Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries

API RECOMMENDED PRACTICE 939-C
FIRST EDITION, MAY 2009

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Downstream Segment

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Introduction

Sulfidation corrosion, also often referred to as sulfidic corrosion, of piping and equipment within the refining industry continues to be a significant cause of leaks leading to equipment replacements, unplanned outages, and incidents associated with large property losses and injuries. The objective of this recommended practice (RP) is to provide practical guidance to inspectors, maintenance, reliability, project, operations and corrosion personnel on how to address sulfidation corrosion in petroleum refining operations.

This document is intended to provide a better understanding of sulfidation corrosion characteristics. Examples of failures are discussed to highlight the common causes. An overview of the two mechanisms of sulfidation corrosion (with and without H_2 present) and the methods used to control and inspect for sulfidation corrosion are summarized. The data herein is a compilation of information extracted from published technical papers, industry information exchanges (NACE and API) and contributions from several owner/operators. Some refining companies have developed proprietary methods to predict sulfidation corrosion and these were not made available as part of this effort.

Common refinery units in which essentially H_2-free sulfidation corrosion occurs are the crude/vacuum, fluid catalytic cracker, coker, and visbreaker units. Hydroprocessing and hydrocracking units experience H_2-free sulfidation corrosion in their feed and distillation sections. They experience sulfidation in the presence of hydrogen in their reaction sections. This sulfidation in the presence of H_2 is typically referred to as H_2/H_2S corrosion.

Included in this RP are:

- background to the degradation mechanism,
- the most common types of incidents and damage observed,
- root causes of sulfidation corrosion,
- methods to predict and monitor the corrosivity of systems,
- materials selection for new and revamped processes,
- inspection and nondestructive examination (NDE) methods used for detecting sulfidation corrosion.

Materials and corrosion specialists should be consulted for additional unit-specific interpretation and application of this RP.

Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries

1 Scope

This recommended practice (RP) is applicable to hydrocarbon process streams containing sulfur compounds, with and without the presence of hydrogen, which operate at temperatures above approximately 450 °F (230 °C) up to about 1000 °F (540 °C). A threshold limit for sulfur content is not provided because within the past decade significant corrosion has occurred in the reboiler/fractionator sections of some hydroprocessing units at sulfur or H_2S levels as low as 1 ppm. Nickel base alloy corrosion is excluded from the scope of this document.

While sulfidation can be a problem in some sulfur recovery units, sulfur plant combustion sections and external corrosion of heater tubes due to firing sulfur containing fuels in heaters are specifically excluded from the scope of this document.

2 Normative References

The following referenced documents are indispensable for the application of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced doucment (inlcuding any amendments) applies.

API 510, *Pressure Vessel Inspection Code: Maintenance Inspection, Rating, Repair, and Alteration*

API 570, *Piping Inspection Code: Inspection, Repair, Alteration, and Rerating of In-service Piping Systems*

API Recommended Practice 571, *Damage Mechanisms Affecting Fixed Equipment in the Refining Industry*

API Recommended Practice 578, *Material Verification Program for New and Existing Alloy Piping Systems*

API Recommended Practice 580, *Risk-Based Inspection*

API Recommended Practice 581, *Risk-Based Inspection Technology*

API Standard 579-1/ASME [1] FFS-1-2007, *Fitness-For-Service*

3 Definitions and Acronyms

For the purpose of this document, the following definitions apply.

3.1 Definitions

3.1.1
low-alloy steels
Steels that contain 1 to 9 % Cr and 0.5 to 1 % Mo.

3.1.2
low-silicon-containing carbon steels
Steels that contain less than 0.10 wt % Si, the minimum limit for ASTM A106 piping.

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[1] ASME International, 3 Park Avenue, New York, New York, 10016, www.asme.org.

3.1.3

material operating envelope

MOE

Documentation describing limits related to unit and equipment specific process parameters for the given materials of construction. Operation within the limits should not adversely affect the mechanical integrity of the equipment and piping. An MOE also defines process monitoring tasks to assure that operating conditions are maintained within the established parameters.

3.1.4

mils/yr

Corrosion rate expressed as 1 mil/yr = 0.001 in./yr; 40 mils = 1 mm.

3.1.5

spec break or **specification break**

The location where a lesser alloy content material is joined or mated up to a higher alloy content material, i.e. 5Cr to carbon steel.

3.1.6

sulfidation

Corrosion of metal resulting from reaction with sulfur compounds in high-temperature environments such that a surface sulfide scale forms often with sulfur penetrating somewhat below the original thickness. The term sulfidic corrosion is consistent with this definition. In this document, sulfidation does not refer to extensive internal attack below the original wall thickness as may occur at temperatures in excess of 1000 °F (538 °C).

3.2 Acronyms

CML	corrosion monitoring location formerly known as TML
Cr	chromium
H_2	hydrogen
H_2S	hydrogen sulfide
Mo	molybdenum
Ni	nickel
PMI	positive materials identification
PWHT	post-weld heat treatment
RT	radiographic testing (inspection), a.k.a. gamma ray or X-ray inspection
S	sulfur
Si	silicon
UT	ultrasonic testing (inspection)

4 Basics of Sulfidation Corrosion

Sulfidation corrosion, also often referred to as sulfidic corrosion, is not a new phenomenon, but was first observed in the late 1800s in a pipe still (crude separation) unit, due to the naturally occurring sulfur compounds found in crude oil. When heated for separation, the various fractions in the crude were found to contain sulfur compounds that corroded the steel equipment. With the advent of fluidized catalytic cracking (FCC) and coking processing, sulfidation corrosion was also experienced in these units [1], [2].

When hydroprocessing was introduced in the 1950s, changes in the corrosion behavior of construction materials were noted. This led to the recognition that a different sulfidation corrosion behavior resulted under hydroprocessing conditions which typically involve the presence of hydrogen. Empirical industry data as well as laboratory research indicates that the sulfidation corrosion rate is a function of a variety of factors including: temperature, the total sulfur concentration, the types of sulfur compounds present, the type of stream (e.g. light gas or heavy oil), the velocity (or flow regime), heat transfer conditions, the presence or absence of hydrogen, and the material of construction.

