVES

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

Specification	Product Forms	Scope
ANSI B16.5	All (also valves)	Standard ASTM materials, dimensions, and pressure temperature ratings
MSS-SP-44	Flanges	Grades F36 through F70, dimensions, chemistry and mechanical properties, but no impacts
MSS-SP-75	All welded fittings except flanges (includes headers)	Grades Y42 through Y70, full materials specification
ASTM A381	Welded pipe [4] (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 (289.6 MPa) through 517.1 MPa (75 ksi), full material specification

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[4] Usually fabricated from HSLA plate, such as A633, Grades C and E or A737.

Note: Other standard specifications exist for low-carbon, manganese, molybdenum, niobium 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 often is specified.

4. ALLOYING ELEMENTS

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

4.1 Chemistry Control

Typical limits for line pipe chemistry are:

- Carbon usually is limited to 0.20% (or lower, e.g., 0.016%) in API X60 to X70 pipe and 0.26% (or lower) in API X52 pipe to enhance weldability. Steels with 0.08% maximum carbon (low-carbon martensite) are used to avoid the need for PWHT in heavy sections.
- Silicon usually is specified as 0.13% to 0.33% in the United States when notch toughness is required. Semi-killed (no minimum silicon) steel is still used in the United States for low-strength steels.
- Manganese often is limited to 0.8% to 1.6%. With less than 0.8% manganese, there is too little manganese to tie up sulfur, although, theoretically, a minimum of 0.4% manganese is needed. Also, a manganese-to-carbon ratio of 4:1 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 3:1 minimum to maximize weldability.
- Nitrogen, if possible, should be limited to 0.009% maximum; however, this usually is possible only with basic oxygen steel. The limit on nitrogen usually is 0.012%. Although some nitrogen is desirable to increase strength, poor base metal and heat-affected zone notch toughness and weld cracking occur as a result of nitride formation when nitrogen is too high. For nitrogen-bearing grades, a 120°C (250°F) preheat for welding usually is required. Where specifications permit nitrogen in excess of 0.01%, the vanadium-to-nitrogen ratio should be specified as 4:1 minimum to avoid embrittlement.
- Aluminum is a deoxidizer and a grain refiner. It also combines with nitrogen to prevent strain age embrittlement. Some specifications require the aluminum-to-nitrogen ratio to be 2:1 or greater to minimize strain-age embrittlement. If aluminum exceeds about 0.05%, it can result in low toughness in weld metal when diluted into the weld metal by high-heat input process, such as submerged arc welding. The low toughness is a result of acicular ferrite formation in the weld. Therefore, aluminum usually is limited to 0.05% maximum.
- 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 usually are limited by cost because double inoculation often is required. Vanadium additions are limited because of poor low-temperature properties, temper embrittlement, and underbead cracking when the concentration becomes too high. PWHT will lower the fracture toughness of vanadium-bearing steels and weld metal, but only reduces toughness of niobium-bearing weld metals.
- Titanium and zirconium occasionally are used as grain refiners. Titanium also is a carbide former and usually is limited to 0.020% to 0.030%. Titanium significantly increases the notch toughness up to 0.020%. However, titanium is harmful to notch toughness when the percentage exceeds 0.040%. The zirconium content usually is 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 usually is less than 0.25% to limit martensite and massive upper bainite formation.
- 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. Misch

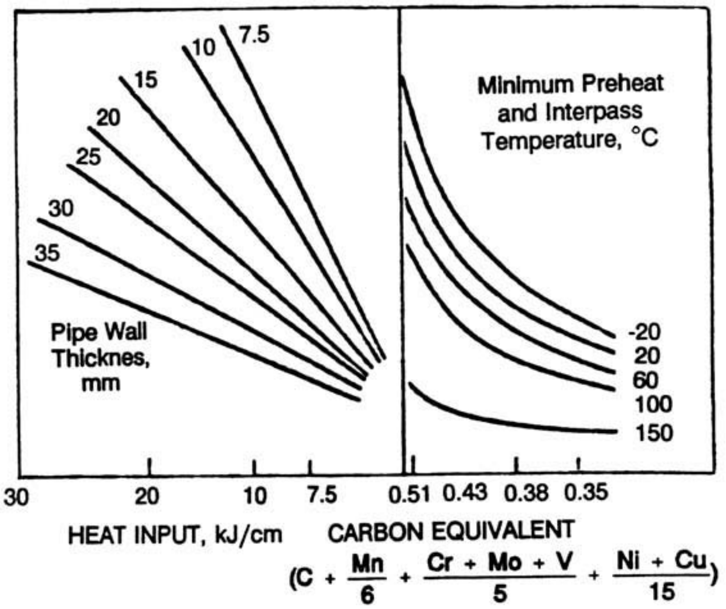

Figure 5.10 - The permissible maximum carbon equivalent for butt welds in line pipe using cellulosic (EXX10) electrodes based on minimum preheat and interpass temperature, pipe wall thickness, and heat input.[6] (Reprinted from *Micro Alloying 75 - Proceedings of Micro Alloying 75 Conference*, October 1, 1975, Union Carbide Corp., Metals Division, New York, NY)

metal is a mixture of elements with atomic numbers of 57 to 71 containing about 50% cerium. Usually, 1.5 times the sulfur level is added. Problems with gas metal-arc welding have been reported when REMs exceed 0.02%.

- Sulfur is kept low (e.g., 0.005% maximum) to enhance notch toughness and resistance to hydrogen-induced cracking. However, when the sulfur is 0.001% or below, weldability problems have occurred in low-heat input processes because of poor fluidity of the weld puddle. Sometimes the sulfur content of the weld filler metal is specified in the 0.01 range to offset the low sulfur in the pipe.

4.2 WELDABILITY CONSIDERATIONS

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 commonly is expressed as the carbon equivalent (CE), defined as either:

$$(1)\ CE = C + \frac{Mn}{4} \quad \text{or} \quad (2)\ C + \frac{Mn}{6} + \frac{(Cr + Mo + V)}{5} + \frac{(Ni + Cu)}{15}$$

Preheat is not required for grades up to API X52 when the CE is less than 0.5 to 0.55 (by definition [1]). Definition (2) is commonly used in specifications. Limiting definition (2) CE to 0.43 for API X60 to X70 grades usually is required. The maximum carbon equivalent, based on preheat and interpass temperature, wall thickness, and heat input (travel speed), can be estimated from Figure 5.10.[6] For example, for 0.42 CE and 25 mm (1 in.) wall pipe, a preheat of 20°C (68°F) would be required for a 12 KJ/cm heat input; however, if the heat input was reduced to 9 KJ/cm, then a 60°C (140°F) preheat would be required.

A refinement to the CE is the parameter P_{cm}, which has been developed to predict hydrogen cracking susceptibility as it relates to weldability. The P_{cm} chemistry parameter, applicable to most low-alloy steels having carbon contents equal to or less than 0.12 wt%, is defined as:

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

The P_{cm} usually is limited to 0.25.
Recently, this approach has been further refined by use of a P_{hm} parameter defined as:

$P_{hm} = P_{cm} + 0.075 \log (H_{ef}) + 0.15 \log (0.017\, K_t\, S_w)$,

where:

H_{ef} = 0.50_{Hf} for cellulosic electrodes
H_{ef} = H_f for low-hydrogen electrodes
H_f = diffusible hydrogen content per 100g of fused metal
K_t = 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
S_w = nominal stress acting on the weld metal, Kgf/mm^2 = ksi/1.42
= $0.050\, R_f$ for R_f less than $20\, S_y$
= $Sy + 0.005\, (R_f - 20\, S_y)$ for R_f greater than $20\, S_y$
S_y = yield strength, kgf/mm^2
R_f = intensity of restraint (kgf/mm^2) = 69 h
h = thickness (mm)

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

Critical T100 (degrees C) = $105{,}000\, (P_{hm} - 0.276)^2$

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

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

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

A third carbon equivalent, CEN, has now become popular. The CEN is defined as:

$$CEN\,(\%) = C + F\left(\frac{Mn}{6} + \frac{Si}{24} + \frac{Cu}{15} + \frac{Ni}{20} + \frac{Cr + Mo + V + Nb + 5B}{5} \right)$$

where: F = 0.75 + 0.25 than (20 [C - 0.12]), thus F = 0.54 for 0.06% C and 1.00 for 0.21% C

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(5) Boron less than 0.001 wt% can be left out of the P_{cm} calculation.

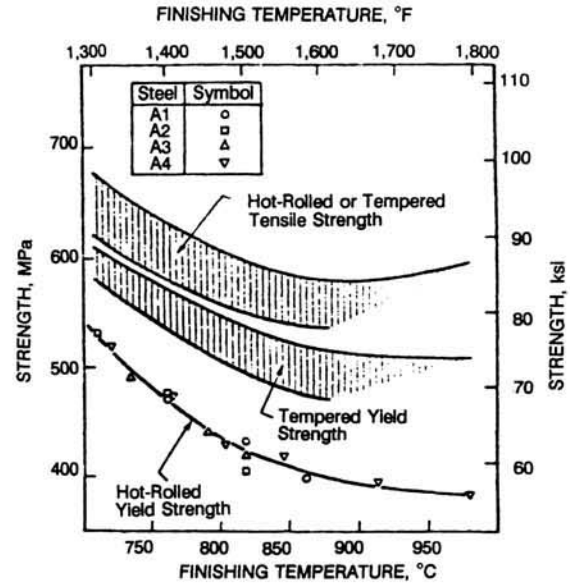

Figure 5.11 - Effect of finishing temperature and tempering on the strength of steels A1 to A4.[7] (Reprinted from *Micro Alloying 75 - Proceedings of Micro Alloying 75 Conference*, October 1, 1975, Union Carbide Corp., Metals Division, New York, NY)

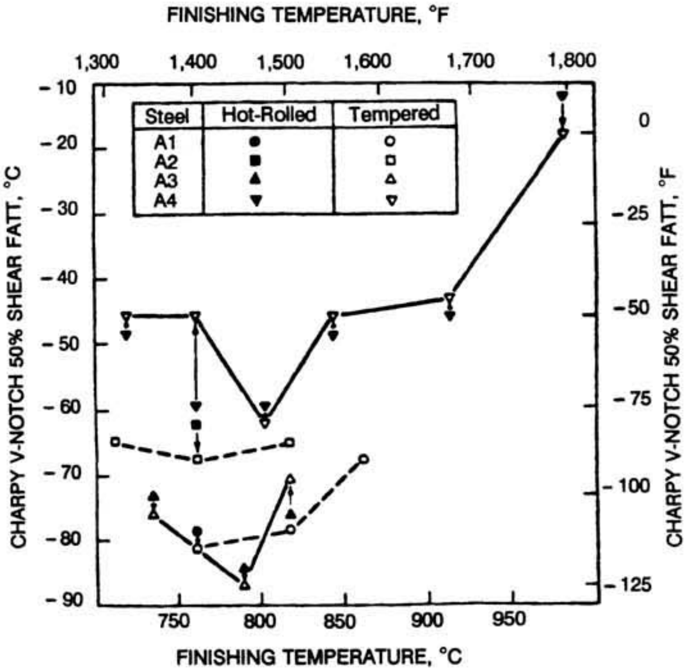

Figure 5.12 - How finishing temperature affects the Charpy V-notch 50% shear fracture-appearance-transition temperature (FATT) of steels A1 to A4.[6] (Reprinted from *Micro Alloying 75 - Proceedings of Micro Alloying 75 Conference*, October 1, 1975, Union Carbide Corp., Metals Division, New York, NY)

5. PROCESSING LINE PIPE

Three major kinds of steel are used for large-diameter line pipe operating under extreme climatic conditions: (1) controlled rolled plate of a precipitation-hardening type containing niobium and vanadium, (2) controlled rolled plate of an acicular-ferrite type, and (3) super-fine grain quenched and tempered plate. Controlled rolling is most common and consists of three stages: (1) simultaneous deformation and recrystallization, (2) low-temperature austenite deformation, and (3) deformation in the mixed austenite-ferrite region.

In the first stage above 1,000°C (1,830°F), austenite grain size is reduced by repeated deformation and recrystallization. In the second stage, between 950°C (1,740°F) and the A_r 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 A_r 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[7] and 5.12;[7] however, optimum mechanical properties occur at a finish rolling temperature of about 810°C (1,490°F). At higher finish-rolling temperatures, bainitic structures appear, causing a deterioration of the fracture appearance transition temperature. With finish-rolling temperatures below 750°C (1,380°F), the brittle fracture resistance also deteriorates.

6. BENDING

High strength line pipe commonly is shop-induction bent. Pipe used for bends must be thick enough to allow for thinning that will occur during bending. Thickness usually is checked ultrasonically after bending. For longitudinally welded pipe, the weld is placed on the neutral axis of the bend. There is a slightly harder and thicker zone in the transition between the bend and the tangent piece. Also, cracking has oc-

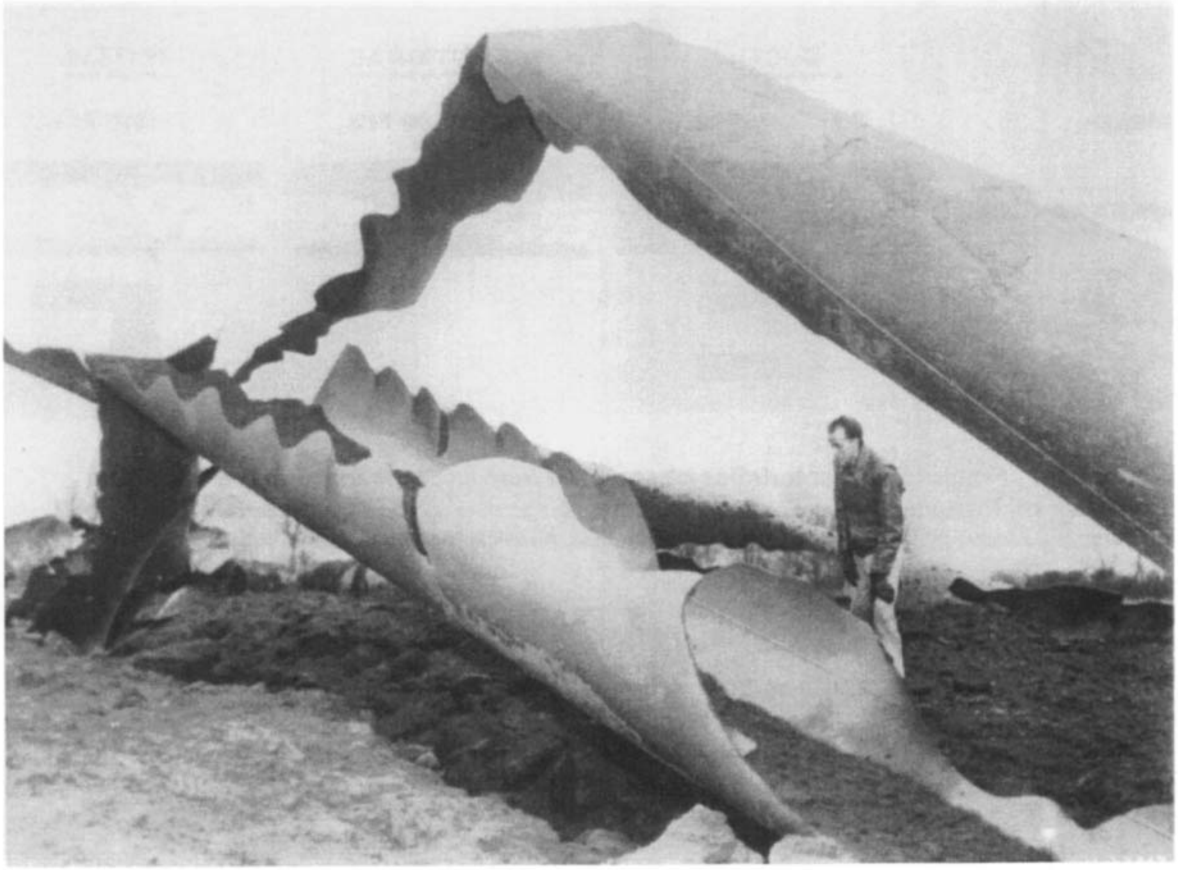

Figure 5.13 - Long distance rupturing of piped tested with gas.[8]
(Reprinted with permission from the Lincoln Electric Co.)

curred as a result of copper contamination on the surface of induction bent pipe; therefore, copper bending shoes should be avoided.

It is important to control carefully bending parameters, such as bending speed, temperature, and water quench. Specifications usually include tests to ensure mechanical properties are not degraded below the minimum requirements and surface inspection, e.g., magnetic particle inspection to ensure no defects have initiated. As mentioned previously, niobium must be greater than 0.025% to prevent a drop in yield strength during induction bending. Many organizations use the International Pipe Association's Voluntary Standard for Induction Bending of Pipe (IPA-VIBS-86) as a basis for a bending specification.

The limits on cold bending of line pipe are contained in Paragraph 841.231 of ASME B31.8. As with cold expansion discussed previously, the maximum strain permitted is limited to a very low level to avoid loss of toughness, etc. For carbon and low alloy steel other than microalloyed steels, such as line pipe, the strain usually is limited by stress corrosion cracking considerations. For example, NACE International MR0175 limits the strain to 5% to avoid sulfide stress cracking (SSC). The strain in a bend can be calculated from the following equation:

$$e_o = \frac{1}{\frac{2R_i}{t} + 1}$$

where:

e_o = the strain on the outside fibers
R_i = the inside radius of the bend
t = the thickness of the pipe

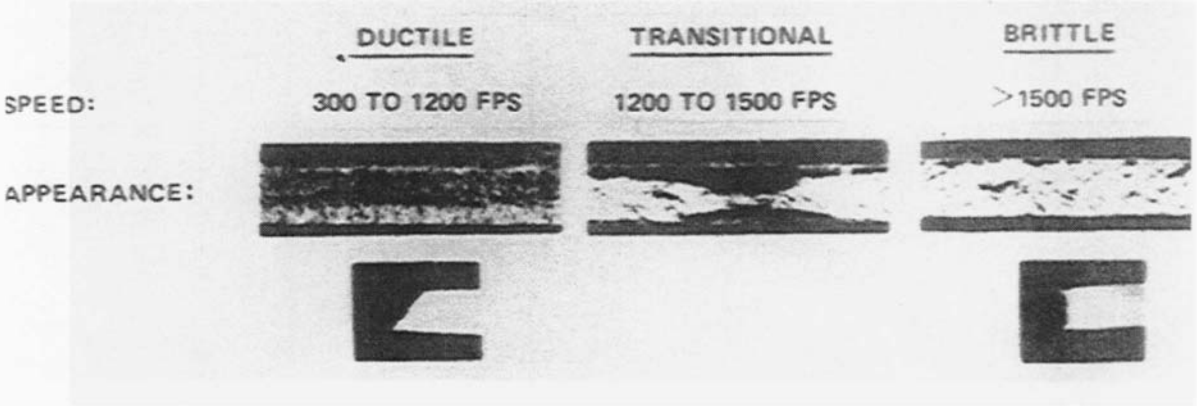

Figure 5.14 - Fracture characteristics observered from line pipe through the transition temperature. [2] **(Reprinted with permission from Sixth Symposium on Line Pipe Research, October 1979, Research sponsored by the Pipeline Research Committee, American Gas Association, Arlington, VA)**

7. FRACTURE

Long pipeline fractures such as the one shown in Figure 5.13[8] can occur in either a brittle or a ductile manner. The fracture appearance and the speed of fracture of ductile and brittle modes are quite different (as shown in Figure 5.14).[2] Various standards have minimum requirements for fracture control. The common ones in the United States are:

- API 5L Appendix SR 5 covers Charpy V-notch testing on pipe with diameters of 115 mm (4.5 in.) or greater. The average shear value of three specimens shall not be less than 60%, and the all heat average shall not be less than 80%.
- API 5L Appendix SR 6 requires 40% minimum shear in a drop-weight tear test on 80% of the heats for 508 mm (20 in.) diameter or larger, API X52 or stronger pipe.

The requirements for Canada are contained in Canadian Standards Association - Z184. Code requirements are, of course, subject to change. In addition to the United States and Canada, a number of other countries have regulations containing specific requirements. Most users specify more than the minimum toughness required by the governing codes or regulations.

7.1 Brittle Fracture

Brittle fractures of line pipe typically follow a sinusoidal path, as shown in Figure 5.15.[2] A high-speed photograph of brittle fracture (Figure 5.16)[2] reveals the advancing tip is well ahead of any significant deformation on the pipe; the crack travels faster than the energy in the pipe can be released. The longest recorded brittle fracture was 13 km (8.1 miles). It occurred in 1960 on a 760 mm (30 in.) diameter API X56 line being gas tested at 60% yield. Research by Battelle reveals that brittle fractures can be avoided in steels other than quenched and tempered ones by specifying 85% average shear area in a drop-weight tear test at the minimum service temperature.(6) This is considerably more stringent than API 5L Appendix SR 6.

Figure 5.17 shows that the % shear in a DWTT only differs slightly from that observed in full scale tests.[2] Meeting the 85% shear criterion also assures that propagating ductile fracture will be arrested. Since the DWTT is applicable only to the pipe base metal, Charpy V-notch test criterion (applicable to both weld

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(6) See API RP5L3 for details of the DWTT.

