

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.

⁽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 hydrotreating 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



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 shut-downs – 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	$C_n H_{2n+2}$	Saturated (-ane suffix) e.g., hexane
2. Olefin or ethylene	$C_n H_{2n}$	Unsaturated (double bond; -ene suffix) e.g., ethylene
3. Naphthenes	$C_n H_{2n}$	Saturated, ring compound, e.g., cyclohexane
4. Aromatic	$C_n H_{2n-6}$	Benzene series
5. Diolefin	$C_n H_{2n-2}$	Two double bonds
6. Cyclic series	$C_n H_{2n-2}$	$C_n H_{2n-8}$, etc. -uncommon
7. Paraffin isomers	$ \begin{array}{c} C-C-C-C-C \\ \qquad \qquad \\ C \qquad \qquad C \end{array} $	

⁽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:

<u>Constituent</u>	<u>Volume %</u>
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 m³ (0.05 ft³) of dissolved hydrogen sulfide per 378 liters (100 gal.) of oil is called sour. However, a crude oil containing less than 0.014 m³ (0.5 ft³) 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 ₂ S	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, Sowell 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 H₂S. 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 H₂S 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/cm² 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

⁽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

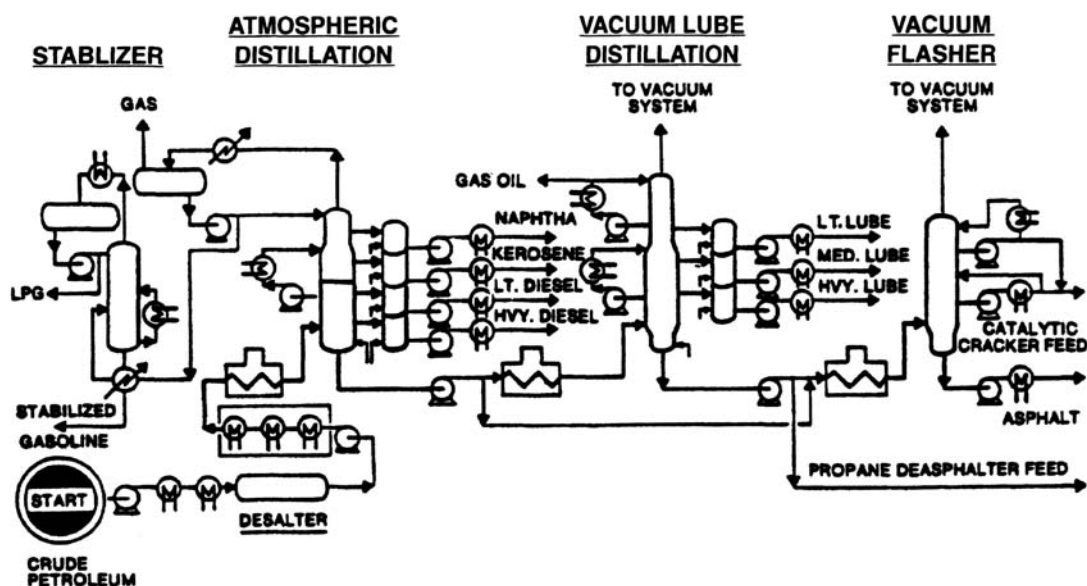


Figure 1.3 - Crude distillation, three stages.¹
(Reprinted with permission from *The Role of Stainless Steels in Petroleum Refining*, April 1977, American Iron and Steel Institute, Washington, DC)

⁽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 proprietary 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

⁽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 hydrosulfurizers, 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 H₂S or NH₃ 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

⁽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 1.4⁶ 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 1.6⁶ 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 1.9¹⁰ 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 1.10¹¹ 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)

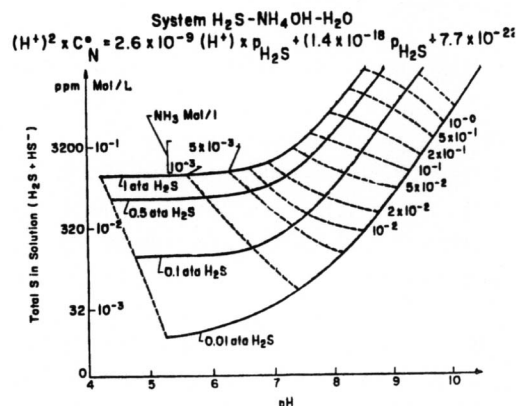


Figure 1.4 - Total S in solution vs pH.⁶
(Reprinted with permission from "Crude Unit Overhead Corrosion," *Hydrocarbon Processing*, May 1972, Gulf Publishing Co., Houston, TX)

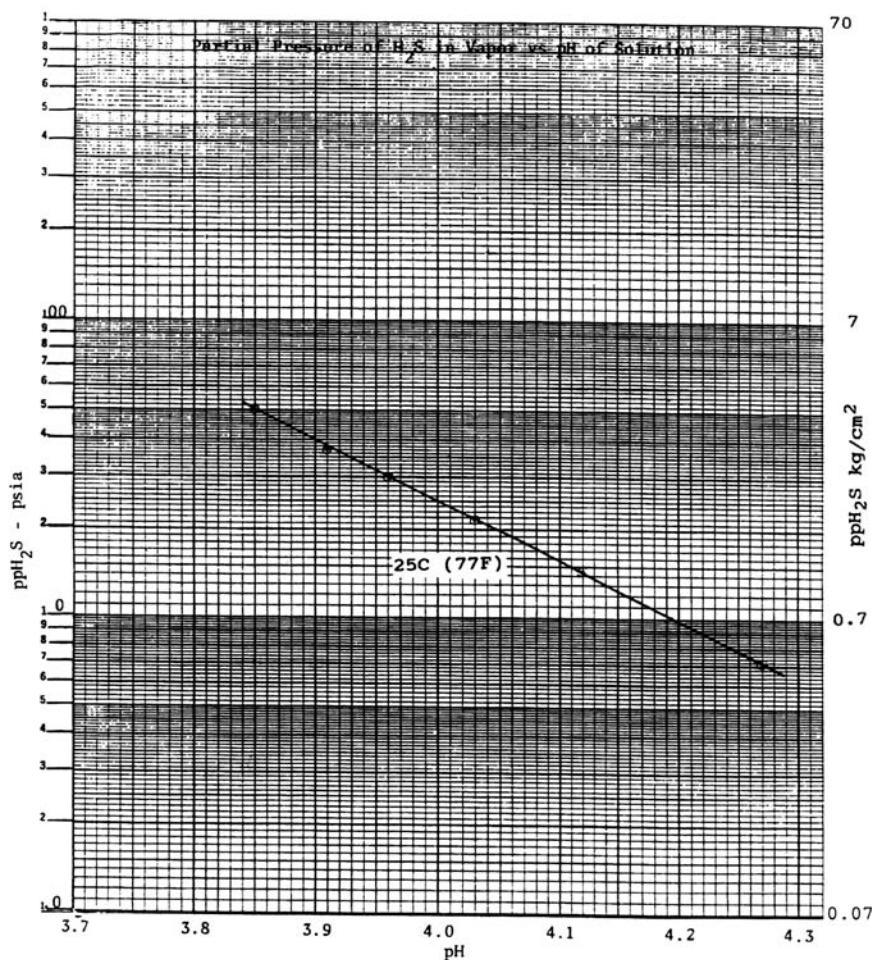


Figure 1.5 - Solubility of H₂S in water. Partial pressure of H₂S in vapor vs pH of solution.⁷
(Reprinted with permission from *Handbook of Chemistry*, 6th Edition, 1979, McGraw-Hill Publishing Co., New York, NY)

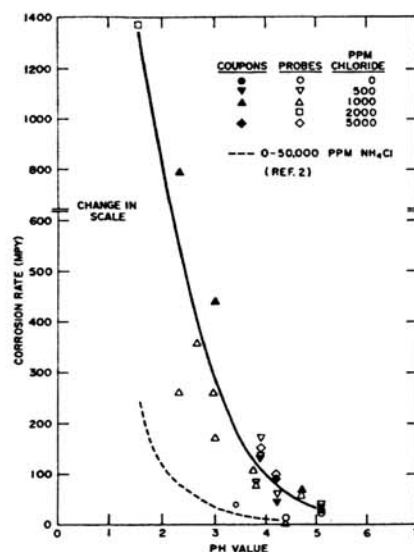
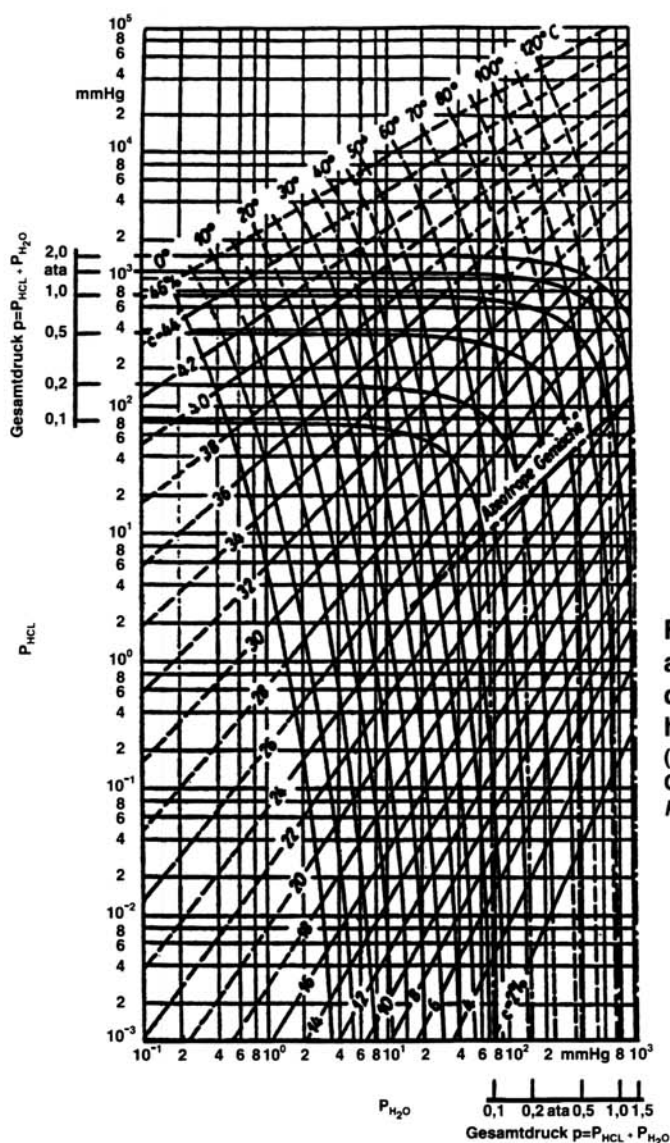


Figure 1.7 - (above) Corrosion of steel in aqueous sulfide solutions. Note the acid corrosion region because of an excess of hydrogen ions at pH values below 4.5.⁸ (Reprinted from "Corrosion of Steel by Sulfides and Cyanides in Refinery Condensate Water," *Materials Protection*, December 1968)

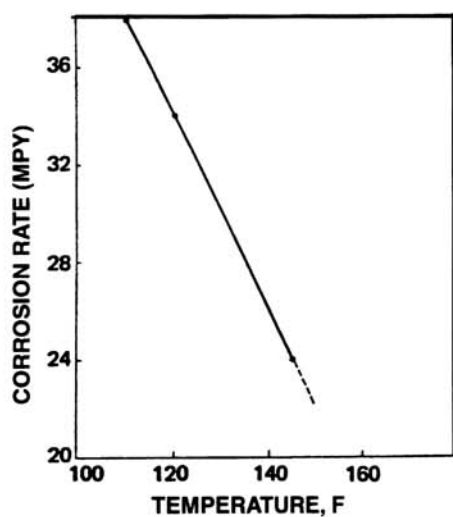


Figure 1.8 - (left) Corrosion rate of steel vs temperature of atmospheric tower sour condensate water.⁹ (Reprinted with permission from "Determination of Refinery Corrosion Rates Using the Pair Technique," *Materials Protection*, June 1969.)

Figure 1.6 - (above left) HCl and H₂O partial pressures over HCl depending on temperature, total pressure, and acid concentration.⁶ (Reprinted with permission from "Crude Unit Overhead Corrosion," *Hydrocarbon Processing*, May 1972, Gulf Publishing Co., Houston, TX)

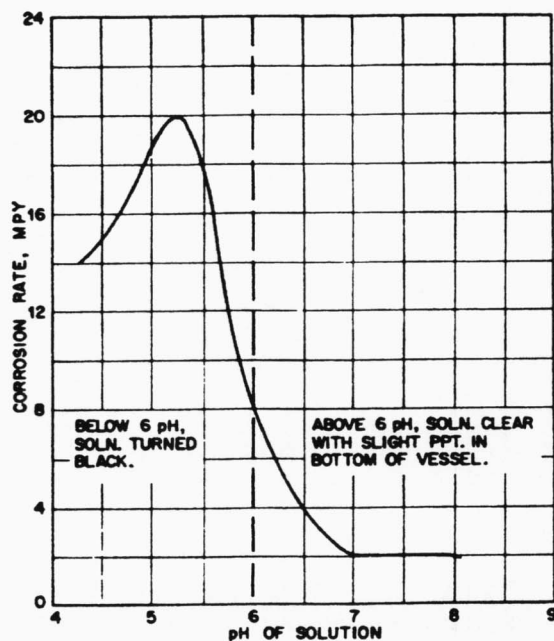


Figure 1.9 - Effect of pH on corrosion rate of iron in solution of the same H_2S activity.¹⁰

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

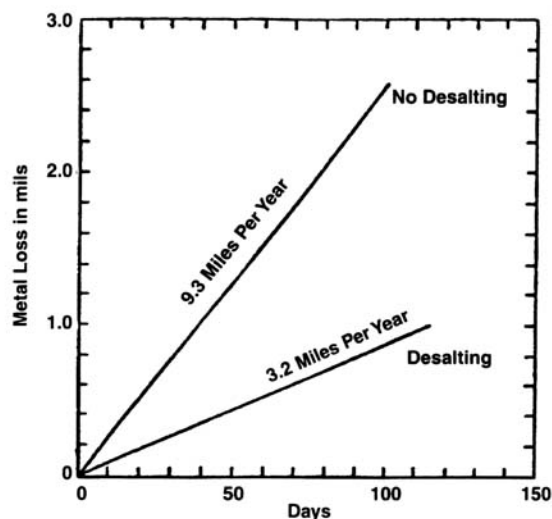


Figure 1.10 - Corrosion rates of steel in a crude unit secondary tower overhead. Desalting produced drastic reduction in corrosion rates.¹¹

(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 corro-

sion 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 1.14¹³ 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.

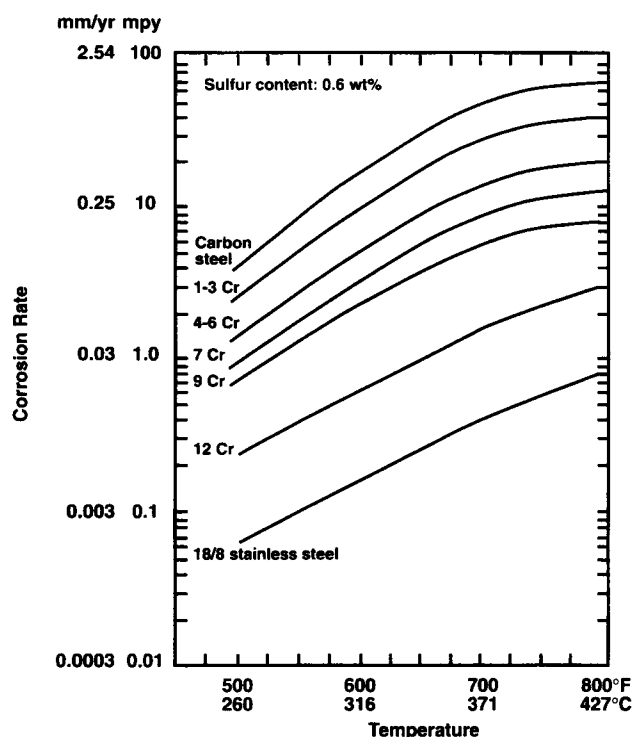
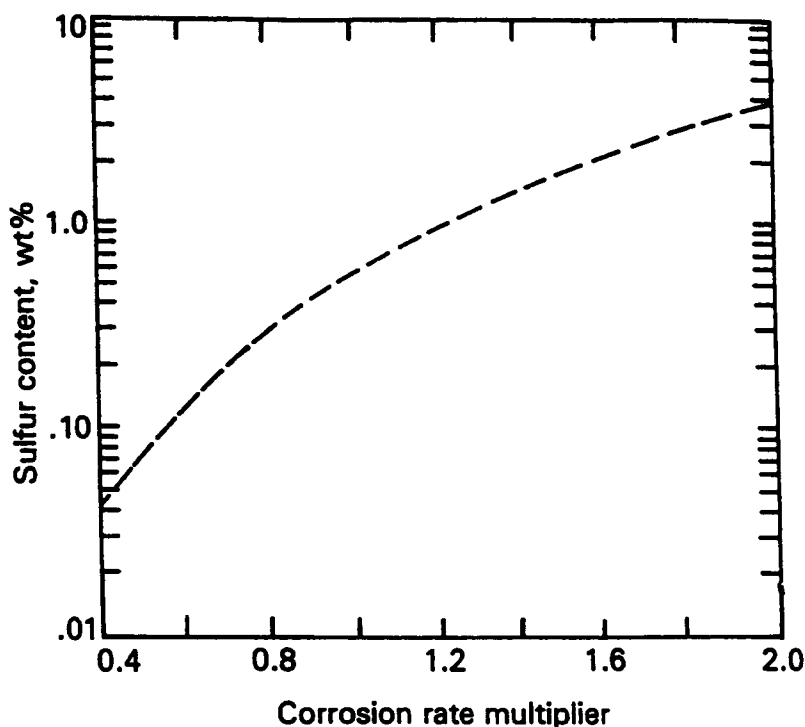


Figure 1.11 - Average corrosion rates of high temperature sulfur corrosion in a hydrogen free environment as compiled from 1961 API questionnaire data from industry-desulfurizing processes and published or reported data-nondesulfurizing processes.¹² (Reprinted from J. Gutzelt, "High Temperature Sulfidic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

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



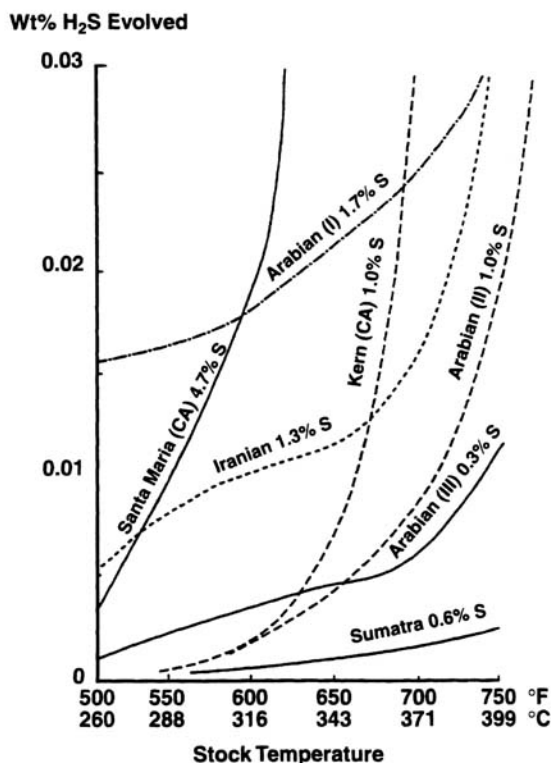


Figure 1.13 - Hydrogen sulfide release from crudes.¹³

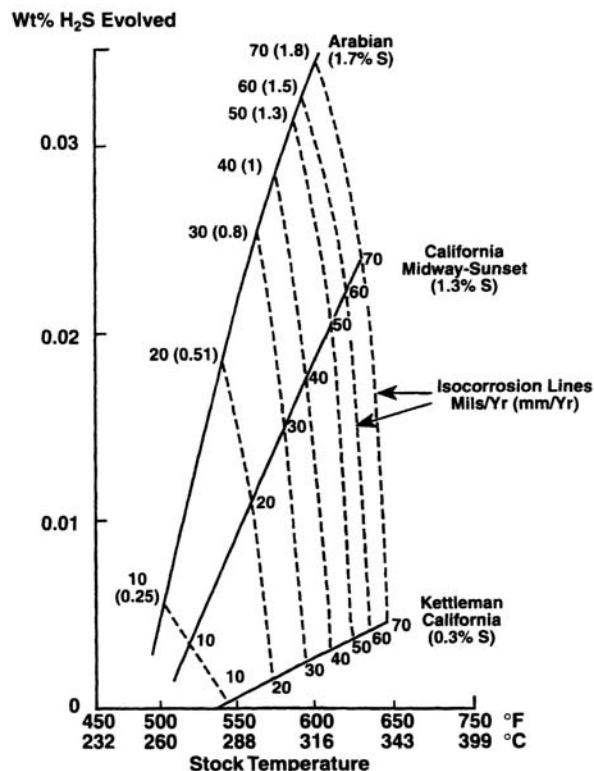


Figure 1.14 - Corrosion of carbon steel furnace tubes.¹³

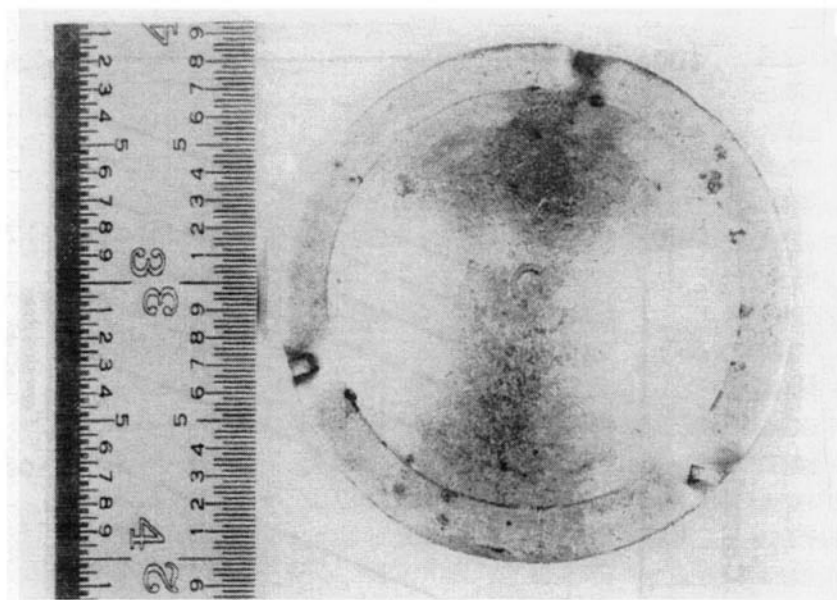
The 5 Cr-1/2 Mo alloy commonly used in furnace tubes corrodes at a measurable rate; the design life usually is 5 to 10 y. Even though metal temperatures are higher than the process temperature in furnace tubes, corrosion rates are always reported as a function of the process temperature. Therefore, furnace 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.