In the absence of hydrogen, corrosion due to sulfur compounds in the crude typically is thought to occur at temperatures above 450 °F (230 °C). As discussed below, the industry relies on a set of curves (the modified McConomy curves [3]) to predict corrosion rates. These curves show that at a given temperature and total sulfur level, steels with increasing chromium content (from carbon steel, to 5Cr to 9Cr to stainless steel) will experience lower corrosion rates. In the presence of hydrogen, i.e. H_2/H_2S corrosion, corrosion starts to increase above about 450 °F (230 °C). The industry relies on a set of curves (the Couper-Gorman curves [4]) to predict the corrosion rate in this environment. These curves relate the amount of H_2S present with temperature to determine the corrosion rate. At a given H_2S content and temperature, increasing Cr content of low to medium alloys makes little or no difference in corrosion rates. It is typically necessary to use 18Cr-8Ni stainless steels in order to achieve a significant improvement in corrosion resistance.

Each crude oil or crude blend has its own unique characteristic chemistry, sulfur compounds, and effect on sulfidation corrosion. Despite the industry's best efforts, the accurate prediction of the resulting H_2-free sulfidation corrosion rate for a specific crude oil and its fractions is an elusive technical challenge. Oil refineries that processed a consistent diet of a particular crude oil or crude blend could often base future predictions on past experience. However, over the past 20+ years, global economics have resulted in many refineries processing tens of different crudes in any given year; thus, minimizing the accuracy, or even feasibility, of predictions based on historical data. Additionally, the verification of the actual corrosion rate experienced while processing a specific crude oil is very difficult.

Sulfidation corrosion results in wastage of the wall thickness of fittings, piping, heater tubes, and pressure vessels. Most industry incidents have occurred in piping components, due to their thinner overall wall thicknesses and their higher population density vs the other equipment types. Although sulfidation corrosion under certain circumstances can be localized, the majority of sulfidation corrosion damage is general or uniform in nature, i.e. present over a fairly large surface area of a given component and not dependent on differenced between local conditions and bulk conditions. As a result when general thinning occurs, ruptures are possible leading to the potential release of large quantities of hydrocarbon streams. Figure 1 to Figure 4 show piping components that experienced H_2-free sulfidation corrosion.

5 Location of Sulfidation Corrosion

Sulfidation corrosion can occur wherever sulfur compounds are present in a hydrocarbon stream and the temperature exceeds approximately 450 °F (230 °C). H_2/H_2S corrosion can also occur in the absence of hydrocarbon. API 571 contains generic process flow diagrams for typical refinery units and identifies where H_2-free sulfidation corrosion and H_2/H_2S corrosion occurs.

H_2-free sulfidation most commonly occurs in the hotter areas of the following types of units: crude, vacuum, coker, visbreaker, and hydroprocessing feed and distillation sections. H_2/H_2S corrosion most commonly occurs in hydroprocessing units such as desulfurizers, hydrotreaters and hydrocrackers downstream of the hydrogen injection point through the reaction section to the separation section.

6 Effects of Process and Material Variables on Corrosion Rates

6.1 Introduction

For the purpose of discussion, sulfidation is presented at three levels of complexity in this document. The first level covers the fundamentals. The second level covers the basic variables to consider in estimating corrosion rates. The third level covers the complicating factors; those second order variables that can at times cause high variability in corrosion rates.

Additionally, sulfidation is considered in this publication to be one of two basic mechanisms: H_2-free sulfidation corrosion and H_2/H_2S corrosion. In some streams there may be small amounts of hydrogen that were not intentionally added, but are liberated from cracking reactions in coking and fluid cat cracking units; however, for the purposes of this document, those streams are referred to as H_2-free.

NOTE There is relatively uniform thinning, which resulted in a sizeable rupture.