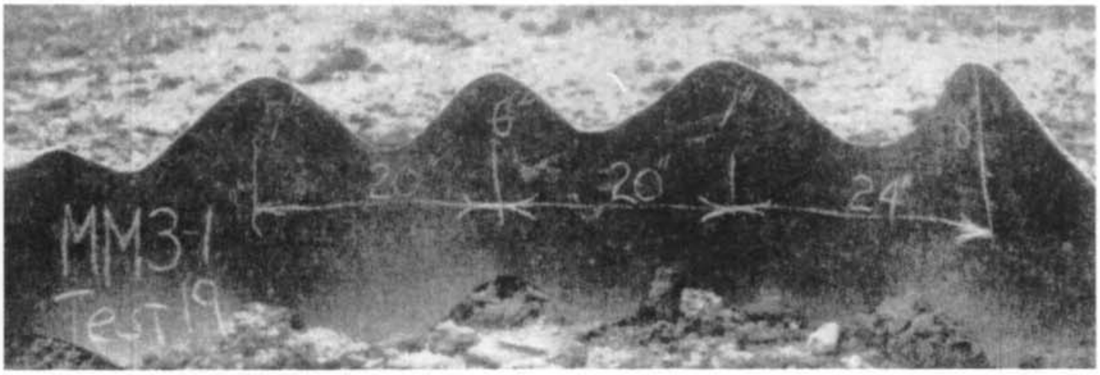

Figure 5.15 - Sinusoidal brittle fracture.[2]
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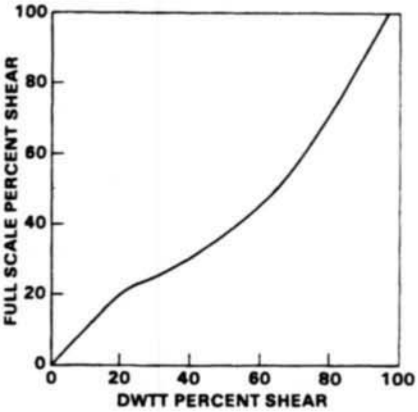


Figure 5.17 - Relationship between DWTT percent shear and full-scale pipe percent shear of the fracture surface.[2] (Reprinted with permission from Sixth Symposium on Line Pipe Research. October 1979, Research sponsored by the Pipeline Research Committee, American Gas Association, Arlington, VA)

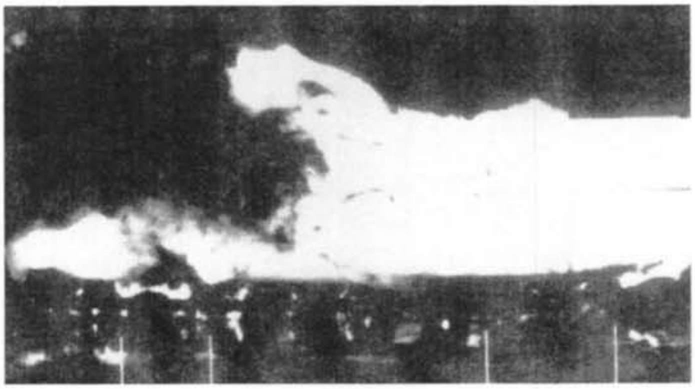


Figure 5.16 - Photo of brittle fracture from high speed movie (3,000 frames/s).[2] (Reprinted with permission from Sixth Symposium on Line Pipe Research. October 1979, Research sponsored by the Pipeline Research Committee, American Gas Association, Arlington, VA)

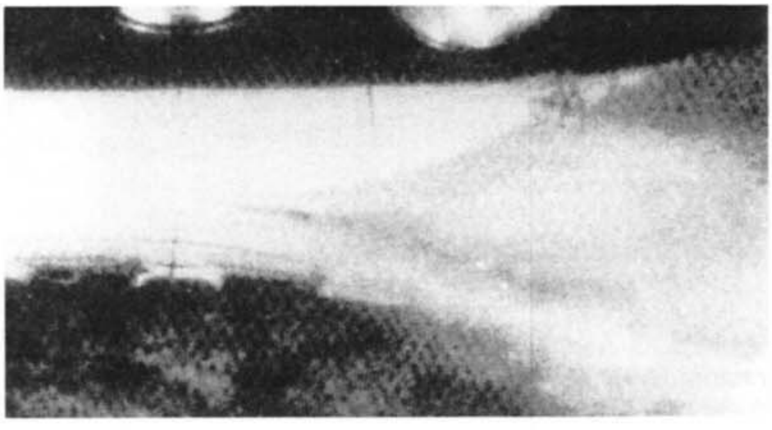
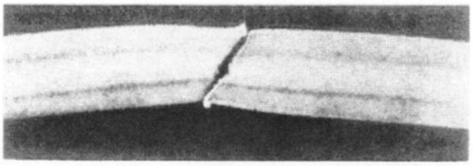
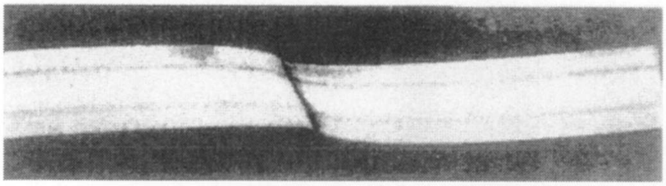


Figure 5.18 - Photo of ductile fracture from high speed movie (3,000 frames/s).[2] (Reprinted with permission from Sixth Symposium on Line Pipe Research, October 1979. Research sponsored by the Pipeline Research Committee, American Gas Association, Arlington, VA)

Figure 5.19 - Ductile fracture of large diameter line pipe showing scalloped fracture edges.[2] (Reprinted with permission from Sixth Symposium on Line Pipe Research, October 1979. Research sponsored by the Pipeline Research Committee, American Gas Association, Arlington, VA)



"Tearing" Shear



"Propagating" Shear

Figure 5.20 - Section across two types of ductile fracture.[2] (Reprinted with permission from Sixth Symposium on Line Pipe Research, October 1979. Research sponsored by the Pipeline Research Committee, American Gas Association, Arlington, VA)

metal and pipe material) commonly is used to assure that ductile fracture will not propagate. The Charpy V-notch approach is discussed in the next section.

7.2 Ductile Fracture

Figure 5.18 shows a high-speed photograph of a line pipe ductile fracture.[2] 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.[2] Ductile fractures do not normally propagate; however, if the 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 300 m (1,000 ft). It occurred in the late 1960s on 915 mm (36 in.) 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 for a 10 mm x 10 mm specimen calculated by the following equation:[9]

$$E_{req.} = K\sigma^2 (Rt)^{1/3}$$

where:

K = 3.56×10^{-5} for metric units and 1.08×10^{-2} for English units
σ = hoop stress, MPa (ksi)
R = pipe radius, millimeters (in.)
t = pipe wall thickness, millimeters (in.)
$E_{req.}$ = Charpy V-notch plateau energy for full size specimen, Joules (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 760 mm, 915 mm, and 1,065 mm (30 in., 36 in., and 42 in.) diameter pipe calculated from this equation are shown graphically in Figure 5.21[6] (A_c for a 10 mm x 10 mm specimen = 80 mm^2 [0.1237-in.^{2}]). The limitation of the Charpy V-notch test is that it is not a full thickness test, whereas the DWTT is. This means that for thicknesses over about

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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 has proposed that for certain pipe geomeries, yield strengths, and stress levels, the Charpy energy required to provide fracture arrest is given by the following formula:

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

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

σ_H = operating stress level (ksi)

R = pipe radius (in.)

t = pipe thickness (in.)

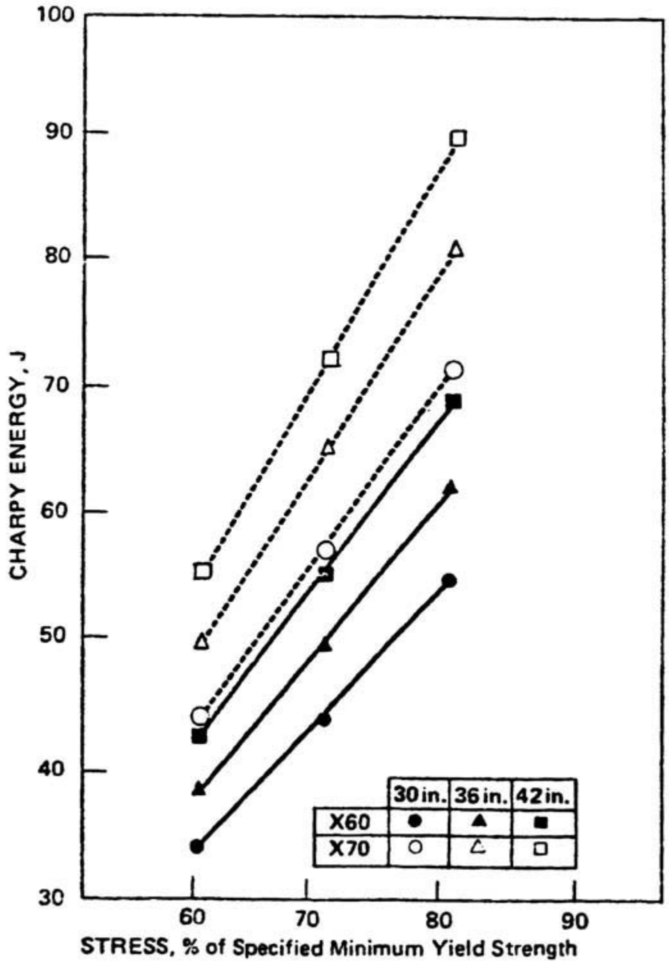

Figure 5.21 - The Charpy V-notch energy needed to produce fracture arrest (after Maxey).[6]
(Reprinted from *Micro Alloying* 75 - *Proceedings of Micro Alloying 75 Conference*, October 1, 1975, Union Carbide Corp., Metals Division, New York, NY)

16 mm (5/8 in.), compensation in the form of increased energy absorption requirements often is specified for thick pipe. It has been recommended that the value calculated from the Battelle equation be increased by 30% when the applied stress is more than 350 MPa (50.8 ksi). Furthermore, the validity of the Battelle equation for X80 material has been questioned. Ongoing research indicates that new criteria of specific fracture energy, crack tip opening angle and specific DWTT energy should be used in lieu of Charpy V-notch energy when designing against ductile fracture in X80 pipe.

When a submarine pipeline is to be installed using a lay barge, the yield strength usually is used for the stress in equations for calculating the fracture toughness requirements. In addition, when the longitudinal stress due to laying exceeds 3/4 of the minimum specified yield strength of the pipe, the minimum yield strength of the round seam weld metal has been required to be 34.5 MPa to 68.9 MPa (5 ksi to 10 ksi) above the minimum yield strength of the pipe. This prevents concentration of the strain in the round seam weld metal, which has resulted in fractures occurring during pipe laying.

Work sponsored by the AISI Committee of Large Diameter Line Pipe Producers yielded an equation similar to Battelle's.[10] 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 which form a chevron pattern. Splits occur in controlled rolled steel but have not been found in quenched and tempered steels. 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 NKK appears to reduce the incidence of splitting or separating. Where splits cannot be avoided, crack arrestors have been proposed. Crack arrestors can be higher toughness pipe, thicker pipe, steel sleeves or glass fiber bands. However, glass fiber bands have not been successful when the fracture ductility (fracture appearance) is in the range of 2% to 15% shear. 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.

8. INTERNAL CORROSION OF PIPING

High-strength line pipe often is used for transporting oil or natural gas, whereas lower-strength pipe often is used for water lines. ERW pipe is subject to grooving corrosion in the weld zone. This can be prevented by limiting the sulfur to 0.012% maximum and by normalizing at 900°C (1,650°F).

Corrosion in water lines primarily is a function of oxygen content in the 4 to 10 pH range. If oxygen is mechanically removed (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 are present, 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 years, depending on the adequacy of the initial surface preparation and the specific type of coating. Internal cathodic protection(7) usually is 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 gas lines, corrosive constituents, such as water, carbon dioxide, and hydrogen sulfide,(8) usually are reduced to a very low level before the fluid enters the line. For oil lines, the water content is limited to 1% maximum.(9) The lost efficiency required to pump the unwanted constituents and the extra wall thickness required for corrosion allowance cannot usually be economically justified. Even with cleanup systems, some water will get into pipelines. Efird and Jasinski have shown that the algebraic product of the wt% total acid number is inversely proportional to the corrosion rate of steel in oil lines containing brine.[11] Corrosion inhibitors usually are added to oil lines when corrosion is anticipated by water settling in low spots, etc. Gas lines usually are 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 done at the wellhead, severe corrosion may occur. The severity of corrosion is a function of the $ppH_2S/ppCO_2$ ratio in wet (i.e., liquid water present) natural gas systems. When this ratio exceeds a certain value, corrosion is controlled by the iron sulfide film that forms on the metal surface. When an iron sulfide film forms on the surface (H_2S dominated system), carbon steel with suitable corrosion inhibitors is adequate in lieu of corrosion-resistant alloys in most cases. This ratio has been reported to be from 1/5,000 to 1/50. Therefore, experience should be checked to determine if carbon steel will be adequate if corrosion inhibitors are used. In the absence of experience to the contrary, most users specify carbon steel in conjunction with inhibitors when the H_2S/CO_2 ratio exceeds 1/50. In order for inhibitors to work the velocity must be

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(7) The reduction of corrosion by shifting the electrochemical corrosion potential of the metal toward a less oxidizing potential by applying an external electric current, i.e., by making it a cathode in an electrochemical circuit.

(8) Typical maximums are water: 112 kg/million std m^3 (7 lbs/million std. ft^3), carbon dioxide: 2% and hydrogen sulfide: 4 ppm.

(9) Corrosion in oil lines is considered water independent if the water is between 0.1 and 1%. Limits on vapor pressure for oil pipelines are used to preclude the presence of corrosive gases.

limited according to the following equation from API RP 14E:

$$V_e = \frac{C}{(\rho_m)^{1/2}}$$

where:

V_e = velocity in m/sec (ft/s)

ρ_m = gas/liquid mixture density in kg/m^3 (lbs/ft^3)

C = empirical constant usually taken as 988 in metric units (100 in English units)(10) for corrosive systems and 1,482 to 1,976 in metric units (150 to 200 in English units) for inhibited systems in continuous service. Salama reports that a constant as high as 4,446 in metric units (450 in English units) is used where solids are not present and pressure drop is not a concern.[12]

An exception to the use of carbon steel with inhibitors when the H_2S/CO_2 ratio exceeds 1/50 would be on an offshore system where the injection of inhibitors may be impractical due to the configuration of the piping, or where ultra high reliability is desired for the line from the platform to the shore. Another exception would be where the mol% H_2S is in the order of 50%; this is in the concentration range where elemental sulfur can form. In the latter case, corrosion is accelerated significantly because under deposit corrosion occurs below the molten sulfur.

When the H_2S/CO_2 ratio is less than 1/50 (CO_2 dominated system), Figure 4.5 in Chapter 4 can be used to estimate corrosion rate on carbon steel. As mentioned in Chapter 4, the higher corrosion rates are based on the deWaard-Lotz equation, which are derived from laboratory tests.[13] DeWaard and Lotz state that calculated rates are affected by the presence of oil, air, scale and the system pH. Corrosion is low when there is more than 15% oil (defined as greater than 50% by weight of C_5+) and there is less than 20% water. Under these conditions, the metal surfaces can be continuously wetted with an oil film, provided the velocity is greater than 1 m/s (3.3 ft/s). Corrosion can still occur in stagnant areas, such as low points, or if only light hydrocarbons are present. Every precaution should be taken to exclude air because it will cause the formation of carboxylic acids, which accelerate corrosion significantly. As mentioned in Chapter 4, the lower corrosion rates in Figure 4.5 are typical of those in systems with scale on the surface. The pH-dependent

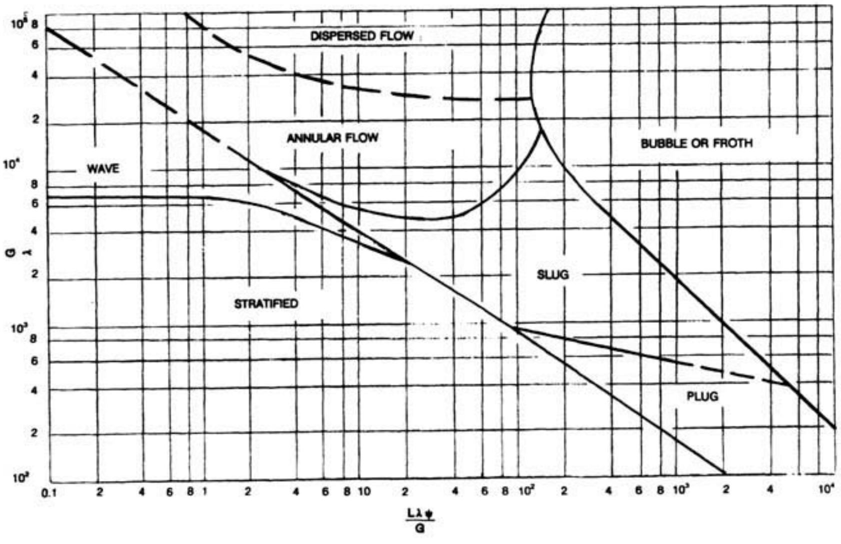

Figure 5.22 - Gas/liquid phase flow.[15]
(Reprinted with permission from "Simultaneous Flow of Oil and Gas," *Oil and Gas Journal*, July 26, 1954)

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(10) Sand entrainment, which accelerates the erosion-corrosion, will reduce the C value significantly.

term that Markin has added to the deWaard-Lotz equation can be used to estimate whether or not a well is corrosive. In addition, Markin has dealt with the effect of mineral deposits, such as calcium and iron carbonates.[14]

In the temperature range where erosion-corrosion occurs in CO_2 dominated systems (above 70°C to 250°C [160°F to 480°F])(11) and in H_2S dominated systems where inhibitors are used, annular flow conditions (see discussion below) are preferred. The adequacy of corrosion inhibitors to prevent corrosion in CO_2 dominated systems is questionable, particularly where annular flow conditions do not exist. Conditions to obtain annular flow, as well as other fluid flow regions, can be determined by use of the graph in Figure 5.22[15] in which the parameters are:

G = mass velocity of the gas phase
in lbs/ h/sq ft of total pipe cross-sectional area
$\lambda = [(P_G/0.075)(P_L/62.3)]^{1/2}$
P_G = density of gas in pounds per cubic ft
P_L = density of liquid in pounds per cubic ft
L = mass velocity of the liquid phase in lbs
per h per sq ft of total pipe cross-sectional area
$\psi = (73/v)[\mu_L(62.3/P_L)^2]^{1}$
v = liquid surface tension in dynes per cm
μ_L = liquid viscosity in centipoise

Even when the system is designed for annular flow, long-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 about 3.0 m/s to 6.1 m/s (10 ft/s to 20 ft/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 28 kPaa (4 psia). Three-phase corrosion inhibitors often prove practical in gas-oil-water systems. Regardless of the type of inhibitor selected, a monitoring system should be installed to check the effectiveness of the inhibitor.

SS is used when velocities exceed about 6.1 m/s (20 ft/s), or bubble or dispersed flow conditions exist. Martensitic SS has performed well, but austenitic SS (e.g., 304L [UNS S30403]) is 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. In addition, the corrosion resistance of martensitic SS is greatly reduced when tempering is done in the 400°C to 590°C (750°F to 1,100°F) range. Where the danger of pitting or stress corrosion cracking from chlorides makes austenitic SS (e.g., 304L [UNS S30403]) a questionable choice, super SS such as UNS S32205 (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 S32205 is reported to be limited to a maximum hydrogen sulfide partial pressure of about 34.5 kPaa (5 psia) at a sodium chloride concentration of one gram per liter at 80°C (176°F) and a pH of 2.7. Therefore, suppliers of super SS should be consulted before selecting one of these materials.

Published data of the resistance of super SS to stress corrosion cracking are shown in Figure 1.19. Resistance to localized corrosion (pitting and crevice corrosion) is shown in Figures 1.18 and 3.19. However, the suppliers of the particular type of super SS should be consulted before selecting one of these materials. Both austenitic and super SS have excellent resistance to erosion-corrosion in velocities up to 26 m/s (85 ft/s). Usually, copper-based alloys are not considered because of poor resistance to hydrogen sulfide,(12) poor resistance to erosion, and low strength. Prevention of corrosion by coatings usually is impracti-

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(11) Above 250°C (480°F) an iron oxide film forms, and inhibitors are not particularly effective.

(12) In copper base alloy gas lines, hydrogen sulfide should be limited to 6.9 milligrams/m ^{3} (0.3 grains per 100 std ft^3). or 4.8 ppm, 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.

cal 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 about 4,480 kPag (650 psig).

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

Transporting synthetic gas has resulted in stress corrosion cracking (SCC) in 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 for preventing this type of SCC.

8.2 Sulfide Stress Cracking

Sulfide stress cracking (SSC) occurs in pipelines, as well as refineries and production wells, as discussed in the previous chapters. The same methods discussed previously (i.e., limiting the macrohardness of welds to HRC 22, or the microhardness of welds to 248 H_v10),(13) are used to avoid failure. However, these limits will not prevent all forms of cracking due to hydrogen sulfide as discussed below. 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 SSC can be estimated by following the procedure in NACE Standard TM0177. 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 in 30 days.

Hydrogen generated from corrosion can cause problems when it recombines in the steel. This results in hydrogen blisters in low-strength steel (e.g., API X42) or a cracking phenomenon called hydrogen-induced cracking (HIC), which is simi-

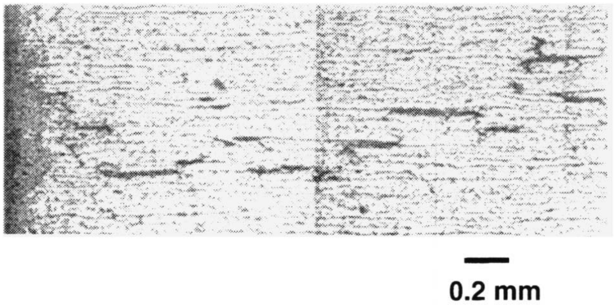

Figure 5.23 - Optical micrograph of HIC penetrating the examined surface (x-z) in the specimen Y.[16]

(Reprinted with permission from "The Test Method of Hydrogen Induced Cracking of Rolled Steels under Wet Hydrogen Sulfide Environment," *Sumitomo Search*, November 1975, Tokyo, Japan)

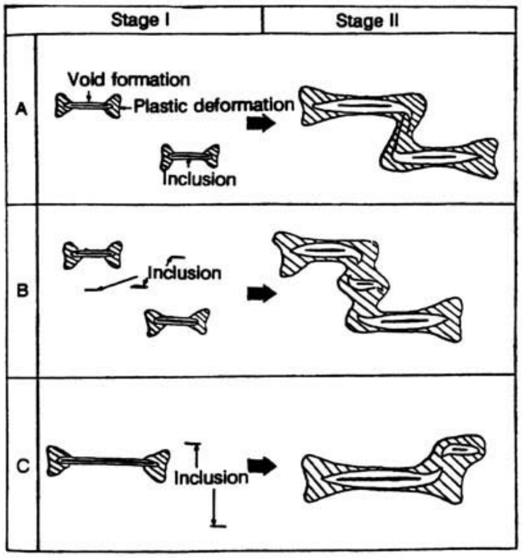

Figure 5.24 - Schematic representation of step-wise cracking process.[16]

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.