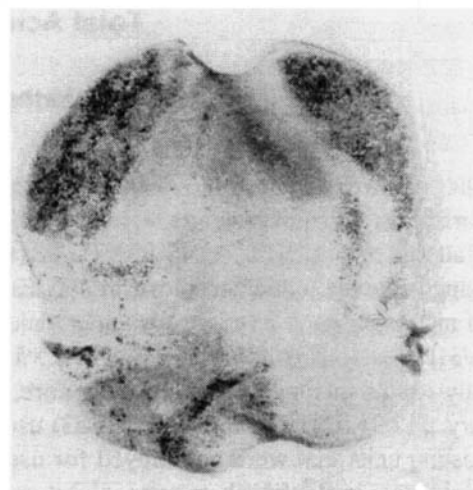
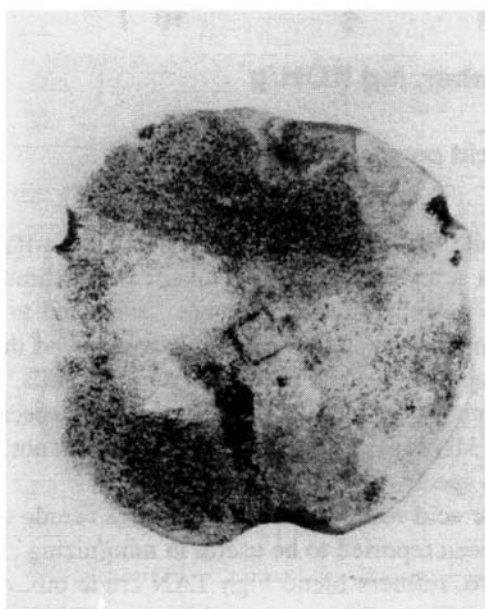
When naphthenic acids are present in sufficient quantities (see previous discussion), alloys with 0-12% chromium, as well as 304/304L (UNS S30400/S30403), 321 (UNS S32100) and 347 (UNS S34700) are severely attacked. Conversely, molybdenum-bearing austenitic SS, e.g., 316/316L (UNS S31600/S31603), 317/317L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

⁽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/

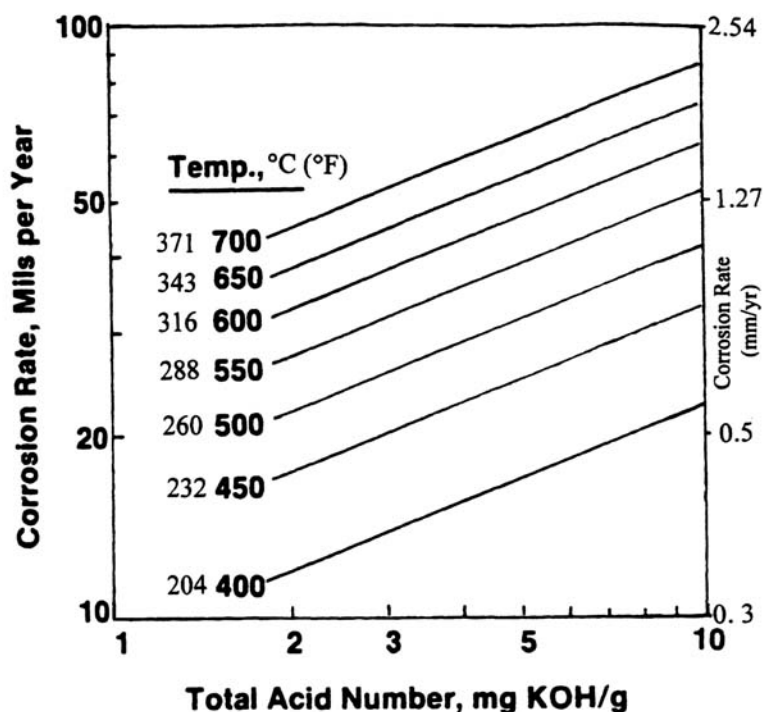


Figure 1.16 - Naphthenic acid corrosion of carbon steel.¹⁴

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 H₂S (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

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

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

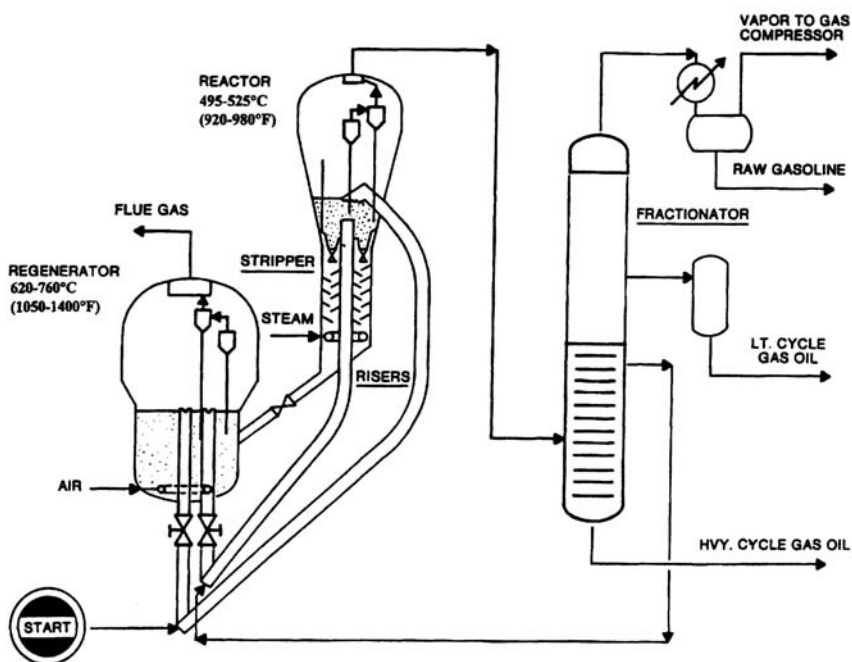


Figure 2.1 - Fluid catalytic cracking.¹
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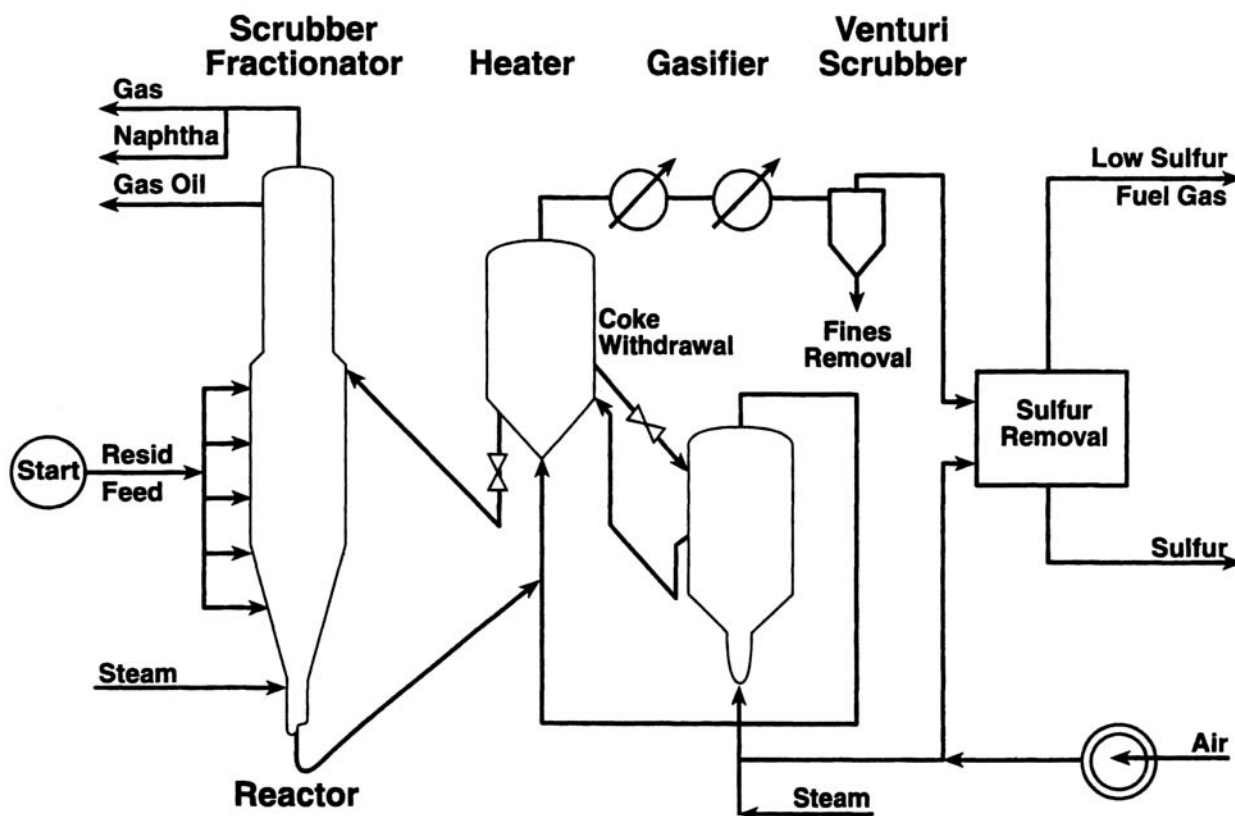


Figure 2.2 - Fluid coking.²
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before it flows to the regenerator. In the regenerator, the catalyst is regenerated by the burning of the coke at about 650°C to 760°C (1,200°F to 1,400°F). Entrained catalyst is again removed from the gases before the gases 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

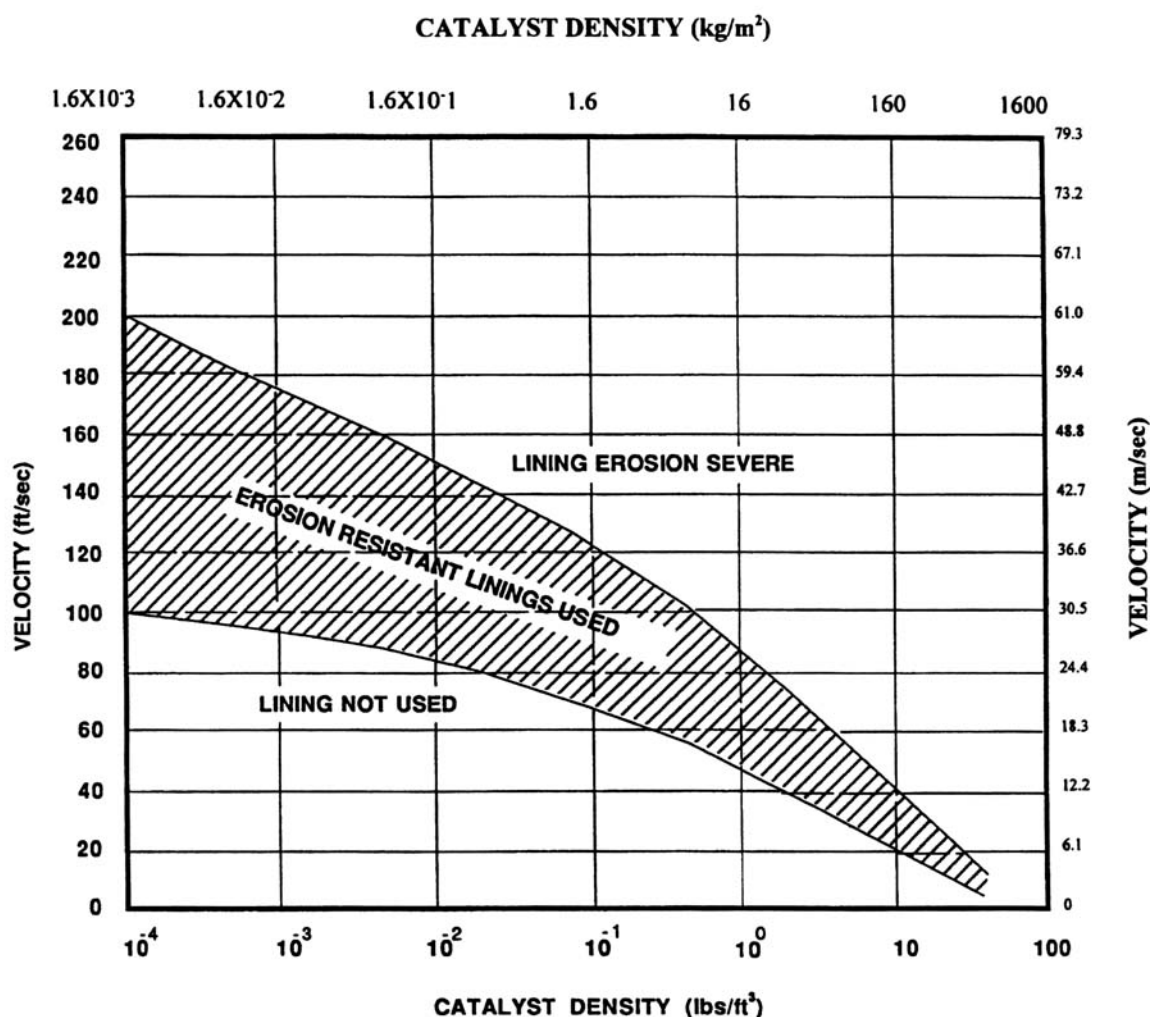


Figure 2.3 - Use of erosion-resistant linings in fluid catalytic cracking units as function of catalyst density and velocity.³

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.

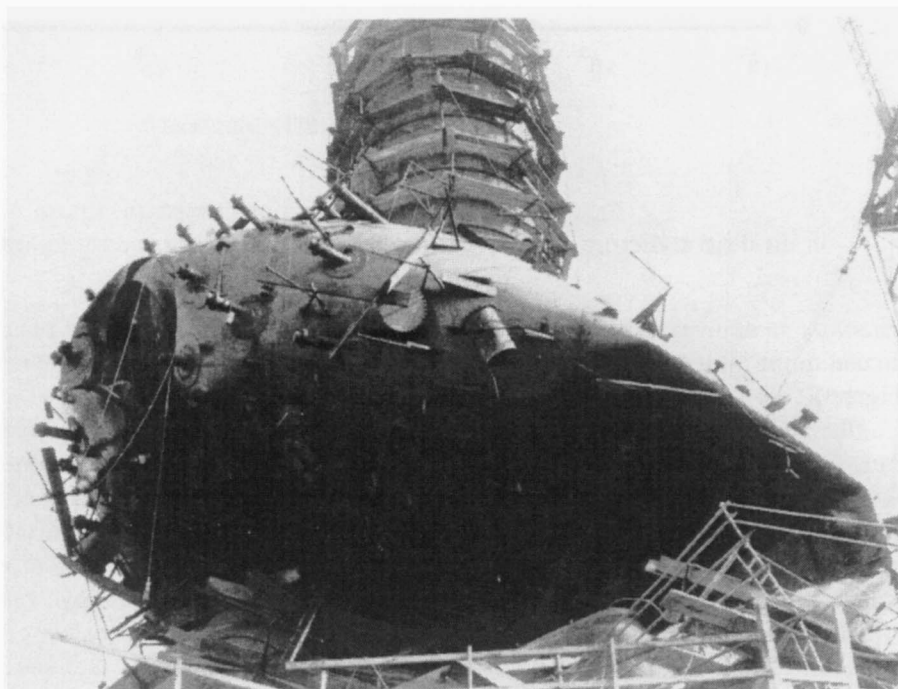
The valves controlling the flow between the reactor and regenerator (or burner) are specially designed slide valves (box-like valves where the gate slides in guides). They have weld overlay hardfacing (e.g., a cobalt base alloy containing 28 Cr, 4 W, 1 C) on the stems, and sliding surfaces and erosion-resistant 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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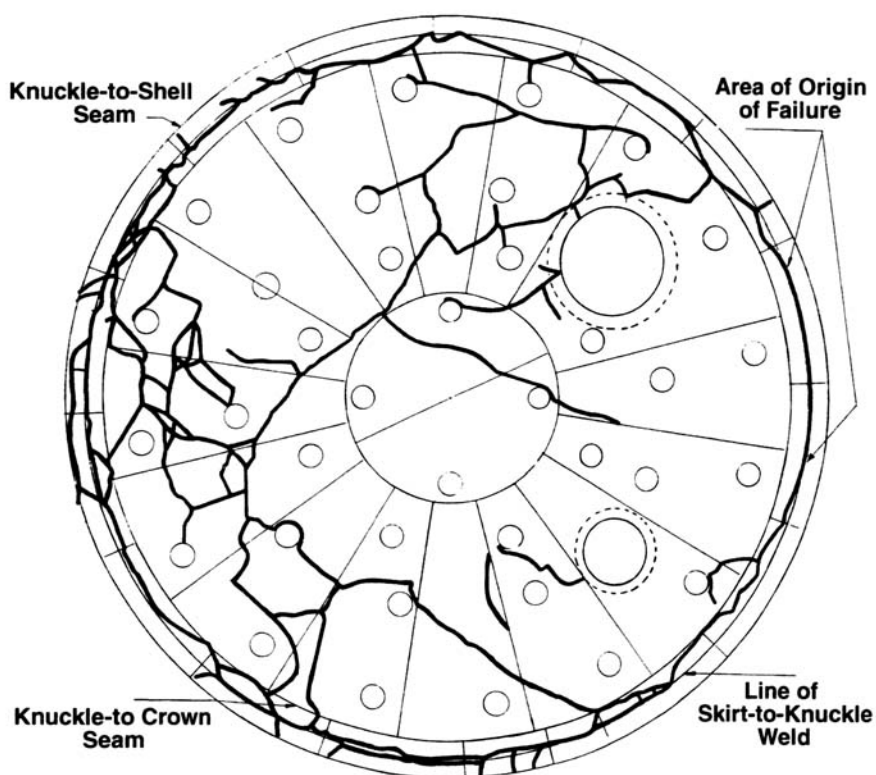
⁽¹⁾ Polythionic acid ($\text{H}_2\text{S}_x\text{O}_6$) or sulfurous acid (H_2SO_3) is formed by the reaction of the iron sulfide scale, water, and oxygen.



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

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

™ Trademark

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.

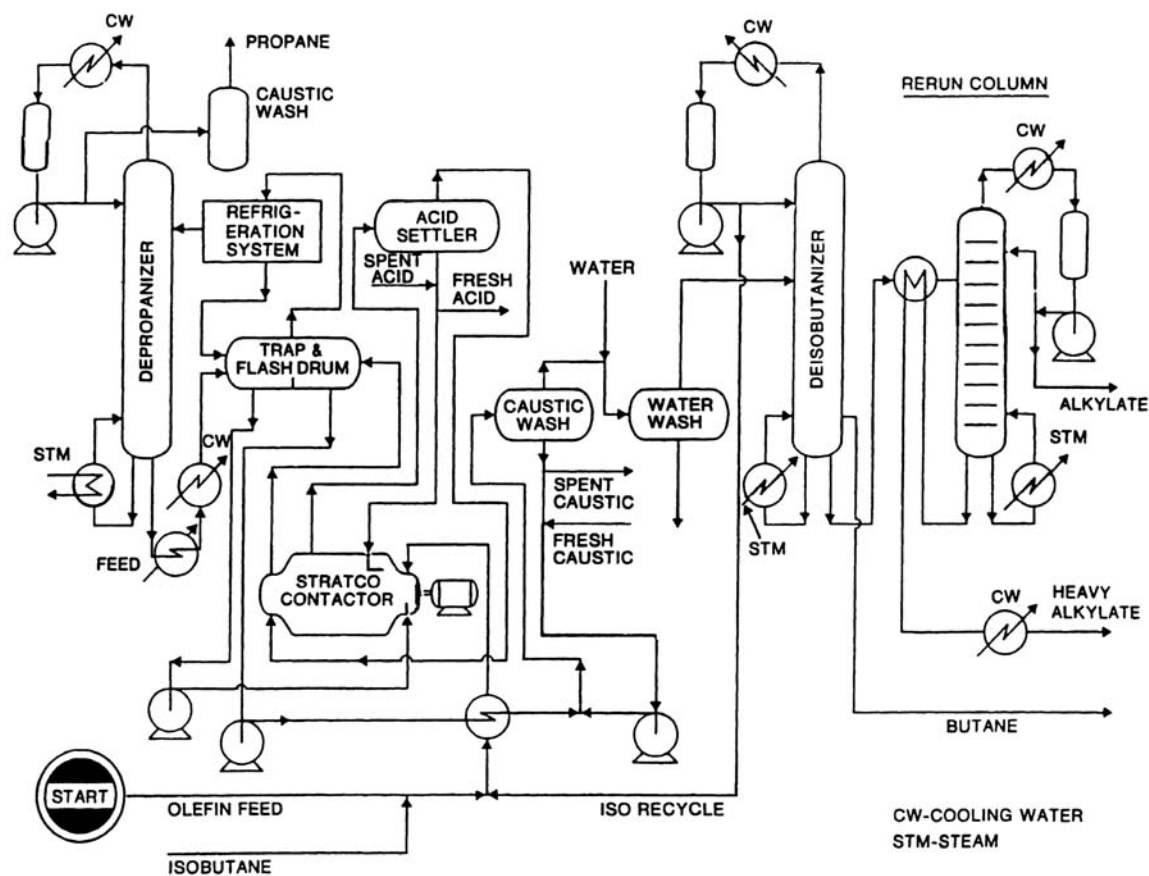


Figure 2.8 - Sulfuric acid alkylation.¹
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Although there have been reports of good performance of 65 Ni-15 Cr-Fe filler metal in coker fractionators up to 400°C (750°F), presumably because of protection by the coke that occurs in coke drums, severe sulfidation 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).

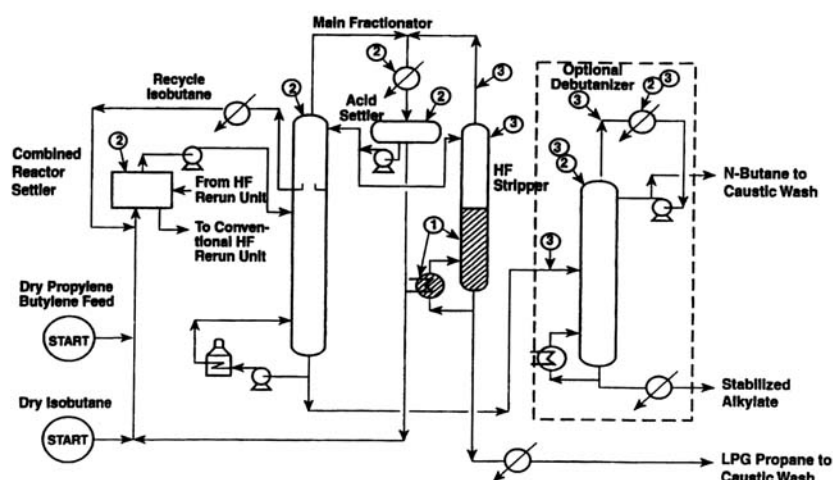
Significant corrosion has been reported in dead legs and socket welds in sulfuric acid systems; therefore, these should be avoided. In addition, hydrogen grooving has occurred on the upper portions of horizontal tanks, manways, nozzles, and piping on surfaces exposed to liquid sulfuric acid. The grooving 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 SO₂ 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
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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 polysulfide⁷ (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

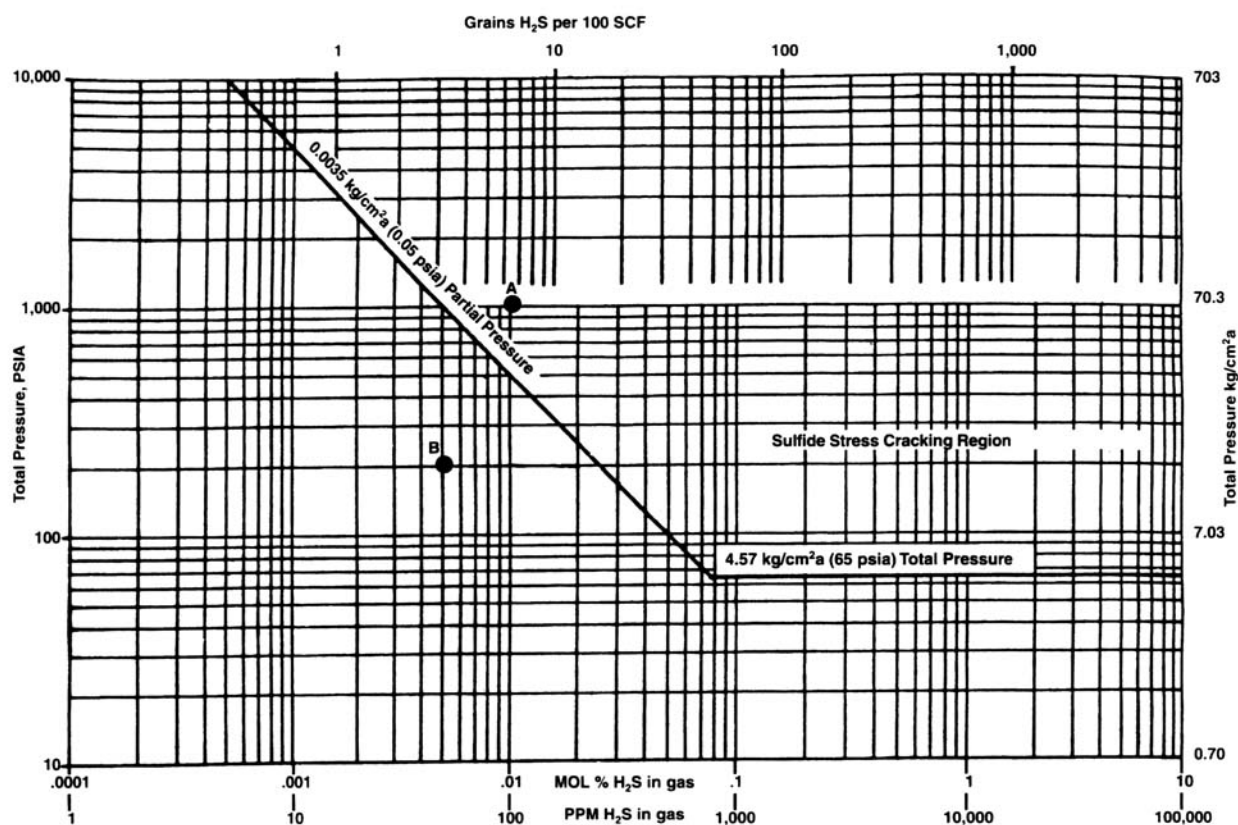


Figure 2.10 - Sour gas systems.⁸

⁽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.