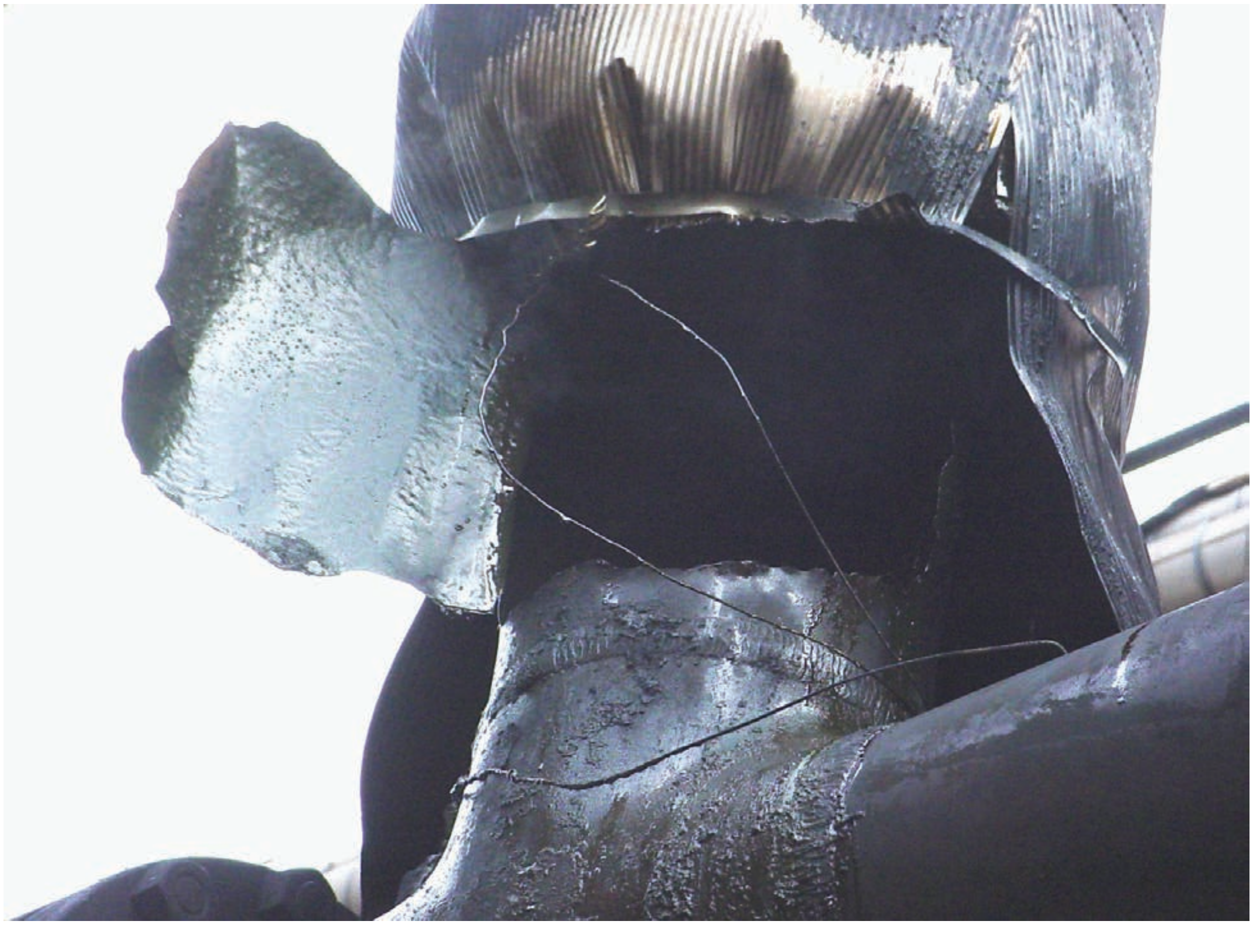
Figure 1—NPS 8 Carbon Steel Piping Failed Due to Sulfidation Corrosion (H_2 Free)

NOTE The Steel Sight Glass Nipple (on right) corroded severely in 2 years in a crude unit (original thickness on left). It was specified as 9Cr.

(Courtesy of ConocoPhillips)

Figure 2—Corroded Carbon Steel Sight Glass Nipple

Crude oils also contain other corrosive constituents that can cause corrosion in H_2-free elevated temperature service. Some crude oils contain organic acids that are often collectively referred to as naphthenic acids. A detailed discussion of the effects of naphthenic acids are outside the scope of this document, but it is important to note that naphthenic acids can dissolve the iron sulfide scale or at the very least render it less protective. Generally, corrosion due to sulfur compounds results in an iron sulfide scale that partially protects the metal from naphthenic acid corrosion. It is often difficult to isolate the individual effects of naphthenic acids and sulfur compounds. However, naphthenic acid never lowers sulfidation corrosion.



NOTE See also sketch in Figure 4.

(Courtesy of BP)

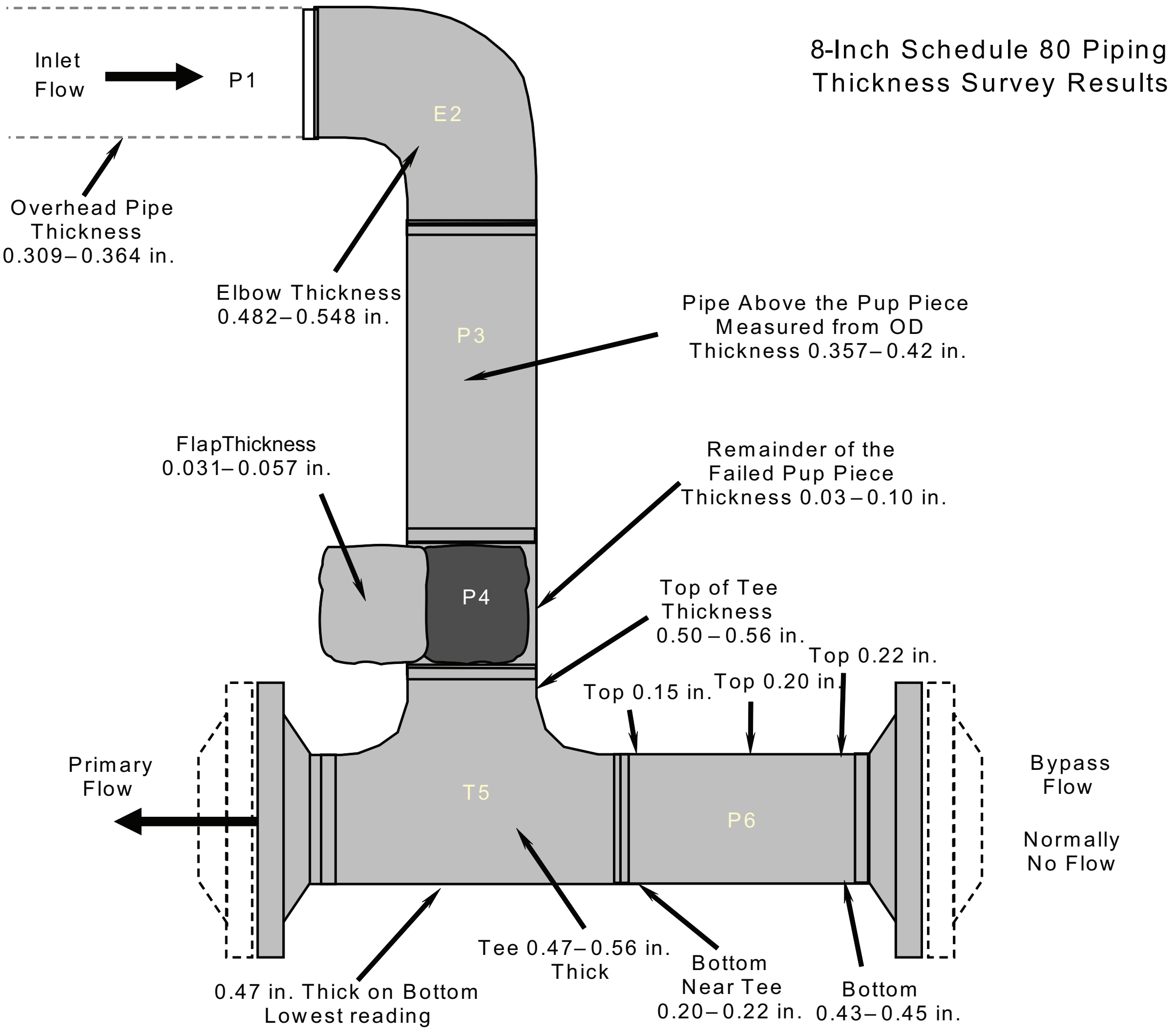
Figure 3—FCC Fractionator Bottoms Carbon Steel Piping Operating at 150 psig (1 MPa) and 650 °F to 700 °F (340 °C to 370 °C)