(Reprinted with permission from "The Test Method of Hydrogen Induced Cracking of Rolled Steels under Wet Hydrogen Sulfide Environment," *Sumitomo Search*, November 1975, Tokyo, Japan)

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(13)Work by TWI indicated that although 248 H_v10 is re quired for the surface exposed to the corrodent, 275 H_v10 is satisfactory for the side not exposed to the corrodent.

lar in appearance to lamellar tearing(14) in medium-strength steels (e.g., API X60). In contrast to SSC (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,[16] and a schematic representation of this stepwise cracking phenomenon is shown in Figure 5.24.[16] The susceptibility to attack is a function of the manganese sulfide stringer morphology. Elongated stringers (or wafers) are most susceptible, whereas lozenge (ellipsoidal) shapes (Type I) are least susceptible. Relative susceptibility to stepwise cracking can be estimated by following the test procedure in NACE Standard TM0284, which consists of exposing an unstressed specimen in hydrogen sulfide-saturated (pH 5) synthetic seawater at ambient temperature and pressure for 96 hours. Low finishing temperatures in thermomechanical rolling can be detected easily 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,
- Requiring 0.25% to 0.3% copper and limiting the sulfur to 0.015% in steel for environments with a pH greater than 5,
- Calcium-argon treating the steel to control the shape and amount of inclusions to produce material with sulfur contents of 0.0009% maximum (9 ppm) and hydrogen 1.5 ppm maximum. As discussed in section 4.1 on chemistry control, unfortunately, steels with very low sulfur levels are more susceptible to cracking during welding than steels with high sulfur levels (0.005% and above).

9. EXTERNAL CORROSION OF UNDERGROUND PIPING

Buried pipelines are subject to external corrosion from groundwater and highly conductive soils. The corrosivity of soils often is estimated based on soil resistivity measurement. The most common measurement method utilizes the "Wenner" four-pin method (ASTM G57). This is used in conjunction with a suitable voltmeter, ammeter, or galvanometer to determine the average resistivities at a desired depth. A general relationship between corrosivity and soil resistivity is:

Soil Resistivity (ohm-centimeter)	**Corrosion Classification**	**Corrosivity Constant (g) Metric (English)**
Less than 2,000	Very corrosive	1.0 (40)
2,000 - 5,000	Corrosive	0.79 (30)
5,000 - 10,000	Moderately corrosive	0.51 (20)
Greater than 10,000	Progressively less corrosive	0.25 (10) or less

Maximum pit depths as a function of time can be estimated by using the equation: $D = g(t)^{1/2}$

where D = pit depth, mm (mils)
g = corrosivity constant
t = time (years)

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(14) Stepwise cracking that occurs in the base metal adjacent to welds due to high through thickness strains caused by weld shrinkage.

The most economical way to prevent external corrosion of underground piping is to coat the pipe and use cathodic protection. Cathodic protection is required because corrosion can be accelerated at pinholes in a coated pipe, particularly when the coating absorbs moisture. Cathodic protection will prevent corrosion at the pinholes in a coating, as well as in areas of coating damage.

9.1 Coatings for Prevention of External Corrosion of Underground Piping

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

- Coal tar enamel
- Asphalt mastic (somastic)
- Asphalt enamel
- Polyvinylchloride tape
- Polyethylene tape
- Polyethylene extrusions
- Fusion-bonded epoxy

Asphalt mastic is a heavy duty system that is shop-applied in thicknesses up to 25.4 mm (1 in.). Although asphalt mastics perform well, they are very costly. Their use usually is limited to river crossing and swamp areas. Coal tar enamel has more than 50 years of successful performance underground; but it is subject to cracking when the temperature is below -7°C (20°F), 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 a feasible material for most pipelines. In addition, coal tar enamels often are ruled out because of long-term deterioration. Asphalt enamel generally is considered inferior to coal tar enamel; therefore, its use is limited. Polyvinylchloride 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 some problems. To obtain a satisfactory coating, careful attention must be given to:

- Materials specifications,
- Coating application and procedures,
- Coating inspection,
- 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:

Polyethylene tape: There is more than 40 years 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. Some pipeline companies will not permit the application to be more than 160 km (100 miles) from where the pipe is to be buried. The most practical method to minimize 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 occurs when cathodic protection current densities become too high) than other types of pipeline coating.

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 also is 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 -23°C to 66°C (10°F to 150°F); however, some tapes (e.g., Tapecoat™ High Temperature Machine Applied) can be used up to 93°C (200°F).

Extruded Polyethylene: Extruded polyethylene has been in general use for about 35 years. The polyethylene is applied by either a forward extrusion or a side extrusion process. The forward extrusion presently is limited to about 610 mm (24 in.) outside diameter pipe. The side extrusion can be used for sizes up to about 3,050 mm (120 in.). Extrusions usually are shop applied but can be applied at the railhead if economics permit. In addition to excellent temperature resistance (-40°C to 66°C [-40°F to 150°F]) and water resistance, the extruded polyethylene coatings have excellent resistance to cathodic disbonding and soil stresses. The commonly used 1.3 mm (50 mil) thickness offers excellent resistance to handling damage. The bonding problems with early applications of the side extrusion appear to have been solved. Field joints often are made with heat-shrinkable sleeves.

Fusion-bonded epoxy: Fusion-bonded epoxy (FBE) 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 FBE (or in properly applied polyethylene tapes or extrusions). FBE displays excellent chemical resistance, excellent resistance to cathodic disbonding, and excellent temperature resistance [-3°C to 66°C (-100°F to 150°F)]. Some formulations can be used up to 93°C (200°F) though there are recent indications of problems with FBE on hot lines. Good temperature resistance is associated with good impact resistance, which minimizes handling damage. A near-white metal-blasted surface (NACE No. 2 SSPC-SP 10, "Near White Metal Blast Cleaning") and freedom from salt contamination(15) are required. Since the fusion-bonded epoxy film is relatively thin (0.3 mm to 0.4 mm [12 mils to 16 mils]), 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 (around 200°C [400°F]), and problems have occurred as a result of improper curing. Curing at lower temperatures results in a more flexible coating, but the softer coating is more prone to disbonding. Field joints are either epoxy coated or taped. One user claims to have had severe disbonding problems. Concern has been expressed that the temperature required to cure the epoxy will cause strain age embrittlement, which reduces the fracture toughness of the steel pipe. To date, the seriousness of the potential strain aging problem is controversial. While some 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.

9.2 Cathodic Protection for External Corrosion Prevention of Underground Piping

All of the above-mentioned coating systems will have some damage and some pinholes. To prevent corrosion in these areas, cathodic protection is applied to cross-country pipelines. Table 5.2 shows how typical current density ranges vary, depending on the type of coating used and the percent of bare surface anticipated.

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(15) Many premature failures of FBE coatings can be traced to salt contamination. Levels greater than 2.0 μ/cm^2, based on ASTM D512, appear to be detrimental. See D. Neal and T. Whitehurst in bibliography.

Table 5.2
Typical Cathodic Protection Design Current Density Ranges

Coating	Bare Surface Area Expected over 20 Year Design Life (%)	Range of Design Current Density Requirements (ma/m^2 [ma/sq ft])
A. **Shop Applied**		
Fusion Bonded Epoxy	2	0.2 - 2.2 (0.02 - 0.2)
Polyethylene Extruded	2	0.2 - 2.2 (0.02 - 0.2)
Coal-tar	3	0.3 - 3.2 (0.03 - 0.3)
Asphalt	3	0.3 - 3.2 (0.03 - 0.3)
Bituminous Mastic	3	0.3 - 3.2 (0.03 - 0.3)
Tapes	5	0.5 - 5.4 (0.05 - 0.5)
B. **Field Applied**		
Coal tar	6	0.6 - 6.5 (0.06 - 0.6)
Asphalt	6	0.6 - 6.5 (0.06 - 0.6)
Bituminous mastics	6	0.6 - 6.5 (0.06 - 0.6)
Tapes	10	1.0 - 10.8 (0.1 - 1.0)
C. **None (bare pipe)**	100	10.8 - 108 (1.0 - 10.0)

It must be emphasized that to assure proper operation of a cathodic protection system, potential measurements must be taken along the system. NACE RP0169 contains recommendations on minimum requirements for control of external corrosion on underground or submerged metallic piping systems.(16) NACE RP0169 was revised recently, so errors arising from soil path IR drop must be considered before using the -0.85 volts vs Cu/CuSO$_4$ half-cell criterion for protection. This is because significant reduction in 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 the use of 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 improperly applied fusion-bonded epoxy coatings have forced lines to be dug up and recoated. The same thing could happen to any line with an improperly applied coating.

In some circumstances, e.g., in salt water, it is necessary to cathodically protect SS, and in other circumstances SS is cathodically protected because it is connected to carbon steel that is being cathodically protected. Austenitic SS polarizes readily. Pitting (the major corrosion mechanism operative in salt water) can be prevented by a protective potential of -0.65 volt vs a saturated calomel electrode (-0.72 volt vs Cu/CuSO$_4$). Ferritic and martensitic SS, including precipitation-hardening SS (as well as titanium and most steels with yield strengths exceeding 63 kg/mm^2 [90 ksi]), can hydrogen embrittle if the potential is more negative than -0.75 volt vs a saturated calomel electrode (-0.82 volt vs Cu/CuSO$_4$). Since it is necessary to polarize carbon steel to at least -0.85 volt vs Cu/CuSO$_4$ for protection (cathodic protection of carbon steel is only 59% effective at -0.82 volt vs Cu/CuSO$_4$), martensitic SS with hardness greater than HRC 22, titanium and super ferritic SS (i.e., those susceptible to hydrogen embrittlement — in the case of titanium, hydriding) should not be coupled to cathodically protected carbon steel.

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(16) NACE RP0177 contains recommendations for AC mitigation for buried pipelines.

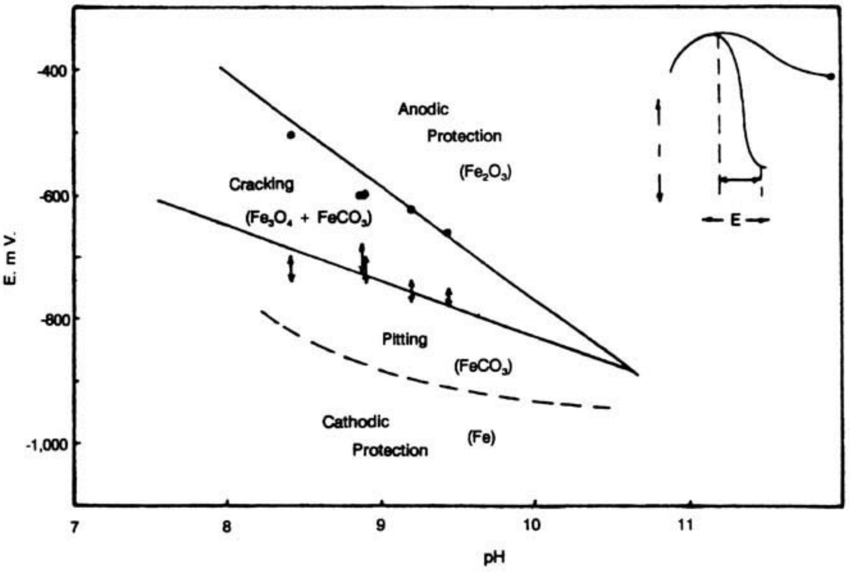

Figure 5.25 - Comparison of the results from stress corrosion tests with those from polarization curves at fast and slow potential sweep rates for different carbonate-bicarbonate solutions, indicating the extent to which the experimentally observed cracking range can be predicted from electrochemical measurements.[17]
(Reprinted with permission from *Materials in Engineering Applications Materials in Engineering Applications*, December 1978, p. 80)

9.3 External Stress Corrosion Cracking of Underground Piping

Throughout the past decade, there have been about two to three reports per year of stress cracking of buried pipelines. The cracking occurs on the outside of the pipe under disbonded coatings of lines under cathodic protection. The failures have been located where the line is warmest (greater than 38°C [100°F]), e.g., within 16 km (10 miles) downstream of 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 a narrow potential-pH band where the material is susceptible (Figure 5.25).[17] This often is the case under disbonded coatings. Most failures have been under coal tar enamel coatings. To date, no failures of fusion-bonded epoxy coated pipelines have been reported. Hydrostatic testing presently is the best means for detecting leaks from SCC. Good surface preparation, most easily attained with shop-applied coatings, currently is the best preventive measure.

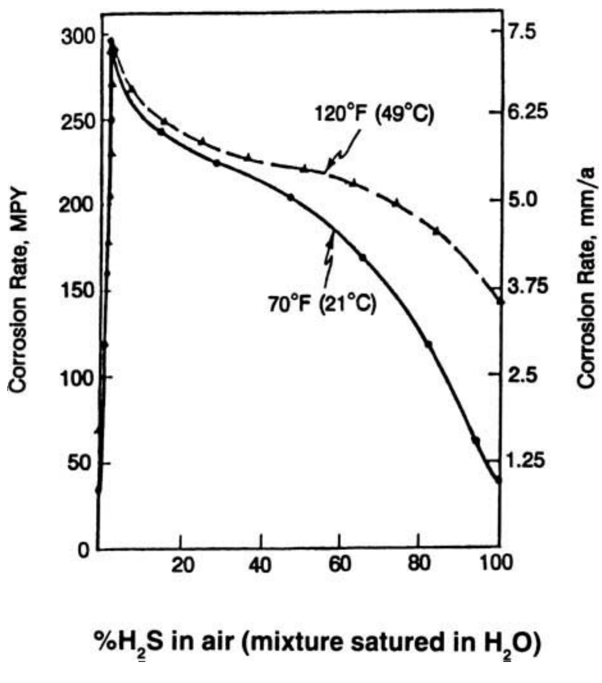

Figure 5.26 - Corrosion rate of wet steel in atmospheres containing H_2S-air mixtures.[18]
(Reprinted with permission from *Anti-Corrosion* September 1981, p. 4)

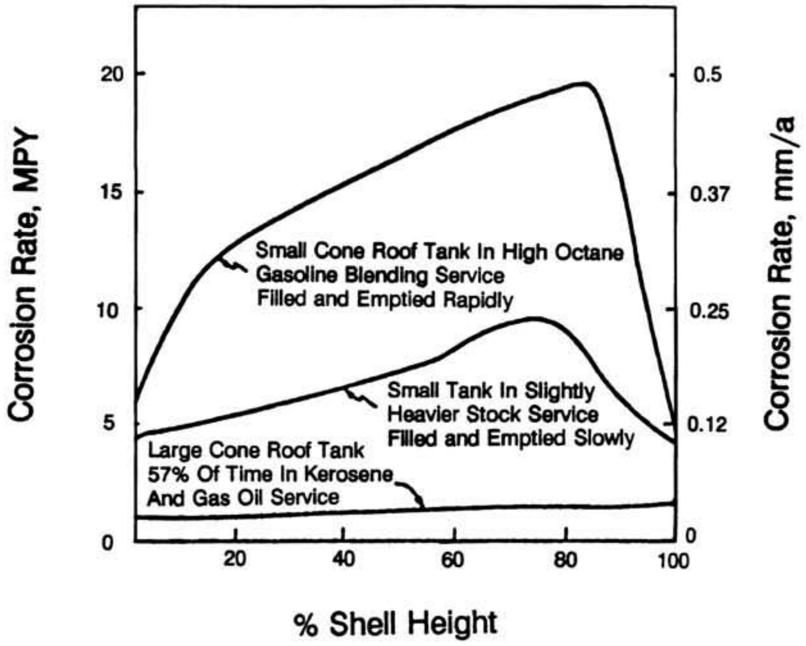

Figure 5.27 - Shell corrosion in cone roof storage tanks handling gasoline.[18]
(Reprinted with permission from *Anti-Corrosion*, September 1981, p. 4)

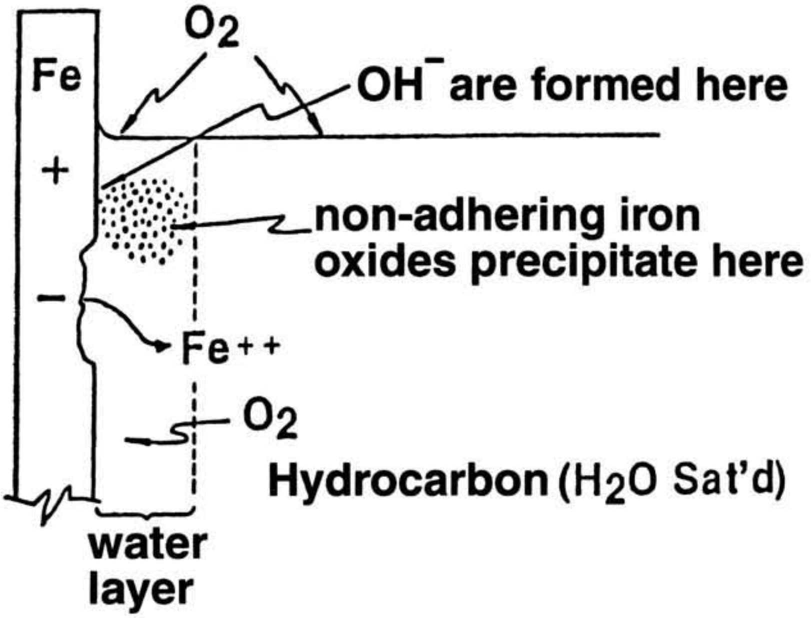

Figure 5.28 - Mechanism of shell-side corrosion in gasoline and light-products storage tank.[18]
(Reprinted with permission from *Anti-Corrosion*, September 1981, p. 4)

10. TANKAGE

Storage tanks built in accordance with API 650 commonly are made of mild steel. API 653 contains requirements for tank inspection, repair, alteration and reconstruction. As discussed in Chapter 1, as a minimum 1.5 mm (1/16 in.) corrosion allowance normally is specified for storage tanks. Where experience indicates a 1.5 mm (1/16 in.) corrosion allowance is not adequate, internal linings usually are specified. Where tanks are lined internally and painted externally, a zero corrosion allowance often is specified. Notch tough steel is required when the design metal temperature is 10°C (50°F) or below (lowest one-day mean temperature of 2°C [35°F] or below). High-strength steels sometimes are 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 SSC. As a minimum, the hardness of the welds should meet NACE RP0472.

10.1 Corrosion in Petroleum Storage Tanks

Corrosion in atmospheric storage tanks can be divided into three zones: (1) the tank roof, (2) the walls, and (3) the bottom. Corrosion on the underside of the tank roof is controlled by the relative amount of air and hydrogen sulfide, as well as the temperature. As can be seen in Figure 5.26,[18] 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 also can 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.[18] Corrosion in light (API density 50 degrees or lighter) is higher than in heavier products because oxygen solubility is higher. Corrosion is high in the 80% to 90% level of the side wall due to the mechanism shown in Figure 5.28.[18] In floating roof tanks, corrosion is found in the area where the major travel of the floating roof occurs (often this is halfway up the tank).[18,19] This corrosion is a result of the oxygen that enters the tank around the roof seals, concentrating in the water layers on the gasoline just beneath the floating roofs. The scale formed in this area is then scraped away by the moving roof, exposing fresh metal to attack. Coatings usually are used to solve this corrosion problem.

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 get to the bottom. Tank bottom corrosion is controlled by coatings and by draining the water from the tank bottom periodically. API RP 652 contains recommendations on lining above-ground petroleum storage tank bottoms. 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 usually is specified for the bottom. When the tank is on soil or other conductive media and water cannot be prevented from contacting the underside of the tank bottom, cathodic protection in accordance with NACE RP0193 normally is applied.

In some locations double bottoms have been used in tanks to minimize leaks into the ground and to facilitate leak detection. The space between the two bottoms often is filled with sand. If the double bottom is a retrofit, accelerated corrosion of the new steel can occur because of the difference in corrosion potential of the new bare material and the old corroded material. Since it is almost impossible to seal the space between the two bottoms, a cathodic protection system usually is used to prevent corrosion. Impressed current cathodic protection is preferred over a sacrificial system because the current requirements often are higher than that which can be obtained from sacrificial anodes. Further information on double bottom tanks is contained in Meyers[20] and McJones.[21] More details on design and corrosion of tanks are contained in Merrick[22] and Meyers.[20]

10.2 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 (-33°C, -42°C, and -162°C [-28°F,

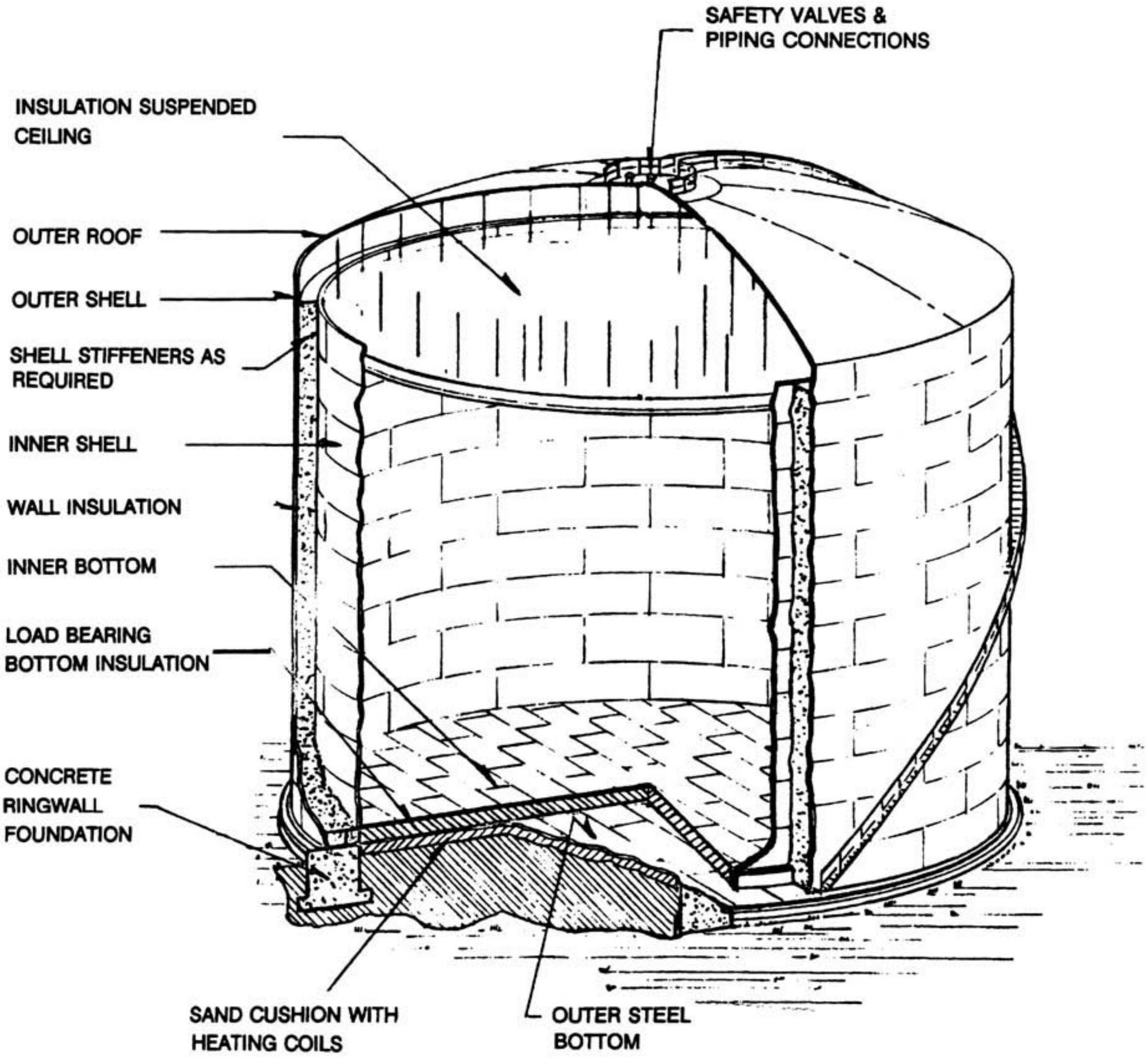

Figure 5.29 - Double wall tank for low-temperature service.