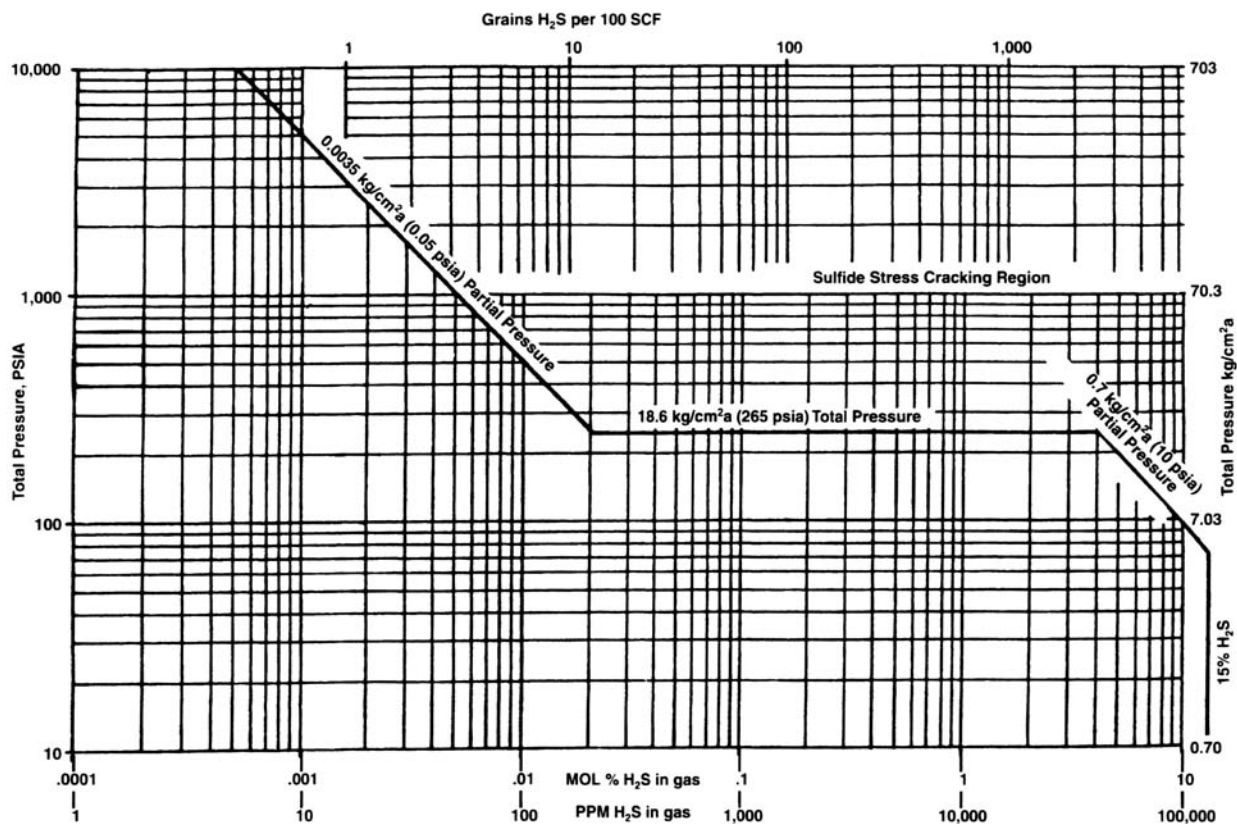


Figure 2.11 - Sour multiphase system.⁸

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 H₂S, i.e., not the total pressure, when determining the potential for SSC. Figures 2.10 and 2.11⁸ 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 H₂S partial pressure as follows:⁹

$$\begin{aligned} \text{pp H}_2\text{S} &> 0.3 \text{ kPaa (0.05 psia) if the water phase pH} > 4.0 \\ \text{pp H}_2\text{S} &> 0.05 \text{ kPaa (0.008 psia) if the water phase pH} < 4.0 \end{aligned}$$

However, this approach is controversial.¹⁰

In refineries, 50 ppm H₂S 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

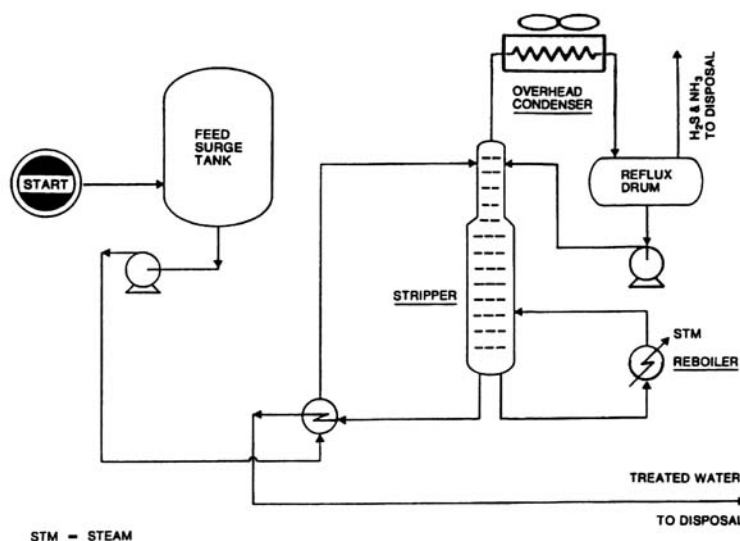
To avoid SSC, the hardness of carbon steels should be limited to 200 Brinell, and the hardness of low alloy steels should be limited to about 235 Brinell. See Chapter 5, Section 6, for limits on cold bends in wet H₂S service. For more detailed requirements on materials resistant to SSC, see NACE Standards MR0175 ("Sulfide Stress Cracking Resistant Metallic Material for Oil Field Equipment") and RP0472⁽⁵⁾ ("Methods

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

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
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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

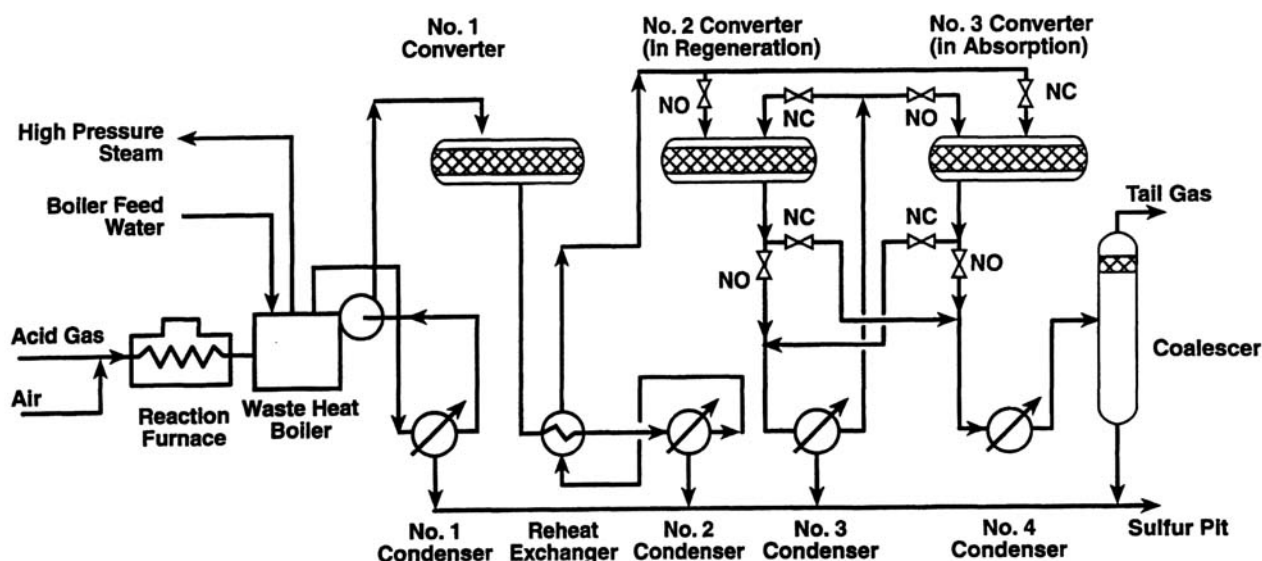


Figure 2.13 - Sulfur plant. ²

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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).

REFERENCES

1. "The Role of Stainless Steels in Petroleum Refining," American Iron and Steel Institute, April (1977).
2. Refinery Process Handbook, *Hydrocarbon Processing* September (1968).
3. Private communication
4. A.G. Harding, E.F. Ehmke, "Brittle Failure of a Large Pressure Vessel," *API Div. Refining*, vol. 42, no. 3 (1962): p. 107.
5. S.K. Brubaker, R.E. Tatnall, "Materials Selection and Design to Minimize Hydrogen Grooving," *Materials Performance* May (1995): p. 59.
6. H.H. Hashium, W.L. Valerioti, "Effect of Residual Copper, Nickel and Chromium on the Corrosion Resistance of Carbon Steel in Hydrofluoric Acid Alkylation Service," CORROSION/93, paper no. 623 (Houston, TX: NACE International, 1993).
7. E.F. Ehmke, "Polysulfide Stops FCCU Corrosion," *Hydrocarbon Processing*, 60, 7 (1981): p. 149.
8. NACE Standard MRO175 (latest revision), "Sulfide Stress Cracking Resistant Metallic Material for Oil Field Equipment" (Houston, TX: NACE).
9. D.R. McIntyre, J.K. Boah, "Review of Sour Service Definitions," *Materials Performance* August (1996): p. 54.
10. L.M. Smith et al., Part 1, D.R. McIntyre, "Technical Forum: Review of Sour Service Definitions," *Materials Performance* April (1997): p. 66.
11. M.S. Cayard et al., "An Exploratory Examination of the Effects of SOHIC Damage on the Fracture Resistance of Carbon Steels," CORROSION/97, paper no. 525 (Houston, TX: NACE, 1997).
12. API Publication 944, Survey of Materials Experience and Corrosion Problems in Sour Water Equipment (Washington, DC: American Petroleum Institute, 1972).
13. API Publication 950, "Survey of Construction Materials and Corrosion in Sour Water Strippers - 1978 (Washington, DC: American Petroleum Institute, 1983).

BIBLIOGRAPHY

- API Publication 942, "Recommended Practice for Welded, Plain Carbon Steel Refinery Equipment for Environmental Cracking Service," (Washington, DC: American Petroleum Institute).
- API Recommended Practice 751, "Safe Operation of Hydrofluoric Acid Alkylation Units, 1st edition (Washington, DC: API, June 1992).
- Bergman, D.J., and G.W.G. McDonald, "Solving Problems in HF Alkylation Units," *Corrosion* 17, 4 (1961): p. 9.
- Bradbury, W.A. "Monolithic Linings for Refinery Service," *Petroleum Refiner* 33, 3 (1954): p. 167.
- Copkson, H.R., and C.F. Cheng, "Stress Corrosion Cracking of Monel in Hydrofluoric Acid," *Corrosion* 12, 12 (1956): p. 647t.
- Dean, S.W., G.D. Grab, "Corrosion of Carbon Steel Tanks in Concentrated Sulfuric Acid Service," *Materials Performance* 25, 7 (1986): p. 48.
- T.F. Degnan, "Effect of Velocity on Life Expectancy of Steel Pipelines in Commercial Strengths of Sulfuric Acid," *Corrosion* 15, 6 (1959): p. 326t.
- Dobis, J.D. et al., "Survey Reveals Nature of Corrosion in HF alky units," *Oil and Gas Journal* 93, 10 (March 6, 1995): p. 63.
- Ehmke, E.F. "Polysulfide Stops FCCU Corrosion," *Hydrocarbon Processing* 60, 7 (1981): p. 149.
- Foroulis, Z.A. "Mechanism of Refinery Corrosion by Aqueous Sour Water Condensates," 6th Middle East Corrosion Conference (Manama, Bahrain: Bahrain Society of Engineers, January 1994): p. 17.
- J. Gutzeit, "Corrosion of Steel by Sulfides and Cyanides in Refinery Condensate Water," *Materials Protection* (Dec. 1968): p. 17.
- J. Gutzeit, "Process Changes for Reducing Pressure Vessel Cracking Caused by Aqueous Sulfide Corrosion," *Materials Protection* (May 1992): p. 60.
- Hansen, R.D. "FCC Slide-Valve Problems Can Be Remedied," *Oil & Gas Journal* 8, 16 (April 18, 1983): p. 139.
- R.L. Hildebrand, "Sour Water Strippers - A Review of Construction Materials," *Materials Performance* 13, 5 (1974): p. 16.
- Holmberg, M.E. and F.A. Prange, "Corrosion in Hydrofluoric Acid Alkylation," *Ind & Eng. Chem.* 37, 11 (1945): p. 1,030.
- INCO Corrosion Engineering Bulletin CEB-1, "Resistance of Nickel and High Nickel Alloys to Corrosion by Sulfuric Acid," (Suffern, NY: INCO, 1983).
- INCO Corrosion Engineering Bulletin CEB-5, "Corrosion Resistance of Nickel-Containing Alloys in Hydrofluoric Acid," Hydrogen Fluoride and Fluorine (Suffern, NY: INCO, 1968).
- Kmetz, J.H., and D.J. Truax, "Carbonate Stress Corrosion of Carbon Steel In Refinery FCC Main Fractionator Overhead Systems," CORROSION/90, paper no. 206 (Houston, TX: NACE, 1990).
- Mason, J.F. Jr. and C.M. Schillmoller, "Corrosion in Sour Water Strippers," *Corrosion* 15, 7 (1959): p. 36.
- McGowin, T.S. and R.A. White, "Coke Drum Fracture Experience," *API Div. Refining*, 52, 3 (1972): p. 778.
- Merrick, R.D. "Refinery Experience with Cracking in Wet H₂S Environments," *Materials Performance*, 27, 1 (1988): p. 30.
- Moore, K.L. "Alloy Stops Corrosion in Fluid Coker," *Petroleum Refiner* 39, 5 (1961): p. 1,949.
- Neumaier, B.W. and C.M. Schillmoller, "What to Do about Hydrogen Blistering," *Petroleum Refinery* 36, 9 (1957): p. 319.
- "Summary of Questionnaire Replies on Corrosion in HF Alkylation Units," *Corrosion* 15, May (1959): p. 33.
- Thornton, D.P. Jr., "Corrosion-Free AF Alkylation," *Chemical Engineering* 77, 14 (July 13, 1970): p. 108.
- Weil, N.A., and F.S. Rapasky, "Experience with Vessels of Delayed Coking Units," *API, Division of Refining*, 38, III (1958): p. 214.

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 hydroprocessing units are hydrosulfurizers (Figure 3.1)¹ and hydrocrackers (Figure 3.2).¹ The primary objective in hydrosulfurizing 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 hydrosulfurizers 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 hydrosulfurizers 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 hydrosulfurizers, 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

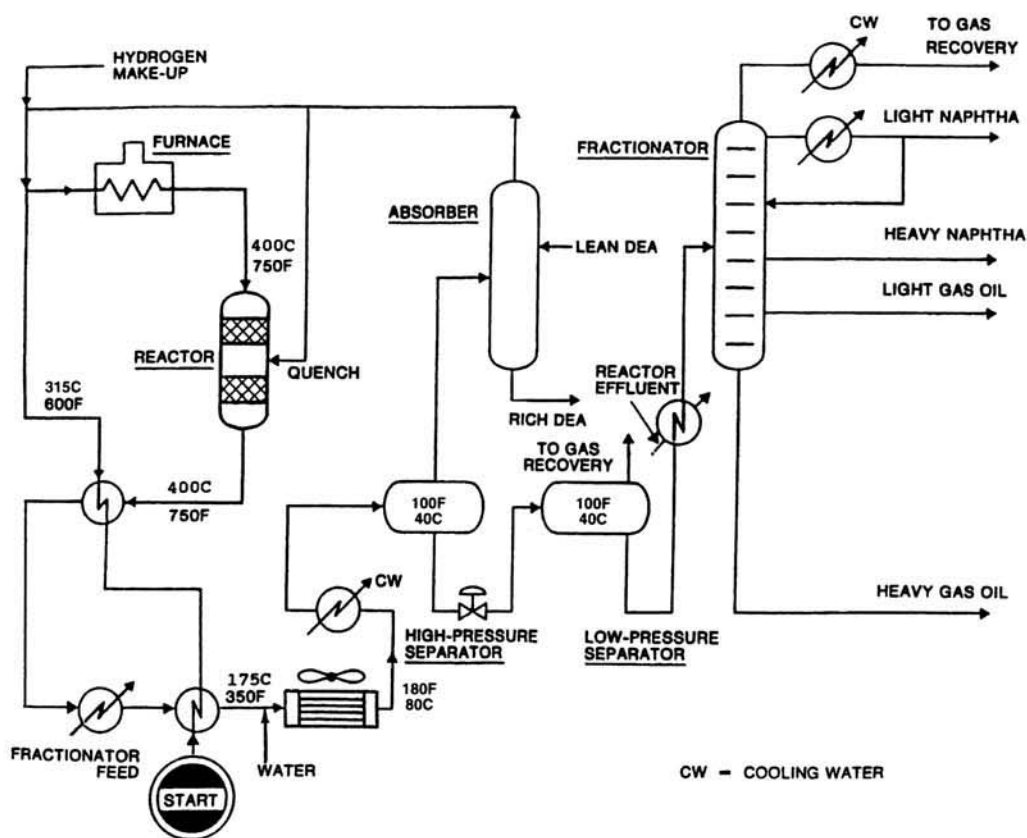


Figure 3.1 - Hydrodesulfurizer.¹

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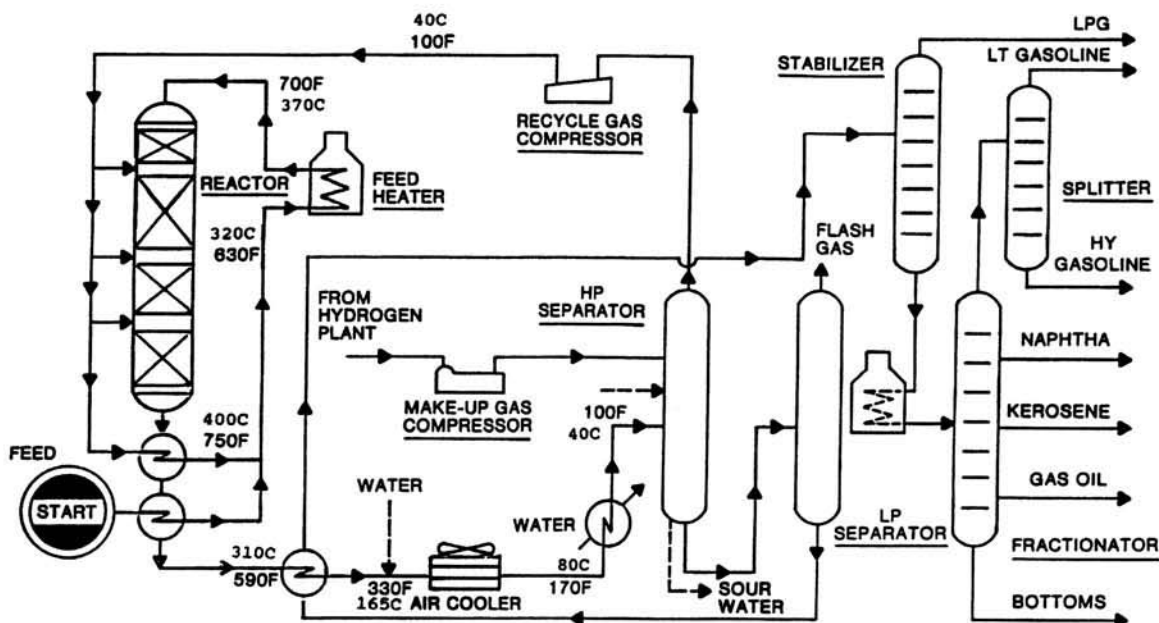
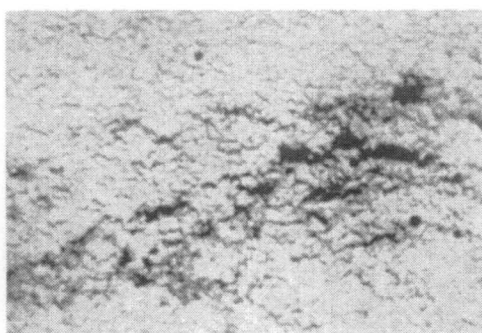


Figure 3.2 - Hydrocracking.¹

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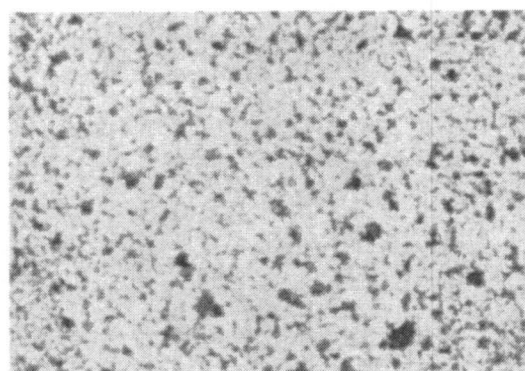


Figure 3.3(a) - (above) Cross section of exchanger. Note cracking in weld metal at right (light colored area) of specimen.²



**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**



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.

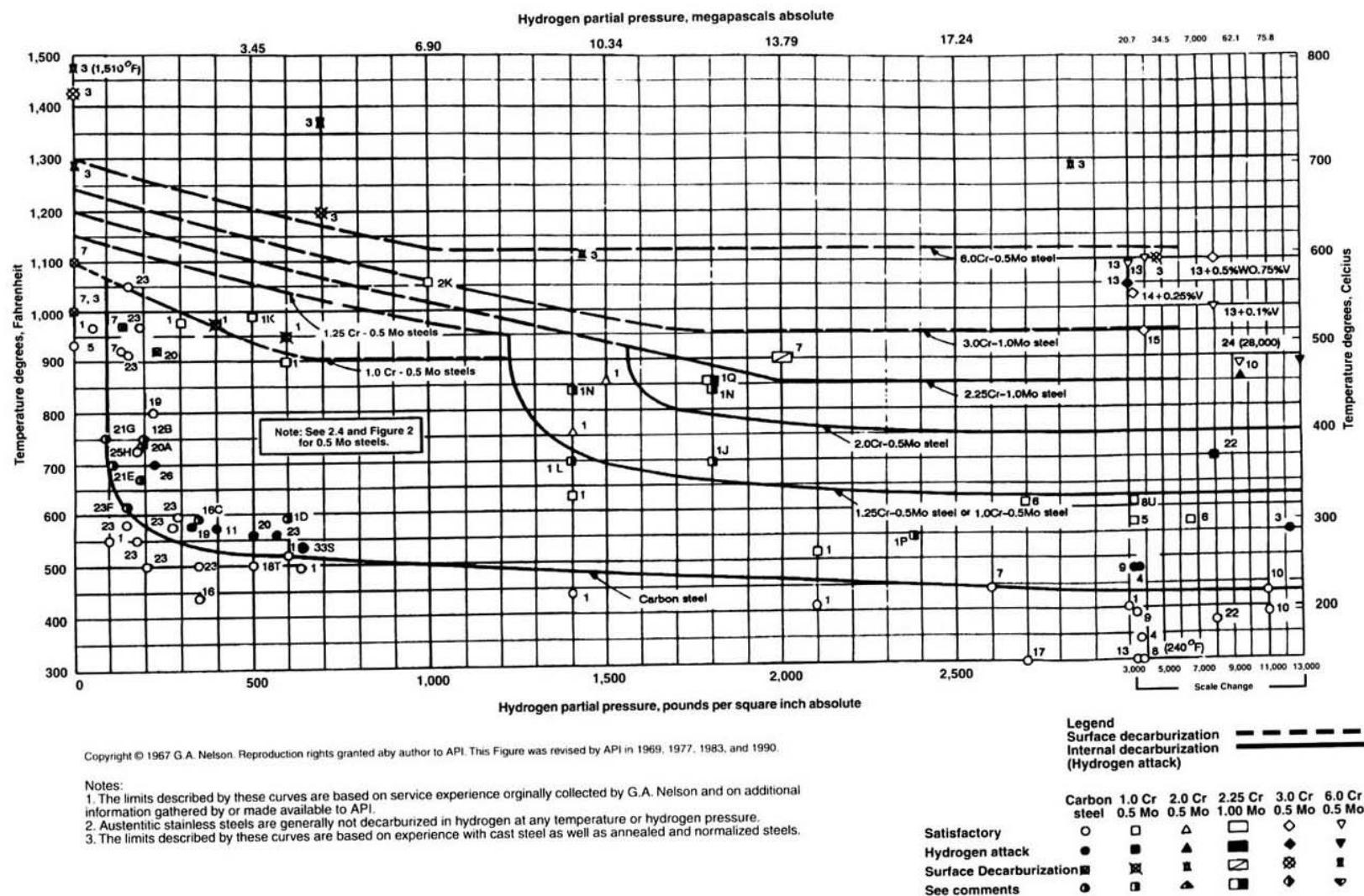


Figure 3.4 - Operating limits for steels in hydrogen service to avoid decarburization and fissuring.³
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API 941 was derived from laboratory work done by Naumann in Germany in the early 1940s.⁴ Since then, it has been revised periodically, based on operating 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 than 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

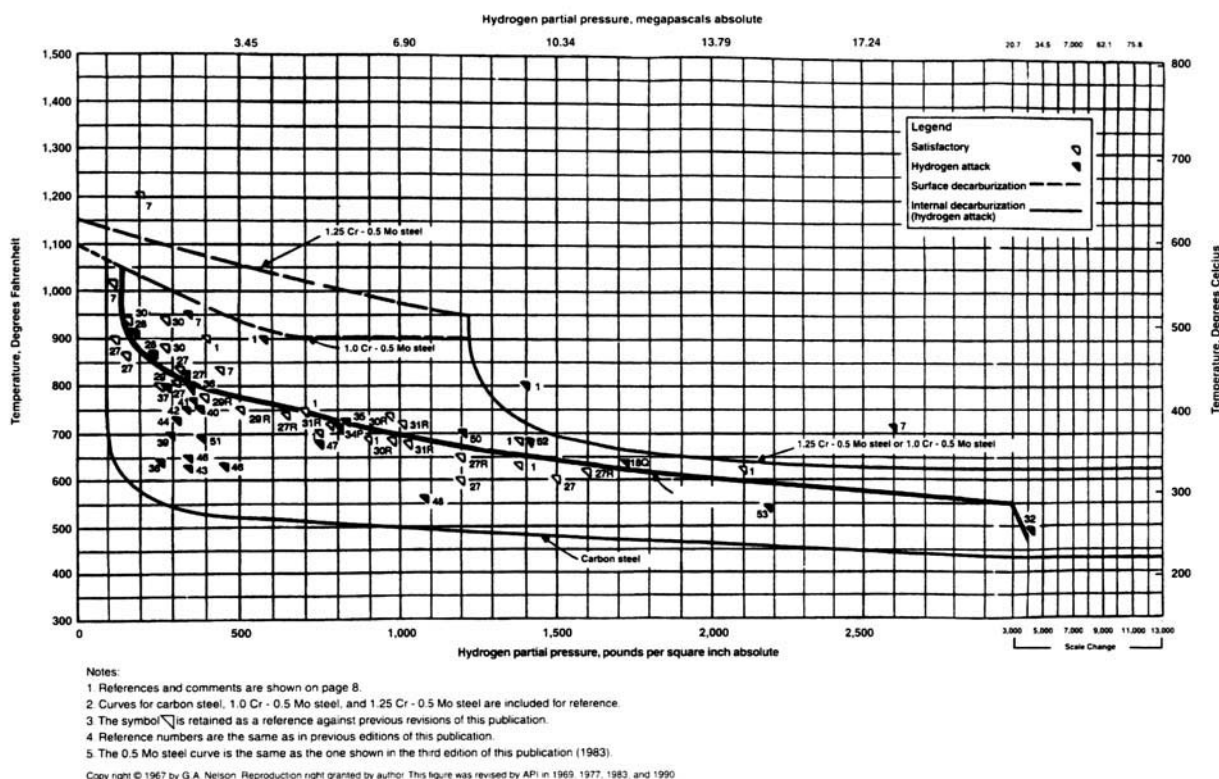
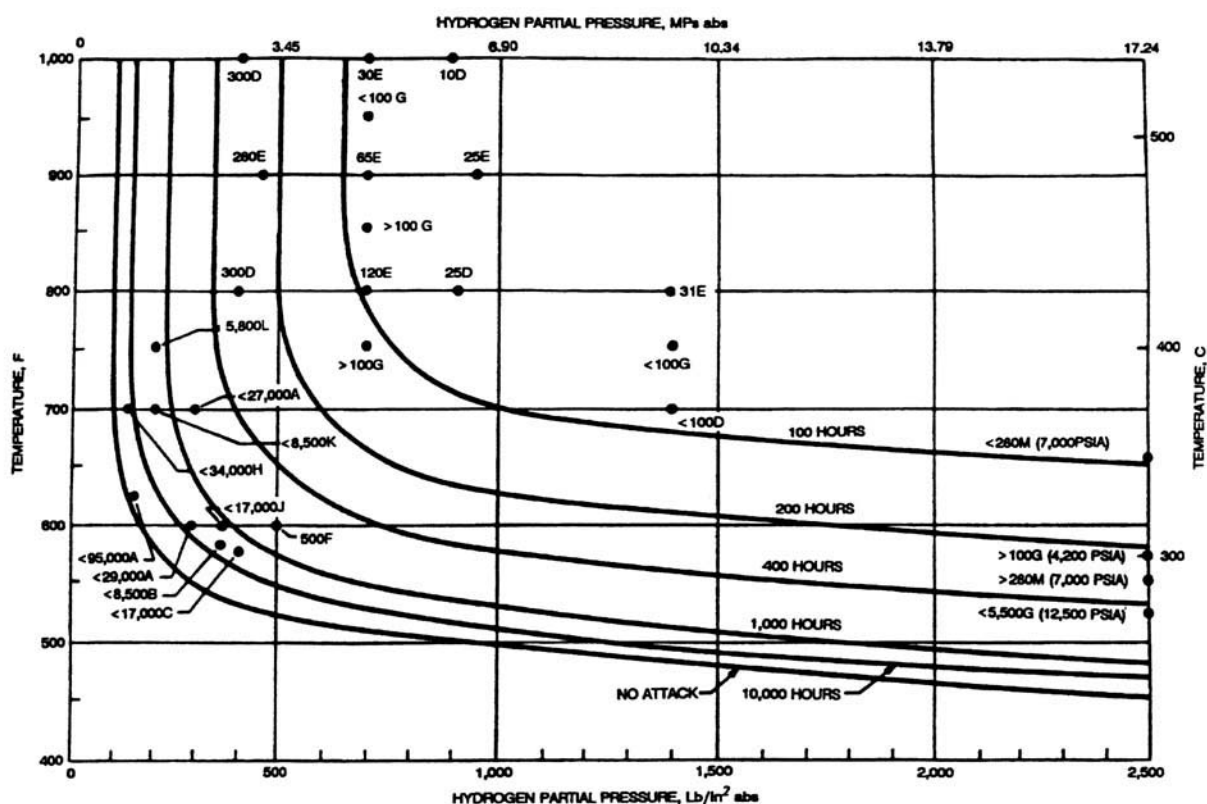


Figure 3.5 - Experience with C-0.5 and Mn-0.5 Mo steels in hydrogen service.³
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alloy selection. Furthermore, records must be kept to ensure the total cumulative time is not exceeded.