6.2 H_2-free Sulfidation

6.2.1 Fundamentals

The fundamentals of H_2-free sulfidation corrosion are covered in Section 4 and Section 5. Sulfidation predominately occurs by direct reaction of sulfur species with the metal surface. H_2-free services are defined as those in which hydrogen is not intentionally added as part of the process.

Carbon steels and some low-alloy steels will corrode in H_2-free process streams in the presence of hydrocarbon-containing sulfur compounds above about 450 °F (230 °C). Corrosion rates can be highly variable and difficult to predict. The basic and complicating variables below affect the ability to predict corrosion rates.



NOTE 1 in. = 25.4 mm and there may be a flow regime effect.

(Courtesy of BP)

Figure 4—FCC Fractionator Bottoms Carbon Steel Piping Shown in Figure 3 Operating at 150 psig (1 MPa) and 650 °F to 700 °F (340 °C to 370 °C)

6.2.2 Basic Variables

6.2.2.1 Temperature and Alloy Content

Carbon steels and low-alloy steels up to and including 9Cr-1Mo can be susceptible to H_2-free sulfidation corrosion. Below 450 °F (230 °C), the corrosion rate is essentially nil. The corrosion rate increases with temperature from approximately 450 °F (230 °C) to about 800 °F (425 °C). The increase is more exponential than linear. The corrosion rate is believed to peak around 800 °F (425 °C) and at higher temperatures the rate decreases [5]. There are several theories as to why there is a peak, ranging from coke formation, destruction of reactive sulfur compounds, to formation of more stable scales (see 7.2 regarding materials selection and this peak).

McConomy [6] developed corrosion rate vs temperature plots for several alloys. These curves represented average corrosion rates from industry data collected in the 1960s primarily from crude heater tubes. In subsequent years, these curves were modified (lowered) because it was found that they were in most cases too conservative for crude unit piping and pressure vessels [3]. These newer curves are referred to as the modified McConomy curves, which are reproduced in Figure B.1. There is significant scatter in the data, so these curves should be used with the knowledge that much higher or lower rates are possible (possibly by a factor of 10).

The curves illustrate the beneficial effect of chromium as an alloying element; the higher the Cr content of the steel, the lower the sulfidation rate, i.e. 9Cr will corrode less than 5Cr, which corrodes less than carbon steel. The exact reason for the beneficial effect of Cr is not clear, but it is believed to be related to the stability and protective nature of the iron-chromium-sulfide scales formed.

6.2.2.2 Sulfur Content and Speciation

The modified McConomy curves are based on a 0.6 % total S content in the crude or fraction and are accompanied by a corrosion rate multiplier for lower and higher sulfur contents. In general, the higher the S content of the stream, the more corrosive the stream will be. This effect is less pronounced than the temperature effect. However, as discussed in Annex B, the situation is more complex. Most crude oils contain a range of sulfur species including H_2S, mercaptans, elemental sulfur, polysulfides, thiophenes, aliphatic sulfides and aliphatic disulfides [7], [8] and each has a different reactivity or affect on corrosion rate. Some companies have performed analyses of crude oil and its fractions for various sulfur compounds and have developed predictive models based on a combination of laboratory and field experience. Nonetheless, it is very difficult for a refinery to accurately assess a crude oil (unknown to them) for corrosion based on total sulfur content alone or a breakdown of the sulfur species.

6.2.3 Complicating Variables

6.2.3.1 Nature of the Hydrocarbon Phase

Sulfur compounds tend to concentrate in heavier liquid fractions, but given the same sulfur content and temperature, light gaseous hydrocarbons appear to be more aggressive. This may be due to different sulfur species, or could be a function of the heavier hydrocarbon wetting the surface and retarding the sulfidation corrosion reaction.

6.2.3.2 Si Content

Carbon steels with low-silicon (< 0.10 %) content can corrode at an accelerated rate when exposed to H_2-free sulfidation corrosion conditions. Refer to Annex C for data showing the relative corrosion rates of high- and low-silicon content steels. In some applications, carbon steel will appear to be adequate based on measured corrosion rates until failure occurs at some undocumented or unidentified low-silicon component. Figure 3 and Figure 4 relate to a failure where there were differences in silicon content amongst the various components and the lower Si content steel components corroded at a greater rate.

6.2.3.3 Flow Regime/Velocity

Carbon and low-alloy steels form a sulfide scale in sulfur-containing streams, which can retard the sulfidation rate. Under high shear stress conditions, the scale can be removed (particularly if naphthenic acid is present) causing accelerated corrosion. One example of high-velocity (high shear stress) effects was the severe sulfidation corrosion of carbon steel balance lines connected to atmospheric bottoms feed pumps. At a flow velocity reported to be at least 180 ft/s (60 m/s), the sulfide protective scale did not form and thus severe corrosion was noted. Components in the same system exposed to lower flow rates did not corrode severely.