-40°F, and -260°F] respectively). However, there have been reports of SCC in fully refrigerated (-33°C [-F]) liquid ammonia storage tanks. Cantwell has reported SCC of LPG spheres as a result of trace amounts of hydrogen sulfide in the LPG.[23] The primary concern in storing these fluids has been 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 contained in Appendix R of API 620 and in BS 7777. More detailed requirements for LNG tanks are contained in Appendix Q of API 620 and in BS 7777. 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. The three basic types of double wall tanks in order of increasing cost are: 1) single containment, 2) double containment, and 3) full containment. The most commonly used type is the single containment shown in Figure 5.29. The single containment tank has a carbon steel outer wall (designed for atmosphere temperature), which is separated from the inner tank by foamed fiberglass (to absorb expansion and contraction) and perlite insulation. An example of a double containment type would be one with a prestressed concrete outer wall either separated from the carbon steel outer wall or lined with carbon steel.

An example of a full containment type is one that has a reinforced concrete roof and a prestressed concrete outer wall. The inner tank on all three types is made of either 9% nickel steel (usually economical for large tanks), 304 SS (UNS S30400), or aluminum (usually economical for small tanks).

Nine percent nickel steel usually is used in the quenched and tempered condition. Modern steelmaking practices have made it possible to obtain high fracture toughness in 9% nickel steel. A Charpy V-notch impact strength of 100 J (74 ft-lbs) at -196°C (-320°F) now commonly is specified. Tempering should be done at 580°C± 6°C (1,075°F ± 10°F). Below 565°C (1,050°F), temper embrittlement can result; above 595°C (1,100°F), austenite will form and upon cooling transform to martensite, thereby lowering the toughness. For 9% nickel steel with thicknesses greater than 25.4 mm (1 in.), fracture mechanics testing should be considered to determine the maximum allowable flaw size. The maximum thickness where good properties can be obtained is 51 mm (2 in.). The minimum thickness should be 9.5 mm (3/8 in.) because of the potential for warpage from the severe blasting required for descaling 9% nickel steel.

Using fracture mechanics testing or BS 7777, design stresses can exceed those allowed by API 620, Appendix Q (218.6 MPa [31.7 ksi]). In these cases, the allowable stress is limited to two-thirds of the yield strength. Although the allowable stresses in BS 7777 are higher than in API 620, Appendix Q, the wall thickness of a tank designed to BS 7777 is thicker than that required by API 620, Appendix Q. This is because BS 7777 requires a full height hydrostatic test while API 620, Appendix Q requires only a partial height hydrostatic test to 1.25 times the LNG load. Because of long successful service of tanks designed to API 620, Appendix Q, there is a trend in the industry away from the full height hydrostatic test.

Since the 65Ni-15Cr-Fe 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 65Ni-15Cr-Fe filler metal is 414 MPa (60 ksi). The 414 MPa (60 ksi) minimum yield strength of 65Ni-15Cr-Fe filler metal minimizes the thickness required in the tank wall and, consequently, the cost.

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Appendix A

General Guide for Materials Selection

SCOPE

This guide covers:

1. Materials and corrosion allowance (CA) for process equipment,
2. Materials for low-temperature services,
3. Materials for wear and abrasion resistance.

EQUIPMENT DESIGN LIFE

Materials selection is based on the following approximate design lives:

1. Large vessels and columns	25 years
2. Small vessels (volume less than 2.2 m^3 (78 ft^3)	10 years
3. Exchanger shells and channels	15 years
4. Air coolers	15 years
5. Furnace tubes and supports	10 years
6. Piping, critical, and 100 mm (4 in.) or larger	15 years
7. Pumps and valves	10 years

CRITERIA FOR MATERIALS SELECTION

1. Materials selection should be based on most severe operating conditions.
2. Process flow diagrams, stream analyses, contaminant levels, upset conditions, safety, reliability, 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 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 SS (UNS S30403 and S31603) are preferred to the regular grades (UNS S30400 and S31600) except for use at operating temperatures higher than 425°C (800°F) and when intergranular stress corrosion or intergranular corrosion is not a problem during operation or downtime. Note: It is common practice for 300 series SS to be made so that it meets both the regular and low carbon grade requirement; thus, it will be stamped, e.g., 304/304L (UNS S30400/S30403).

TABLE A-1
Typical ASTM Specifications for Materials

Material (UNS No. as applicable)	Plate	Pipe	Tubing	Forgings & Fittings	Bars	Castings
Cast Iron						A48, A126 A278
Carbon Steel	A285, A515 A516, A537 A737	A53, A106 A671, A672 A691	A214, A179 A192, A210	A105, A181 A266, A234	A29, A575 A576, A663 A675	A216
Carbon-1/2 Mo	A204	A335	A161, A209	A182, A234		A217
1 Cr-1/2 Mo, 1-1/4 Cr-1/2 Mo, & 2-1/4 Cr-1 Mo	A387	A335	A199 A200 A213	A182 A336 A234	A29 A739	A217
5Cr-1/2 Mo	A387	A335	A199, A200 A213	A182, A234		A217
12Cr, CA15	A240		A268	A182	A479	A217
Austenitic Stainless 304, 304L, 316, 316L, 321, 347, 310, CF3, CF3M, CF8, CF8C, CF8M	A240	A312 A358	A213 A249 A271	A182 A336 A403	A479	A351 A744
HK40(J94204) & HP modified						A297
Duplex 2205 SS (S32205)	A240	A790	A789	A182, A815	A276	
6 MoSS (N08367)	B688	B675	B676			
Alloy 800 (N08800)	B409	B407	B163, B407	B366, B564	B408	
Alloy 825 (N08825)	B424	B423	B163, B704	B366	B425	
904L (N08904)	B625	B673, B677	B674, B677		B649	
Alloy 20 (N08020)	B463	B464, B474	B468	B462	B472	A351
Copper (C10200)	B152	B42	B75, B111			
Admiralty Brass (C44300)			B111			
Naval Brass (C46500)	B171				B124	
70-30 Cu-Ni	B171	B467, B608	B111, B395			
Titanium Gr.2 (R50400)	B265	B337	B338	B381	B348	B367
Alloy 400 (N04400)	B127	B165	B163, B165	B564	B164	A494
Alloy 625 (N06625)	B443	B444	B444, B704	B446		
Alloy C276 (N010276)	B575	B622	B622, B626	B574		A494
Ni Resist TP2 (F41002)						A436
Aluminum	B209	B241	B234	B247	B211	

General Guidelines for Materials Selection and Corrosion Allowances

1. Materials typically used for the following environments are contained in Tables A-2 through A-17. It is important to note that the materials listed are typical and that there can be exceptions.

- General - hydrocarbon with low sulfur contents, non-corrosive 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 wt% and 1.0 wt%
- Hydrocarbon plus hydrogen
- Hydrocarbon plus hydrogen and hydrogen sulfide
- Sour water and desalter water
- Carbonate
- Low pressure wet carbon dioxide
- High pressure wet carbon dioxide
- Amine
- Acid gas
- Liquid sulfur
- Untreated, aerated water
- Caustic
- Valve trim

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

CI = cast iron
CS = carbon steel
1 Cr = 1 Cr-1/2 Mo
1-1/4 Cr = 1-1/4 Cr-1/2 Mo
5 Cr = 5 Cr-1/2 Mo
9 Cr = 9 Cr-1 Mo

12 Cr = Types 405, 410, 410S, CA15 (UNS S40500, S41,000, S41008, J9II59)
18-8 = Types 304, 316, 321, 347, CF8, CF8M, CF8C (UNS S30400, S31600, S32100, S34700, J92600, J92900, J92710)
SS = stainless steel

3. The numerals after a material designation indicate the minimum nominal corrosion allowances in millimeters (mm) as follows:

- 1.3 mm (0.050 in.) for SS furnace tubes unless otherwise specified
- 1.5 mm (0.063 in.) for piping unless otherwise specified
- 2.5 mm (0.100 in.) for 1 Cr - 5 Cr furnace tubes and typical minimum thickness for clad
- 3.0 mm (0.125 in.) for carbon steel furnace tubes, for TEMA Class R heat exchangers, and for sour water piping with hydrogen sulfide partial pressures less than 0.07 MPaa (10 psia)
- 4.5 mm (0.188 in.) for sour water vessels and heat exchangers with hydrogen sulfide partial pressures less than 0.07 MPaa (10 psia)
- 6 mm (0.250 in.) for vessels and heat exchangers with hydrogen sulfide partial pressures greater than 0.07 MPaa (10 psia) or carbon dioxide partial pressures less than 0.03 MPaa (4 psia)

TABLE A-2

SERVICE

General Hydrocarbon (S < 0.2 wt%
H_2S<0.01 mol% in gas,
<50 ppm in fluid,
ppH_2<0.7 MPaa/100 psia)
Steam, Air, Treated Cooling
Tower Water and Other
Noncorrosive Services

OPERATING TEMPERATURE

F: 100, 200, 300, 400, 500, 600, 700, 800, 900, 1,000, 1,100, 1,200, 1,300, 1,400

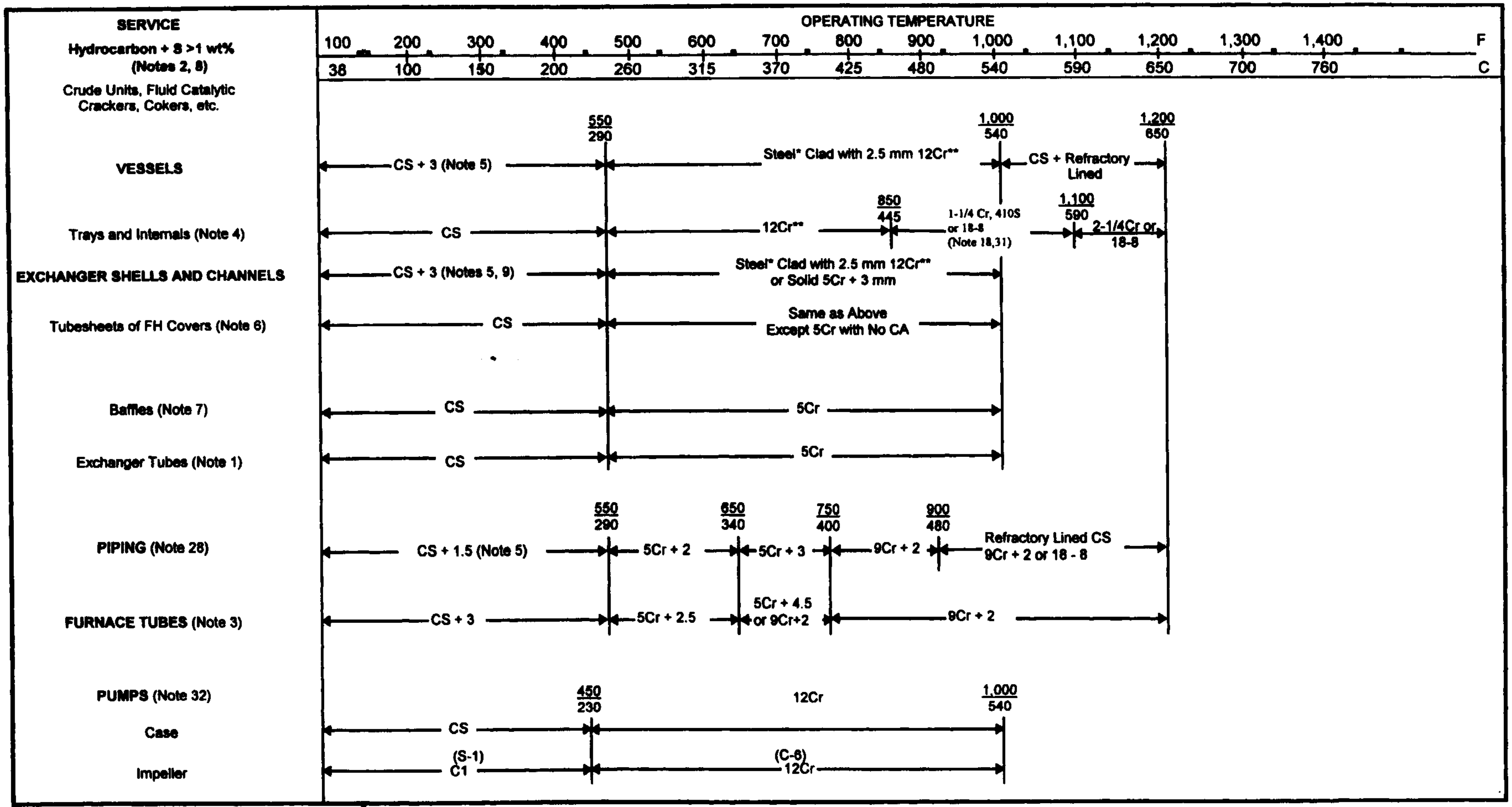
C: 38, 100, 150, 200, 260, 315, 370, 425, 480, 540, 590, 650, 700, 760

SERVICE	100 F / 38 C – 450 F / 230 C	450 F / 230 C – 750 F / 400 C	750 F / 400 C – 825 F / 441 C	825 F / 441 C – 1,000 F / 540 C	1,000 F / 540 C – 1,100 F / 590 C	1,100 F / 590 C and above
VESSELS	CS + 1.5*	CS + 1.5*	CS + 1.5*	1-1/4Cr + 3**	1-1/4Cr + 3**	
Trays and Internals (Note 4)	CS	CS	CS	1-1/4Cr**	1-1/4Cr**	
EXCHANGER SHELLS AND CHANNELS	CS + 3*†	CS + 3*†	CS + 3*†	1-1/4Cr + 3**†	1-1/4Cr + 3**†	
Tubesheets of FH Covers (Note 6)	CS	CS	CS	1-1/4Cr**	1-1/4Cr**	
Baffles (Note 7)	CS	CS	CS	1-1/4Cr**	1-1/4Cr**	
Exchanger Tubes (Note 1, 35)	CS	CS	CS	1-1/4Cr**	1-1/4Cr**	
PIPING	CS + 1.5*	CS + 1.5*	CS + 1.5*	1-1/4Cr + 1.5**	1-1/4Cr + 1.5**	
FURNACE TUBES (Note 2, 3)	CS + 3	CS + 3	1-1/4Cr + 2.5**	1-1/4Cr + 2.5**	2-1/4Cr + 2.5**	SS or Alloy 800H + 1.3
PUMPS (Note 32)						
Case	CS (S-1) (Note 33)	CS (S-4)	CS (S-4)			
Impeller	CS	CS	CS			

NOTES:

*See Note 2, 26
**See Note 8
†See Note 9

TABLE A-3



NOTES:

*See Note 2, 28

**See Note 18, 29

†See Note 8

TABLE A-4

SERVICE Hydrocarbon • S > 0.2 wt% • Naphthenic Acid (TAN > 1.8) (Notes 2, 8, 29)	OPERATING TEMPERATURE 100 200 300 400 500 600 700 800 900 1,000 1,100 1,200 1,300 1,400 F 38 100 150 200 260 315 370 425 480 540 590 650 700 760 C	
	450 230	850 455
VESSELS	CS + 3 (Note 5)	Steel* Clad with 2.5 mm 316L**
Trays and Internals (Note 4)	CS	316L**
EXCHANGER SHELLS AND CHANNELS	CS + 3 (Notes 5, 9)	Steel* Clad with 2.5 mm 316L**
Tubesheets of 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)	316L + 1.5**
FURNACE TUBES (Note 3)	CS + 3	316L + 1.3** or 316Ti+1.3**
PUMPS (Note 32)		
Case	CS (S-1)	316** (A-8)
Impeller	C1	316**

NOTES:

*See Note 2

**See Note 29

TABLE A-5

OPERATING TEMPERATURE

F: 100, 200, 300, 400, 500, 600, 700, 800, 900, 1,000, 1,100, 1,200, 1,300, 1,400

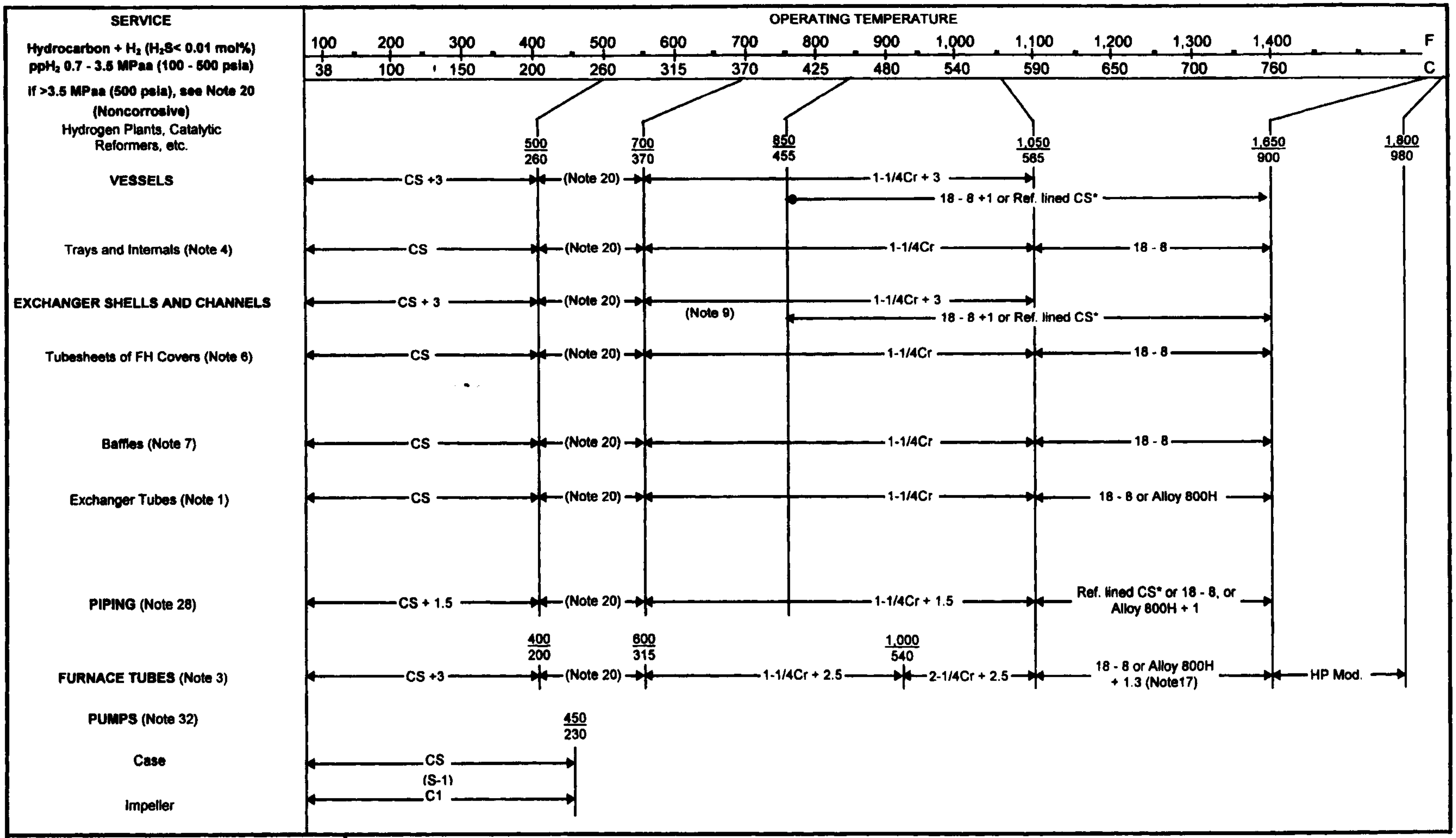
C: 38, 100, 150, 200, 260, 315, 370, 425, 480, 540, 590, 650, 700, 760

SERVICE Hydrocarbon + S (0.2 - 1 wt%) Crude Units, Fluid Catalytic Crackers, Cokers, etc.	450 230	550 290	650 340	825 441
VESSELS	CS + 3 (Note 5)			CS Clad with 2.5 mm 12Cr**
Trays and Internals (Note 4)	CS			12Cr
EXCHANGER SHELLS AND CHANNELS	CS + 3 (Notes 5, 9)			CS Clad with 2.5 mm 12Cr** or Solid 5Cr + 3
Tubesheets of FH Covers (Note 6)	CS			CS Clad with 2.5 mm 12Cr**
Baffles (Note 7)	CS			5Cr
Exchanger Tubes (Note 1)	CS			5Cr
PIPING (Note 28)	CS + 1.5 (Note 5)		CS +3	5Cr + 1.5
FURNACE TUBES (Note 3)	CS +3		5Cr + 2.5	
PUMPS (Note 32)				
Case	CS (S-1)	CS (S-4)	CS (S-6)	12Cr (C-6)
Impeller	C1	CS	12Cr	12Cr