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/cm² 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/cm² a (1,991 psia) until the stream reaches the pressure letdown valve.



References

- A. AMOCO Oil Company, private communication to API Subcommittee on Corrosion, 1960.
- B. A.R. Cluffreda and W.D. Rowland, "Hydrogen Attack of Steel in Reformer Service," *Proceedings*, 1957, Vol. 37, American Petroleum Institute, New York, pp. 116-128.
- C. C.A. Zapffe, "Boiler Embrittlement," *Transactions of the ASME*, 1944, Vol. 66, pp. 81-126.
- D. R.E. Allen, R.J. Jansen, P.C. Rosenthal, and F.H. Vitovec, "The Rate of Irreversible Hydrogen Attack of Steel at Elevated Temperatures," *Proceedings*, 1961, Vol. 41, American Petroleum Institute, New York, pp. 74-84.
- E. L.C. Weiner, "Kinetics and Mechanism of Hydrogen Attack of Steel," *Corrosion*, 1961, Vol. 17, pp. 109-115.
- F. J.J. Hur, J.K. Deichler, and G.R. Worrell, "Building a Catalytic Reformer," *Oil and Gas Journal*, October 29, 1956, No. 78, pp. 103-107.
- G. F.K. Naumann, "Influence of Alloy Additions to Steel Upon Resistance to Hydrogen Under High Pressure," *Technische Mitteilungen Krupp*, 1938, Vol. 1, No. 12, pp. 223-234.
- H. M. Hasegawa and S. Fujinaga, "Attack of Hydrogen on Oil Refinery Steels," *Tetsu To Hagane*, 1960, Vol. 46, No. 10, pp. 1349-1352.
- I. T.C. Evans, "Hydrogen Attack on Carbon Steels," *Mechanical Engineering*, 1948, Vol. 70, pp. 414-416.
- J. Air Products, Inc., private communication to API Subcommittee on Corrosion, March 1960.
- K. API Refinery Corrosion Committee Survey, 1957.
- L. I. Class, "Present State of Knowledge in Respect to the Properties of Steels Resistant to Hydrogen Under Pressure," *Stahl und Eisen*, August 18, 1960, Vol. 80, pp. 1117-1135.

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

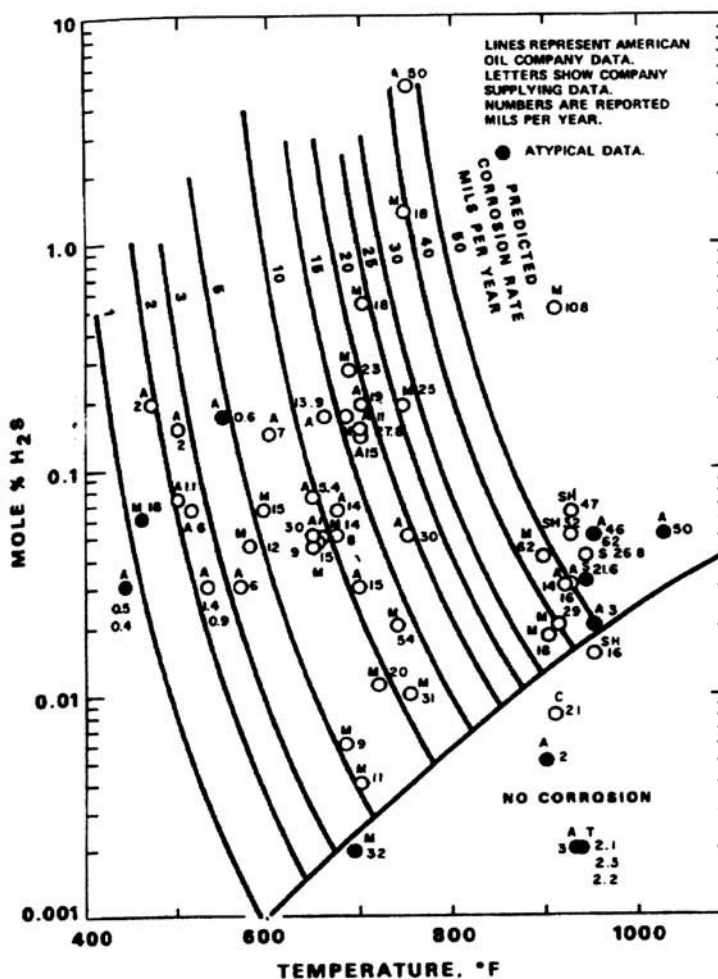
When the temperature exceeds 288°C (550°F) in hydrogen-hydrogen sulfide mixtures, severe corrosion occurs on carbon and low-alloy steels. Corrosion rates of various materials as a function of mole % hydrogen sulfide (based on only the constituents in the vapor phase) vs temperature for both gas oil and 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 H₂S. 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.

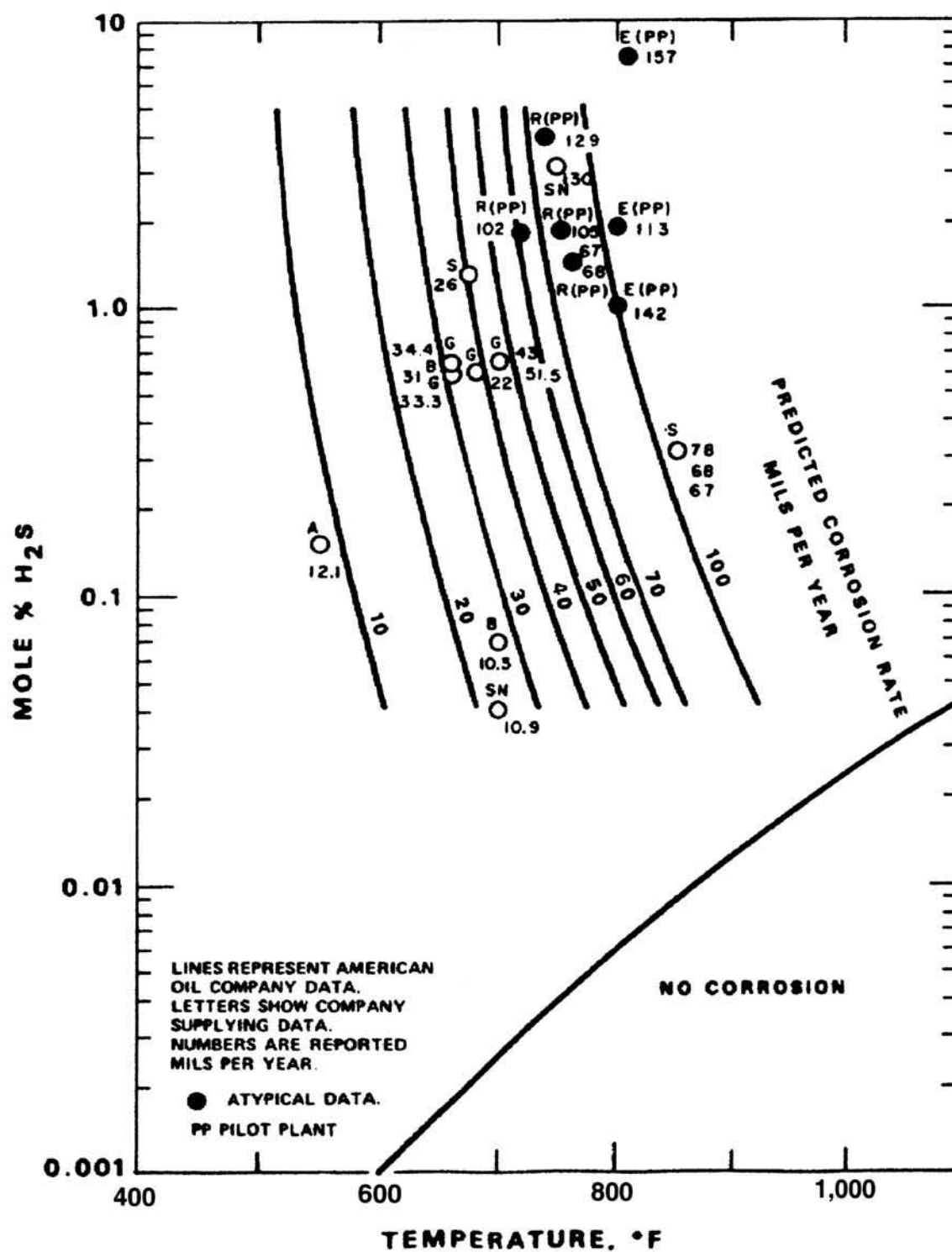
The 12 Cr alloy occasionally is used up to 345°C (650°F) when the hydrogen sulfide concentration is less than 1 mol%. Aluminized (diffusion-coated aluminum) carbon and low-alloy steel also display excellent resistance to hydrogen sulfide in these environments; however, attack can occur at breaks in the 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.

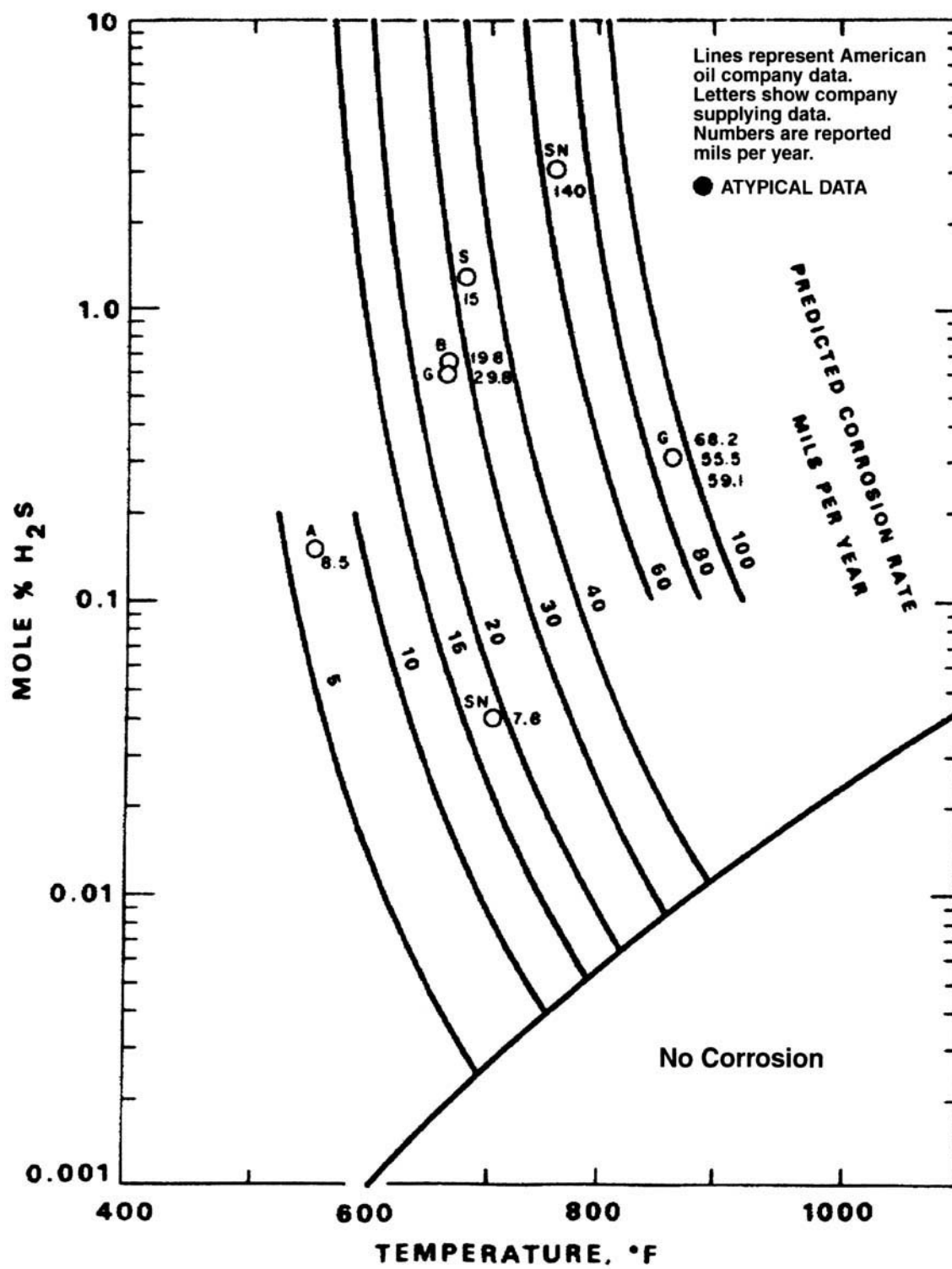
Figure 3.7 - Isocorrosion curves for carbon, low alloy, and stainless steels as a function of mole percent H₂S and temperature.⁶

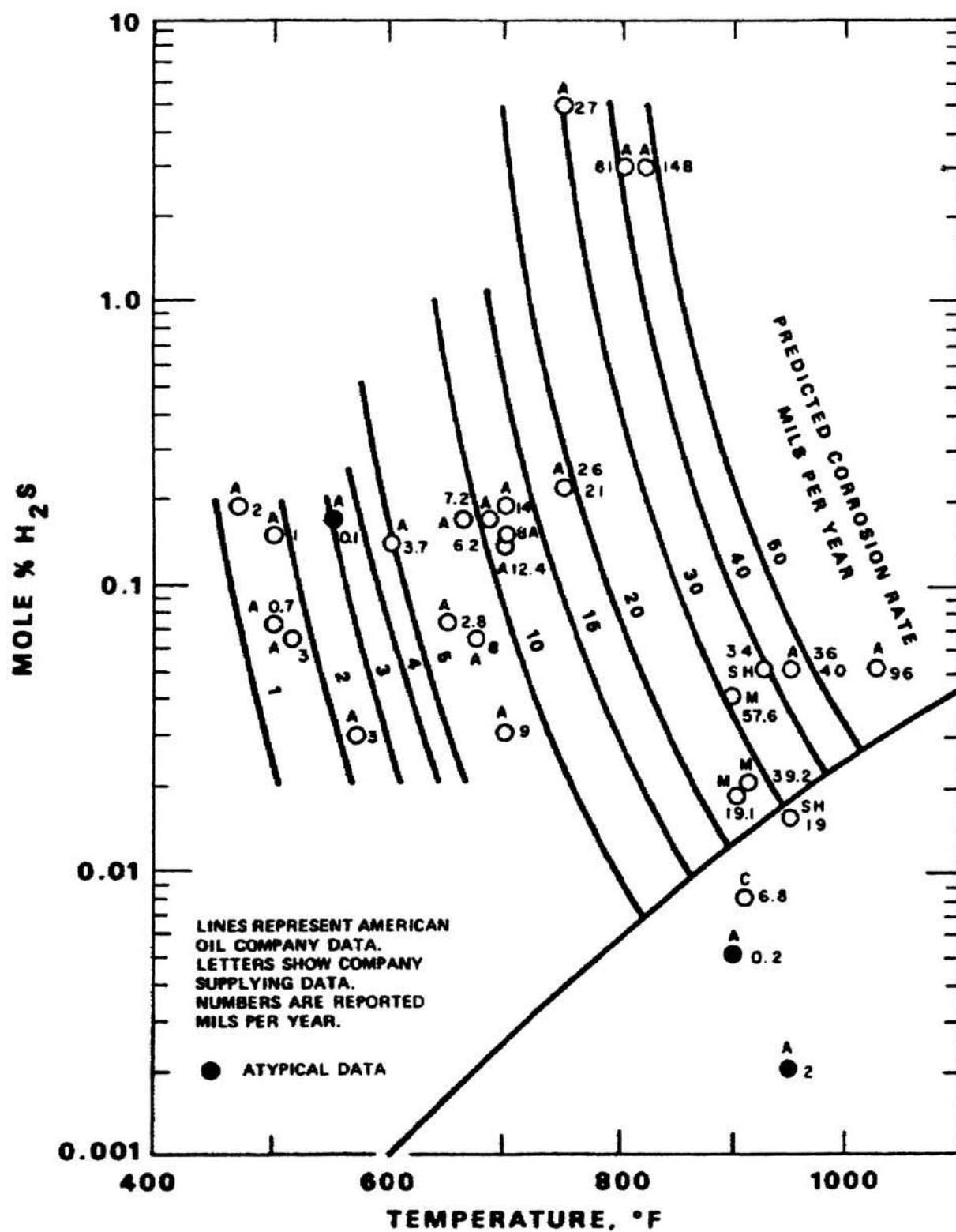
(Reprinted from "Computer Correlations to Estimate High Temperature Hydrogen Sulfide Corrosion in Refinery Streams," *Materials Protection*, January 1971)

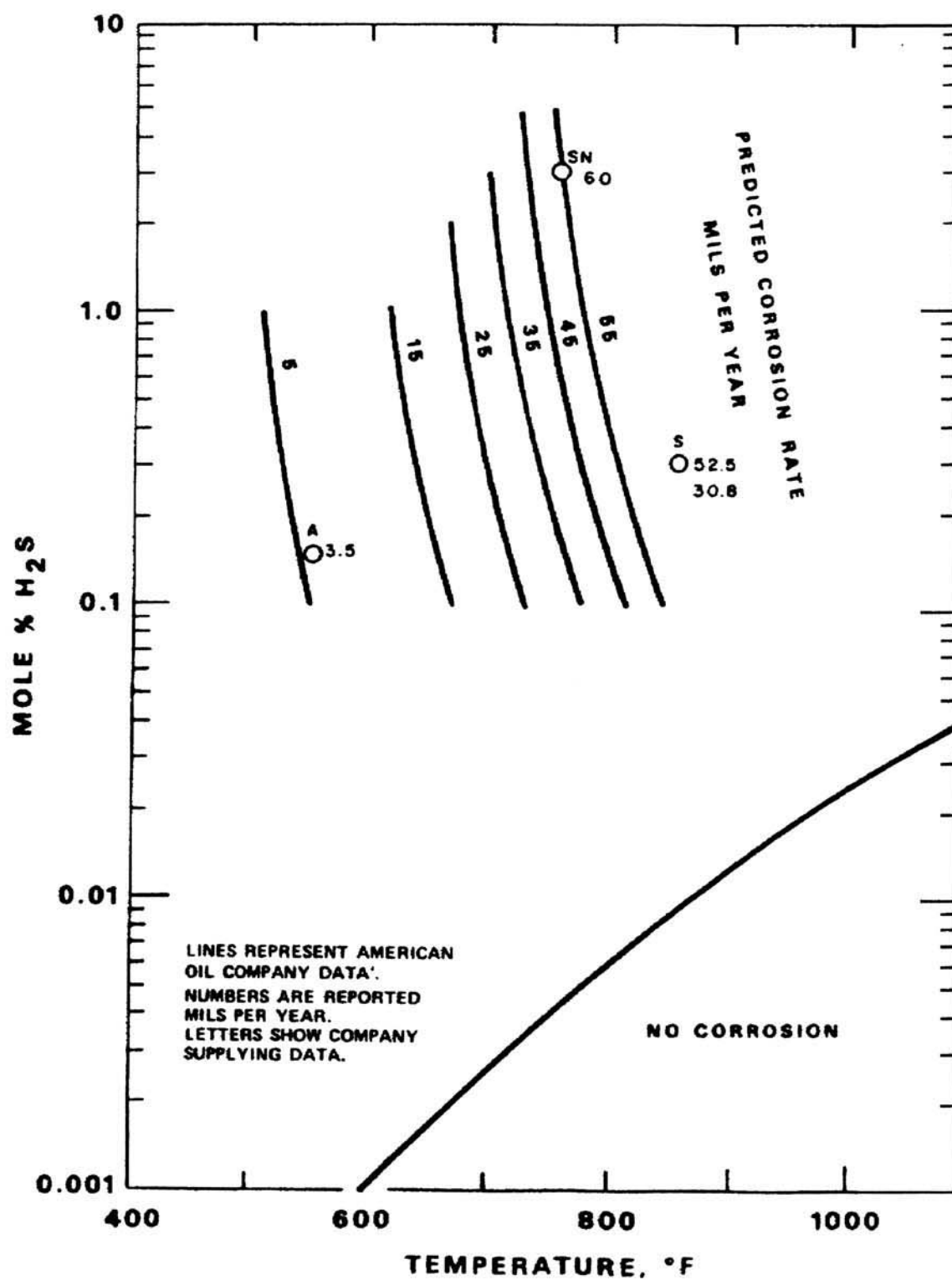
Figure 3.7(a) - Carbon steel, naphtha diluent.⁶



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

Figure 3.7(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

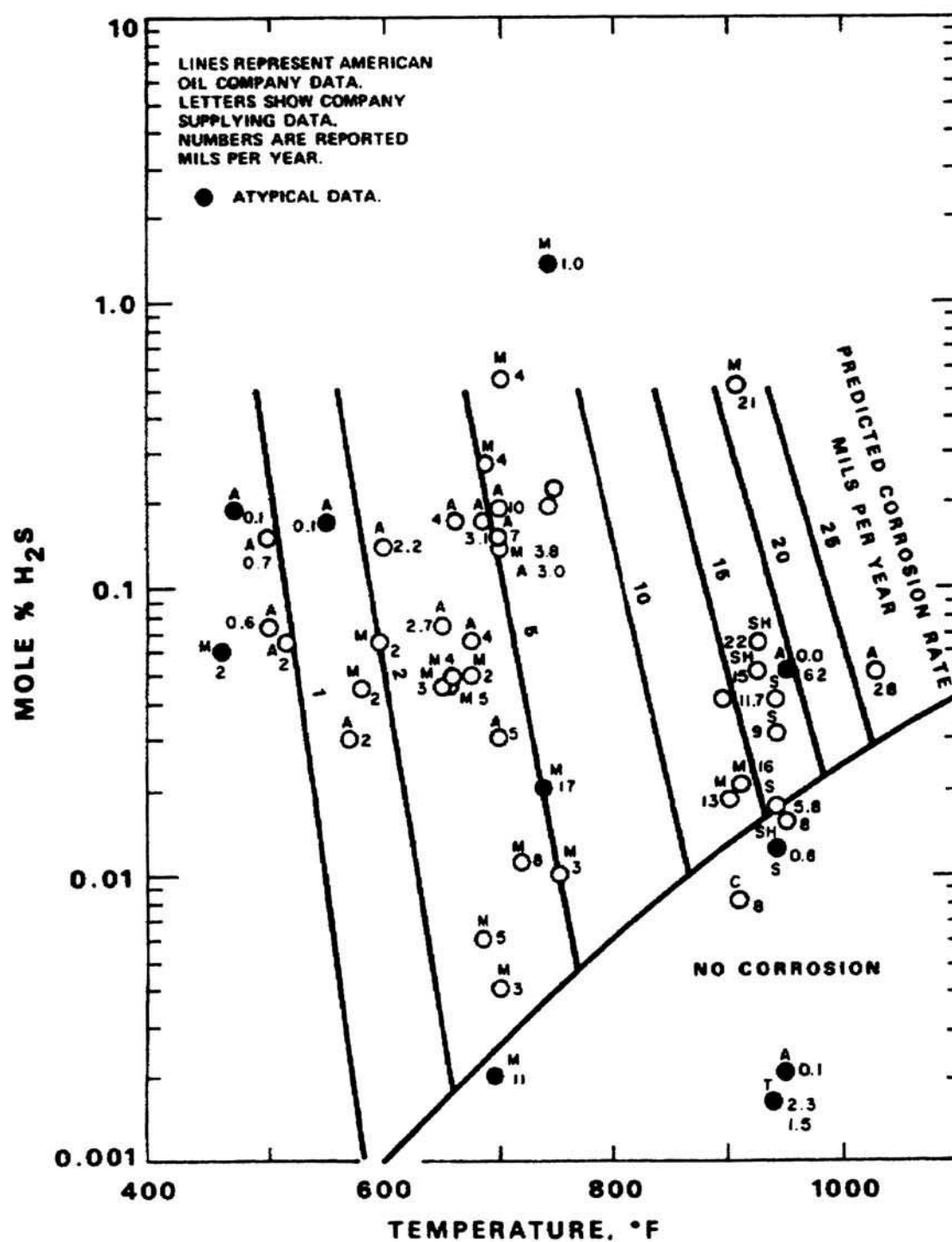


Figure 3.7(g) - Cr stainless steel, naphtha diluent.⁶

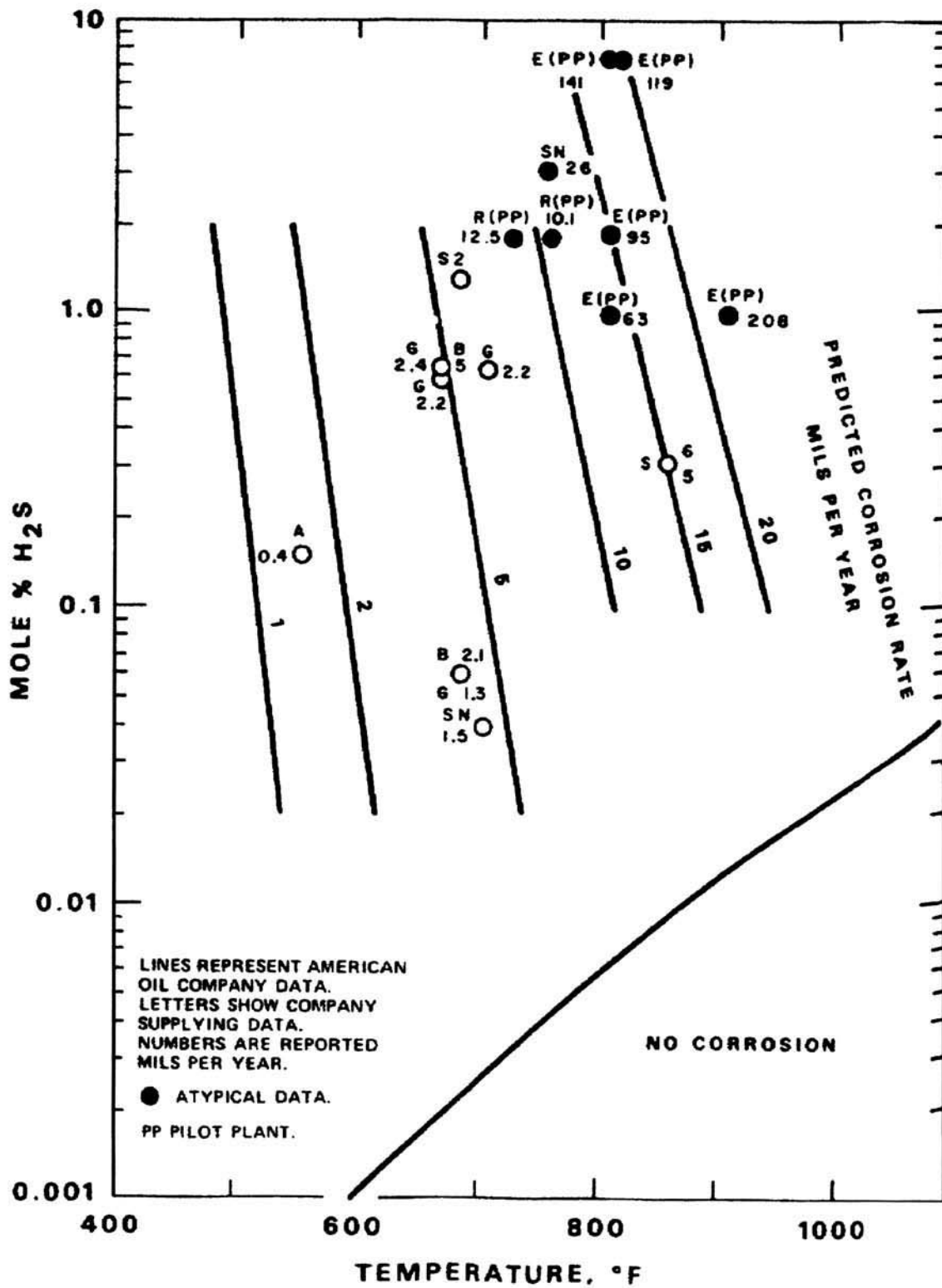


Figure 3.7(h) - 12% Cr stainless steel, gas oil diluent.