No flow or very low flow can also be detrimental. This can contribute to stratification of corrosive species, and cause preferential attack. In some cases, such as a column bottoms, low velocity or long residence time can allow more H_2S to evolve.

Another key factor appears to be whether the surface is wetted or not, with higher rates expected if surface wetting is not present (perhaps six times higher, see 6.3.3.1).

6.2.3.4 Coking

Coking in general will reduce the rate of corrosion in non-heat transfer components, by isolating the steel or alloy surface from the hydrocarbon fluid stream. An example of this is found in coke drums where 12Cr linings have cracked but the shell did not corrode as severely as expected due to coking. Under heat transfer conditions, such as those in fired heater tubes, the presence of a coke layer can increase the metal temperature resulting in an increase in corrosion rate.

6.2.3.5 Stripping Steam/Reboiling

The degree of stripping in sidestream strippers in the crude unit and in the FCC main fractionator can affect the buildup of H_2S. If columns are not adequately stripped, the associated bottoms systems can experience higher corrosion rates. One refiner reported that when the stripping steam rate was reduced for energy savings, severe corrosion occurred in a carbon steel area of the FCC main fractionator vessel. The degree of reboiling can also affect the H_2S content, with lesser amounts of steam leading to less effective stripping and concentration of higher levels of H_2S in the bottoms of towers.

6.2.3.6 Pressure

The total system pressure does not appear to be a major variable for H_2-free sulfidation corrosion.

6.2.3.7 "H_2-free, Low-sulfur Streams" in Hydrotreater Distillation Sections

This mechanism is not well understood. NACE Publication 34103 [9] published in 2002, summarizes the available information. It is treated here as a special case of H_2-free sulfidation although the observed corrosion rates often are more in line with those expected with H_2/H_2S corrosion. Corrosion has been found to be particularly severe in the hotter fractionator reboiler circuits (see 6.3.3).

6.2.3.7.1 Temperature and Alloy Content

The higher the temperature, the more corrosive the stream will be. NACE Publication 34103 [9] shows corrosion rates have approached or exceeded those found in hydrogen-containing environments similar to the Couper-Gorman curves for various alloys. Depending on temperature, alloying to a minimum of 300 Series stainless steel (SS) was needed to be resistant.

6.2.3.7.2 Sulfide Content

Typically, the measurable *total sulfide* (total sulfur species or compounds) content is very low, often below 50 ppm and can be as low as 1 ppm. Using the standard curves based on *total sulfide* content or mole % H_2S in these streams would not predict corrosion. Experience is often far different and not easily predicted. Several hypotheses exist that the corrosion is caused by mercaptans at low concentrations or the low *total sulfide*/low H_2 content as discussed in 6.3.3.2.

6.2.3.7.3 Flow Regime/Velocity

Flow rate does appear to have an effect, because most corrosion observed has occurred in areas of higher shear stress, such as in elbows. However, severe corrosion has been observed in the top portions of carbon steel, 5Cr and 9Cr horizontal heater tubes where higher H_2S levels are present due to stratified flow, lack of oil wetting, and/or somewhat higher temperatures.

6.3 H_2/H_2S Corrosion

6.3.1 Fundamentals

The fundamentals of H_2/H_2S corrosion are covered in Section 4 and Section 5. Simply put, carbon steels and low-alloy steels will corrode in the presence of H_2 and H_2S above about 450 °F (232 °C). A fundamental difference of H_2/H_2S corrosion vs H_2-free corrosion is that low-alloy steels up through 12Cr are less effective in avoiding H_2/H_2S corrosion than in H_2-free streams. The 18Cr-8Ni stainless steels are most commonly used to obtain acceptable corrosion resistance.

6.3.2 Basic Variables

6.3.2.1 Temperature and Alloy Content

Corrosion starts to occur in this service at temperatures in excess of about 450 °F (232 °C). Corrosion increases with temperature. Couper-Gorman curves were developed for predicting corrosion rates in H_2/H_2S streams and are included in Figure B.3 to Figure B.10. It was found that the oil fraction affects the corrosion rate in this environment. Consequently, there are separate curves for naphtha and gas oils. These curves illustrate that gas oil services are generally more corrosive. Some companies do not differentiate between oil types *and use the more conservative gas oil rather than naphtha services curve*.

There is little improvement found by increasing the chromium content of the alloy until the 300 Series SS (18Cr-8Ni alloys) or higher alloys are used, i.e. carbon steel, 5Cr and 9Cr corrode at a similar rate in this environment.

6.3.2.2 Sulfur (H_2S) Content

The Couper-Gorman curves show that the corrosion rate increases with increasing concentrations of H_2S on a mole % basis. Some companies have also created curves that are a function of partial pressure of H_2S. Examples of such curves are included in Figure B.11 through Figure B.13 [10].

6.3.3 Complicating Variables

6.3.3.1 Flow Regime/Velocity/Hydrocarbon Phase

In most cases, the 300 Series SS are used in more aggressive services. They typically are not affected severely by velocity (high or low), whereas, carbon steel and low-alloy steels are more sensitive to velocity (shear stress). An important complicating variable is whether or not the metal is exposed to liquid phase or vapor phase conditions. All other factors being equal, the corrosion rate may be about six times higher when the metal surface is exposed to vapor vs liquid (see Figure B.11 and Figure B.12) [10].

6.3.3.2 Effect of H_2 Partial Pressure

Increasing hydrogen levels reduces the sulfur activity and tends to reduce corrosion rates [10].

This effect is not readily apparent when they are large levels of hydrogen and H_2S present, such as in the reaction section of hydroprocessing units. However, this could help explain why increased corrosion rates are observed in the distillation sections of hydroprocessing units after the hydrogen treat gas is removed.