NOTES:

**See Note 18, 28, 29

TABLE A-6



NOTES:

*See Note 15
Ref. = Refractory

TABLE A-7

OPERATING TEMPERATURE

F: 100 200 300 400 500 600 700 800 900 1,000 1,100 1,200 1,300 1,400

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

SERVICE			
Hydrocarbon + H_2 + H_2S ppH_2 <10.34 MPaa (1,550 psia) H_2S>0.01 mol% Hydrodesulfurizers, Hydrocrackers, etc.	450 230		550 290 — 925 495
VESSELS	CS + 3*	**	1-1/4Cr** or 2-1/4Cr** Clad with 2.5 mm 321 or 347
Trays and Internals (Note 4)	CS*	**	321 or 347
EXCHANGER SHELLS AND CHANNELS	CS + 3*	**	Same as Vessel
Tubesheets of 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 (Note 28)	CS + 1.5	**	321 or 347 + 1.5
FURNACE TUBES (Note 3)	CS +3 (350 175)	**	321 or 347 + 2.5
PUMPS (Note 32)			
Case	CS (S-1)		
Impeller	C1		

NOTES:

*See Note 5
**See Note 20

TABLE A-8

SERVICE	OPERATING TEMPERATURE
Sour Water **Desalter Water**	100 200 300 400 500 600 700 800 900 1,000 1,100 1,200 1,300 1,400 F 38 100 150 200 260 315 370 425 480 540 590 650 700 760 C
	300 150
VESSELS	
H_2S pp < 70 kPaa (10 psia) or 1,000 ppm	CS + 4.5*
H_2S pp > 70 kPaa (10 psia) or 1,000 ppm	CS + 6*
Trays and Internals (Note 4)	CS + 3*
EXCHANGER SHELLS AND CHANNELS	Same as Vessel
Tubesheets of FH Covers (Note 6) Air, H.C. or treated water on the other side	CS + 4.5*
Baffles (Note 7)	CS
Exchanger Tubes (Note 1)	
ppH_2S < 70 kPaa (10 psia)	CS 12GA min *
ppH_2S > 70 kPaa (10 psia)	CS 12GA min * or 2205 or Ti
Untreated water otherside	2205 or Ti
PIPING (Note 28)	
ppH_2S < 70 kPaa (10 psia)	CS + 3*
ppH_2S > 70 kPaa (10 psia)	CS + 6* or 316L
FURNACE TUBES (Note 3)	
PUMPS (Note 32)	
Case	CS
Impeller	(S-8) 18 - 8

NOTES:

*See Notes 13, 24

TABLE A-9

OPERATING TEMPERATURE

F: 100, 200, 300, 400, 500, 600, 700, 800, 900, 1,000, 1,100, 1,200, 1,300, 1,400

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

SERVICE **Carbonate** **CO_2 Removal (Note 25)** Hydrogen Plant, Gas Treating Plant, etc.	100 F (38 C) – 150 F (65 C)	150 F (65 C) – 300 F (150 C)
VESSELS	CS + 3	CS + 3
Trays and Internals (Notes 4, 11)	CS*	CS*
EXCHANGER SHELLS AND CHANNELS	CS + 3*	CS + 3*
Tubesheets of FH Covers (Note 6)	CS *	CS *
Baffles (Note 7)	CS*	CS*
Exchanger Tubes (Note 1)	CS*	CS*
PIPING	CS + 1.5*	CS + 1.5*
FURNACE TUBES (Note 3)		
PUMPS (Note 32)		
Case	CS (S-1)	SS (A-7)
Impeller	CS	SS

NOTES:

*Notes 10, 12, 21

**Notes 10, 12

TABLE A-10

SERVICE	OPERATING TEMPERATURE
Low Pressure Wet CO_2 **(pp CO_2 >0.7 kPaa (0.1 psia) <27.6 kPaa (4 psia)** **Regenerator Top & Overhead)** Hydrogen Plant, Gas Treating Plant, etc.	F: 100, 200, 300, 400, 500, 600, 700, 800, 900, 1,000, 1,100, 1,200, 1,300, 1,400 C: 38, 100, 150, 200, 260, 315, 370, 425, 480, 540, 590, 650, 700, 760
VESSELS	← CS + 6 or 304L* → Dew Point
Trays and Internals (Note 4)	← 12Cr →
EXCHANGER SHELLS AND CHANNELS	← CS + 6 or 304L* →
Tubesheets of FH Covers (Note 6)	← CS or 304L →
Baffles (Note 7)	← CS or 304L →
Exchanger Tubes (Note 1)	← CS 10GA min or 304L → (Notes 12, 19)
PIPING	
Before Condensation	← CS + 1.5 →
Two Phase Flow	← CS + 6* →
FURNACE TUBES (Note 3)	
PUMPS (Note 32)	
Case	← CS → (S-6)
Impeller	← 12Cr →

NOTES:

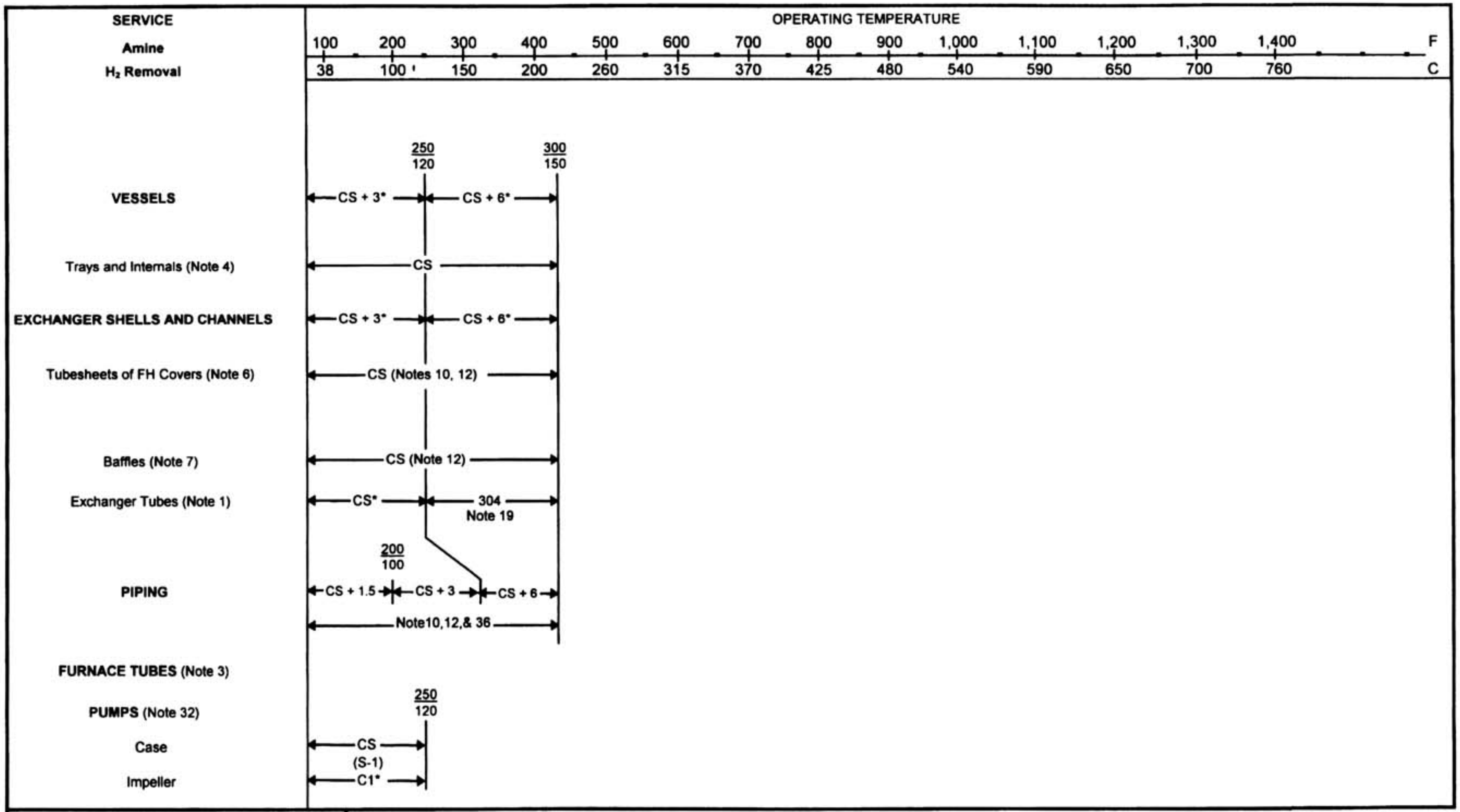
*Note 12

TABLE A-11

SERVICE	OPERATING TEMPERATURE	
High Pressure **Wet CO_2 - H_2 Mixtures** **(pp CO_2 >0.03 MPaa [4 psia])** Hydrogen Plant, Gas Treating Plant, etc.	F: 100, 200, 300, 400, 500, 600, 700, 800, 900, 1,000, 1,100, 1,200, 1,300, 1,400 C: 38, 100, 150, 200, 260, 315, 370, 425, 480, 540, 590, 650, 700, 760	
	120/50	Dew Point
VESSELS	CS + 6	CS Clad with 2.5 mm 304L
Trays and Internals (Note 4)	12Cr or 304L	12Cr or 304L
EXCHANGER SHELLS AND CHANNELS	CS + 6	CS Clad with 2.5 mm 304L
Tubesheets of FH Covers (Note 6)	CS + 6	CS Clad with 2.5 mm 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



NOTES:

*See Notes 5, 10

TABLE A-13

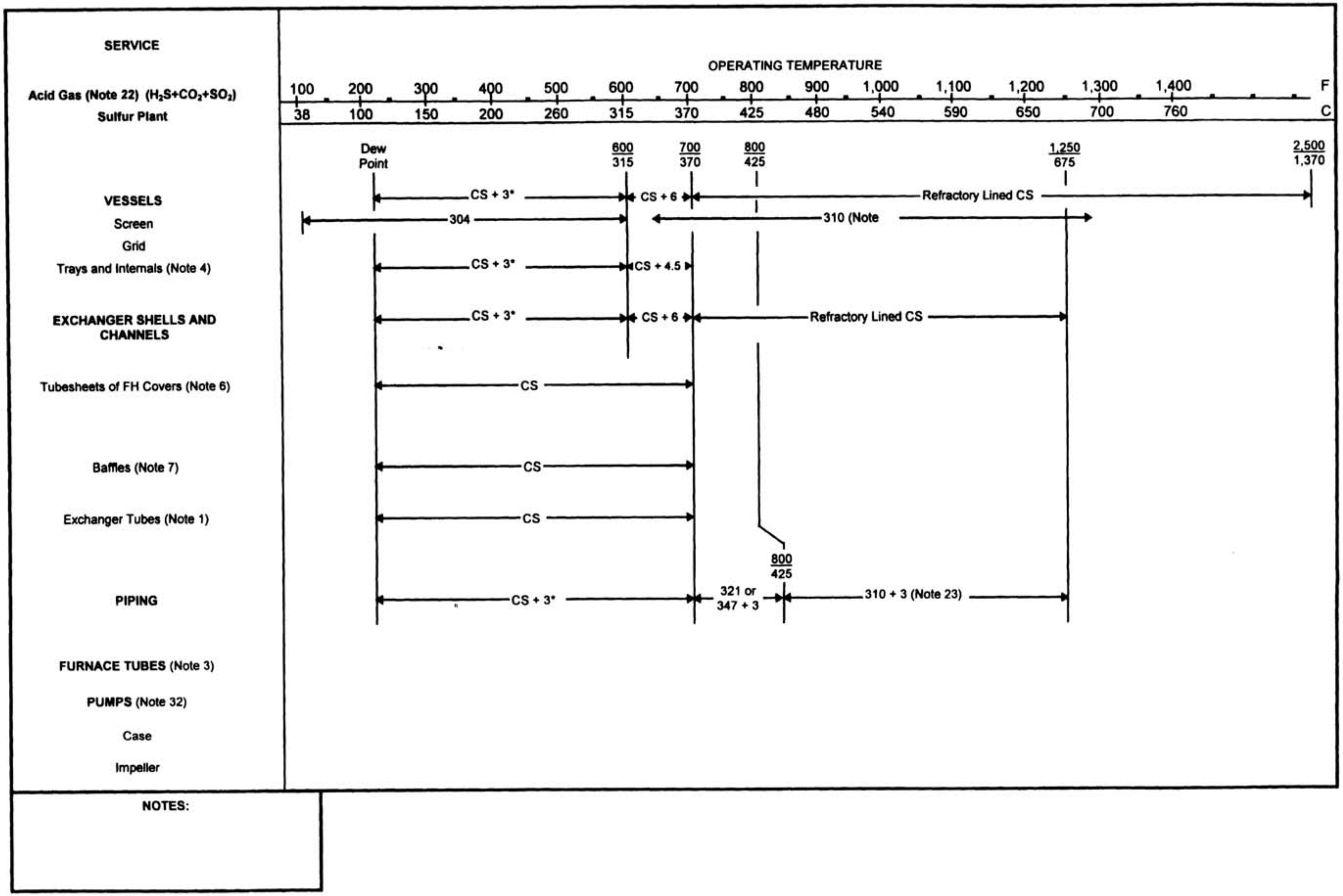
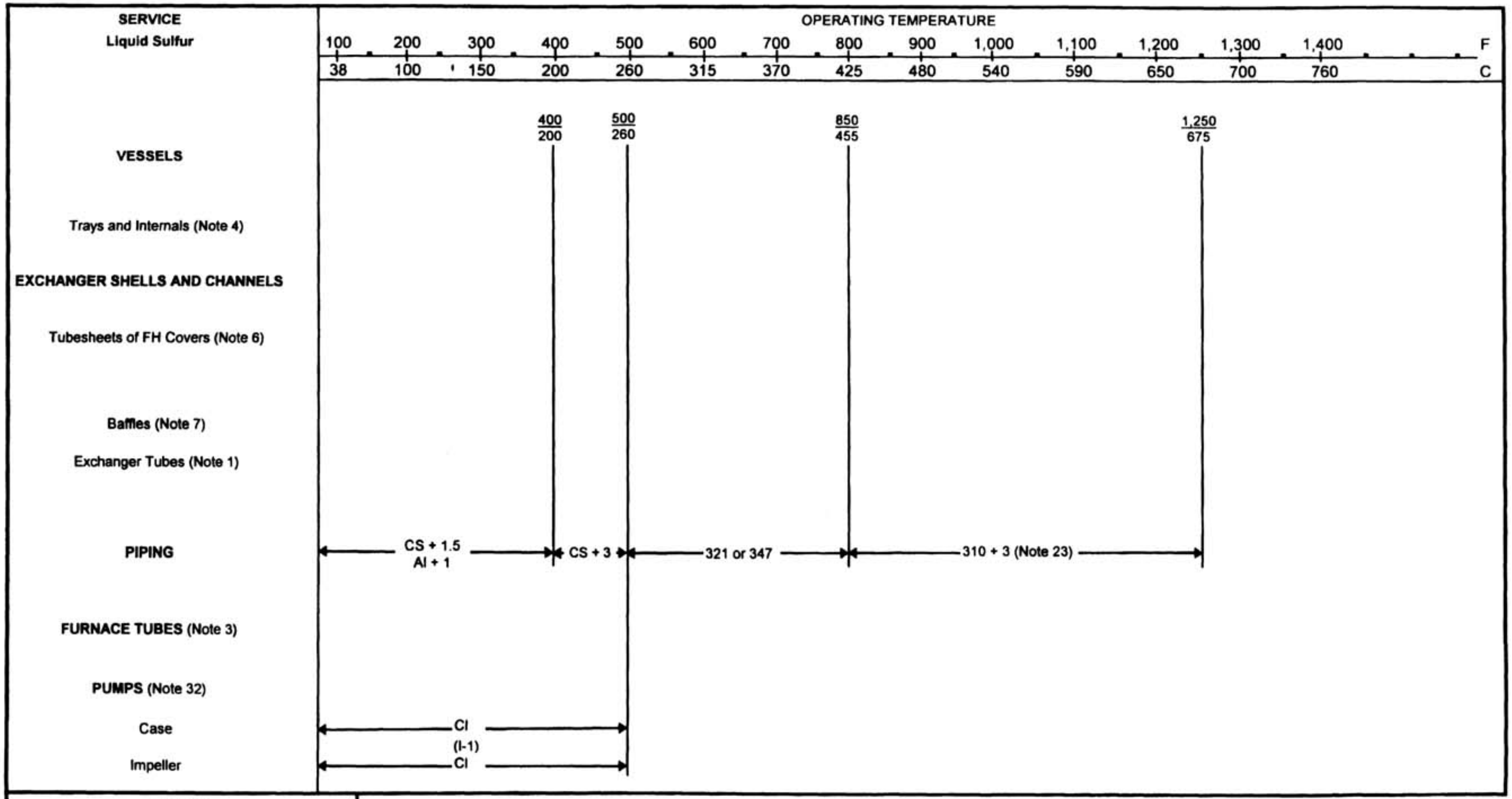

SERVICE
Acid Gas (Note 22) ($H_2S+CO_2+SO_2$)
Sulfur Plant
OPERATING TEMPERATURE
100 200 300 400 500 600 700 800 900 1,000 1,100 1,200 1,300 1,400 F
38 100 150 200 260 315 370 425 480 540 590 650 700 760 C
Dew Point
600/315
700/370
800/425
1,250/675
2,500/1,370
VESSELS
CS + 3*
CS + 6
Refractory Lined CS
Screen
304
310 (Note
Grid
Trays and Internals (Note 4)
CS + 3*
CS + 4.5
EXCHANGER SHELLS AND CHANNELS
CS + 3*
CS + 6
Refractory Lined CS
Tubesheets of FH Covers (Note 6)
CS
Baffles (Note 7)
CS
Exchanger Tubes (Note 1)
CS
800/425
PIPING
CS + 3*
321 or 347 + 3
310 + 3 (Note 23)
FURNACE TUBES (Note 3)
PUMPS (Note 32)
Case
Impeller
NOTES:

TABLE A-14



NOTES:

TABLE A-15

SERVICE **Untreated, Aerated Water**	OPERATING TEMPERATURE 100 200 300 400 500 600 700 800 900 1,000 1,100 1,200 1,300 1,400 F 38 100 150 200 260 315 370 425 480 540 590 650 700 760 C
	300 150
VESSELS	CS + 2.5 mm 90 Cu-10 Ni Clad
Trays and Internals (Note 4)	
EXCHANGER SHELLS AND CHANNELS	CS + 2.5 mm 90Cu -10 Ni Clad
Tubesheets of FH Covers (Note 6)	Naval Brass or 70Cu-30Ni*
Baffles (Note 7)	Naval Brass or 70Cu-30Ni*
Exchanger Tubes (Note 1)	Admiralty Brass or 70Cu-30Ni*
PIPING	Cement Lined CS
FURNACE TUBES (Note 3)	
PUMPS (Note 32)	
Case	CI
Impeller	(I-2) Al Bronze

NOTES:

*See Note 27

TABLE A-16

SERVICE Caustic NaOH, KOH	OPERATING TEMPERATURE 10 – 30 wt % to 200/100	 200/100 – 250/125	 250/125 – 400/200	 50 wt% to 170/75	 170/75 – 400/200
VESSELS	CS + 1.5*	CS + 6	Alloy 400 + 1.5	CS + 3*	Alloy 400 + 1.5
Trays and Internals (Note 4)	CS*		Alloy 400	CS*	Alloy 400
EXCHANGER SHELLS AND CHANNELS	CS + 1.5*	CS + 6	Alloy 400 + 1.5	CS + 3*	Alloy 400+ 1.5
Tubesheets of FH Covers (Note 6)	CS*		Alloy 400	CS*	Alloy 400
Baffles (Note 7)	CS*		Alloy 400	CS*	Alloy 400
Exchanger Tubes (Note 1)	CS*	Alloy 400		CS*	Alloy 400
PIPING	CS + 1.5*	CS + 6 (Note 14)	Alloy 400 + 1.5	CS + 3*	Alloy 400 + 1.5
FURNACE TUBES (Note 3)					
PUMPS (Note 32)					
Case	CS (S-1)	Alloy 400 (Note 34)		CS* (S-1)	Alloy 400 (Note 34)
Impeller	CI*	Alloy 400		CI*	Alloy 400

Temperature scale: 100, 200, 300, 400 F; 38, 100, 150, 200 C

NOTES:

*See Note 10

Table A-17 - Valve Trim

Environment	Valve Trim Material (Note 16)
1. General Service	
a) Treated Water	
b) Steam Δp <1.03 MPag (150 psig) in multiphase flow	12 Cr
< 3.4 MPag (500 psig) in single phase flow	12 Cr
Δp >1.03 MPag (150 psig) in multiphase flow or	
>3.4 MPag (500 psig) in single phase flow	Stellite 6™ (UNS R30006)
2. Hydrocarbon, Carbonate, Wet CO_2, Acid Gas, Liquid Sulfur	
a) Carbon and low alloy steel piping	12 Cr
b) 321 or 347 (UNS S32100 or S34700) piping	18-8
3. Sour Water, Desalter Water	18-8 or 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	Alloy 400 (UNSN04400)

Notes for Tables A-2 through A-17

1. The thickness of exchanger tubes should be that specified in the Exchanger Design Criteria. Where a gauge is specified, the thickness must be checked for adequacy with regard to pressure. Alternatively, a corrosion allowance of 0.25 mm (0.01 in.) to 1.5 mm (0.06 in.) can be specified.

2. Above 400°C (750°F), use silicon-killed (not aluminum-killed) carbon steel. Above 440°C (825°F), use 1 Cr-1/2 Mo or 1-1/4 Cr-1/2 Mo.