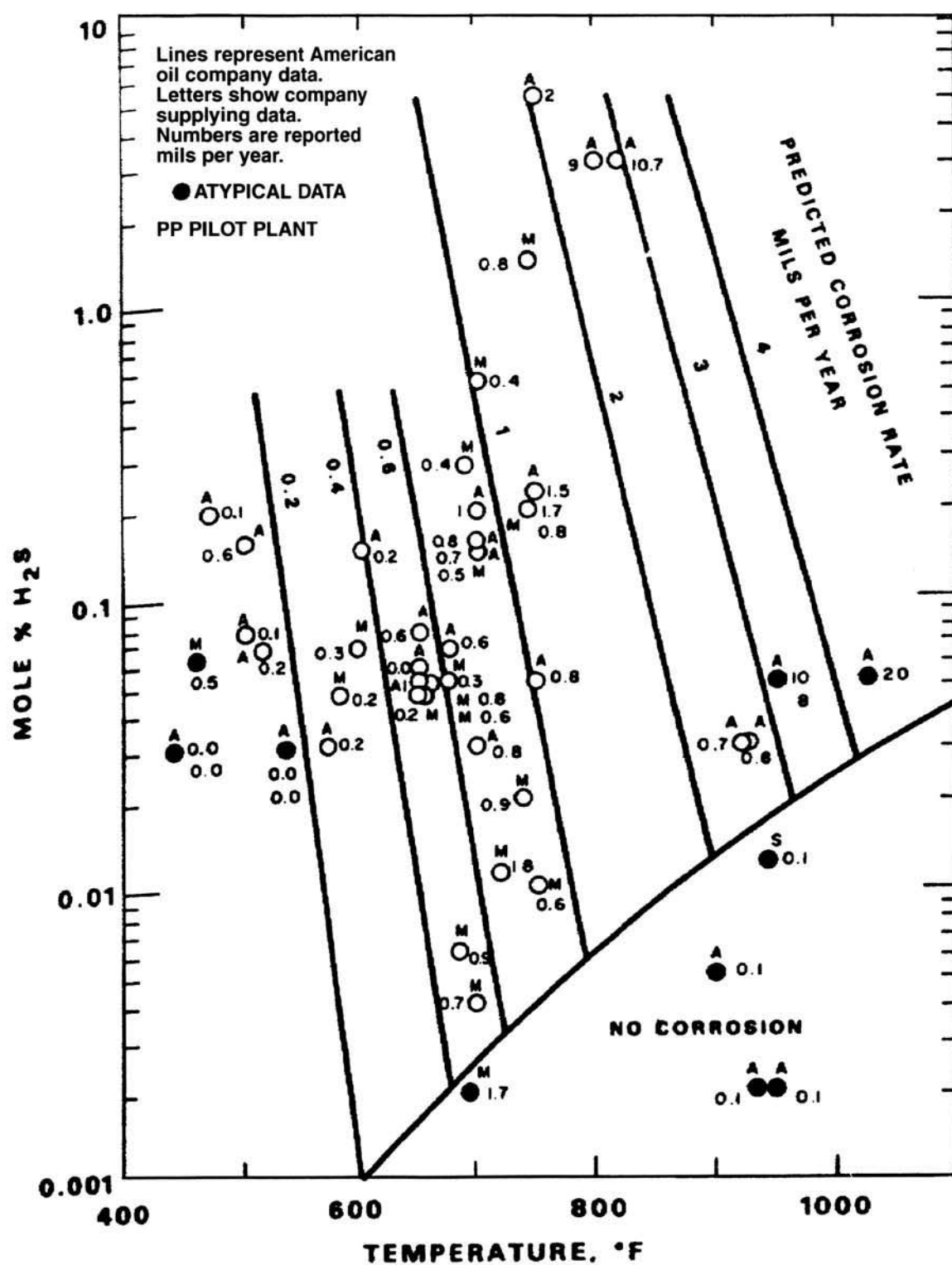
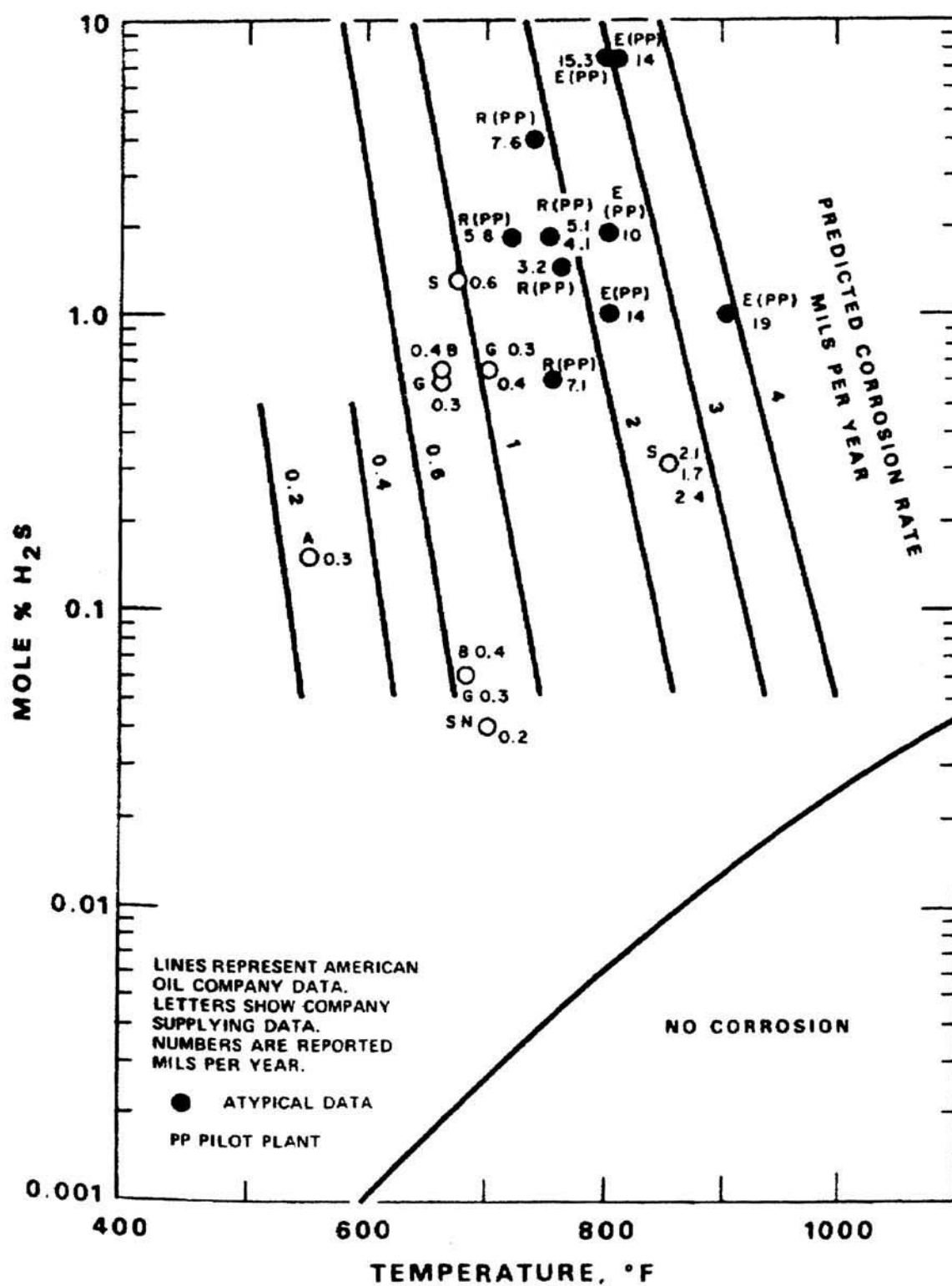


Figure 3.7(i) - 18-8 stainless steel, naphtha diluent.⁶

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

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)TM unit, a hot potassium carbonate absorption system, a monoethanolamine (MEA) absorption system or a SulfinolTM unit to purify the hydrogen by removing the carbon dioxide.

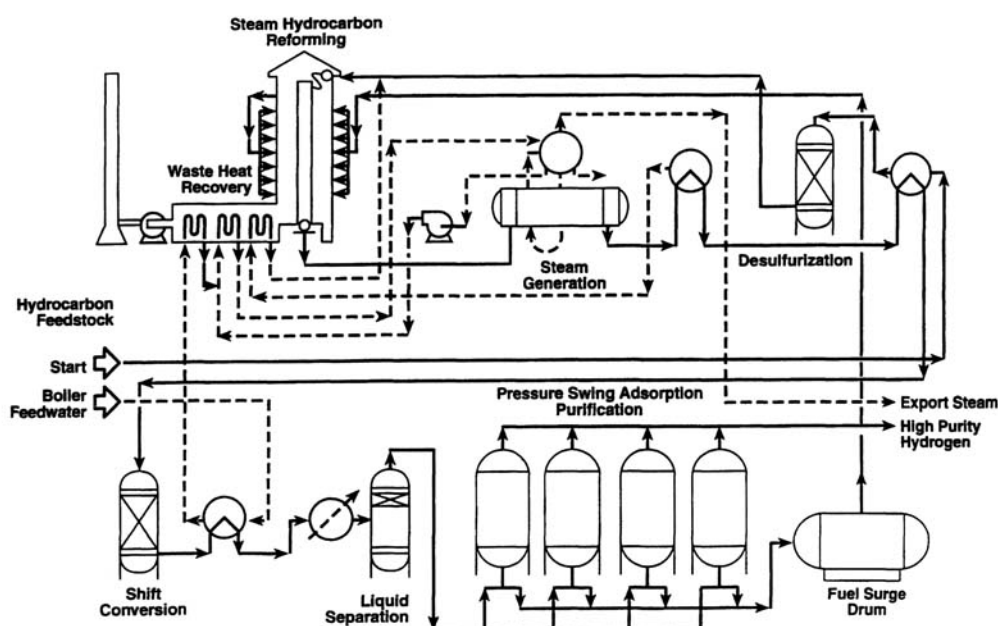


Figure 4.1 - Hydrogen¹

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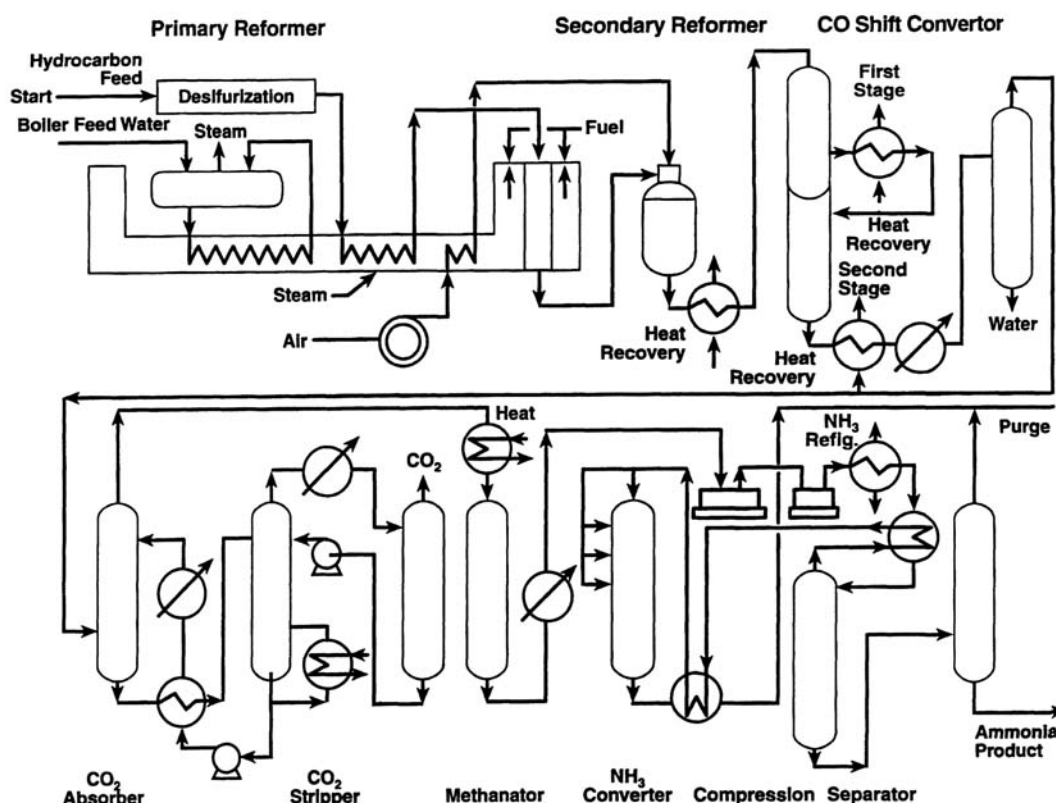


Figure 4.2 - Ammonia.¹

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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

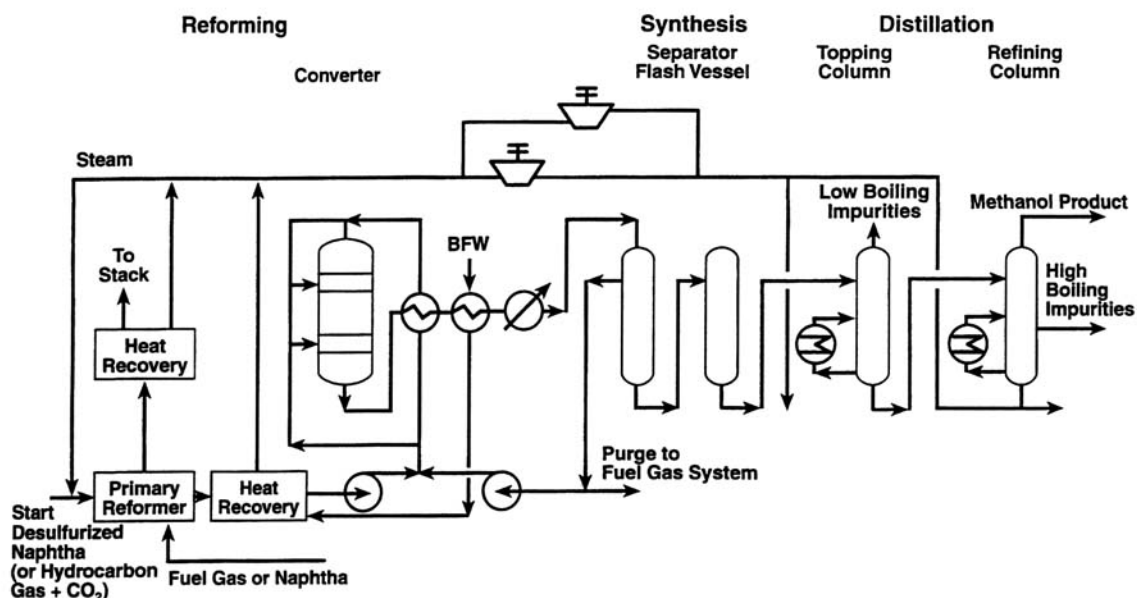


Figure 4.3 - Methanol.¹ (Reprinted with permission from "Refinery Process Handbook," *Hydrocarbon Processing*, Houston, TX: Gulf Publishing, 1968)

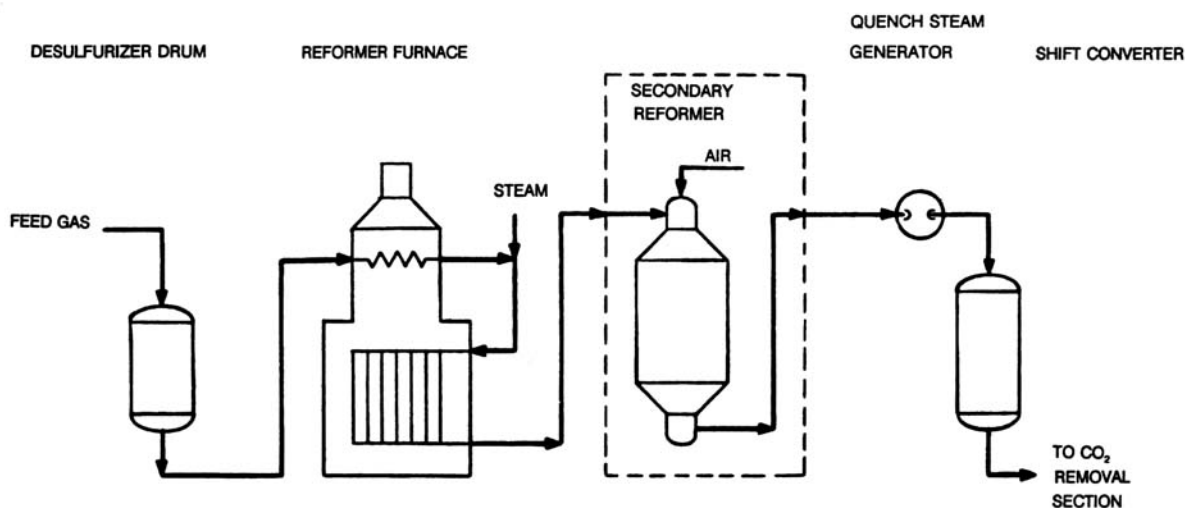


Figure 4.4 - High temperature front end section of reforming plant.²

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-1 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 “pigtailed.” Pigtailed 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 pigtailed 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) pigtailed 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 pigtailed.

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

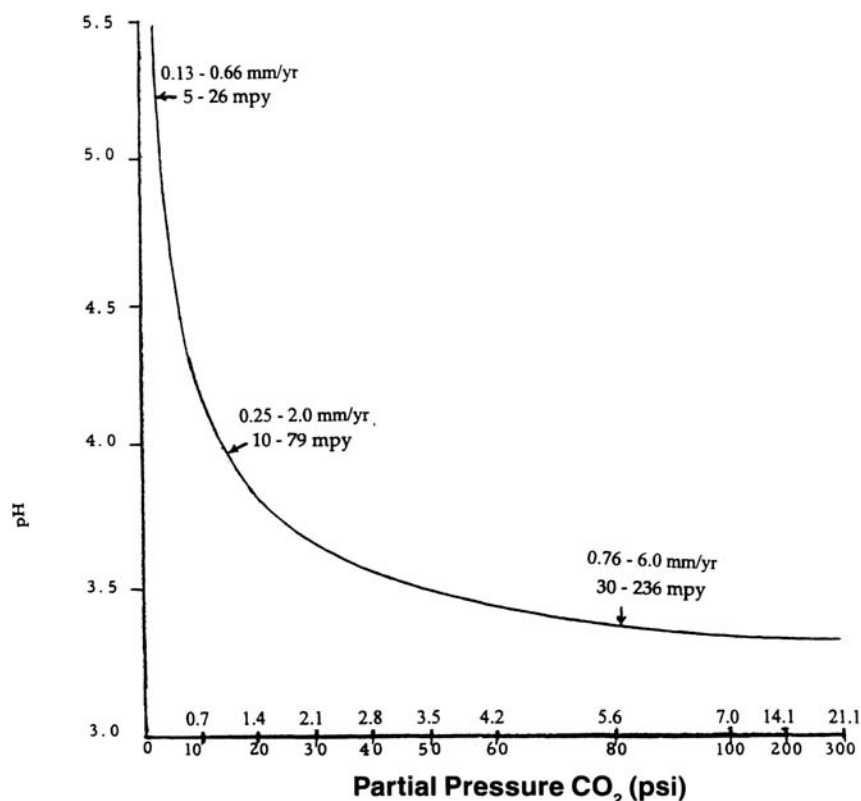


Figure 4.5 - Relationship between pH, carbon dioxide partial pressure, and estimated corrosion rate on carbon steel at 38°C (100°F).²

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)

⁽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

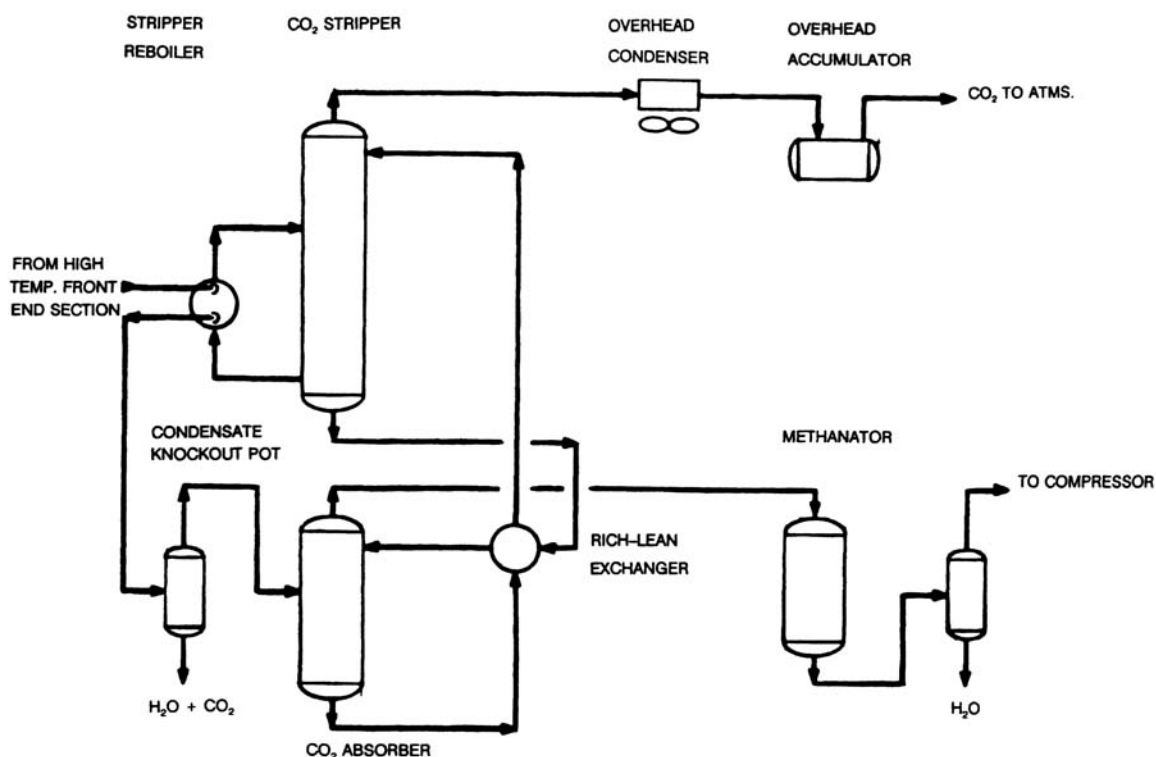


Figure 4.6 - Carbon dioxide removal section of reforming plant.²

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 SCC, most operators require stress relief for process temperatures above 60°C (140°F). This is because SCC 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

<u>Amine</u>	<u>wt%</u>	<u>Rich loading (mol/mol)</u>	<u>Total lean loading (mol/mol)</u>
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 Methanol Plants

Methanol plants are very similar to ammonia plants; high-temperature reformer furnaces and high-pressure (multilayer) converters are used. High corrosion rates on carbon steel occur 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.