6.3.3.3 Coking

Coking is not much of an issue in regards to sulfidation corrosion in light oil hydrotreaters. Heavy oil hydrotreaters and hydrocrackers can have coking issues; typically, coking reduces the corrosion rate in non-fired equipment such as pressure vessels and piping. However, several operators have reported increased corrosion rates after fired heater tubes experienced coking.

6.3.3.4 Stripping Steam

The degree of stripping does not significantly affect sulfidation in light oil hydrotreaters. However, steam injection to shorten furnace residence time can be a major contributor to sulfidation corrosion in heavy oil hydrotreaters and hydrocrackers. The effect of the stripping steam may be two-fold: a primary effect may be that the shorter residence time does not allow the sulfur vapors to evolve and disengage, so that more corrosion occurs further downstream in the hotter sections of columns and piping circuits that might otherwise be expected to be sulfur-free.

7 Practical Guidelines for Avoiding Sulfidation Corrosion Failures

This section first covers actions that refineries can take to avoid failures due to sulfidation corrosion of existing equipment, emphasizing inspection planning and strategy. Then, materials selection considerations for new equipment are covered.

7.1 For Existing Units and Components

There are a number of steps that refineries can take to limit the likelihood of a sulfidation corrosion failure.

7.1.1 Create and Implement an Inspection Plan for Components in Sulfidation Corrosion Service

The first step is to create an inspection plan. Equipment operating at conditions under which H_2-free sulfidation or H_2/H_2S corrosion can occur must be identified. Based on factors such as the consequence of failure, the anticipated corrosion rate, and the past inspection results, a plan is devised consisting of an inspection date, scope, method and interval for follow-up inspection. API 581 contains tables that can be used to estimate possible corrosion rates. In most cases, sulfidation corrosion is generalized, so an effective inspection can consist of targeted point thickness readings. The following are some issues that may need to be considered when planning inspections.

— Increases in operating temperatures and operating severity over many years can lead to unexpected increases in corrosion rates.

— The partitioning effect of sulfur compounds into certain streams; heavier streams may contain more and different sulfur types.

— Flow regime or stratification in horizontal lines, heater tubes, and deadlegs. The top of the tube or pipe may corrode more because of H_2S vapor blanketing and in heaters higher temperature. Vertical heater tubes are prone to accelerated corrosion on the top return bends and bottom fired heaters may experience more corrosion on the hotter bottom surfaces. Vertical deadlegs can also be prone due to chimney effects, leading to accumulation of higher concentrations of sulfidation corrosion causing species. Finned tubes may operate hotter and corrode more than adjacent unfinned tubes.

— High-velocity areas and injection points may be more prone to corrosion due to flashing and turbulence that reduces the adherence of the protective scale. Notable areas are the hydrogen injection points in hydrotreaters, around control valves, and downstream of orifice plates.

— High-temperature line supports can act as cooling fins, if the component operates above the peak of the sulfidation corrosion curve. A support can act as a cooling fin and lead to locally higher corrosion in the cooler part of the line, such as in an FCC reactor overhead line.

— Specification breaks, i.e. where a higher alloy adjoins a lower alloy. There is no “galvanic” effect, but these locations tend to be areas where the lower alloy may be marginal.

7.1.2 Perform Inspections

There are various techniques that can be used to detect and track sulfidation corrosion.

a) *Conventional Methods*. The vast majority of inspections are conducted by conventional straight beam UT thickness readings at defined thickness monitoring locations (TMLs) and are highly effective. TMLs should be chosen taking into account actual wall temperatures and other variables affecting sulfidation corrosion rate as noted in 4.6.

   If UT readings are taken at high temperature, special probes, couplants, and calibration techniques are needed to account for the difference of sound velocity vs temperature. Properly qualified procedures and technicians are required if readings are to be taken with the piping hot. If monitoring known areas of active corrosion, a good practice is to take baseline readings cold (i.e. during a shutdown) followed by a set of baseline readings at high temperature right after start-up, so that subsequent in-service readings can be compared more easily. RT is a very common and highly effective inspection technique for small bore piping. Where localized corrosion is suspected, line or area scanning (manual or automated) UT and profile RT are used.

b) *Other Methods*. Other commercially available techniques that can be used to detect sulfidation include the following; however, most are newer and even more operator sensitive.

   — *Real Time RT Scanners*. These have a display and a crawler mechanism to move a source along while displaying the inspection image in “real time,” that is, without the need for developing film as in conventional RT. Wall thicknesses can be measured with reasonable accuracy. This method is particularly beneficial for detecting localized corrosion. The primary limitation pertains to access constraints in congested parts of piping systems. An advantage is that insulation does not need to be removed in order to perform this inspection. Lower power hand-held devices can also be effective for measuring the wall thickness locally.

   — *Pulsed Eddy Current*. There are several types of these tools available under a number of different trade names. All of them essentially work by producing an eddy current and measuring perturbations in the field to derive a wall thickness. Some companies do not endorse its use for detecting sulfidation corrosion or only consider it for rough screening. Similar to RT scanners, an advantage is that insulation does not need to be removed in order to perform this inspection.

   — *UT Mapping*. This type of UT equipment is comprised of line or area scanners that map and give data representation of thickness over a large area. Due to temperature limitations, these are normally performed at shutdowns. In addition, insulation must be removed. Although electromagnetic acoustic transducer methods do not require contact or couplant, they can be large and cumbersome.

   — *Guided Wave UT*. There are several types of guided wave UT methods available that can inspect up to 150 ft under ideal surface conditions or much less if the surface is scaled or coated. Two rings of insulation at each end of the piping length to be inspected are stripped to allow access with a ring of transducers. This method is affected by coating condition, numbers of elbows and welds, etc. Due to temperature limitations, this type of inspection is performed during shutdowns.

   — *Inspection Pigs for Heater Tubes*. There are several types of pigs that can be inserted at the inlet of a heater and transverse the convection and radiant sections of a fired heater while taking continuous UT thickness readings. Tubes typically need to be pig cleaned prior to the inspection and there are limitations on bend radius.