3. Materials selection for furnace tubes in non-hydrogen containing hydrocarbon plus sulfur services is based on the assumption that the metal temperature is 50°C (100°F) higher than the internal fluid temperature. To avoid excessive oxidation the outside skin temperatures should not exceed 530°C (1,000°F) for carbon steel, 650°C (1,200°F) for 1-1/4 Cr to 9 Cr and 930°C (1,700°F) for 18-8 SS. When austenitic SS is specified for temperatures above 530°C (1,000°F), "H" grades should be used, and cold forming should be prohibited where creep strength governs the allowable stress unless it is followed by solution annealing. Cold forming of carbon steel furnace and boiler tubes, e.g., cold bends, should be prohibited unless followed by stress relief.

4. Corrosion allowance (CA) for trays and internals:

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

5. Use only silicon-killed steels for temperatures above 232°C (450°F). For areas where sour water collects, see Table A-8.

6. Where not covered by TEMA and the material specified for both sides is the same, corrosion allowance should be 0.75 x the sum of the corrosion allowances for each side up to 6 mm (1/4 in.) maximum. Where not covered by TEMA and alloy requirements for two sides are different and solid alloy tube sheet is used, use corrosion allowance for higher alloy side as the total corrosion allowance. Where cladding is required on the tubeside, the minimum thickness of cladding should be 10 mm (3/8 in.) so that at least one of the grooves for rolling will be in the cladding.

7. Baffles should be 6 mm (1/4 in.) minimum thickness; no other corrosion allowance need be used.

8. Where 1-1/4 Cr-1/2 Mo is specified, 1 Cr-1/2 Mo also may be used. Do not use 1 Cr-1/2 Mo in hydrogen service if hydrogen partial pressure is greater than 0.7 MPaa (100 psia) above 480°C (900°F). Do not use 1 Cr-1/2 Mo in general service above 530°C (1,000°F).

9. A corrosion allowance of 3 mm (1/8 in.) should be used on carbon steel and low alloy 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%, stress relieve for service temperatures above 60°C (140°F). For 30% to 50% caustic, the service temperature where stress relief is required decreases from 60°C (140°F) to 48°C (118°F). 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 12 Cr 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 >2.5 m/s [8ft/s]) e.g., downstream of control valves, the rich carbonate inlet of a carbonate regenerator, reboiler tubesheets, baffles, etc., use 304 SS (UNS S30400) plus 1 mm (1/32 in.) corrosion allowance. Do not use miters; long-radius elbows are preferred. Piping specifications usually contain other limitations on miters.

13. Hardness of completed carbon and low-alloy steel welds should not exceed 200 Brinell. Valve trim should be 18 Cr-8 Ni SS and meet NACE Standard MR0175. For piping, if the ammonium bisulfide concentration exceeds 4% or the product of the mol% H_2S and the mol% NH_3 exceeds 0.05, use materials recommended for ppH_2S >70 kPaa (10 psia).

14. Use alloy 400 (UNS N04400) valve trim for caustic service above 93°C (200°F).

15. The metal temperature should not exceed that where carbon steel starts to lose its resistance to hydrogen attack.

16. If the service temperature will exceed 480°C (900°F), check with a materials engineer.

17. Stress corrosion cracking of 300 series SS may result if solids carry-over exceeds 1 ppm.

18. Do not use type 405 SS (UNS S40500) above 343°C (650°F). When welding is anticipated, use 410S SS (UNS S41008) rather than 410 SS (UNS S41000).

19. For U-bends, heat treat the entire 18 Cr-8 Ni SS tube at 1,000°C (1,850°F) minimum after bending. Where a 1000°C (1850°F) minimum heat treating temperature is not practical, 900°C (1,650°F) may be used. Use 321 (UNS S32100) or 347 SS (UNS S34700) if only the U-bends can be heat treated.

20. To choose between carbon or alloy steels in hydrogen service, see API 941. The corrosion allowance given in the table must be applied.

21. See Table A-10 for recommended materials for the 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 900°C (1,650°F) for 4 hours after completion to prevent polythionic acid cracking during downtime.

24. Unless more restrictive velocities are specified, the maximum velocity should not exceed 6 m/s (20 ft/s) in mixed phase flow piping where the ammonium bisulfide concentration exceeds 4% or the product of the mol% H_2S and the mol% NH_3 exceeds 0.05. Use 2205 (UNS S32205) for tubes and 309L (UNS S30903) clad headers in mixed phase flow where the ammonium bisulfide concentration exceeds 4% and 2205 (UNS S32205) piping where the ammonium bisulfide concentration exceeds 8%. For control valves where high turbulence occurs due to a pressure drop of greater than 3.8 MPag (2,000 psig), use Stellite™ 6 (UNS R30006) valve trim and 304L (UNS S30403) piping for 10 diameters downstream of the control valve.

25. Do not use nickel or cobalt base alloys, e.g., alloy 600 (UNS N06600), alloy 400 (UNS N04400), Colmonoy™, etc.; Stellite™ (UNS R30006) may be used.

26. The 1.5 mm (1/16 in.) corrosion allowance should be used where the vessel is externally coated (painted) and either internally lined or where experience has shown that the corrosion rate is essentially nil e.g., pure hydrocarbons, dry steam, etc.

27. The choice between brass and copper nickel alloys is contingent upon 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. Admiralty (UNS C44300) is usually limited to a process inlet temperature of 177°C (350°F) for cooling service. Aluminum bronze (UNS C61400) or copper nickel alloys often are used when the process inlet temperature is 177°C to 232°C (350°F to 450°F). Aluminum bronze (UNS C61400) has a somewhat higher tolerance for hydrogen sulfide than copper nickel alloys.

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

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

Regardless of the sulfur content, when hydrocarbons have a TAN above 1.5 mg of KOH/gm and the temperature is above 230°C (450°F), use 316L (UNS S31603) - except use 317L (UNS S31703) for California crude oils. For castings, use CF8M (UNS J92900) or CG8M (UNS J93000) provided the ferrite content is 8% minimum.

30. When 18 Cr-8 Ni SS is specified, any grade may be used; however, unstabilized regular carbon (0.08% carbon maximum) grades usually are not used for operating temperatures above 425°C (800°F). For temperatures above 425°C (800°F), stabilized grades should be used if there is a possibility of intergranular attack during downtime. For 321 (UNS S32100) or 347 SS (UNS S34700) in thickness in excess of 13 mm (1/2 in.), restricted chemistry (0.04% to 0.05%C, 0.015 max. P & max. S, Cr/Ni>1.6) should be used. In addition, 347 (UNS S34700) should be limited to 19 mm (3/4 in.) maximum to avoid problems associated with welding. Types 309 (UNS S30900), 310 (UNS S31000), 316 (UNS S31600), 321 (UNS S32100), and 347 (UNS S34700) should be used with caution for operating temperatures above 600°C (1100°F) because of the possibility of sigma phase embrittlement.

31. When experience shows that coking will occur above 455°C (850°F), 1-1/4 Cr-1/2 Mo can be used up to 590°C (1,100°F) and 2-1/4 Cr-1 Mo can be used up to 650°C (1,200°F). Conversely, if coking does not occur or if high velocities occur that will prevent coke lay-down, SS is required. The choice between 410S (UNS S41008) and 18-8 depends on the anticipated loading. This is because 410S will lose some room temperature ductility due to 475°C (885°F) embrittlement. Thus, 410S should be limited to parts with relatively low stress levels.

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

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

34. See note 9 in Table G-1 of API 610 (1996).

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

36. When ammonia is present in the stripper overhead system, ammonium bisulfide forms. This requires 316L for reflux piping.

Table A-18
Chemical Compositions of Some Common Stainless Steels, Special Stainless Steels and High Nickel Alloys

Alloys		Chemical Compositions, weight %																*CPI or
UNS No	P (G)-No.	C	Mn	P	S	Si	Cr	Ni	Mo	Fe	Cu	N	Ti	Nb	Al	Co	W	V	PRE_N
304L UNS S30403	8 (Gr 1)	0.03 max	2.00 max	0.045 max	0.03 max	0.75 max	18.00 20.00	8.00 12.00		64.95 74.00		0.00 0.10							18.0 21.6
316L UNS S31603	8 (Gr 1)	0.03 max	2.00 max	0.045 max	0.03 max	1.50 max	16.00 18.00	10.00 14.00	2.00 3.00	61.30 72.00		0.00 0.10							22.6 29.5
2205 UNS S32205	10H (Gr 1)	0.03 max	2.00 max	0.03 max	0.02 max	1.00 max	21.00 23.00	4.50 6.50	2.50 3.50	63.72 71.86		0.14 0.20							31.5 37.8
CD-4MCu J93370		0.04 max	1.00 max	0.03 max	0.04 max	1.00 max	24.50 26.50	4.75 6.00	1.75 2.25	59.89 66.25	2.75 3.25								30.3 33.9
SAF 2507 UNS S32750	10H (Gr 1)	0.03 max	1.20 max	0.035 max	0.02 max	0.80 max	24.00 26.00	6.00 8.00	3.00 5.00	58.77 66.76	0.50 max	0.24 0.32							37.7 47.6
Alloy 20 UNS N08020	45	0.07 max	2.00 max	0.045 max	0.035 max	1.00 max	19.00 21.00	32.00 38.00	2.00 3.00	40.85 44.00	3.00 4.00			8XC 1.00					25.6 30.9
904L UNS N08904	45	0.02 max	2.00 max	0.045 max	0.035 max	1.00 max	19.0 23.0	23.0 28.0	4.0 5.0	49.90 42.00	1.00 2.00								32.2 39.5
6XN UNS N08367	45	0.03 max	2.00 max	0.04 max	0.03 max	1.00 max	20.00 22.00	23.50 25.50	6.00 7.00	41.40 50.32	0.75 max	0.18 0.25							42.7 49.1
254SMO UNS S31254	8 (Gr 4)	0.015 max	1.00 max	0.03 max	0.01 max	0.80 max	19.50 20.50	17.50 18.50	6.00 6.50	51.43 56.32	0.50 1.00	0.18 0.22							42.2 45.5
25-6Mo UNS N08926		0.02 max	2.00 max	0.03 max	0.01 max	0.50 max	19.00 21.00	24.00 26.00	6.00 7.00	41.69 50.35	0.50 1.50	0.15 0.25							41.2 48.1
1925hMo UNS N08925	45	0.02 max	1.00 max	0.045 max	0.03 max	0.50 max	19.00 21.00	24.00 26.00	6.00 7.00	42.71 50.10	0.80 1.50	0.10 0.20							40.4 47.3
20Mo-6 UNS N08026	45	0.03 max	1.00 max	0.03 max	0.03 max	0.50 max	22.00 26.00	33.00 37.20	5.00 6.70	24.51 38.00	2.00 4.00								38.5 48.1
Sanicro 28 UNS N08028	45	0.03 max	2.50 max	0.03 max	0.03 max	1.00 max	26.00 28.00	30.00 34.00	3.00 4.00	29.01 40.40	0.60 1.40								35.9 41.2
Alloy+A21 800 UNS N08800	45	0.10 max	1.50 max		0.015 max	1.0 max	19.0 23.0	30.0 35.0		39.50 min	0.75 max		0.15 0.60		0.15 0.60				19.0 23.0
Alloy 825 UNS N08825	45	0.05 max	1.00 max		0.03 max	0.50 max	19.50 23.50	38.00 46.00	2.50 3.50	22.22 38.50	1.50 3.00				0.20 max				27.8 35.1
Alloy 625 UNS N06625	43	0.10 max	0.50 max	0.015 max	0.02 max	0.5 max	20.00 23.00	55.92 68.85	8.00 10.00	5.00 max			0.40 max	3.15 4.15	0.40 max				46.4 56.0
C276 UNS N10276	44	0.01 max	1.00 max	0.04 max	0.03 max	0.08 max	14.50 16.50	50.99 63.50	15.00 17.00	4.00 7.00						2.50 max	3.00 4.50	0.35 max	73.9 87.5

*CPI (Critical Pitting Index) or PRE_N (Pitting Resistance Equivalent, nitrogen included) = %Cr + 3.3 x (%Mo + %W) + 16 x %N

General Guidelines for Materials for Low-Temperature Services

1. This guide defines low-temperature as any temperature below +57°C (+135°F).

2. Materials listed in Table A-19 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 Boiler and Pressure Vessel Code, Section VIII, Division 1 (UCS-66) and Division 2 (AM 204)
- ASME B31.3 Chemical Plant and Petroleum Refinery Piping (323.2)

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

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

5. Select low-temperature steels for fracture-critical structural members designed for tensile stress levels greater than 40 MPa (6 ksi), and specify a minimum Charpy V-notch impact energy absorption of 27 joules (20 ft-lbs) for base metal, heat affected zones, 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 heat affected zones.

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-19

MINIMUM DESIGN TEMP		PLATES		STRUCTURAL NONPRESS	PIPING	TUBING	FORGINGS & FITTINGS	CASTINGS	FASTENERS
C	F	SHELLS AND HEADS	TRAYS						
		COMPLY WITH CODES – NO SPECIAL FRACTURE TOUGHNESS REQUIREMENTS							
57	135	APPLICATIONS FOR ASME BOILER AND PRESSURE VESSEL CODE, SECT. VIII	①	A36 OR A283	API 5L GR. B, A53 GR. B, A106 GR. B OR A671	NO SPECIAL REQUIREMENT	A105 OR A234 ③ ④	A216 GRADE WCB ④	
-6	20	DIVISIONS 1 AND 2: FOLLOW FIGURE USC-66 FOR DIVISION 1 AND FIGURE AM-218.1 FOR DIVISION 2 FOR MAT'L SELECTION AND IMPACT TEST REQUIREMENTS.		FOR NON-CRITICAL A36, OTHERWISE SAME AS PLATE FOR PIPING	A53 GR.B SEAMLESS A106 GR. B OR A671 ④		A105 A234 A727 OR A758 ③ ④	A352 GRADE LCB (NOT IMPACT TESTED) ④ ⑭	A193 GRADE B7 A194 GRADE 2H
-17	0				A106 GR. B OR A524 ④		A707 GR. L1 (ONLY). A727 OR A758 ④ ⑫		
-30	-20	PREFERRED MATERIAL: A 516 (ALL GRADES) ② ④ ⑪ ⑭	SAME AS VESSEL EXCEPT NO SPECIAL REQUIREMENTS FOR BOLTED TRAYS <10GA	⑮	A333 GR. 6 ④ ⑭	A334 GRADE 6 OR A179 ④ ⑦ ⑭	A350 GR. LF1 OR LF2, A420 GR. WPL6 OR A707 GR. L2 (ONLY) ④ ⑭	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 REQUIREMENTS	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 -74C/-100F A352 GR. LC3	
-100	-150	A553 OR A353 ② ⑬ ⑯ (TO -196 C/ -320 F)	A353 OR A553 TYPE 1		A333 GR. 8 ⑯	A334 GRADE 8 ⑯	A522 TP. ⑯ A420 (WPL8)	A351 GRADE CF8 ⑩	A320, GR. B8 A194, GR. 8 ANNEALED
		A240 TYPE 304 ⑤	TYPE 304		A312 TP. 304 ⑤	A213 TP304 ⑤	A182 GR. F 304 ⑤		
		B209 AL ALLOY 5063/5456	ALUMINUM		B241 (6061)	B234 (6061)	B247/361 (6061)		B211 TP 2024-T6
-200	-325	A240 TYPE 304 ⑤ ⑨	TYPE 304 ⑤ ⑨		A312 ⑤ TP. 304 ⑨	A213 ⑤ TP. 304 ⑨	A182, F 304 ⑤ ⑨ A403, WP 304	A351 GRADE CF8 , ⑤ ⑨	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 FOOTNOTE NUMBERS ON THE FOLLOWING PAGES

Notes for Table A-19

1. Bolted trays: No special requirements
   Welded trays: No special requirements up to and including 13 mm (1/2 in.) thick. Same as vessel shell above 13 mm (1/2 in.) 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% radiographed and magnetic particle inspected.

3. For forgings in thicknesses greater than 25 mm (1 in.), consider restrictive carbon content, e.g., 0.32 maximum, to enhance weldability. 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 -46°C (-50°F) *without* impact testing under the following (exempt) conditions:

<u>Applicable</u> <u>Code</u>	<u>Summary</u> <u>of</u> <u>Rules</u>
a. ASME Section VIII, Div. 1 paragraphs UCS-66 and UCS-67 (and Figures UCS-66 and UCS-66.1) *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 also may be reduced 15°C (30°F) 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 applicable material curve in Figure UCS-66, *except* impact testing is mandatory for: (1) All material thicknesses greater than 102 mm (4 in.) for welded construction. (2) All material thicknesses greater than 152 mm (6 in.) for non-welded materials with a MDMT less than 49°C (120°F). Also exempt from impact tests are: (1) ANSI B16.5 or B16.47 ferritic steel flanges with a MDMT not colder than -30°C (-20°F), (2) All UCS materials less than 2.5 mm (0.098 in.) thick and UCS nuts provided such CS materials are used at MDMTs not colder than -46°C (-50°F), (3) All P-No. 1 Group 1 or 2 materials 25 mm (1 in.) and less provided the vessel is hydrostatically tested, has an MDMT between 343°C (650°F) and -29°C (-20°F), and shock or cyclic loading is not a controlling condition. See UG-20 for additional exemptions. (4) Materials listed in Table UG 84.3 are exempt from additional tests provided the MDMT is warmer than the test temperature.

Note: Welding Procedure Qualification Tests must include weld and heat affected zone impact tests unless specifically exempted by paragraph UCS-67.

b. ASME Section VIII, Div. 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, *except* impact testing is mandatory for:

(1) All material thicknesses greater than 76 mm (3 in.) when the MDMT is lower than 49°C (120°F), and
(2) All material thicknesses greater than 51 mm (2 in.) which have been subjected to accelerated cooling (during heat treatment) when the MDMT is lower than 49°C (120°F).

Also exempt from impact tests are materials used in vessels with MDMT not colder than -46°C (-50°F) *and* design stress intensities not higher than 41 MPa (6,000 psi).

These exemptions *do not* apply to vessels in lethal service.

c. ASME B31.3, Section 323.2.2
(and Table 323.2.2)

Impact tests are not required when the MDMT is below -29°C (-20°F) but at or above -46°C (-50°F) and *both* the maximum operating pressure does not exceed 25% of the maximum allowable design pressure at ambient temperature *and* the combined longitudinal stress (from pressure, dead weight and displacement strain) does not exceed 41 MPa (6,000 psi).

Note: This exemption is not applicable for Category M (hazardous) fluid service.

5. Type 304 (UNS S30400) is listed because it is the least costly of the acceptable materials. Other 300 series SS may be needed due to 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 -254°C (-425°F) and higher with the following exceptions:

Applicable Code	Summary of Rules
a. ASME Section VIII, Div. 1 Para. UHA-51	Grades other than 304, 304L, 316, 316L and 347 (UNS S30400, S30403, S31600, S31603 and S34700) are not exempt from impact tests at temperatures of -200°C (-325°F) and higher if they are materials: 1) with allowable carbon contents in excess of 0.10%; 2) in cast form; 3) which have not been solution heat treated; or 4) in the form of weld metal *unless* they are otherwise exempted by Paragraph UHA-51.
b. ASME Section VIII, Div. 2, Para. AM-213	Same exceptions from impact tests as Division 1 except types 316 and 316L (UNS S31600 and S31603) are not in first category exempt from testing down to -254°C (-425°F). UHA 213.1 has exemptions for stress intensities less than 41.4 MPa (6,000 psi).
c. ASME B31.3, Section 323.2.2 (and Table 323.2.2)	Essentially the same exceptions from impact tests as ASME VIII, Div. 2 with slight variations. See Table A-18 and check all product forms; because, for some types, the lowest exempt temperature varies with product form or material specification.

6. Impact testing of ASTM A193 Grade B7 studs (but not ASTM A194 Grade 2H nuts) is required by ASME Section VIII, Div. 1 for temperatures below -40°C (-40°F), by ASME VIII, Div. 2 for temperatures below -29°C (-20°F), but not by ASME B31.3 above -46°C (-50°F) *if* the material is quenched and tempered.

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

8. Impact tests of aluminum are required only under ASME B31.3 for service below -270°C (-452°F). Notched tensile tests to prove ductility are required for wrought products for service below -270°C (-42°F). Notched tensile tests to prove ductility are required for cast products for service below -200°C (-325°F) by ASME Section VIII, Division 1.

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

10. Impact tests are required for austenitic SS castings by ASME Section VIII, Divisions 1 and 2 and under ASME B31.3 for castings in the non-solution annealed condition.

11. ASTM specification A20 lists impact properties generally achievable using standard mill practices.

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

13. Transverse Charpy V-notch impact testing shall be specified as a supplemental requirement.
14. For postweld heat treatment requirements, see:

a. ASME Section VIII, Division 1, Paragraph UCS-56.(1)
b. ASME Section VIII, Division 2, Paragraph AF-402.
c. ASME B31.3, Table 331.1.1.

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

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

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(1) Reductions in the minimum postweld heat treatment temperature (permitted by Table UCS-56.1) should not be allowed for materials which must meet the fracture toughness requirements of Figure UCS-66. Postweld heat treatment should be considered for pressure vessels with walls 25.4 mm (1 in.) or thicker to minimize the possibility of brittle fracture during hydrostatic test. In some cases, this will allow a 15°C (30°F) reduction in impact testing exemption temperature (see ASME VIII, Div. 1, UCS-68).

General Guidelines for Materials 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 (2) [UNS F45000], Type A, Class III, (3) Type A, etc.);
- Triten™ OPS-T200X(4) (plate, pipe, and overlay);
- Austenitic cast irons;
- Martensitic steels;
- Abrasion-resistance steels; (5)
- Austenitic manganese steels;
- Hardfacing alloys (Lincoln Faceweld™ No. 12 [CrCx], MG Industries™ Alloy 770 and 790 [UNS W74510 ob], Stellite™ 6 & 21 (UNS R30006 and R30021), Stoody™ 100 HC [25 Cr, 4.3 C, 1.6 Mn, 1.1 Mo, bal. Fe] etc.);
- Rubber (nitrile) or polyurethane lining;
- Ceramic lining (basalt, high density alumina ceramic, mullite bonded silicon carbide fused cast) manufactured by Abresist™, 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 27 joules (20 ft-lbs) at the design temperature and a minimum hardness of HRC 50.

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(2) HB 550-650
(3) HB 450-650
(4) HB 550-600
(5) HB 250-450

Appendix B

Rules of Thumb for Materials of Construction for Refineries

1. **The effect of temperature in the absence of hydrogen or corrosives in process streams:**
   Below -100°C (-150°F): 18 Cr-8 Ni SS, aluminum or 9% nickel steel required.