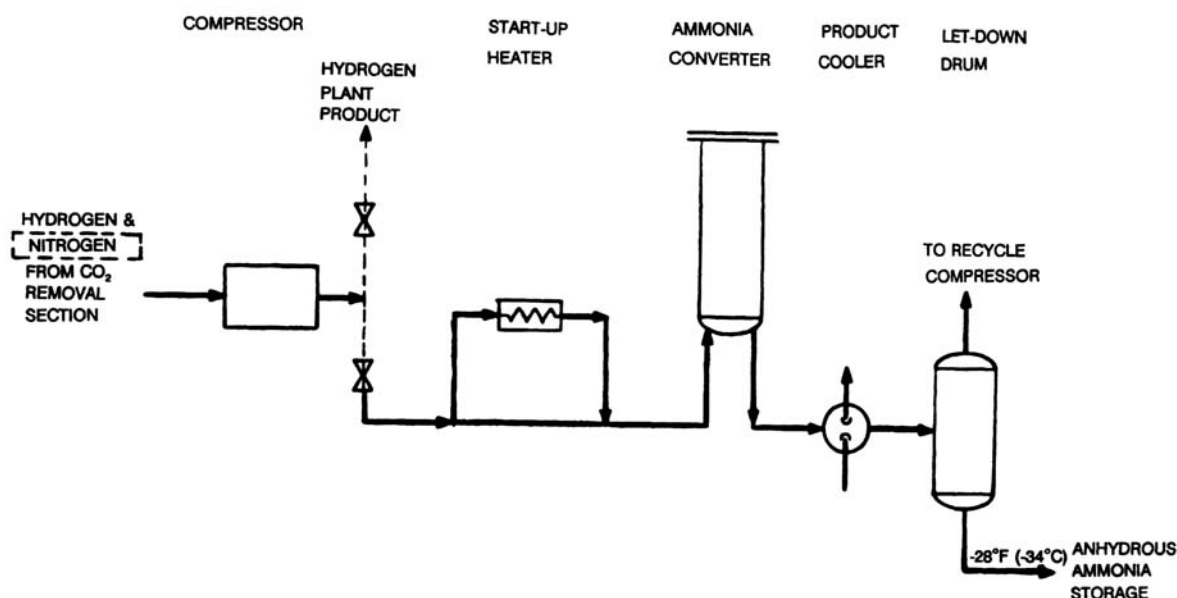


Figure 4.7 - High pressure section of reforming plant.²

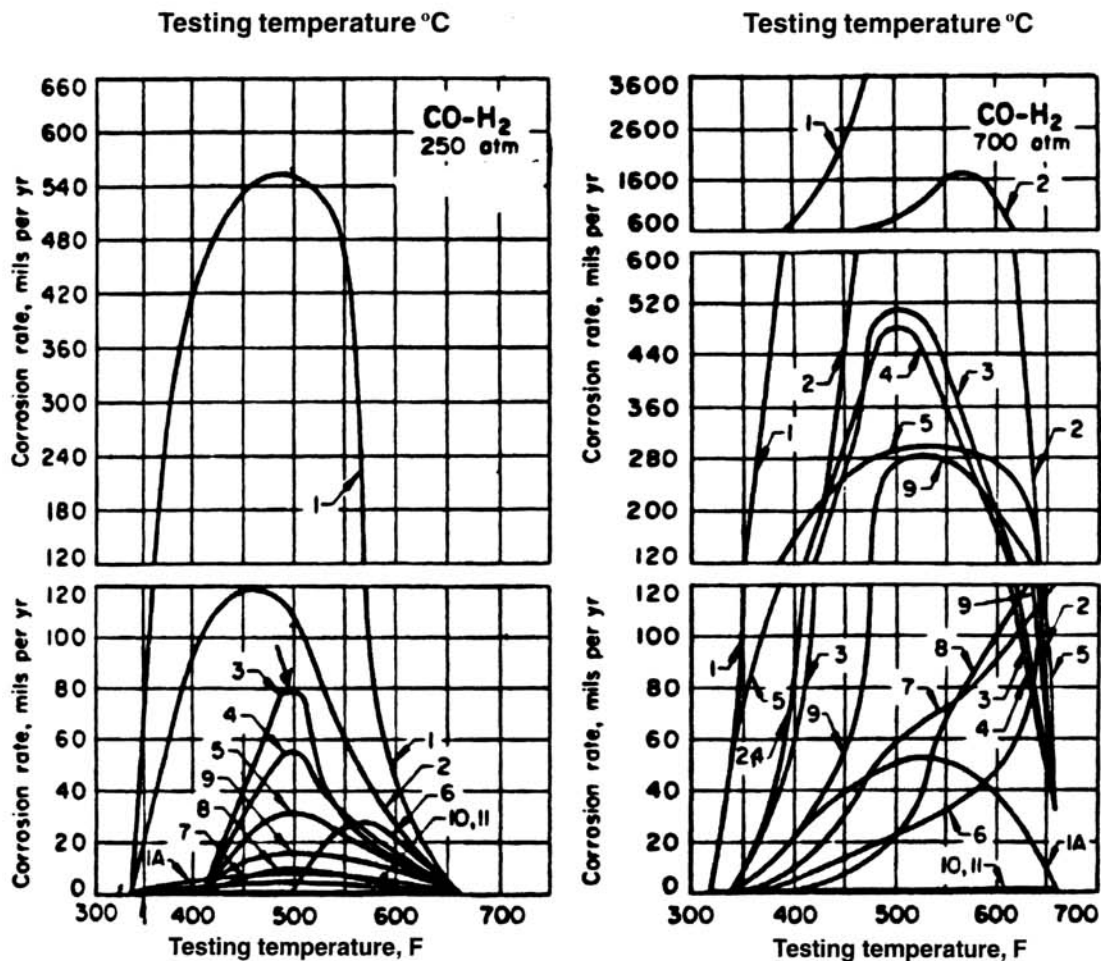
2.5 Other Common Processes

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 N04400) 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., VitonTM, nitrile, etc., are suitable for MTBE. Some refiners have had success with KalrezTM and other proprietary materials. Specially formulated urethanes have been used for vapor seals in storage tanks where PTFE has failed. VitonTM 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-H₂. 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)

REFERENCES

1. Refinery Process Handbook, *Hydrocarbon Processing* (September 1968): p. 231.
2. R.A. White, "Materials of Construction for Ammonia and Hydrogen Plants," NACE Western Regional Meeting (Houston, TX: NACE, 1965).
3. M.S. Dupart et al., "Understanding Corrosion in Akanolamine Gas Treating Plants," Parts 1 and 2, *Hydrocarbon Processing*, 75 (April and May 1993): p. 75, 89.
4. V.A. Dokuchaev, Y. I. Archakov, "Study of the Stress Corrosion Cracking Tendency of Steel St. 3 in Hydrogen Sulfide-Saturated Monoethanolamine," *Kontrol, Remont Zashch. Rorroz. Neftezavod. Oborud.* (1982): p. 60. and R.N. Parkins, Z.A. Foroulis, "Stress Corrosion Cracking of Mild Steel in Monoethanolamine Solutions," *Materials Performance* 26, 1 (1988): p. 19.
5. H.I. McHenry, T.R. Shives, D.T. Read, J.D. McColskey, C.H. Brady and P.T. Purtscher, "Examination of a Pressure Vessel that Ruptured at the Chicago Refinery of the Union Oil Company on July 23, 1984," Report NBSIR-86/3049 (Washington, DC: National Bureau of Standards, 1986)
6. Z.A. Foroulis, "Stress Corrosion Cracking of Carbon Steel in Hot Potassium Carbonate/Bicarbonate Solutions," *Boshoku Gijutsu* 36, 11 (1987): p. 689.
7. *Metals Handbook*, 8th edition, T. Lyman, editor, vol. 1 (ASM, 1961): p. 580.

BIBLIOGRAPHY

- "API Survey Shows Few Amine Corrosion Problems," *Petroleum Refiner*, 46, 11 (1968): p. 281.
- API Recommended Practice 951, "Guidelines for Avoiding Corrosion and Cracking Problems in Amine Units" (Washington, DC: American Petroleum Institute).
- Atkins, K.T.G., D. Fyfe, and J.D. Rankin, "Corrosion in Carbon Dioxide Removal Plant Towers," *AIChE Safety in Air and Ammonia Plants*, 16 (Sept. 1974): p. 39.
- Avery, R.E., and H.L. Valentine, "High Temperature Piping Systems for Petrochemical Processing (INCO)," *Chemical Engineering Progress*, 64, 1 (1968): p. 89.
- Bagdasarian, A.J., et al., "Stress Corrosion Cracking of Carbon Steel in DEA and 'ADIP' Solutions," *Materials Performance* 30, 5 (1991): p. 63.
- Banks, W.G., "Corrosion in Hot Carbonate Systems," *Materials Protection* 6, 11 (1967): p. 37.
- Baumert, K.L., et al., "Hydrogen Attack of Carbon - 0.5 Molybdenum Piping in Ammonia Synthesis," *Materials Performance* 25, 7 (1986): p. 34.
- Bienstock, D., and J.H. Field, "Corrosion Inhibitors for Hot-Carbonate Systems," *Corrosion* 17, 12 (1961): p. 87.
- Bienstock, D., and J.H. Field, "Corrosion of Steels in Boiling Potassium Carbonate Saturated with Carbon Dioxide and Hydrogen Sulfide," *Corrosion* 17, 7 (1961): p. 89.
- Blanc, C., et al., "Amine-Degradation Products Play No Part in Corrosion of Gas-Sweetening Plants," *Oil and Gas Journal* 80, 46 (Nov. 15, 1982): p. 128.
- Cherrington, D.C., and A.R. Ciuffreda, "How to Design Piping Systems for Hydrogen Service," *Oil and Gas Journal* 65, 21 (May 22, 1967): p. 102.
- Ciuffreda, A.R., and B.N. Greene, "Hydrogen Plant Shutdowns Reduced," *Hydrocarbon Processing* 51, 5 (1972): p. 113.
- Ciuffreda, A.R., and B.E. Hopkinson, "Survey of Materials and Corrosion Experience in Reformer Hydrogen Plants," *API Division of Refining* 52, 3 (1972): p. 549.
- Dawson, J.J., "Behavior of Welded Pressure Vessels in Agricultural Ammonia Service," *Welding Journal* 35, 6 (1956): p. 568.
- Deegan, D.C., and B.E. Wilde, "Stress Corrosion Cracking Behavior of ASTM A517 Grade F Steel in Liquid Ammonia Environments," *Corrosion* 29, 8 (1973): p. 310.
- deWard, C., U. Lotz, and D.E. Milliams, "Predictive Model for CO₂ Corrosion Engineering in Wet Natural Gas Pipelines," *Corrosion* 47, 12 (1991): p. 976.
- Dingman, J.C., et al., "Minimize Corrosion in MEA Units," *Hydrocarbon Processing* 45, 9 (1966): p. 285.
- Dokuchaev, V.A., and Y.I. Archakov, "Study of the Stress Corrosion Cracking Tendency of Steel St. 3 in Hydrogen Sulfide-Saturated Monoethanolamine," *Kontrol, Remont Zashch. Rorroz. Neftezavod. Oborud.* (1982): p. 60.
- Dunn, C.L. et al., "First Plant Data from Sulfinol Process," *Hydrocarbon Processing* 44, 4 (1965): p. 137.
- Edeleanu, C., ed., *Materials Technology in Steam Reforming Processes* (London, UK: Pergamon Press, 1966).
- Foroulis, C.A., "Stress Corrosion Cracking of Carbon Steel in Hot Potassium Carbonate/Bicarbonate Solutions," *Boshoku Gijutsu* 36, 11 (1987): p. 689.
- Gutzeit, J., and J.M. Johnson, "Stress Corrosion Cracking of Carbon Steel Welds in Amine Service," *Materials Performance* 25, 7 (1986): p. 18.
- Hall, A.M., et al., "Some Properties of HF, HH, HK and HN Alloys," ASME Publication 68-PVP-6 (1968).
- Ihrig, H.R., "Attack of Hydrogen-Nitrogen Mixtures on Steels," *Ind. & Eng. Chem.* 41, 11(1949): p. 2,516.
- Kobrin, G., and E.S. Kopecki, "Choosing Alloys for Ammonia Services," *Chemical Engineering* 85, 28 (Dec. 18, 1978): p. 115.
- Lang, F.S., and J.F. Mason Jr., "Corrosion in Amine Gas Treating Solutions," *Corrosion* 14, 2 (1958): p. 105t.
- Loginow, A.W., and E.H. Phelps, "Stress Corrosion Cracking of Steels in Agricultural Ammonia," *Corrosion* 18, 8 (1962): p. 229t.

- Market, J.W., "Metal Dusting in the Process Boiler of a Methanol Plant," American Institute of Chemical Engineers Annual Meeting, paper no. 94b (November 25-30, 1984).
- Moltley, J.R., and D.R. Fincher, "Inhibition of Monoethanolamine Solutions," *Materials Protection* 2, 10 (Aug. 1963): p. 27.
- Moore, K.L., "Corrosion of Furnace Tubes by Residual Welding Slag," *Corrosion* 16, 1 (1960): p. 26t.
- Moore, K.L., "Corrosion Problems in a Refinery Diethanolamine System," *Corrosion* 16, 10 (1960): p. 111.
- Moran, J.J., et al., "Behavior of Stainless Steels and Other Engineering Alloys in Hot Ammonia Atmospheres," *Corrosion* 17, 4 (1961): p. 115 (191t).
- Parkins, R.N., and Z.A. Foroulis, "Stress Corrosion Cracking of Mild Steel in Monoethanolamine Solutions," *Materials Performance* 26, 1 (1988): p. 19.
- Pease, G.R., "Corrosion of Nickel-Chromium, Iron Alloys by Welding Slags," *Welding Journal* 35, 9 (1956): p. 469-S.
- Polderman, L.D., et al., "Degradation of Monoethanolamine in Natural Gas Treating Service," *Oil and Gas Journal* 54, 2 (May 16, 1955): p. 180.
- Polderman, L.D., and A.B. Steel, "Degradation of Diethanolamine in Gas Treating Service," *Oil and Gas Journal* 55, 3 (July 30, 1956): p. 206.
- Prange, F.A., "Corrosion in a Hydrocarbon Conversion System," *Corrosion* 15, 12 (December, 1959): p. 619t.
- Prescott, G.R., Letter to Editor of *Materials Protection*, 10, 12: Questionable. Magnetic Technique for Detection of Premature Failures (Dec. 1971).
- Richert, J.P., et al., "Stress Corrosion Cracking of Carbon Steel in Amine Systems," *Materials Performance* 26, 1 (1988): p. 9.
- Roach, D.B., "Defects and Damage in Cast Heater Tubes," *Materials Evaluation* 30, 11 (1972): p. 229.
- Scott, B., et al., "Corrosion History of Hot Potassium CO₂ Absorber," *AIChE Safety in Air and Ammonia Plants* 28 (1988): p. 127.
- Sheilan, M., and R.F. Smith, "Hydraulic-Flow Effect on Amine Plant Corrosion," *Oil and Gas Journal* 82, 47 (November 19, 1984): p. 138.
- Sutcliffe, J.M., et al., "Stress Corrosion Cracking of Carbon Steel in Carbonate Solutions," *Corrosion* 28, 8 (Aug. 1972): p. 313.
- Townshend, P.E., G.T. Colegate and T.L. Van Waart, "Carbon Dioxide Corrosion at Low Partial Pressures in Major Submarine Gas Pipelines," *Soc. Pet. Eng'rs of AIME*, paper 3741 (1972).
- Williams, E., and H.P. Leckie, "Corrosion and Its Prevention in a Monoethanolamine Gas Treating Plant," *Materials Protection* 7, 7 (1968): p. 21.
- Wong, H.A., et al., "Corrosion-Inhibition System Passes Severest Test at Chevron's Princess MEA Plant," *Oil and Gas Journal* 83, 45 (November 11, 1985): p. 100.

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

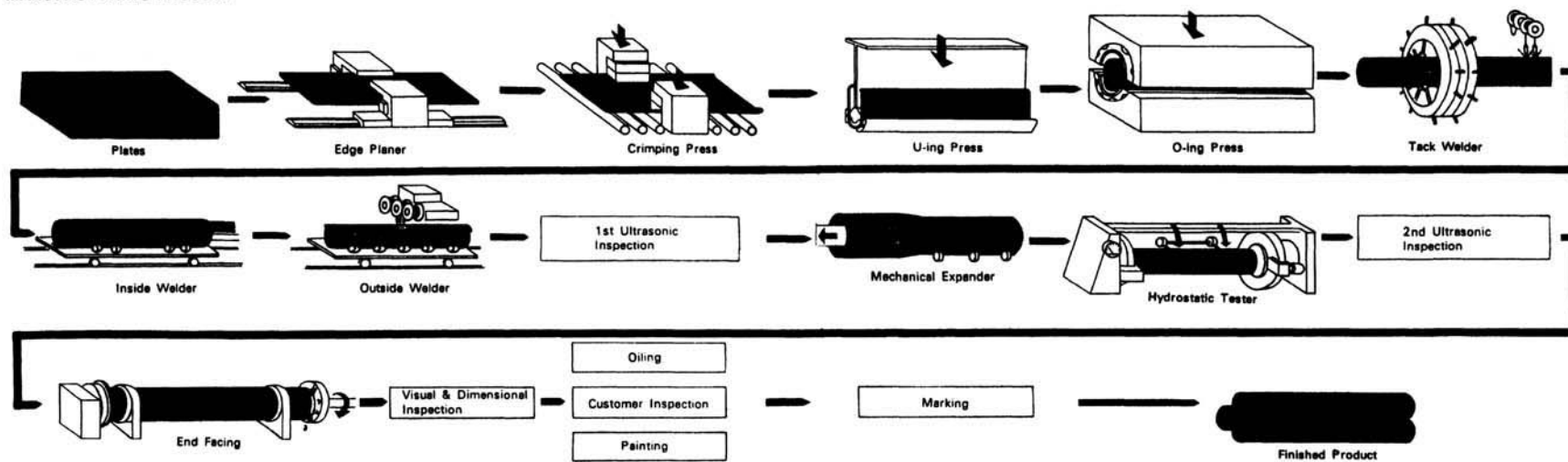
The process for manufacturing electric resistance welded (ERW) pipe is shown schematically in Figure 5.3.¹ In this process, coils rather than plate are formed, then continuously electric resistance welded. Figure 5.4² shows a typical cross section of an ERW weld. In contrast to the submerged arc weld, 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

⁽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.

MANUFACTURING PROCESS



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

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

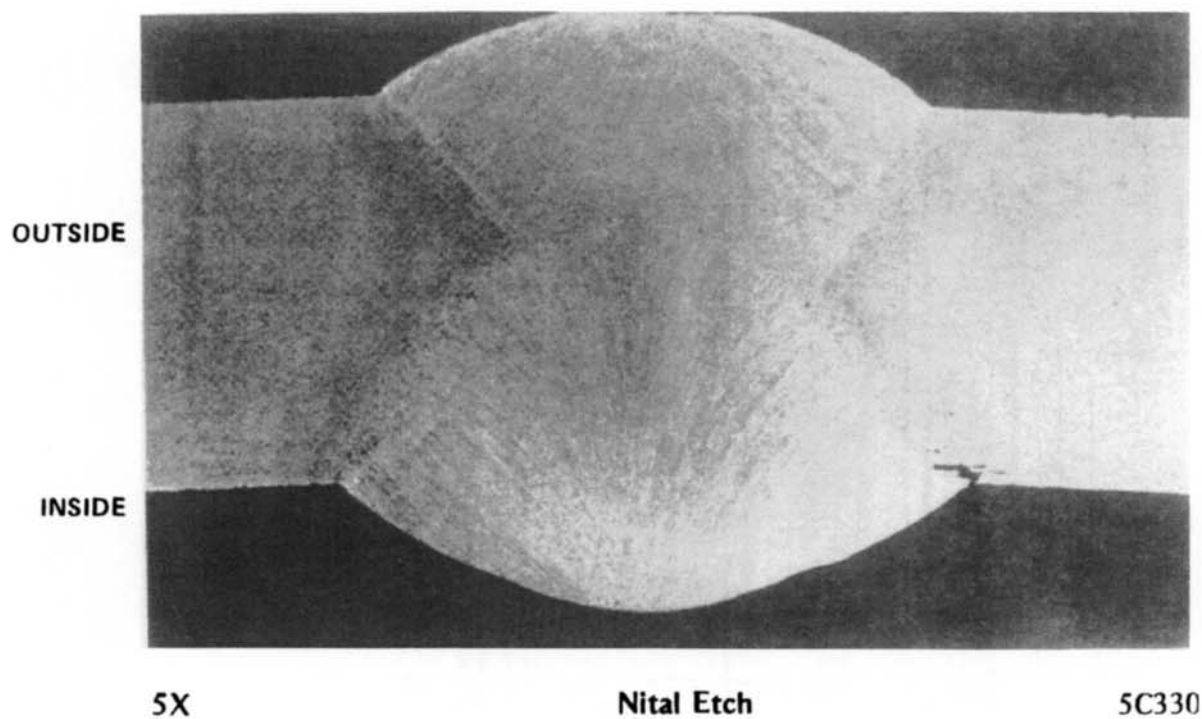


Figure 5.2 - Toe cracks in the HAZ of a DSA weld.²

(Reprinted with permission from Sixth Symposium on Line Pipe Research, October 1979.
Research sponsored by the Pipeline Research Committee, American Gas Association, Arlington, VA)

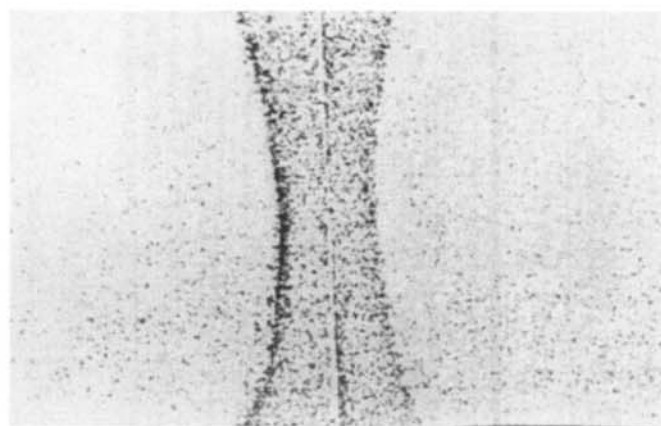
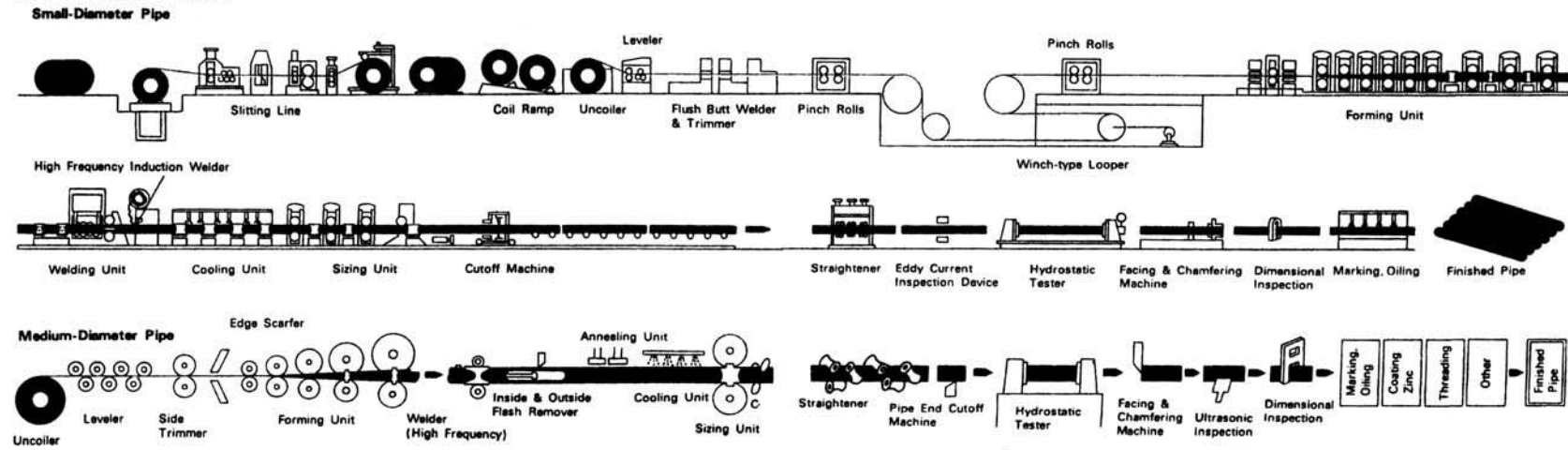


Figure 5.4 - High frequency weld.²

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MANUFACTURING PROCESS



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:

- 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

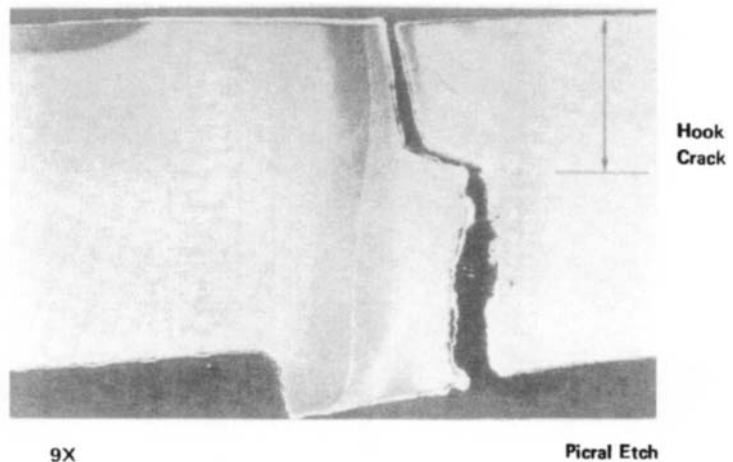


Figure 5.5 - Appearance of a hook crack in ERW weld.²
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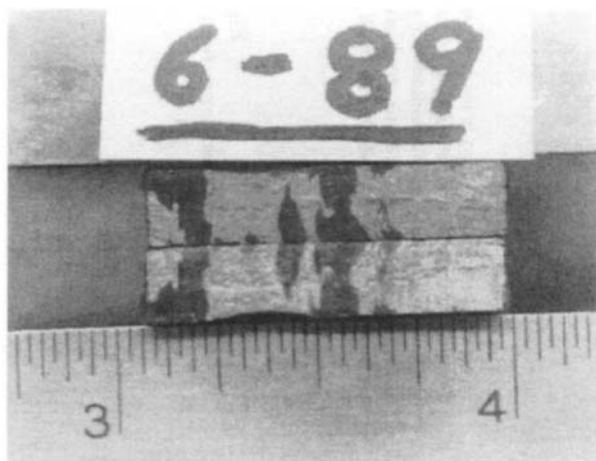


Figure 5.6 - Through wall penetrators in ERW weld.³

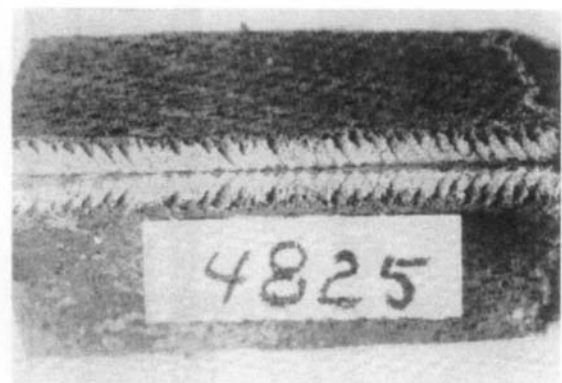
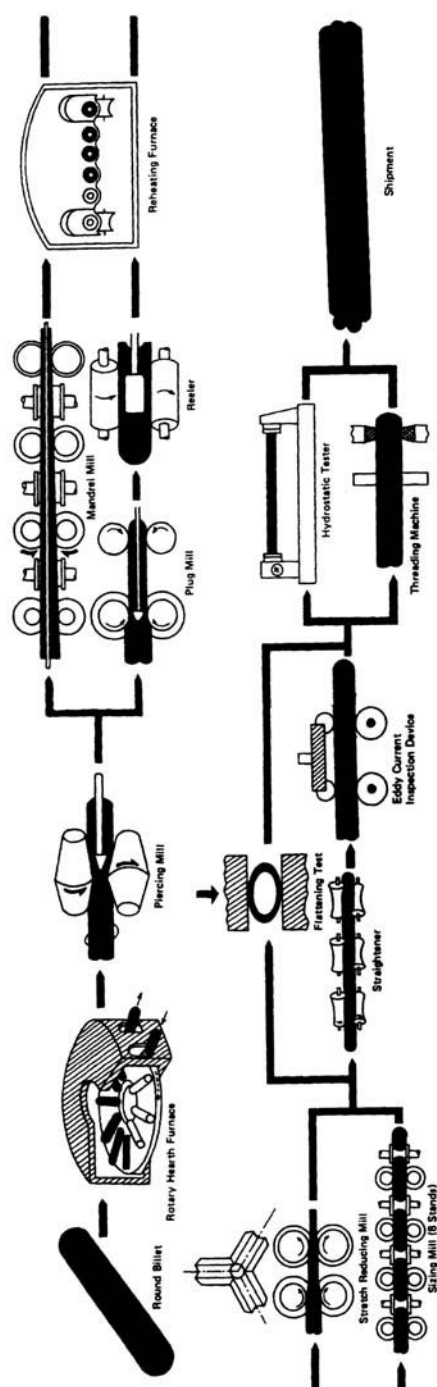


Figure 5.7 - Stitch weld (intermittent fusion) in ERW weld.⁴
(Reprinted with permission from API Bulletin 5T1, "Nondestructive Testing Terminology," 9th ed., May 1987, American Petroleum Institute, Washington, DC)

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 withdrawal of the mandrel or the plug, the rolled shell is reheated before being processed on a stretch reducing mill or a sizing mill where the desired OD and wall thickness are obtained.