7.1.3 Evaluate Thickness Readings

Thickness readings should be grouped by common corrosion circuits and evaluated for trends. Additional readings may be needed if the remaining thickness is approaching the minimum required thickness. Once a component is noted as approaching the minimum thickness, API 579-1/ASME FFS-1-2007 can be used to evaluate the corrosion profile and damage for acceptability for continued service. Fitness-For-Service (FFS) assessments typically require periodic monitoring to be conducted to ensure that the estimated future corrosion rate is not exceeded.

7.1.4 Perform Retrospective PMI

Many refineries have instituted retrospective PMI programs (see API 578) for alloy piping systems. Methods vary, but many programs include stripping all insulation. Others have used radiographic methods or long range guided wave UT methods to find all welds and selectively strip insulation at the welds. This allows access to the piping on either side as well as the weld.

A number of PMI instruments are available. They belong to either the optical spectroscopic or X-ray fluorescence types of analyzers. They can be used on-line or during downtimes to determine alloy content of the outside weld bead and the base metal or fitting adjacent to the weld. These instruments should have the sensitivity to determine that the Cr, Ni, and Mo levels are within the ASTM limits.

If a rogue material is identified, a risk assessment should be performed to determine if and when it should be replaced. Small bore piping and fittings such as vents and drains are typical areas where incorrect materials are often found. Refineries should implement policies and procedures to prevent the reuse of carbon steel or alloy piping at temperatures exceeding 450 °F (230 °C) without confirmation of the chemistry. Material control is particularly important for maintenance repairs or replacements. Some refineries have adopted programs specifying that alloy verification is required for 100 % of all alloy components at the point of installation.

7.1.5 Perform a Low-Si Carbon Steel Inspection Program

Thickness surveys are appropriate for both carbon steel and low-alloy piping systems. However, carbon steel represents a special case. As mentioned above, carbon steels with low-Si (< 0.10 %) content can corrode at an accelerated rate when exposed to sulfidation corrosion conditions. Typically, fittings have higher silicon content, while piping is the most likely component to have low-Si content.

Some refiners have instituted an approach similar to PMI for identification of these materials. These approaches may involve an initial risk assessment to focus inspections on the circuits representing the highest risk. When mill certificates are available, some operators have used them to determine whether low-Si (< 0.010 wt %Si) steels were procured and will try to locate the low-Si spools.

Many field portable instruments used for PMI cannot identify silicon to the level needed to distinguish between high- and low-Si-containing steel. Chemical verification requires that metal shavings of all components be taken and analyzed in a lab.

As an alternative, insulation can be stripped and each piping segment can be exposed for UT inspection, hammer testing, or inspected with a technique that does not require access to determine thickness. Sulfidation corrosion is typically relatively uniform, so straight beam UT thickness readings are sufficient. If readings are taken with the piping in service, a qualified procedure incorporating high-temperature calibration and/or adjustment to the thickness measured is needed along with qualified UT operators. Unless the chemistry has been verified, however, the current operating conditions/stream composition may have been benign and if conditions become more severe in the future, the corrosion rate could increase. If a low-Si content material is identified, a risk assessment should be performed to determine if and when it should be replaced. Unless all components in a carbon steel system have been checked for either silicon content or thickness, the inspector should assume that low-Si steel may be present in the system and may corrode at much higher than nominal rates under some conditions (see Annex C).

7.1.6 Define an Operating Envelope for Each Part of the Unit Where Sulfidation Corrosion is Possible

A systematic study should be performed to define operating limits for those sections of the unit where sulfidation corrosion is a concern. This typically will address temperature and S content. A materials operating envelope [11] also defines sampling and monitoring requirements.

7.1.7 Institute Corrosion Monitoring

Corrosion probes can be used to better understand the sulfidation corrosion behavior of a particular crude slate or feed. For sulfidation corrosion, the electrical resistance type of probe is suitable, but the materials need to be compatible with high-temperature service. The probes work on the concept that as a sensing wire or tube is corroded, the electrical resistance changes due to the change in cross-sectional area. Many refiners have standardized on tubular vs wire loop probes for such services since they tend to be more robust. Some refiners test the probes at temperature prior to installation to ensure that data will be generated by the probe once it is commissioned. There are fixed and retractable probes; the fixed type being more common in high-temperature services. Retractable probes require more elaborate access fittings and there is always a safety concern when retracting or inserting probes during unit operation. The probes can be outfitted with transmitters or wiring to send signals to the control house and be collected by the plant operations monitoring software system. Response of the probes depends on the element type and thickness and may take a few days to stabilize in order to obtain reliable data. Ideally, monitoring data is combined with the crude or stream composition and levels and types of sulfur compounds to trend these factors with observed corrosion rates.

7.1.8 Inject Inhibitors for Corrosion Control

Some of the same phosphoric acid based inhibitors that are used for naphthenic acid control have been shown in laboratory tests to also inhibit sulfidation corrosion. At this time, however, inhibitors are not typically used to control sulfidation corrosion.

7.1.9 Replace or Upgrade the Material

If sulfidation corrosion is occurring at a high rate where the component life is limited or future operating conditions will be more severe than in the past, replacing the material in-kind (perhaps with a heavier schedule for piping) or upgrading to a more sulfidation corrosion resistant material should be considered. In-kind replacement requires that regular and frequent inspections will be required to ensure that corrosion rates are manageable. It is preferable to specify higher alloy for better corrosion resistance to minimize the reliance on inspection.

7.2 New and Replacement Components

7.2.1 Materials Selection Guidance

Most refiners, process licensors, and engineering and construction companies maintain guides for materials selection for components that will be exposed to potential sulfidation corrosion conditions. Guidance for materials selection for oil refinery applications is also provided in a book published by NACE [12]. Materials are selected based on the proposed maximum operating conditions and by referring to the appropriate proprietary prediction curves, modified McConomy curves or Couper-Gorman curves (which may be adjusted based on experience). For example, during materials selection, rarely is all of the peak in corrosion rate at 800 °F (425 °C) for H_2-free services taken into consideration.