   Below -45°C (-50°F): Impact-tested low-alloy (nickel) steels required.

   Below -29°C (-20°F): Most codes require impact tests of carbon steel unless the stress is below 41,370 kPa (6, 000 psi) (See specific code requirements).

   Below 16°C (60°F): Brittle fracture of steel over approximately 13 mm (1/2 in.) thick possible. See Figure AM218.1 of ASME Section VIII , Division 2 or Figure UCS-66 of ASME Section VIII, Division 1, for specific thickness-temperature relationships.

   Above 345°C (650°F): Do not use 17 Cr steel, and avoid 12 Cr steel because of embrittlement. To avoid graphitization, use silicon-killed carbon steels only (e.g., ASTM A106, ASTM A515).

   Above 440°C (825°F): 1 Cr minimum is required for continuous service to avoid graphitization; however, furnace tubes are usually limited by oxidation.

   Above 540°C (1,000°F): 1-1/4 Cr (595°C [1,100°F] max.) to 9 Cr required to resist oxidation.

   Above 595°C (1,100°F): 2-1/4 Cr (650°C [1,200°F] max.) to 9 Cr required to resist oxidation.

   Above 650°C (1,200°F): 18 Cr-8 Ni SS required to resist oxidation; however, embrittlement due to formation of sigma phase is possible in some grades. Avoid cold work.

   Above 930°C (1,700°F): Use 25 Cr-12 Ni SSs (limited to non-pressure parts) e.g., 309 (UNS S30900) and HH (UNS J93503) or 25 Cr-20 Ni, e.g., 310 (UNS S31000) or HK-40 (UNS J94204) to resist oxidation.

   Above 1,095°C to 1,205°C (2,000°F to 2,200°F): Refractory-lined materials required.

2. **Hydrocarbon + sulfur, hydrogen free (e.g., crude units, cokers)**
   Above 230°C (450°F): Use 316L SS (UNS S31603) when total acid number of the crude oil exceeds 1.5 mg to 1.8 mg KOH/gm. Type 317L (UNS S31703) may be required for some crude oils, such as those from California.

   Above 288°C (550°F): Solid 5 Cr or 12 Cr clad required for crude oils containing over 1 wt% sulfur in absence of operating experience or hydrogen sulfide evolution data. For all hydrogen sulfide use 9 Cr minimum.

Above 345°C (650°F): Solid 5 Cr or 12 Cr clad required for crude oils containing 0.1wt% to 1.0 wt% sulfur in absence of operating experience or hydrogen sulfide evolution data. Consider all killed steel when sulfur content is below 0.2wt % to 0.3 wt %.

Above 400°C (750°F): Use 9 Cr in lieu of 5 Cr.

Above 540°C to 595°C (1,000°F to 1,100°F): 1 Cr 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 205°C (400°F): See API Standard 941 for 1 Cr, 1-1/4 Cr - 1/2 Mo, etc., based on hydrogen partial pressure. Avoid the use of C-1/2 Mo in hydrogen service. Be sure to calculate the hydrogen partial pressure based on gaseous products only. Beware of furnace tubes and exchangers, as the API Standard 941 curve is based on metal temperature.

4. **Hydrocarbon + hydrogen + hydrogen sulfide greater than 0.01 mol%**
   Above 205°C (400°F): Same as Number 3 above.

   Above 288°C (550°F): 321 or 347 SS (UNS S32100 or 34700) cladding or solid. Consider 12 Cr (343°C [650°F] maximum). Avoid 304 and 316 SS (UNS S30400 and S31600) because of intergranular stress corrosion cracking during downtime. Also avoid low carbon grades (e.g., 304L, 316L [UNS S30403, S31603]) SS 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: 304L SS (UNS S30403), (316L [UNS S31603], or alloy 20 [UNS N08020] required in many cases).

   Above 370°C (700°F): 18 Cr-8 Ni SS required.

   Above 425°C (800°F): 310 SS (UNS S31000) required (thermally stabilize after welding).

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

6. **Monoethanolamine (MEA) and Diethanolamine (DEA)**
   All temperatures: Stress relieve carbon steel welds and cold bends.

   Above 135°C (275°F): 304 SS (UNS 30400) exchanger tubes to 141°C (285°F) maximum (based on metal temperature).

7. **Potassium carbonate**
   Above 60°C (140°F): Stress relieve carbon steel. The use of 18 Cr-8 Ni SS required in reboilers and where there is turbulence (e.g., velocity exceeds 2.4 m/s [8 ft/s]). Do not use alloy 400 (UNS N04400), alloy 600 (UNS N06600) or Colmonoy™. Stellite™ 6 (UNS R30006) is acceptable.

8. **Carbon dioxide in water**
   Above 50°C (120°F): Use 304L SS (UNS S30403) to dew point when the carbon dioxide partial pressure exceeds 28 kPaa (4 psia). Aluminum is acceptable under the following conditions:

   a. pH between 4 and 8,
   b. no carbonate carryover,

c. copper less than 0.1 ppm and chloride less than 50 ppm;
d. velocity less than 30 m/s (100 ft/s) for mist-free gas; less than 18 m/s (60 ft/s) for up to 5 % moisture; less than 3.0 m/s (10 ft/s) for gas loaded with condensate.

9. Sulfuric acid alkylation

Below 38°C (100°F): Carbon steel good in 70% to 99% H_2SO_4 for velocities less than 0.6 m/s (2 ft/s). Use alloy 20 (UNS N08020) in valves and in high velocity areas.

10. Hydrogen sulfide

Below water dew point: When the hydrogen sulfide partial pressure is greater than 0.34 kPaa (0.05 psia), cracking of steels and some nonferrous materials can occur when hardness exceeds 235 Brinell HRC 22. See NACE Standard MR0175. For carbon steel the hardness limit should be 200 Brinell (HRB 95). See NACE Standard RP0472. Avoid use of cement linings or alloy 400 (UNS N04400) for sour water. See Number 14 for corrosion allowance on carbon steel exposed to sour water.

Above 200°C (400°F): Alloy 400 (UNS N04400) has no tolerance for hydrogen sulfide (gaseous or in aqueous solution).

11. Sodium and potassium hydroxide

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

Above 150°C (300°F): Alloy 400 (UNS N04400) or alloy 200 (UNS N02200) required to resist corrosion (based on metal temperature).

12. Aqueous chlorides

a. Maximum chloride content to avoid pitting and crevice corrosion:

304L (UNS S30403)	200 ppm
316L (UNS S31603)	1,000 ppm

Limitations
- pH 6 to 8
- Residual chlorine less than 2 ppm
- Absence of corrosion-inducing bacteria
- 50°C (120°F) maximum
- Absence of manganese in the water

b. Stress corrosion cracking (SCC)

Above 50°C (120°F): SCC of 18 Cr-8 Ni SS is possible; therefore, alternative materials often are chosen. In the case of units containing significant amounts of hydrocarbon, precautions during shutdown are often sufficient to avoid SCC. Solution annealing at 980°C (1,800°F) or stress relieving at 900°C (1,650°F) is required for 18 Cr-8 Ni SS U-bent exchanger tubes. Type 321 or 347 SS (UNS S32100 or S34700) is required when only U-bent portion of exchanger tubes is heat treated.

13. Boiler feedwater

Above 120°C (250°F): Use 12 Cr pumps (CA15 [UNS J91150] or CA6NM [UNS J91540]).

14. Corrosion allowance on carbon steel

(Metric equivalents are not numerical equivalents but are the commonly used equals.)

a. 1.5 mm (1/16 in.): Use on vessels and piping in non-corrosive service unless otherwise specified.

b. 2.5 mm (1/10 in.): Common minimum thickness for cladding.

c. 3.0 mm (1/8 in.): Minimum required for furnace tubes per API 560. Many refiners require as a minimum on vessels. Use on heat exchangers unless otherwise specified since no money is saved by specifying 1.5 mm (1/16 in.) because 3 mm (1/8 in.) is a TEMA Class R Standard. Use for sour water piping when the hydrogen sulfide partial pressure exceeds 70 kPaa (10 psia).

d. 4.5 mm (3/16 in.): Primarily used for sour water vessels and exchangers where the hydrogen sulfide partial pressure is less than 70 kPaa (10 psia).

e. 6.0 mm (1/4 in.): Maximum corrosion allowance. Primarily used for wet carbon dioxide equipment when the carbon dioxide partial pressure is less than 30 kPaa (4 psia) and for sour water equipment when the hydrogen sulfide partial pressure exceeds 70 kPaa (10 psia).

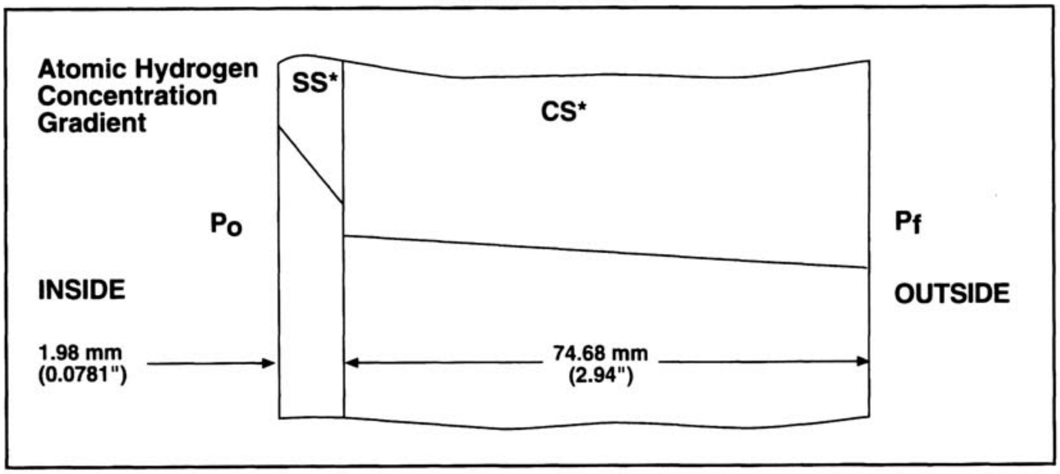
Appendix C

Hydrogen Partial Pressure Calculations

A. PROBLEM

Determine the equilibrium hydrogen partial pressure, P_i, at the carbon steel side of the stainless steel/ carbon steel interface in an 18 Cr-8 Ni stainless steel clad carbon steel vessel given the following information:

VESSEL VALVE



Temperature:	399°C (750°F)	
Partial Pressure H_2	Inside = 33.4 kg/cm^2a (475 psia)	= P_O
	Outside = 0	= P_f

Diffusion Coefficients:

SS (stainless steel)	10^{-6} cm^2/s (1.55 x 10^{-7} $in.^2/s$)
CS (carbon steel)	10^{-4} cm^2/s (1.55 x 10^{-5} $in.^2/s$)

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.*

Fick's first law of diffusion[1] through a solid (metal)

$$J = -D \frac{\partial C}{\partial X}$$

where J = Flow per unit area
D = Diffusion coefficient
C = Concentration
X = Metal thickness

Predicts that at steady state conditons

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

Then hydrogen flow through the SS clad layer can be expressed as

$$J_S = -D_S \frac{\Delta C}{\Delta t_s} = -D \frac{C_0 - C_i}{t_s} \qquad \textbf{(1)}$$

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

However, Sievert's Law[2] relates atomic hydrogen concentration within the metal to partial pressure by:

$$C = KP^{(1/2)} \qquad \textbf{(2)}$$

where K = Constant
C = Hydrogen concentration
P = Pressure (ATM)

Substituting Equation 2 into Equation 1 yields:

$$J_S = -D_S \frac{K_S\,(P_O^{(1/2)} - P_i^{(1/2)})}{t_s} \qquad \textbf{(3)}$$

Similarly for CS backing metal:

$$J_c = -D_C \frac{K_C\,(P_i^{(1/2)} - P_f^{(1/2)})}{t_C}$$

which reduces to

$$J_C = -D_C \frac{K_C \, P_i^{(1/2)}}{t_C} \tag{4}$$

Since P_f = 0 from initial conditions

Since flow through CS must equal flow through SS then:

$$J_S = J_C$$

and, combining Equation 3 and Equation 4:

$$-D_S \frac{K_S \, (P_O^{(1/2)} - P_i^{(1/2)})}{t_S} = -D_C \frac{K_C \, P_i^{(1/2)}}{t_C} \tag{5}$$

Rearranging and solving Equation 5 for P yields:

$$P_i = \left[\frac{Po^{1/2}}{1 + \frac{(t_s K_C D_C)}{(t_C K_S D_S)}} \right]^2 \tag{6}$$

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 (See section E, Calculation of Sievert's Law Constants) into Equation 6 yields:

$$P_i = \left[\frac{(475)^{1/2}}{1 + \frac{(0.0781)(0.326)(10}{(2.94)(3.0)(10^{-6})}} \right.$$

$$P_i = 20.1 \text{ kg/cm}^2\text{a} (286 \text{ psia})$$

D. DISCUSSION

Results obtained with the model described above appear to be quite reasonable. An important assumption contained in the model is number 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 on page 175).

Existing literature consistently reports a higher hydrogen solubility in γ-iron than in α-iron.[2] Therefore, since the crystal structure of the clad vessel wall changes from face-centered cubic (γ) 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 1 becomes $J_S = D_S (C_0 - C_{CS})/t_S$) 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.

This alternative model, in effect, 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 also is 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. Carbon steel at temperatures: 399°C (750°F):

$$S = 42.7\ P^{(1/2)} \exp(-3{,}280/T) \qquad \text{(DMIC Report 219)}^{2}$$

where S = Solubility of hydrogen in ppm
P = Pressure in atmospheres
T = Temperature in degrees K

for P = 33.4 kg/cm² (475 psia) and T = 399°C (750°F) = 673°K (1,210°R)

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

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

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

$$K_C = \frac{C}{p^{(1/2)}} = \frac{1.8}{(475/14.7)^{1/2}}$$

$$K_C = 0.326$$

2. Stainless Steel

Solubility data[3] for type 347 stainless steel

Temperature	371°C (700°F)
Pressure	105.5 kg/cm² a(1,500 psia)
Hydrogen concentration	30 ppm

Substituting into Sieverts' Equation (Equation 2) and solving for K yields

$$K_s = \frac{C}{p^{(1/2)}} = \frac{30}{(1500/14.7)^{1/2}}$$

$$K_s = 3.0$$

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1. R.E. Reed-Hill, *Physical Metallurgy Principles* (New York, NY: Van Nostrand, 1964): p. 257.
2. E.E. Fletcher, A.R. Elsea, "Hydrogen Movement in Steel-Entry, Diffusion and Elimination," Defense Metals Information Center Report 219 (June 1965).
3. T.P. Groeneveld, A.R. Elsea, "Effect of Hydrogen on the Properties of Reactor Steels at Temperatures Below 400°F" (December 1971). Unpublished Report to American Petroleum Institute.

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Appendix D

A. UOE Double Submerged Arc Welded X65 and X70 Line Pipe

1.0 SCOPE

Pipe shall be manufactured in accordance with API Specification for Line Pipe, API Standard 5L, (latest edition). In addition, it shall comply with the provisions and requirements of this specification.

2.0 PROCESS OF MANUFACTURE AND MATERIAL

2.1 Steel shall be made by the electric furnace or basic oxygen process. Steel shall be fully killed. If continuous casting is used, magnetic stirring, squeeze rolling or other proven techniques shall be used to prevent center line segregation.

2.2 Pipe shall be cold U-O formed with the principal rolling direction of the plate corresponding with the longitudinal axis of the pipe.

2.3 Formed pipe shall be longitudinally welded by the submerged arc welding process, using at least one pass from the inside and at least one pass from the outside single seam.

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

2.5 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.

2.6 The manufacturer shall perform all fabrication and welding in accordance with an established written procedure. The first production pipe shall be sectioned and tested. Tests shall verify that physical and chemical properties, as well as nondestructive testing, meet the requirements of the specification. In addition, microhardness traverses across the weld and heat affected zone shall be performed. The hardness shall not exceed 280 HV_{10} 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.

2.7 The pipe manufacturing procedure, including details of the steel making route, shall be submitted to the buyer for approval as part of the manufacturer's bid. As a minimum, the submittal shall include a description of the following:

- Steel making method and desulfurization practice,
- Casting method, including a description of all special practices associated with casting, such as tundish shrouding and treatment of "intermix" continuous cast slabs containing a mixture of two steel heats,
- Plate rolling schedule, including final pass percent reduction and methods of temperature and thickness control,
- Welding procedures and qualification test data to support longitudinal welding and manual repair welding,
- Heat treatment procedures,
- Ultrasonic testing procedure for final acceptance, including the number of probes, probe orientations, probe angles and frequency, and diagrams showing the probe coverage of the weld zone.

3.0 CHEMICAL PROPERTIES AND TESTS

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

	Weight %
Carbon	0.16 maximum
Manganese	0.8-1.6
Silicon	0.15 - 0.35
Phosphorus	0.020 maximum
Sulfur	0.005 maximum
Calcium	0.006 maximum
Copper	0.35 maximum
Chromium	0.30 maximum
Molybdenum	0.20 maximum
Nickel	0.30 maximum
Titanium	0.030 maximum
Boron	0.0003 maximum
Niobium (Columbium)	0.05 maximum
Vanadium	0.08 maximum
Niobium (Columbium) + Vanadium	0.10 maximum
Nitrogen	0.010 maximum
Aluminum (Total)	0.025 - 0.05
Aluminum (Soluble)	2 times Nitrogen (minimum)
Total of Nb + V + Ti + Cu + Cr + Mo	0.5 maximum

3.2 The manufacturer shall state in the quotation the nominal (aim) chemical composition and steel making route for pipe on the order. Intentional alloy additions other than niobium or vanadium will not be permitted without approval of the buyer. Aim chemical compositions and mill control limits on alloying elements shall be subject to buyer's approval prior to placement of the order.

3.3 The carbon equivalent shall comply with API 5L, Appendix E, SR18. In addition, the P_{cm} parameter based on a product analysis and calculated using the following formula, shall not exceed 0.20.

$$P_{cm} = C + \frac{Si}{30} + \frac{Mn + Cu + Cr}{20} + \frac{Ni}{60} + \frac{Mo}{15} + \frac{V}{10} + 5B$$

where B refers to the Boron content of the steel.

3.4 Both heat and product analyses shall be furnished.

3.5 Analyses shall be taken from each lot of pipe.

4.0 MECHANICAL PROPERTIES AND TESTS

4.1 Pipe tensile properties shall conform to the requirements of the applicable grade as shown in Table 4.1 of API Standard 5L; however, the yield strength shall not exceed 552 MPa (80,000 psi) for X65 and 586 MPa (85,000 psi) for X70 material. In addition, the yield-to-tensile strength ratio shall not exceed 0.93.

4.2 Tensile properties shall be measured on one sample per lot of pipe, except where more than one heat of steel is represented in a lot. Tensile tests shall be performed on samples from all heats represented in the lot.

4.3 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 E, SR5 of API 5L.

4.3.1 Specimens shall be Charpy V-notch Type A.

4.3.2 Temperature of testing shall be (**state design temperature**).

4.3.3 To be acceptable, the minimum average of the three tests shall be at least 47.5 J (35 ft-lbs), and no individual test shall be less than 38 J (28 ft-lbs)(1) based on full size (10 mm x 10 mm) specimens. Percent shear area shall also be reported.

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

4.4 Drop weight tear testing on 508 mm (20 in.) diameter and larger pipe shall be carried out at 0°C (+32°F) in accordance with Appendix E, SR6 of API 5L, except that 100% of the heats shall exhibit 85% or more shear fracture area.

5.0 HYDROSTATIC TESTS

5.1 Each length of pipe shall be given a mill hydrostatic test which will produce in the pipe wall a hoop stress of 95% of the minimum specified yield strength (MSYS). Test pressure shall be maintained for at least 10 seconds. The manufacturer shall submit for approval a full description of their hydrostatic test stand end seals and their calculations if they propose to apply Appendix E, SR14. When it is agreed that SR14 will be applied, the minimum hoop stress shall be 92% of the MSYS.

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(1) The minimum Charpy V-notch impact requirement should be based on the equation:

$C_V = K\sigma^2 (Rt)^{1/3}$,

where $K = 3.56 \times 10^{-5}$ for metric units and 1.08×10^{-2} for English units

σ = the hoop stress, MPa (ksi)

R = pipe radius mm (inch)

t = pipe wall mm (inch)

C_v = plateau energy for full size specimen, Joules (ft-lbs)

5.2 The weld seam shall be positioned such that any pinhole leaks or weepers are clearly visible to the hydrotest operator or the designated full time mill inspector.

5.3 Hydrostatic test gauges shall be calibrated prior to commencement of 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.

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

6.0 DIMENSIONS, WEIGHTS AND LENGTHS

6.1 The pipe shall be furnished in 12.2 m (40 ft) nominal lengths. Each shipment shall have a minimum average length of 10.7 m (35.0 ft). The maximum length shall be 13.7 m (45.0 ft), and the minimum length shall be 5.8 m (19.0 ft). Not more than 10% of the lengths in any shipment shall be less than 7.9 m (26.0 ft).

6.2 Jointers shall not be furnished.

6.3 Tolerances on pipe diameter, wall thickness, and weights shall be as specified in API 5L Table 6.3, except that the minimum wall thickness (not including locally ground areas) for 60% of the pipe joints shall have equal to or greater than the specified wall thickness. The wall thickness at any area, including ground areas, shall be at least 92% of the minimum specified wall.

6.4 Pipe ends shall be smoothly beveled to an angle of 30 degrees +5, - 0 degrees, up to 16 mm (5/8 in.) 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 1.5 mm (1/16 in.) ± 0.4 mm (1/64 in.) for 95% of the circumference. The remaining 5% may vary between 0.8 mm (1/32 in.) minimum and 2.4 mm (3/32 in.) maximum.

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

6.6 Through any cross section over the pipe length, the maximum and minimum internal diameters shall satisfy the following relationship:

$$\frac{D_{max} - D_{min}}{D_{max} + D_{min}} \times 100 \leq 0.5\% \quad \textbf{OR} \quad \frac{D_{max} - D_{min}}{2 \times \text{Nominal D}} \times 100 \leq 0.5\%$$

7.0 PIPE ENDS AND THREAD PROTECTORS

Each pipe shall be fitted with bevel protectors to prevent damage during shipment. Pipe 356 mm (14 in.) in diameter and larger that is not internally mill coated shall be fitted with metal bevel protectors.