Besides 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 Kawasaki 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

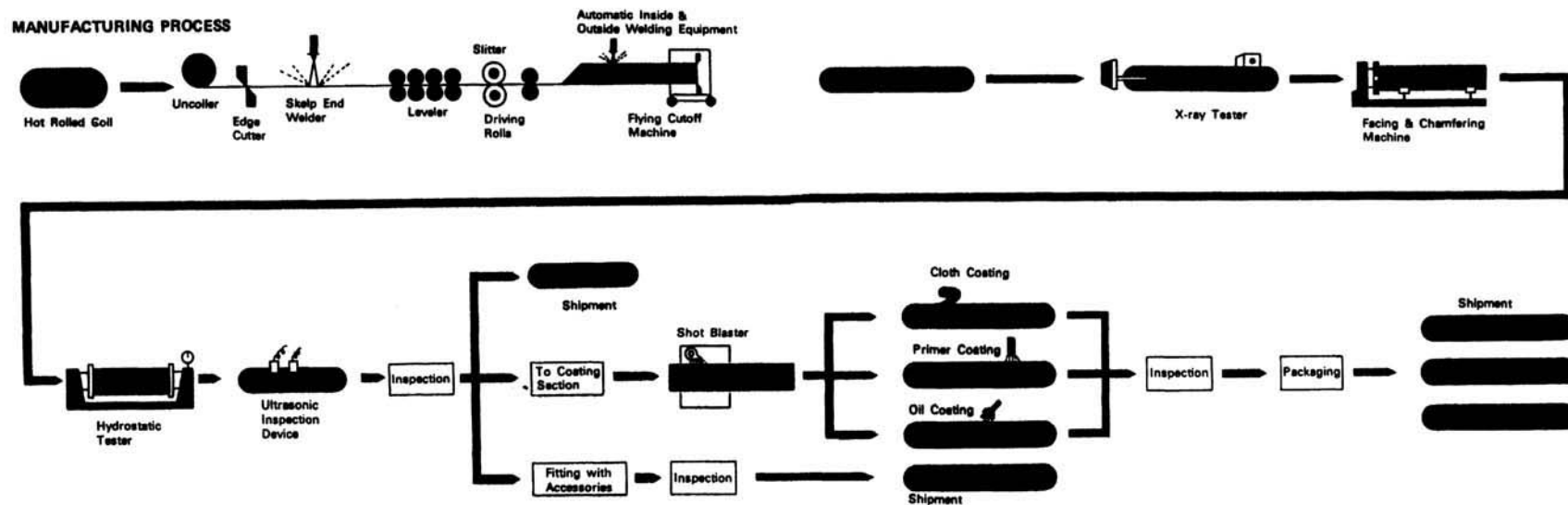
API specification 5L is the principal line pipe specification. It combines the previous API 5L, 5LX, and 5LS. The selection of a grade depends on the strength-to-weight ratio and the pumping costs. ASTM specifications (e.g., A381) often are used for compressor station pipe, particularly for extruded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

<u>Specification</u>	<u>Product Forms</u>	<u>Scope</u>
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

⁽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

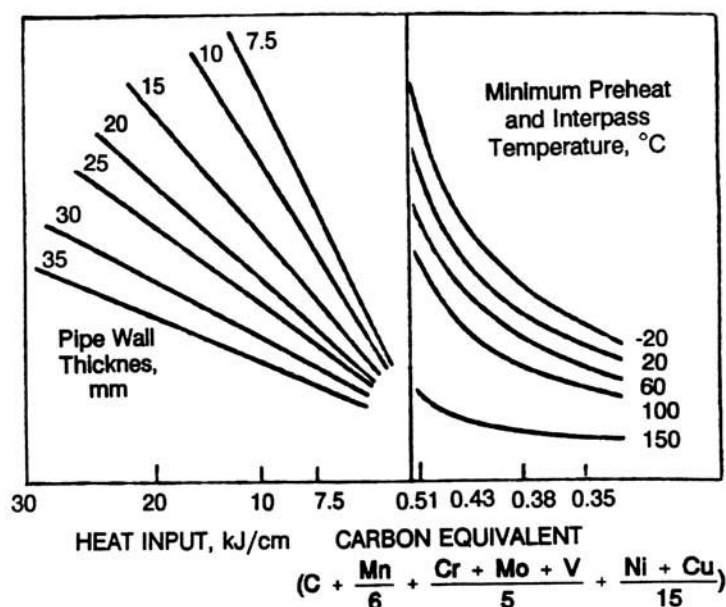


Figure 5.10 - The permissible maximum carbon equivalent for butt welds in line pipe using cellulosic (EXX10) electrodes based on minimum preheat and interpass temperature, pipe wall thickness, and heat input.⁶ (Reprinted from *Micro Alloying 75 - Proceedings of Micro Alloying 75 Conference*, October 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:

$H_{ef} = 0.50 H_f$ 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 $20 S_y$

= $S_y + 0.005 (R_f - 20 S_y)$ 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 $100^\circ C$ ($212^\circ F$), called critical T100, is calculated where:

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

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 ($212^\circ F$) 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

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

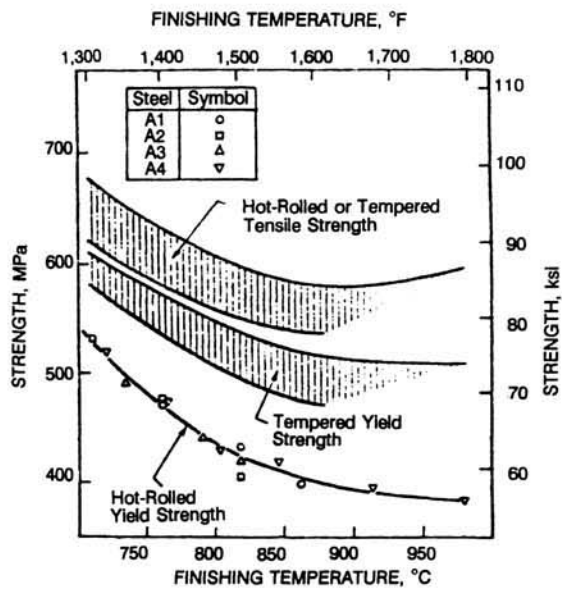


Figure 5.11 - Effect of finishing temperature and tempering on the strength of steels A1 to A4.⁷ (Reprinted from *Micro Alloying 75 - Proceedings of Micro Alloying 75 Conference*, October 1, 1975, Union Carbide Corp., Metals Division, New York, NY)

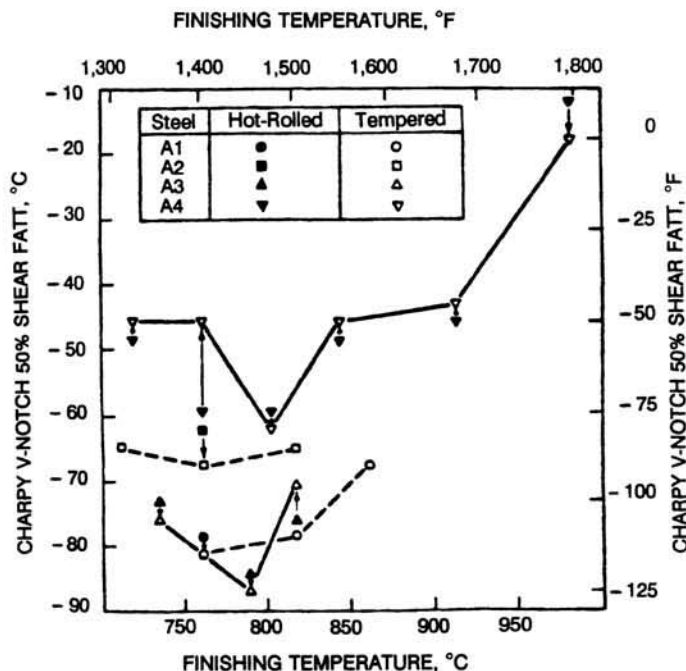


Figure 5.12 - How finishing temperature affects the Charpy V-notch 50% shear fracture-appearance-transition temperature (FATT) of steels A1 to A4.⁶ (Reprinted from *Micro Alloying 75 - Proceedings of Micro Alloying 75 Conference*, October 1, 1975, Union Carbide Corp., Metals Division, New York, NY)

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_1 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_1 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 5.11⁷ 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-

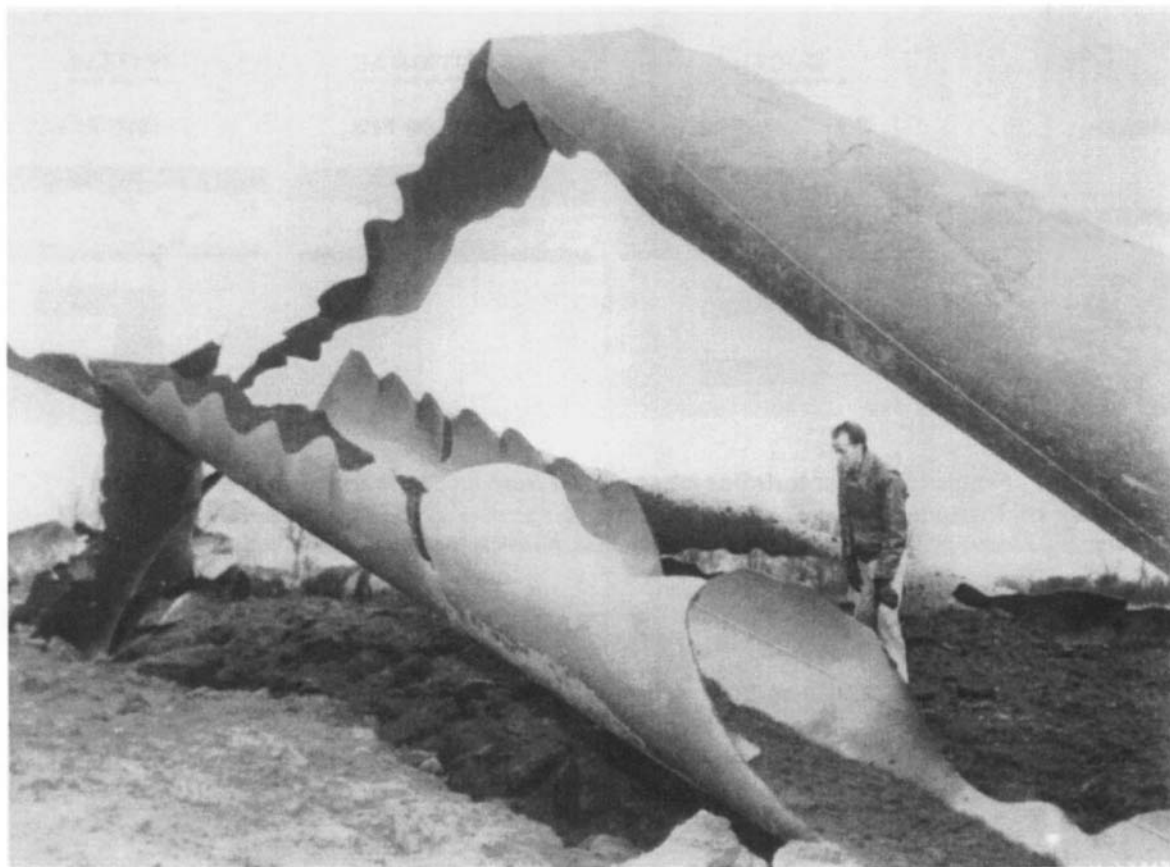


Figure 5.13 - Long distance rupturing of piped tested with gas.⁸
(Reprinted with permission from the Lincoln Electric Co.)

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

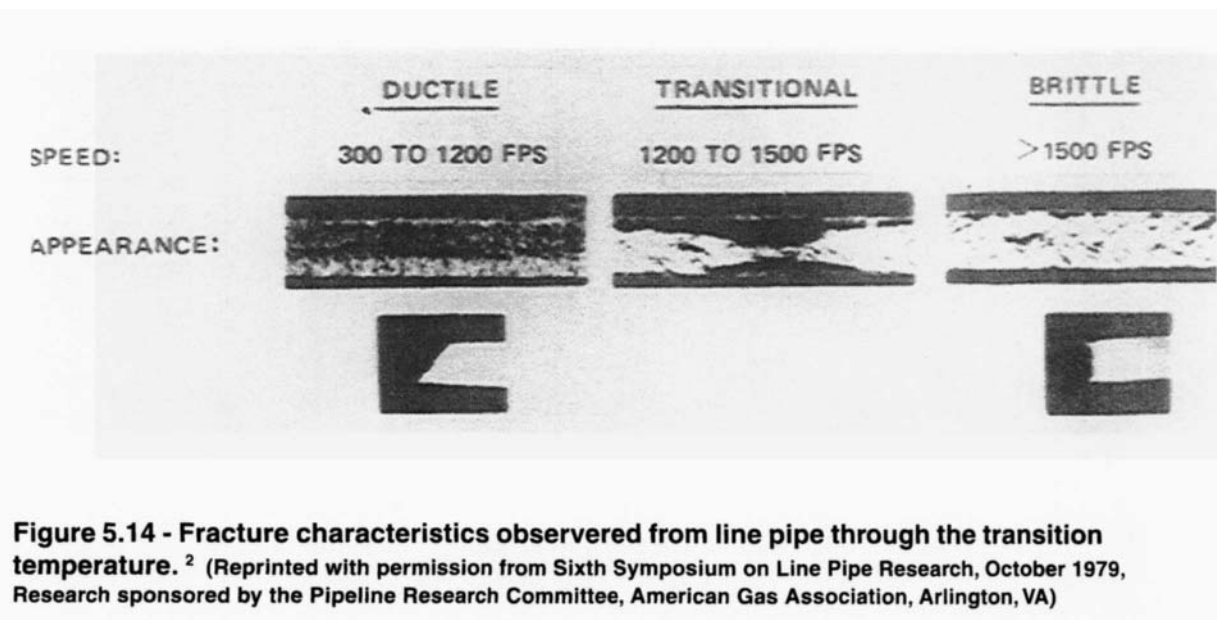
It is important to control carefully bending parameters, such as bending speed, temperature, and water quench. Specifications usually include tests to ensure mechanical properties are not degraded below the minimum requirements and surface inspection, e.g., magnetic particle inspection to ensure no defects 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



7. FRACTURE

Long pipeline fractures such as the one shown in Figure 5.13⁸ 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

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



Figure 5.15 - Sinusoidal brittle fracture.²

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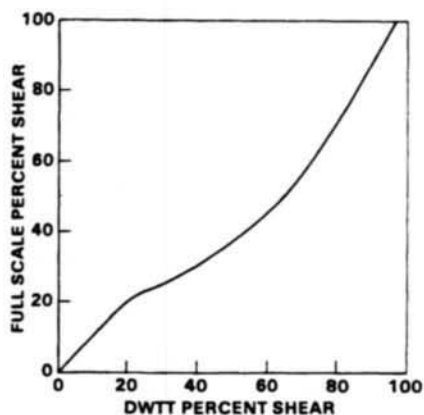


Figure 5.17 - Relationship between DWTT percent shear and full-scale pipe percent shear of the fracture surface.²

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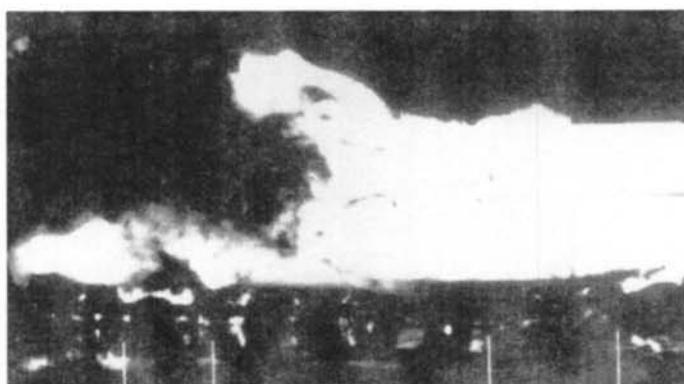


Figure 5.16 - Photo of brittle fracture from high speed movie (3,000 frames/s).² (Reprinted with permission from Sixth Symposium on Line Pipe Research, October 1979, Research sponsored by the Pipeline Research Committee, American Gas Association, Arlington, VA)

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)

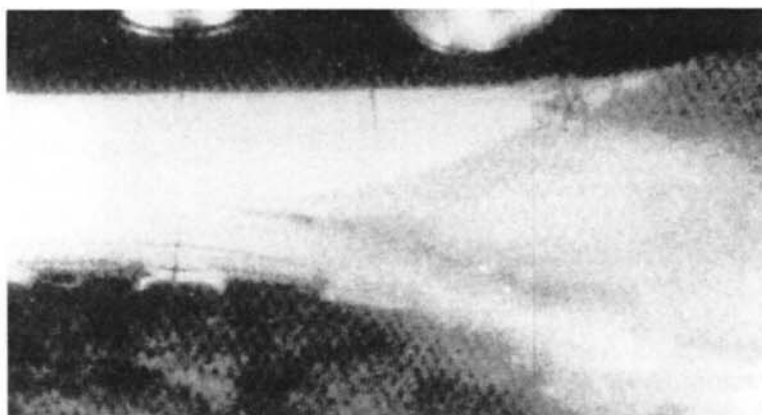
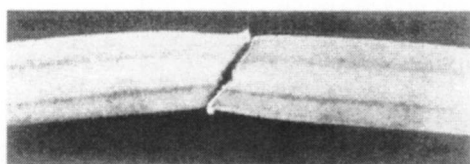


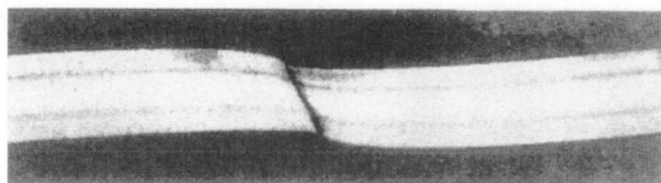


Figure 5.19 - Ductile fracture of large diameter line pipe showing scalloped fracture edges.²
(Reprinted with permission from Sixth Symposium on Line Pipe Research, October 1979. Research sponsored by the Pipeline Research Committee, American Gas Association, Arlington, VA)



"Tearing" Shear

23506



"Propagating" Shear

23226

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

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

where:

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

σ = 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 5.21⁶ (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

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 geometries, yield strengths, and stress levels, the Charpy energy required to provide fracture arrest is given by the following formula:

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

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

σ_n = operating stress level (ksi)

R = pipe radius (in.)

t = pipe thickness (in.)

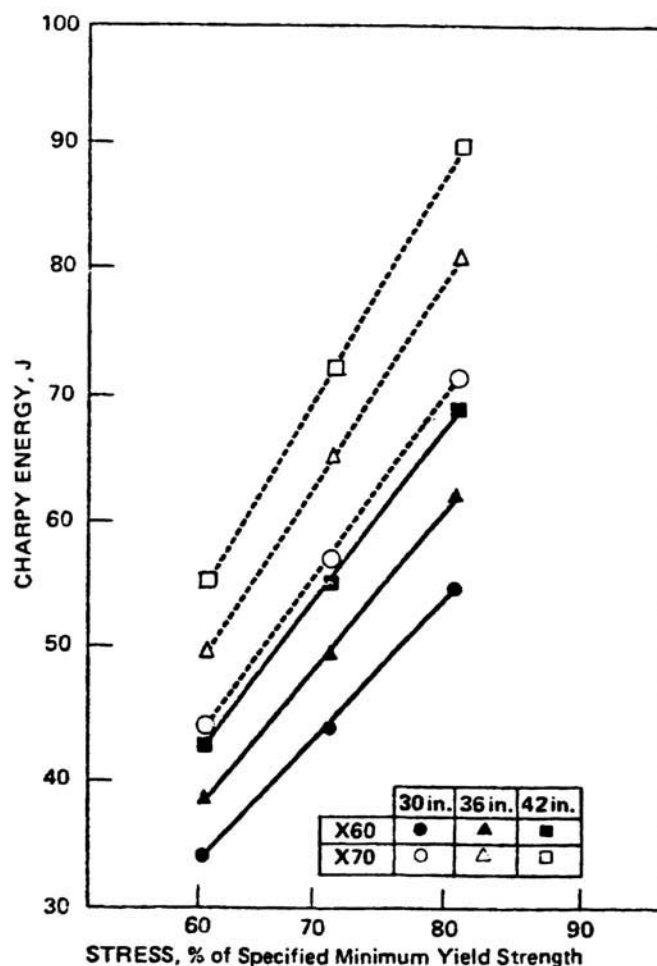


Figure 5.21 - The Charpy V-notch energy needed to produce fracture arrest (after Maxey).⁶

(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 me-

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	12 Cr	= Types 405, 410, 410S, CA15 (UNS S40500, S41,000, S41008, J9II59)
CS	= carbon steel		
1 Cr	= 1 Cr-1/2 Mo	18-8	= Types 304, 316, 321, 347, CF8, CF8M, CF8C
1-1/4 Cr	= 1-1/4 Cr-1/2 Mo		(UNS S30400, S31600, S32100, S34700, J92600, J92900, J92710)
5 Cr	= 5 Cr-1/2 Mo		
9 Cr	= 9 Cr-1 Mo	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	OPERATING TEMPERATURE															
	100	200	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400		F
General Hydrocarbon (S < 0.2 wt% H ₂ S < 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	38	100	150	200	260	315	370	425	480	540	590	650	700	760		C
VESSELS																
Trays and Internals (Note 4)																
EXCHANGER SHELLS AND CHANNELS																
Tubesheets of FH Covers (Note 6)																
Baffles (Note 7)																
Exchanger Tubes (Note 1, 35)																
PIPING																
FURNACE TUBES (Note 2, 3)																
PUMPS (Note 32)																
Case																
Impeller																

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

TABLE A-3

SERVICE		OPERATING TEMPERATURE																F		
Hydrocarbon + S >1 wt% (Notes 2, 8)		100	200	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400		C			
Crude Units, Fluid Catalytic Crackers, Cokers, etc.		38	100	150	200	260	315	370	425	480	540	590	650	700	760					
VESSELS						550 290	Steel* Clad with 2.5 mm 12Cr**					1,000 540	CS + Refractory Lined				1,200 650			
		CS + 3 (Note 5)																		
Trays and Internals (Note 4)		CS				12Cr**				850 445	1-1/4 Cr, 410S or 18-8 (Note 18,31)		1,100 590	2-1/4Cr or 18-8						
EXCHANGER SHELLS AND CHANNELS		CS + 3 (Notes 5, 9)				Steel* Clad with 2.5 mm 12Cr** or Solid 5Cr + 3 mm														
Tubesheets of FH Covers (Note 6)		CS				Same as Above Except 5Cr with No CA														
Baffles (Note 7)		CS				5Cr														
Exchanger Tubes (Note 1)		CS				5Cr														
PIPING (Note 28)		CS + 1.5 (Note 5)				550 290	5Cr + 2		650 340	5Cr + 3		750 400	9Cr + 2		Refractory Lined CS 9Cr + 2 or 18-8					
FURNACE TUBES (Note 3)		CS + 3				5Cr + 2.5		5Cr + 4.5 or 9Cr+2		9Cr + 2										
PUMPS (Note 32)						450 230	12Cr					1,000 540								
Case		CS																		
Impeller		(S-1) C1				(C-6) 12Cr														

NOTES:

*See Note 2, 28

**See Note 18, 29

†See Note 8

TABLE A-4

SERVICE	OPERATING TEMPERATURE														
Hydrocarbon • S > 0.2 wt% •	100	200	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	F
Naphthenic Acid (TAN > 1.8) (Notes 2, 8, 29)	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**									
PUMPS (Note 32)						or 316Ti+1.3 [™]									
Case	CS					316**									
	(S-1)					(A-8)									
Impeller	C1					316**									

NOTES:

*See Note 2

**See Note 29

TABLE A-5

SERVICE		OPERATING TEMPERATURE															
Hydrocarbon + S (0.2 - 1 wt%)		100	200	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	F	
Crude Units, Fluid Catalytic Crackers, Cokers, etc.		38	100	150	200	260	315	370	425	480	540	590	650	700	760	C	
VESSELS		CS + 3 (Note 5)					650 340	CS Clad with 2.5 mm 12Cr**								825 441	
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)					550 290	CS + 3	5Cr + 1.5								
FURNACE TUBES (Note 3)		CS + 3						5Cr + 2.5									
PUMPS (Note 32)							450 230		650 340								
Case		CS					CS	CS	12Cr								
		(S-1)					(S-4)	(S-6)	(C-6)								
Impeller		C1					CS	12Cr	12Cr								
NOTES:																	
**See Note 18, 28, 29																	

TABLE A-6

SERVICE	OPERATING TEMPERATURE															
	100	200	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	F	
Hydrocarbon + H ₂ (H ₂ S < 0.01 mol%) ppH ₂ 0.7 - 3.5 MPaa (100 - 500 psia) If >3.5 MPaa (500 psia), see Note 20 (Noncorrosive) Hydrogen Plants, Catalytic Reformers, etc.	38	100	150	200	260	315	370	425	480	540	590	650	700	760	C	
VESSELS				500 260		700 370		850 455		1,050 585		1,650 900		1,800 980		
	CS + 3				(Note 20)				1-1/4Cr + 3							
										18 - 8 + 1 or Ref. lined CS*						
Trays and Internals (Note 4)	CS				(Note 20)				1-1/4Cr				18 - 8			
EXCHANGER SHELLS AND CHANNELS	CS + 3				(Note 20)		(Note 9)		1-1/4Cr + 3							
										18 - 8 + 1 or Ref. lined CS*						
Tubesheets of FH Covers (Note 6)	CS				(Note 20)				1-1/4Cr				18 - 8			
Baffles (Note 7)	CS				(Note 20)				1-1/4Cr				18 - 8			
Exchanger Tubes (Note 1)	CS				(Note 20)				1-1/4Cr				18 - 8 or Alloy 800H			
PIPING (Note 28)	CS + 1.5				(Note 20)				1-1/4Cr + 1.5				Ref. lined CS* or 18 - 8, or Alloy 800H + 1			
FURNACE TUBES (Note 3)		400 200			(Note 20)	800 315			1-1/4Cr + 2.5	1,000 540			2-1/4Cr + 2.5	18 - 8 or Alloy 800H + 1.3 (Note 17)	HP Mod.	
PUMPS (Note 32)				450 230												
Case	CS															
Impeller	(S-1) C1															

NOTES:

*See Note 15

Ref. = Refractory

NOTES:

*See Note 15
Ref. = Refractory

TABLE A-7

SERVICE	OPERATING TEMPERATURE															F
	100	200	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400		
	38	100	150	200	260	315	370	425	480	540	590	650	700	760	C	
Hydrocarbon + H ₂ + H ₂ S ppH ₂ <10.34 MPaa (1,550 psia) H ₂ S>0.01 mol% Hydrosulfurizers, Hydrocrackers, etc.																
VESSELS																
Trays and Internals (Note 4)																
EXCHANGER SHELLS AND CHANNELS																
Tubesheets of FH Covers (Note 6)																
Baffles (Note 7)																
Exchanger Tubes (Note 1)																
PIPING (Note 28)																
FURNACE TUBES (Note 3)																
PUMPS (Note 32)																
Case																
Impeller																
NOTES:																
*See Note 5																
**See Note 20																

NOTES:

*See Note 5

**See Note 20

150

TABLE A-9

SERVICE	OPERATING TEMPERATURE															
	100	200	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	F	C
Carbonate CO ₂ Removal (Note 25) Hydrogen Plant, Gas Treating Plant, etc.	38	100	150	200	260	315	370	425	480	540	590	650	700	760		
VESSELS			$\frac{300}{150}$													
Trays and Internals (Notes 4, 11)			CS + 3													
EXCHANGER SHELLS AND CHANNELS			CS*													
Tubesheets of FH Covers (Note 6)			CS + 3*													
Baffles (Note 7)			CS *													
Exchanger Tubes (Note 1)			CS*													
PIPING			CS + 1.5*													
FURNACE TUBES (Note 3)																
PUMPS (Note 32)			$\frac{150}{65}$													
Case			CS (S-1)												SS (A-7)	
Impeller			CS												SS	
NOTES: *Notes 10, 12, 21 **Notes 10, 12																

152

TABLE A-11

SERVICE	OPERATING TEMPERATURE															
	100	200	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	F	C
High Pressure Wet CO ₂ - H ₂ Mixtures (pp CO ₂ > 0.03 MPaa [4 psia]) Hydrogen Plant, Gas Treating Plant, etc.	38	100	150	200	260	315	370	425	480	540	590	650	700	760		
VESSELS	120 50 Dew Point															
	← CS + 8 →	← CS Clad with 2.5 mm 304L →														
Trays and Internals (Note 4)	← 12Cr or 304L →															
EXCHANGER SHELLS AND CHANNELS	← CS + 8 →	← CS Clad with 2.5 mm 304L →														
Tubesheets of FH Covers (Note 6)	← CS + 8 →	← CS Clad with 2.5 mm 304L →														
Baffles (Note 7)	← CS →	← 304 →														
Exchanger Tubes (Note 1)	← 10GA CS →	← 304 (Note 19) →														
PIPING	← CS + 8 (Note 12) →	← 304L + 1 →														
FURNACE TUBES (Note 3)																
PUMPS (Note 32)																
Case	← CS (S-6) →	← 18-8 (A-7) →														
Impeller	← 12Cr →	← 18-8 →														
NOTES:																

154

SERVICE		OPERATING TEMPERATURE															F C
		100	200	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400		
Amine H ₂ Removal		38	100	150	200	260	315	370	425	480	540	590	650	700	760		
VESSELS		250 120 CS + 3" 300 150 CS + 6"															
Trays and Internals (Note 4)		CS															
EXCHANGER SHELLS AND CHANNELS		CS + 3" CS + 6"															
Tubesheets of FH Covers (Note 6)		CS (Notes 10, 12)															
Baffles (Note 7)		CS (Note 12)															
Exchanger Tubes (Note 1)		CS* 304 Note 19															
PIPING		200 100 CS + 1.5" CS + 3" CS + 6" Note 10, 12, & 36															
FURNACE TUBES (Note 3)																	
PUMPS (Note 32)		250 120 CS (S-1) C1*															
Case																	
Impeller																	
NOTES:																	
*See Notes 5, 10																	

TABLE A-13

SERVICE	OPERATING TEMPERATURE	
	F	C
Acid Gas (Note 22) (H ₂ S+CO ₂ +SO ₂) Sulfur Plant	100 200 300 400 500 600 700 800 900 1,000 1,100 1,200 1,300 1,400	38 100 150 200 260 315 370 425 480 540 590 650 700 760
	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

SERVICE Liquid Sulfur	OPERATING TEMPERATURE															
	100	200	300	400	500	600	700	800	900	1,000	1,100	1,200	1,300	1,400	F	C
	38	100	150	200	260	315	370	425	480	540	590	650	700	760		
VESSELS				400 200	500 260			850 455				1,250 675				
Trays and Internals (Note 4)																
EXCHANGER SHELLS AND CHANNELS																
Tubesheets of FH Covers (Note 6)																
Baffles (Note 7)																
Exchanger Tubes (Note 1)																
PIPING																
				CS + 1.5 Al + 1	CS + 3		321 or 347							310 + 3 (Note 23)		
FURNACE TUBES (Note 3)																
PUMPS (Note 32)																
Case					CI											
Impeller					(I-1) CI											
NOTES:																

TABLE A-15

SERVICE	OPERATING TEMPERATURE	
Untreated, Aerated Water	100 200 300 400 500 600 700 800 900 1,000 1,100 1,200 1,300 1,400	F C
	38 100 150 200 260 315 370 425 480 540 590 650 700 760	
VESSELS	← CS + 2.5 mm 90 Cu-10 Ni Clad → 300 150	
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				OPERATING TEMPERATURE				F	C
	100 38	200 100	300 150	400 200	100 38	200 100	300 150	400 200		
	10 - 30 wt %				50 wt %					
VESSELS	200 100	250 125	400 200		170 75	400 200				
Trays and Internals (Note 4)	CS + 1.5"	CS + 6"	Alloy 400 + 1.5"		CS + 3"	Alloy 400 + 1.5"				
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	Cl*		Alloy 400		Cl*		Alloy 400			
NOTES:										
*See Note 10										

Table A-17 – Valve Trim

<u>Environment</u>	<u>Valve Trim Material (Note 16)</u>
1. General Service	
a) Treated Water	
b) Steam $\Delta p < 1.03$ MPag (150 psig) in multiphase flow	12 Cr
< 3.4 MPag (500 psig) in single phase flow	12 Cr
$\Delta p > 1.03$ MPag (150 psig) in multiphase flow or	
> 3.4 MPag (500 psig) in single phase flow	Stellite 6™ (UNS R30006)
2. Hydrocarbon, Carbonate, Wet CO₂, 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) $< 100^{\circ}\text{C}$ (200°F)	12 Cr
b) $> 100^{\circ}\text{C}$ (200°F)	18-8
5. Untreated Water $< 100^{\circ}\text{C}$ (200°F)	Bronze
6. Caustic	
a) 10-30 wt%, $< 100^{\circ}\text{C}$ (200°F)	12 Cr
b) 10-30 wt%, $> 100^{\circ}\text{C}$ (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:

	<u>Removable</u>	<u>Welded In</u>
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 $93^\circ C$ ($200^\circ F$).
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 $480^\circ C$ ($900^\circ F$), 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 $343^\circ C$ ($650^\circ F$). 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 $1,000^\circ C$ ($1,850^\circ F$) minimum after bending. Where a $1000^\circ C$ ($1850^\circ F$) minimum heat treating temperature is not practical, $900^\circ C$ ($1,650^\circ F$) 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 $900^\circ C$ ($1,650^\circ F$) 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 StelliteTM 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), ColmonoyTM, etc.; StelliteTM (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
		SHELLS AND HEADS	TRAYS						
C	F	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 MATL 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)	A193 GRADE B7
-17	0	PREFERRED MATERIAL: A 516 (ALL GRADES) ② ④ ① ①④			A106 GR. B OR A524 ④		A707 GR. L1 (ONLY). A727 OR A758 ④ ①②	④ ①④	A194 GRADE 2H
-30	-20		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 MATLS AND IMPACT TEST REQUIREMENTS A203 GRADE D ② ①	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				A333 GRADE 3			A352 GRADE LC2 TO -74C/-100F A352 GR. LC3	
-100	-150	A553 OR A353 ② ①③ ①④ (TO -196 C/ -320 F) A240 TYPE 304 ⑤			A333 GR. 8 ①⑥ A312 TP. 304 ⑤ B241 (6061)		A522 TP. ①⑥ A420 (WPL8) A182 GR. F 304 ⑤ B247/361 (6061)	A351 GRADE CF8 ①①	A320, GR. B8 A194, GR. 8 ANNEALED B211 TP 2024-T6
-200	-325	B209 AL ALLOY 5063/5456 ALUMINUM A240 TYPE 304 ⑤ ⑨	TYPE 304 ⑤ ⑨		A312 ⑤ TP. 304 ⑨ B241 ⑧	A213 ⑤ TP. 304 ⑨ B234 ⑧	A182, F 304 ⑤ ⑨ A403, WP 304 B247/361 ⑧	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			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:

Applicable Code

- 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.

Summary of Rules

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 CodeSummary 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).

⁽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), Stoddy™ 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.

⁽²⁾ HB 550-650

⁽³⁾ HB 450-650

⁽⁴⁾ HB 550-600

⁽⁵⁾ HB 250-450

INDEX

Index Terms

Links

A

Abrasion resistance	170			
Acceleration of galvanic corrosion rate	29			
Acid gas service	155	159		
Air coolers	75			
Alkalinity				
methyl orange	20			
phenolphthalein	20			
Alkylation	2	37		
hydrofluoric acid	45			
sulfuric acid	44	173		
Alloying elements, in line pipe steel	115	182	188	
Aluminizing	61	99		
Aluminum foil, for SCC prevention	80			
Amines, neutralizing	10			
Amine units	2	96	154	159
Ammonia				
high-pressure conversion	98			
as neutralizer	10	12	79	
Ammonia plants	91	92		
Ammonium bisulfide	76	78	96	
Ammonium chloride	11	75	83	
Asphalt enamel	129	130		
Asphalt mastic	129	130		
ASTM specifications	142			
Atmospheric compatibility of metals	31			

B

Bacteria, sulfate-reducing	134
Bellows, expansion. <i>See</i> Expansion bellows	
Bending, line pipe	118

This page has been reformatted by Knovel to provide easier navigation.

<u>Index Terms</u>	<u>Links</u>			
Biocides	20			
Boiler feedwater	32	173		
Brittle fracture	40	41	43	74
	120	171		
C				
Calcareous deposits	20			
Calcium treatment, and HIC	49	127		
Carbonate stress corrosion cracking	42	97	132	
Carbon dioxide				
high-pressure wet	153			
low-pressure wet	152	159		
removal of	94	151		
in water	172			
Carbon equivalent	116			
Carbon steels				
in alkylation plants	44	46		
corrosion allowances	174			
in crude units	12			
in hydrocracker air coolers	75			
in hydroprocessing units	57			
isocorrosion curves	61	77		
naphthenic acid corrosion	17			
in reforming plants	94			
in regenerators	38			
in steam	30			
in sulfur plants	51			
water corrosion	21	25	29	
Carburization, catastrophic. <i>See</i> Metal dusting				
Cast iron, water corrosion	20			
Catalysts	37	55		
Catalytic cracking. <i>See</i> Fluid catalytic cracking				
Catalytic reforming	1	81		
Cathodic protection	124	130	132	
Caustic injection	9			
Caustic service	158	159		

<u>Index Terms</u>	<u>Links</u>			
Chlorides	83	173		
Chlorination, and seawater corrosion	25			
Chromate inhibitors	27			
Cladding. <i>See also</i> Roll bond cladding				
on hydroprocessing reactors	71			
for restoration	43			
vs. weld overlay	5			
Coal tar enamel	129	132		
Coatings. <i>See also</i> Organic coatings				
for underground piping	129			
Coke drums	42			
Coking. <i>See</i> Delayed coking; Fluid coking				
Condensate. <i>See</i> Steam and condensate				
Condenser tubes, under velocity conditions	23			
Continuously regenerated catalytic reforming	81			
Coolers	75			
Cooling water				
materials selection for	30			
systems	19			
Copper and alloys				
condenser tubes, under velocity conditions	23			
water corrosion	22	26	30	
Corrosion allowances	4	21	143	174
Corrosion fatigue cracking	32			
Corrosion inhibitors. <i>See</i> Inhibitors				
Corrosion rates	13	20	23	95
	100	133	134	
<i>See also</i> Isocorrosion curves				
Cor-ten	84			
cracking; Thermal fatigue				
CRCR. <i>See</i> Continuously regenerated catalytic reforming				
Crevice corrosion	25			
Critical pitting temperature	24	25		
Critical preheat temperature	117			
Crude oil				
atomic structure	5			

<u>Index Terms</u>	<u>Links</u>			
corrosive constituents	6			
desalting	9	14		
distillation unit	8			
neutralization number	7			
refinery processing of	2			
Crude units	5			
corrosion in	8			
equipment and piping	14			
overhead systems	8			
Cyanides, corrosive effect	46			
Cyclones	39			
D				
Dead legs, corrosion in	19			
Dealloying	22			
DEA. <i>See</i> Diethanolamine				
Deasphalting, solvent	99			
Decoking	42			
Delayed coking	42			
DeLong diagram	71	72		
Delta ferrite, in SS weld metals	72			
Department of Transportation	105			
Desalting	9	12	150	159
Desulfurizers. <i>See</i> Hydrodesulfurizers				
Diethanolamine	173			
Disbonding, of weld overlay	72			
Distillates, sulfur in	6			
Distillation	1	8		
Double-submerged arc welding (DSAW), line pipe	106	108	181	
Ductile fracture	121	122		
E				
Electric resistance welding (ERW), line pipe	106	108	187	
Epoxy, fusion-bonded	129	130	132	
Erosion-corrosion	22	23	30	125
Expansion bellows	40	42	81	

This page has been reformatted by Knovel to provide easier navigation.

<u>Index Terms</u>	<u>Links</u>			
External corrosion, of underground piping	128			
F				
Failures				
amine absorber	96			
fluid coker burner vessel	40	41		
FBE. <i>See</i> Fusion-bonded epoxy				
FCC. <i>See</i> Fluid catalytic cracking				
Feed-effluent exchangers and piping	74			
Ferrite, delta. <i>See</i> Delta ferrite				
Fiber-reinforced plastic	27	30		
Filler metals				
for clad restoration	43			
for dissimilar welds	18			
Fittings, line pipe	114			
Flare tips	85			
Flue gases	84			
Fluid catalytic cracking	1	37		
Fluid coking	37			
Fractionation equipment	46	81		
Freshwater, corrosion in	20			
Furfural	99			
Furnace tubes	144			
Fusion-bonded epoxy	129	130	132	
G				
Galvanic corrosion	25	27		
Gas lines, dehydration of	124			
Graphitic corrosion	22	39	171	
Guniting	38			
H				
Hardfacing	16	31	40	84
Heat exchangers	5	19	74	144
Heat treatment, postweld. <i>See</i> Postweld				

<u>Index Terms</u>	<u>Links</u>			
heat treatment				
HIC. <i>See</i> Hydrogen-induced cracking				
Hook cracks	110			
Hydriding, of Ti tubes in seawater	26			
Hydrocarbon environments,				
materials selection	144	159	171	
Hydrochloric acid, in crude units	10			
Hydrocracking	2	37	55	
Hydrodealkylation units	99			
Hydrodesulfurizers	55			
Hydrofluoric acid alkylation	45			
Hydrogen attack	57			
Hydrogen blistering	47	127		
Hydrogen flaking	71	72	73	
Hydrogen-induced cracking	49	80	127	194
Hydrogen partial pressure calculations	175			
Hydrogen plants	2	91	92	
Hydrogen sulfide				
release from crudes	16			
removal of	94			
in sour systems	46	173		
and storage tank corrosion	134			
Hydroprocessing units	55			
Hydrostatic testing	40	132	183	190
Hydrotreating	1			
I				
Inhibitors	10	22	27	32
	96	124	128	
Injection				
caustic	9			
of inhibitors	10			
quills	10			
Inspection	32	110	183	190
Intergranular stress corrosion cracking	74	85		
Internal corrosion, of line pipe	124			

<u>Index Terms</u>	<u>Links</u>		
Isocorrosion curves	61	77	
Iso-pH curves	77		
J			
J factor	73		
K			
Kalrez	99		
Knockout pots	96		
L			
Langelier's Index	20		
Line pipe			
bending	118		
brittle fracture	120		
chemistry control	115		
ductile fracture	121	122	
electric resistance welded	106	108	187
external corrosion	128		
fittings and valves	114		
helical seam	112	113	
internal corrosion	124		
manufacture	105	181	188
materials selection	144		
processing	118		
seamless	111		
specifications	112	114	
underground	128		
UOE	106	107	181
wall thickness, minimum	106		
weldability	116	194	
Linings. <i>See</i> Refractory linings			
Liquid metal embrittlement	29		
Low-alloy steels			
in hydroprocessing reactors	71		

<u>Index Terms</u>	<u>Links</u>		
isocorrosion curves	63		
Low-temperature service	164		
M			
Magnesium chloride	10		
Materials selection			
alkylation plants	44		
catalytic reformers	81		
coke drums	42		
cooling water	30		
and corrosion allowances	143		
criteria	141		
crude units	5		
flare tips	85		
flue gas scrubbers	84		
general guidelines	4	141	
hydrogen, methanol, and ammonia plants	92		
hydroprocessing units	55		
line pipe	105		
low-temperature services	164		
reactors and regenerators	38		
refineries	171		
sour water strippers	46		
for specific environments	143		
sulfur plants	51		
tanks	134		
utilities	19		
wear and abrasion resistance	170		
MEA. <i>See</i> Monoethanolamine			
Mercaptan	99		
Mercury, and gas corrosion	126		
Metal dusting	83	98	
Methanol plants	91	92	98
Methyl orange alkalinity	20		
Methyl tertiary butyl ether	101		
Microbiologically influenced corrosion	20		

<u>Index Terms</u>	<u>Links</u>		
Monoethanolamine	172		
absorption system	91		
MTBE. <i>See</i> Methyl tertiary butyl ether			
N			
Naphtha			
defined	1		
heavy	11		
Naphthenic acid corrosion	7	17	146
Neutralization, in overhead systems	10		
Neutralization number	7		
Nickel and alloys			
chemical compositions	163		
for expansion bellows	40	42	
for pigtails	94		
O			
Organic coatings	22	84	124
Overhead systems			
carbon steel	12		
corrosion protection in	8		
Overlay. <i>See</i> Weld overlay			
Oxygen scavengers	25	27	
P			
Penetrators	110		
pH			
and carbonate SCC	42		
control of	10	12	
and corrosion rate of carbon steel in seawater	26		
and erosion-corrosion	32		
and hydriding	26		
and hydrocracker corrosion	78		
iso-pH curves	77		
and Langelier Index	20		

<u>Index Terms</u>	<u>Links</u>			
and sour service	48			
Phenolphthalein alkalinity	20			
Phenol production	99			
Pigtails	94			
Pipe. <i>See</i> Line pipe; Underground piping				
Pitting of SS	24			
Polyethylene extrusions	128	129	130	
Polyethylene tape	128	129	130	
Polymerization	2	99		
Polysulfides, for cyanide removal	47			
Polythionic acid	61	75		
Postweld heat treatment	49	71	80	
Potassium carbonate	97	172		
absorption unit	91			
Potassium hydroxide	173			
Pressure swing adsorption (PSA) unit	91	96	98	
Pumps				
in crude units	19			
materials selection	144			
R				
Reactors	38	71		
Refineries				
materials selection	171			
processes	1			
Refractory linings	38	83	84	85
	94	171		
Regenerator vessels	38			
Residuum	1	37	84	
Roll bond cladding	4			
S				
Salt water, corrosion in	25			
Secondary reformers, in ammonia plants	92	94		
Shell-side corrosion	133			
Sidecut stripper columns	19			

This page has been reformatted by Knovel to provide easier navigation.

<u>Index Terms</u>	<u>Links</u>		
Sievert's law constants	178		
Sigma phase embrittlement	71	94	171
Sodium chloride	10		
Sodium hydroxide	173		
SOHIC. <i>See</i> Stress-oriented hydrogen-induced crackmg			
Soil resistivity	128		
Solvent treating	99		
Sour water			
characteristics	46		
materials selection	150	159	
Sour water strippers	2	49	50
Stainless steels			
in air coolers	76	78	
in amine units	98		
cathodic protection	131		
chemical compositions	163		
for clad restoration	43		
for feed-effluent exchangers and piping	74		
H grades	30		
for high-temperature lines	40		
in hydroprocessing reactors	71		
isocorrosion curves	67		
for line pipe	126		
naphthenic acid corrosion	17		
pitting in water	24		
for refractory linings	39		
in steam	30	32	
in sulfur plants	51		
Steam and condensate	30		
Step cooling	73		
Stepwise cracking	128		
Stitch welds	110		
Storage tanks			
ammonia	98	134	
double-wall	134	135	

<u>Index Terms</u>	<u>Links</u>			
low-pressure, low-temperature	134			
LPG and LNG	135			
petroleum	132			
Stress corrosion cracking	30	74	80	96
	126	132	174	
<i>See also</i> Carbonate SCC; Intergranular SCC; Transgranular SCC				
Stress-oriented hydrogen-induced cracking	49	96		
Sulfidation	61			
Sulfide attack in seawater	26			
Sulfide stress crachng	47	127		
Sulfinol units	91			
Sulfur				
in crude oil	6	14		
in flue gases	84			
liquid	156	159		
Sulfuric acid alkylation	44			
Sulfurous acid	75			
Sulfur plants	2	50	155	172
T				
Tanks. <i>See</i> Storage tanks				
TAN. <i>See</i> Total acid number				
Tape, polyethylene	129	130		
Temperature				
critical pitting, for SS	24	25		
critical preheat	117			
Temper embrittlement	71	72	73	
Thermal fatigue (crachng)	1	42	85	
Titanium and alloys				
in sour water strippers	50			
for tubing	11	25	30	
Total acid number	7	146		
Toughness, and thermal fatigue	42			
Transgranular stress corrosion cracking	74	80		

<u>Index Terms</u>	<u>Links</u>		
U			
Underground piping			
cathodic protection	130		
coatings for	129		
external corrosion	129		
stress corrosion cracking	131		
UOE line pipe	106	107	181
Urethanes	99		
Utilities, materials selection for	20		
V			
Vacuum columns	19		
Valves			
in crude units	19		
line pipe	114		
in regenerators	40		
Valve trim, materials selection	159		
Vanadium pentoxide	84		
Velocity, and water corrosion	23	26	
Vessels. <i>See also</i> Regenerator vessels			
materials selection	144		
Visbreaker columns	19		
Viton	99		
W			
Water, untreated and unaerated	157	159	
Water lines, corrosion in	124		
Wear resistance	170		
Weld overlay			
on hydroprocessing reactors	71		
ring gasket grooves, cracking in	81		
vs. cladding	4		
Weld slag, catastrophic oxidation	94		
Welds and welding. <i>See also</i> Hardfacing			
defects	110		

<u>Index Terms</u>	<u>Links</u>			
dissimilar welds	18			
DSAW line pipe	106	107	108	181
duplex SS welds, delayed cracking in	27			
ERW line pipe	106	108	187	
in hydroprocessing reactors	71			
line pipe weldability	116	194		
postweld heat treatment	49	71	80	
weld metal, fissures in	57			
Wet steam. <i>See</i> Steam and condensate				

X

X factor	73
----------	----

Z

Zinc coatings	22
---------------	----