8.0 COUPLINGS

(No requirements in addition to API 5L)

9.0 NONDESTRUCTIVE INSPECTION

9.1 The full body of all plate used for manufacturing pipe shall be ultrasonically examined to detect gross laminations. Examination shall be in accordance with ASTM A 435 or other mill standard technique acceptable to the buyer. In addition to the required "grid" scan, the area scanned shall include 100% of the as-trimmed edges for the longitudinal weld seam and the edges which represent the final ends of the pipe after plate forming and welding. The scan pattern shall be such that it will detect all indications 19 mm x 100 mm [3/4 in. x 4 in.] and larger. In the event pipe ends must be cut back after this examination, the examination shall be repeated on the final pipe ends.

Mill procedures shall be submitted to the buyer for permission to proceed prior to production. To be acceptable, lamellar-type defects shall not exceed 100 mm (4 in.) in the longitudinal direction or 19 mm (3/4 in.) in the transverse direction throughout the body of the plate. The limit along the scanned edges of the plate shall be 19 mm (3/4 in.) in any direction. Laminations exposed at a plate edge are rejectable regardless of size.

9.2 The ultrasonic examination 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 mill's internal quality control and subject to buyer's mill representative's review.

9.3 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:

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

9.3.2 Probes for detecting weld area defects shall be positioned to detect both transverse and longitudinal defects.

9.3.3 Calibration shall be performed at the same rate of speed used in production testing.

9.3.4 Both the 1.5 mm (1/16 in.) side drilled hole (located on the center line of the weld seam) and the N5 notch specified in paragraph 9.15 of API 5L shall be used to calibrate the equipment. Four (4) longitudinal N5 notches located at each of the weld toes and two (2) transverse N5 notches, one on the ID surface and one on the OD surface, shall be used. Defects that exhibit indications of cracks or lack of penetration also shall be investigated as above.

9.4 Each end of the longitudinal welds shall be radiographed covering a distance of at least 200 mm (8 in.) after expansion and hydrostatic testing. Radiographic film shall be Kodak Type AA or equivalent, and each film shall contain a 2% penetrameter. The H & D film density shall be in the range of 2.0 to 3.0. A film density up to 3.5 is permitted in the plate. If the wire type penetrameters are used, the sensitivity demonstrated by the smallest visible wire shall be at least 2.0 %. The manufacturer shall submit for the buyer's approval their pipe wall thickness vs proposed sensitivity range for the wire penetrameters. All penetrameter thicknesses shall be based on the base metal thickness.

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

9.6 All pipe containing injurious defects exceeding the limits of Section 9 of API Standard 5L shall be rejected unless repairs are permitted in accordance with paragraph 10.0 of this specification.

9.7 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.

9.8 Residual magnetism shall be measured at four locations on each of the beveled ends of the finished pipe subsequent to any handling by electromagnetic lifting devices. The maximum permitted residual magnetism shall be 30 gauss measured with a buyer-approved gaussometer. At least 5 lengths per 100 shall be examined. In no case shall less than 2 lengths be measured during an 8 hour shift. Any pipe exceeding this limit shall be demagnetized the full length and retested to determine the gauss level. Any pipe still exceeding 30 gauss shall be rejected.

10.0 WORKMANSHIP, VISUAL INSPECTION, AND REPAIR OF DEFECTS

10.1 Defects not exceeding 8.0% of the specified wall thickness may be removed by grinding and blending to a smooth contour, provided the remaining wall thickness at the ground area is not less than 92% of the specified wall thickness.

10.2 No welding repairs shall be permitted under the following circumstances: after expansion, within 152 mm (6 in.) of the pipe ends, or at any time on the parent pipe or plate. When repairs of defects are not permitted, the rejected area shall be removed as a compete ring.

10.3 Injurious weld defects in excess of 8.0% 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.

10.4 Prior to repair, welding defects shall be completely removed, and the cavity shall be thoroughly cleaned and nondestructively examined.

10.5 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 heat-affected zone. Acceptance criteria shall be the same as specified in Section 4.0 of this specification.

10.6 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. Back to back (ID to OD) repairs are not permitted, except when small hydrostatic test weeper leaks are repaired. In addition, the total weld repaired length shall not exceed 5% of the total seam weld length per pipe.

10.7 All weld repairs shall be x-rayed. The film coverage shall extend at least 100 mm (4 in.) beyond the ends of the repair weld.

10.8 Dents in excess of those permitted in paragraph 10.3 of API 5L are unacceptable and shall not be repaired.

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

11.0 MARKING AND COATING

11.1 Pipe markings prescribed in API Standard 5L, Section 11 and Appendix E, SR3 shall be paint-stenciled on the inside of the pipe, except those on pipe with a nominal outside diameter of 305 mm (12 in.) and under. These markings 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.

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

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

11.4 Color banding for all wall thicknesses may be required. When requested, a stripe approximately 51 mm (2 in.) 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.

11.5 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 (**latest edition**), and the external coating shall meet the requirements of (**list specification**).

12.0 TRANSPORTATION

12.1 Pipe shall be loaded for shipment in accordance with API RP 5L1, "Recommended Practice for Railroad Transportation of Line Pipe," or API RP 5LW, " Recommended Practice for Transportation of Line Pipe on Barges and Marine Vessels," whichever is applicable.

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

12.3 Evidence of transit fatigue cracking shall cause the entire load to be provisionally rejected until the balance of the load can be adequately inspected and it can be demonstrated that the remaining pipe is free of cracks.

B. Electric Resistance or Electric Induction Welded X65 and X70 Line Pipe for Submarine Pipelines and Sour Service

1.0 SCOPE

Pipe shall be manufactured in accordance with API Specification for Line Pipe, API Standard 5L, (**latest edition**). In addition, it shall comply with the provisions and requirements of this specification.

2.0 PROCESS OF MANUFACTURE AND MATERIAL

2.1 Steel shall be made by the electric furnace or basic oxygen process. Steel shall be fully killed. If continuous casting is used, magnetic stirring, squeeze rolling, or other proven techniques shall be used to prevent center line segregation.

2.2 Pipe shall be cold U-O formed from plate or skelp.

2.3 Formed pipe shall be longitudinally welded by the high frequency electric resistance welding or high frequency electric induction process, single seam.

2.4 The longitudinal weld seam and heat affected zone shall be normalized at a temperature of at least 870°C (1,600°F) after welding as verified with a buyer-approved method. The weld shall be allowed to cool below 650°C (1,200°F) prior to water quenching. The adequacy of normalizing shall be demonstrated by metallurgical sampling (including a microhardness traverse 1 mm above the ID surface) prior to start of production welding, at least once per heat thereafter and at other times when requested by the buyer's inspector because of process upset conditions.

2.5 Sufficient crop shall be taken from the lead end of each pipe run to assure tempering of martensite has been achieved on the remaining weld. Verification by metallographic examination shall be performed to demonstrate this.

2.6 Skelp produced in multiples of the final width is prohibited for sizes over 8 in. nominal diameter except when the steel is manufactured by the continuously cast method.

2.7 Pipe may be cold expanded as permitted by API 5L. Cold expansion shall be limited to a maximum of 1.5%. The manufacturer shall demonstrate and document in their quality manuals and procedures that expansion does not exceed this amount.

2.8 The manufacturer shall perform all fabrication, welding, and inspection activities in accordance with an established written procedure. The first production pipe shall be sectioned and tested. The testing shall verify that the mechanical properties, chemical composition, and nondestructive testing meet the specification requirements. In addition, microhardness traverses across the weld and heat affected zone shall be performed. The hardness shall not exceed 248 HV_{10} at any location.

2.9 The pipe manufacturing procedure, including all relevant production history on 508 mm (20 in.) and greater diameter pipe furnished for high pressure gas service, shall be submitted to the buyer for approval as part of the manufacturer's bid. As a minimum, the submittal shall include a description of the following:

- Steel making method and desulfurization practice;
- Casting method, including a description of all special practices associated with casting, such as tundish shrouding and treatment of "intermix" continuous cast slabs containing a mixture of two steel heats;
- Skelp or plate rolling schedule, including final pass % reduction and methods of temperature and thickness control;
- Heat treatment procedures;
- Ultrasonic testing procedure for final acceptance, including the number probes, probe orientations, probe angles and frequency, and diagrams showing the probe coverage of the weld zone.

3.0 CHEMICAL PROPERTIES AND TESTS

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

	Weight%
Carbon	0.16 maximum
Manganese	0.8-1.6
Silicon	0.15 - 0.35
Phosphorus	0.020 maximum
Sulfur	0.005 maximum
Calcium	0.006 maximum
Copper	0.350 maximum
Chromium	0.300 maximum
Molybdenum	0.200 maximum
Nickel	0.300 maximum
Titanium	0.030 maximum
Boron	0.0003 maximum
Niobium (Columbium)	0.050 maximum
Vanadium	0.080 maximum
Niobium (Columbium) + Vanadium	0.100 maximum
Nitrogen	0.010 maximum
Aluminum (Total)	0.025 - 0.05
Aluminum (Soluble)	2 times Nitrogen (minimum)
Total of Nb + V + Ti + Cu + Cr + Mo	0.5 maximum

3.2 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 niobium or vanadium will not be permitted without approval of the buyer. Aim chemical compositions and mill control limits on alloying elements shall be subject to buyer's approval prior to placement of the order.

3.3 The carbon equivalent shall comply with API 5L Appendix E, SR18.

In addition, the P_{cm} parameter based on a product analysis and calculated using the following formula shall not exceed 0.20.

$$P_{cm} = C + \frac{Si}{30} + \frac{Mn + Cu + Cr}{20} + \frac{Ni}{60} + \frac{Mo}{15} + \frac{V}{10} + 5B$$

where B refers to the boron content of the steel.

3.4 Both heat and product analyses shall be furnished. Product samples from the same heat shall be taken from lengths made from different coils.

3.5 Analyses shall be taken from each lot of pipe.

4.0 MECHANICAL PROPERTIES AND TESTS

4.1 Both longitudinal and transverse plate and weld tensile properties shall conform to the requirements of the applicable grade as shown in Table 4.1 of API Standard 5L; however, the yield strength shall not exceed 552 MPa (80,000 psi) for X65 and 586 MPa (85,000 psi) for X70 material. In addition, the yield to tensile strength ratio shall not exceed 0.93.

4.2 Both longitudinal and transverse tensile properties shall be measured on one sample per lot of pipe, except where more than one heat of steel is represented in a lot, tensile tests shall be performed on samples from all heats represented in the lot.

4.3 Flattening tests shall be made as required by Paragraph 4.10 of API 5L.

4.4 Three sets of three Charpy impact test specimens shall be taken from pipe body, heat-affected zone, and weld fusion zone, respectively. These samples shall be taken from each heat of steel furnished on the order. The samples shall be tested in accordance with Appendix E, SR5 of API 5L.

4.4.1 Specimens shall be Charpy V-notch Type A.

4.4.2 Temperature of testing shall be (**state design temperature**).

4.4.3 To be acceptable, the minimum average of the three tests shall be at least 95J (70 ft-lbs), and no individual test shall be less than 81 J (60 ft-lbs)(2) based on full size (10 mm x 10 mm) specimens. Where necessary to obtain full size specimens, the pipe shall be flattened prior to machining the specimens. Percent shear area also shall be reported.

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

4.5 Drop weight tear testing on 508 mm (20 in.) diameter and larger pipe shall be carried out at 0°C (+32°F) in accordance with Appendix E, SR6 of API 5L, except that 100% of the heats shall exhibit 85% or more shear fracture area.

4.6 A hardness test shall be carried out on one pipe per heat or lot of 100 pipe lengths, whichever produces the greatest test frequency. Three traverses across the base metal, heat-affected zone, and weld fusion zone shall be made. One traverse shall be approximately 1 mm below the OD surface. One traverse shall be approximately 1 mm below the ID surface. One traverse shall be at the pipe mid thickness. No individual hardness reading shall exceed 248 HV_{10}.

5.0 HYDROSTATIC TESTS

5.1 Each length of pipe shall be given a mill hydrostatic test which will produce in the pipe wall a hoop stress of 100% of the minimum specified yield strength (MSYS). Test pressure shall be maintained for at least 10 seconds. If distortion occurs, the test pressure may be reduced to 95% of MSYS provided the pressure is maintained for at least 20 seconds. The manufacturer shall submit for approval a full description of their hydrostatic test stand end seals and their calculations if they propose to apply Appendix E, SR14.

5.2 The weld seam shall be positioned such that any pinhole leaks or weepers are clearly visible to the

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(2) The minimum Charpy V-notch mpact requirement should be based on the equation:

$C_V = K\,\sigma^2\,(Rt)^{1/3}$,

where K = 3.56 x 10^{-5} for metric units and 1.08 x 10^{-2} for English units

σ = the hoop stress, MPa (ksi),

R = pipe radius, mm (inch)

t = pipe wall, mm (inch)

C_V = plateau energy for full size specimen, Joules (ft-lbs) hydrotest operator or the designated full time mill inspector.

5.3 Hydrostatic test gauges shall be calibrated prior to commencement of production, at least once a week thereafter and after any hydrostatic failure of end seals or pipe body. Certified dead weight testers shall be used for calibrations. A buyer representative shall witness the calibration of all gauges.

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

6.0 DIMENSIONS, WEIGHTS, AND LENGTHS

6.1 The pipe shall be furnished in 12.2 m (40 ft) nominal lengths. Each shipment shall have a minimum average length of 10.7 m (35 ft). The maximum length shall be 12.8 m (42.0 ft), and the minimum length shall be 11.6 m (38.0 ft).

6.2 Jointers shall not be furnished.

6.3 Tolerances on pipe diameter wall thickness and weights shall be as specified in API 5L Table 6.3 except as follows:

- The pipe diameter away from the ends shall be ± 3 mm (± 1/8 in.) of the nominal diameter.
- The inside pipe diameter within 102 mm (4 in.) of each pipe end shall be ± 1.5 mm (± 1/16 in.) of the nominal diameter (less 2 times the nominal wall thickness) when measured on the inside surface of the pipe.
- The tolerance on the wall thickness shall be +15%, -0%.

6.4 Pipe ends shall be smoothly beveled to an angle of 30 degrees +5, - 0 degrees, up to 16 mm (5/8 in.) 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 1.5 mm (1/16 in.) ± 0.4 mm (1/64 in.) for 95% of the circumference. The remaining 5% may vary between 0.8 mm (1/32 in.) minimum and 2.4 mm (3/32 in.) maximum. The price for beveling shall be quoted separately.

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

6.6 Through any cross section over the pipe length, the maximum and minimum internal diameters shall satisfy the following relationship:

$$\frac{D_{max.} - D_{min.}}{D_{max.} + D_{min.}} \times 100 \le 0.5\% \qquad \textbf{OR} \qquad \frac{D_{max.} - D_{min.}}{2 \times \text{Nominal D}} \times 100 \le 0.5\%$$

6.7 Misalignment of the skelp edges at the longitudinal weld shall not exceed 5% of the specified wall thickness.

6.8 The depth of internal flash trim shall not infringe on the specified minimum wall thickness.

7.0 PIPE ENDS AND THREAD PROTECTORS

Each pipe shall be fitted with bevel protectors to prevent damage during shipment. Pipe 356 mm (14 in.) in diameter and larger that is not internally coated shall be fitted with metal bevel protectors.

8.0 COUPLINGS

(No requirements in addition to API 5L)

9.0 NONDESTRUCTIVE EXAMINATION

9.1 The full body of all plate or skelp used for manufacturing pipe shall be ultrasonically examined to detect gross laminations. Examination shall be in accordance with ASTM A 435 or other mill standard technique acceptable to the buyer. In addition to the required "grid," the area scanned shall include 100% of the as-trimmed edges of the ERW seam and the edges which represent the final ends of the pipe after forming and welding. The scan pattern shall be such that it will detect all indications 19 mm x 100 mm (3/4 in. x 4 in.) and larger. In the event the pipe ends must be cropped back after this examination, the examination shall be repeated. Mill procedures shall be submitted to the buyer for permission to proceed prior to production. To be acceptable, lamellar-type defects shall not exceed 100 mm (4 in.) in the longitudinal direction or 19 mm (3/4 in.) in the transverse direction throughout the body of the plate or skelp. The limit along the scanned edges shall be 19 mm (3/4 in.) in any direction. Laminations exposed at a plate edge are rejectable regardless of size.

9.2 The ultrasonic examination required by API 5L paragraph 9.1 (b) 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 buyer's mill representative's review.

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

9.3.1 The test pipe shall be run at the start of each shift, at least once during the shift and at other times when requested by the buyer's inspector.

9.3.2 Probes for detecting weld area defects shall be positioned to detect both transverse and longitudinal defects.

9.3.3 Calibration shall be performed at the same rate of speed used in production testing at least twice per shift. The test piece shall be made from production pipe from the same order.

9.3.4 Both the 1.5 mm (1/16 in.) vertically drilled hole (located on the center line of the weld seam) and the N5 notch specified in paragraph 9.15 of API 5L shall be used to calibrate the equipment. Four (4) longitudinal N5 notches located at each of the weld toes and two (2) transverse N5 notches, one on the ID surface and one on the OD surface, shall be used. Defects that exhibit indications of cracks or lack of penetration also shall be investigated as above.

9.4 All ultrasonic equipment shall be proven capable of detecting weld area flaws within the pipe camber and weld skewing range of the pipe handled.

9.5 The manufacturer shall demonstrate the extent of weld length coverage during calibration. Manual ultrasonic examination of the pipe ends shall be performed to maintain 100% coverage.

9.6 All pipe containing injurious defects exceeding the limits of Section 9 of API Standard 5L shall be rejected unless repairs are permitted in accordance with paragraph 10.0 of this specification.

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

9.8 Residual magnetism shall be measured at four locations on each of the beveled ends of the finished pipe subsequent to any handling by electromagnetic lifting devices. The maximum permitted residual magnetism shall be 30 gauss measured with a buyer-approved gaussometer. At least 5 lengths per 100 shall be examined. In no case shall less than 2 lengths be measured during an 8-h shift. Any pipe exceeding this limit shall be demagnetized the full length and retested to determine the gauss level. Any pipe still exceeding a 30 gauss level shall be rejected.

10.0 WORKMANSHIP, VISUAL INSPECTION, AND REPAIR OF DEFECTS

10.1 Defects may be removed by grinding and blending to a smooth contour provided the remaining wall thickness is at least 92% of the specified wall thickness, except that any crack in the weld area (weld or HAZ) found by visual or other NDE method is cause for permanent rejection of the affected joint. Hook cracks or "up-turned fiber" defects may be ground or cut out as a ring provided the absence of other hook crack areas on the joint is demonstrated by wet magnetic particle or other nondestructive examination method acceptable to the buyer.

10.2 No welding repairs are permitted on the weld zone or the parent pipe or plate.

10.3 Dents in excess of those permitted in paragraph 10.3 of API 5L are unacceptable and shall not be repaired.

10.4 Arc burn produced during the manufacture or inspection of the pipe are injurious defects and shall be removed by cutting off a ring of pipe. As a reference method for confirming the existence of an arc burn, the area may be buffed with a wire brush or sanding disc and etched with a 5% Nital solution.

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

11.0 MARKING AND COATING

11.1 Pipe markings prescribed in API Standard 5L, Section 11 and Appendix E, SR3 shall be paint-stenciled on the inside of the pipe, except that on pipe with a nominal outside diameter of 305 mm (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.

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

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

11.4 Color banding for all wall thicknesses may be required. When requested, a stripe approximately 51 mm (2 in.) 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.

11.5 Pipe shall be furnished bare with no lacquer or oil, 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 external coating shall meet the requirements (**List specification**).

12.0 TRANSPORTATION

12.1 Pipe shall be loaded for shipment in accordance with API RP 5L1, “Recommended Practice for Railroad Transportation of Line Pipe,” or API RP 5LW, “Recommended Practice for Transportation of Line Pipe on Barges and Marine Vessels,” whichever is applicable.

12.2 Pipe that travels onboard ships shall be stowed below deck.

12.3 Evidence of transit fatigue cracking shall cause the entire load to be provisionally rejected until the balance of the load can be adequately inspected and it can be demonstrated that the remaining pipe is free of cracks.

13.0 HYDROGEN-INDUCED CRACKING TEST

13.1 The manufacturer shall demonstrate that each heat of line pipe furnished is resistant to hydrogen-induced cracking (HIC).

13.2 For the first five heats of pipe furnished, one pipe shall be selected for removal of a test coupon. Thereafter, one pipe for every 10 heats shall be selected for coupon removal. Tests shall be conducted and evaluated in accordance with NACE International Standard TM0284. Acceptance criteria shall be:

- Crack length ratio: 8% maximum
- Crack sensitivity ratio: 1% maximum

14.0 FIELD WELDABILITY TEST

14.1 The manufacturer shall demonstrate the field weldability of each X-grade on the order by performing a girth welding procedure qualification test on pipe of the maximum carbon equivalent furnished.

14.2 The weld shall be made with the shielded metal arc process using cellulosic electrodes and the vertical down technique. Preheat shall be limited to that necessary to remove moisture from the pipe, approximately 38°C (100°F).

14.3 At least four macrosections shall be taken from opposite quadrants of the weld and examined for HAZ cracking. Additionally, three microhardness traverses (one each 1 mm below the OD and ID surfaces, and one at the pipe mid-wall) shall be made on each macrosection. The hardness shall not exceed 248 HV_{10}

15.0 WELD AREA CORROSION TEST

15.1 The manufacturer shall demonstrate that each heat of line pipe furnished is resistant to preferential weld area corrosion in both the as-welded and seam normalized conditions.

15.2 Two complete rings, one from the as-welded lead end of the pipe and one from the middle of the run, shall be removed for testing. Each ring shall be immersed in a bath of artificial seawater with the pH adjusted with acetic acid to not higher than 4. The test shall be carried out at a temperature of 40°C (104°F) for 14 days. At the conclusion of the test the weld area shall be closely examined and the maximum depth of the corrosion penetration measured. The depth of attack in the weld area shall not exceed that in the body of the pipe by more than a factor of 1.25.

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