Corrosion rates for sulfidation corrosion can also be estimated using the tables in API 581. The tables are derived from the above-mentioned curves.

An appropriate corrosion allowance is added for the anticipated sulfidation corrosion rate at the maximum operating temperature. During design, some companies use a multiplier on the calculated corrosion rate or use a safety factor on some operating conditions to have a greater confidence that the likelihood of sulfidation corrosion exceeding the design rates is minimal. It is likely that the crude slate will change over the years (in some units, it changes frequently), which is one reason to check “sensitivity” factors in the design.

7.2.2 H_2-free Services

Where no prior experience or information is available, the modified McConomy curves would indicate the following materials selections for resistance to sulfidation corrosion (not considering the effect of naphthenic acid corrosion or mercaptan corrosion) in H_2-free, 2 wt % S environments is as follows. These selections could vary depending on sulfur species, hydrocarbon phase, flow regime and the other operating variables discussed in 6.2.

— Carbon steel for temperatures up to 525 °F (275 °C). Use fully killed steels to assure silicon content > 0.10 wt %.

— 5Cr-0.5Mo for temperatures between 525 °F and 620 °F (275 °C and 325 °C).

— 9Cr-1Mo above 620 °F (325 °C).

— 300 Series SS can also be used to virtually eliminate sulfidation corrosion.

7.2.3 H_2/H_2S Services

For H_2/H_2S environments, the Couper-Gorman curves show that with high mole % H_2S at metal temperatures above about 500 °F (260 °C), 300 Series SS are the preferred choice. For lower severity services, such as naphtha and kerosene hydrotreaters with lower mole % H_2S levels, low-alloy Cr-containing alloy steels, including 12Cr steels, have been used successfully.

7.2.4 Heater Tubes

For heater tube material selection for corrosion avoidance, the design should assume a metal inner film temperature of 50 °F to 200 °F (28 °C to 111 °C) higher than the process outlet temperature. This temperature delta varies based on coking tendency and heater design.

7.2.5 Linings or Cladding

Linings or claddings of higher alloys are often used in heat exchangers, drums and towers. A cost savings is achieved as the backing material is a lower cost material. Use of linings or claddings is especially advantageous in high pressure services which require thick wall components.

7.2.6 Piping Components

All carbon steel piping components should be specified to have a 0.10 wt % minimum Si content for improved sulfidation corrosion resistance as discussed in 6.2.3.2 and Annex C. This is generally achieved by requiring the use of ASTM A106 piping. Most piping today is triple-stamped and meets ASTM A106, ASTM A53 and API 5L. Most refineries do not allow single-stamped ASTM A53 pipe to be used. Pressure vessels are typically made of ASTM A515 or ASTM A516 steel, which contain sufficient silicon content in the specification.

7.2.7 Scaling

Most companies specify materials to limit the corrosion rate to below 10 mils/year (0.25 mm/year) in order to avoid an excessive corrosion allowance and scale formation. This may lead to selecting “higher alloy” materials in order to avoid an excessive scale formation. Iron sulfide scale can be voluminous, and as it spalls off it can clog reactor beds, pumps, instrumentation, etc. Plugging reactor catalyst beds with corrosion products from upstream components can reduce run lengths and be a substantial cost factor.

7.2.8 Specification Break

Care must be taken to critically examine all specification breaks in piping systems. Many of these pipe class changes result from sulfidation corrosion concerns. For example, the bypass piping around an exchanger which has carbon steel inlet piping and stainless steel outlet piping will have a pipe class change which needs to be carefully designed.

7.2.9 PMI Program

Refineries should institute and maintain a PMI program per API 578 to verify that the correct alloy has been installed in all sulfidation services. Some refineries have adopted programs that specify that alloy verification is required for 100 % of all alloy components at the point of installation.

7.2.10 Materials Operating Envelope (MOE)

For new units it is advisable to create an MOE or corrosion monitoring plan to guide future operation. For new components in an existing unit, the MOE should be reviewed and modified if needed.

8 Limitations of Current Knowledge Base

The guidance provided in this document is based upon industry experience. Sulfidation corrosion rate prediction remains an elusive goal. Individual refining companies have spent many years and significant resources trying to improve the predictive tools. Nevertheless, the ability to take a crude oil that is unknown to a particular refinery and predict the sulfidation corrosion behavior for that refinery has proven to be very difficult.

Publicly available tools should be considered as rough guides with the understanding that predicted corrosion rates are an average value with a fairly large scatter band. There are industry initiatives, such as the ASSET [2] [13] program, but the amount of information for conditions typically encountered in refineries is very limited.

Some important unresolved issues are:

- hydrotreater distillation corrosion mechanism;
- the fundamental effect of hydrogen on the corrosion rate;
- the effect of modern steelmaking techniques, i.e. generally lower Cr content in the specification range than years ago when corrosion rate curves were compiled.

9 Incidents

The industry has experienced numerous failures as a result of sulfidation corrosion, mostly of piping. Incidents documented by Marsh Consulting [14] total close to $400 million in the period of 1984 through 2001 for five incidents documented to involve sulfidation corrosion. To prepare this document, industry sources such as NACE STG 34 Refining Industry Corrosion Minutes and the API Subcommittee on Corrosion and Materials Minutes were reviewed for publicly reported incidents of sulfidation corrosion [15], [16]. In addition, a survey was conducted in 2005 to identify additional incidents to assist in the preparation of these RP guidelines.

A total of 45 incidents identified during preparation of this RP have been grouped into a summary chart, shown in Figure 5, and classified by primary root cause. Some examples of specific incidents and further details regarding the categories listed in the pie chart are included in Annex A.

Low-Si content failures are the most common mechanism. Current generation refinery carbon steel piping materials available in North America are typically triple-stamped ASTM A106/A53/API 5L and contain greater than 0.10 % Si.

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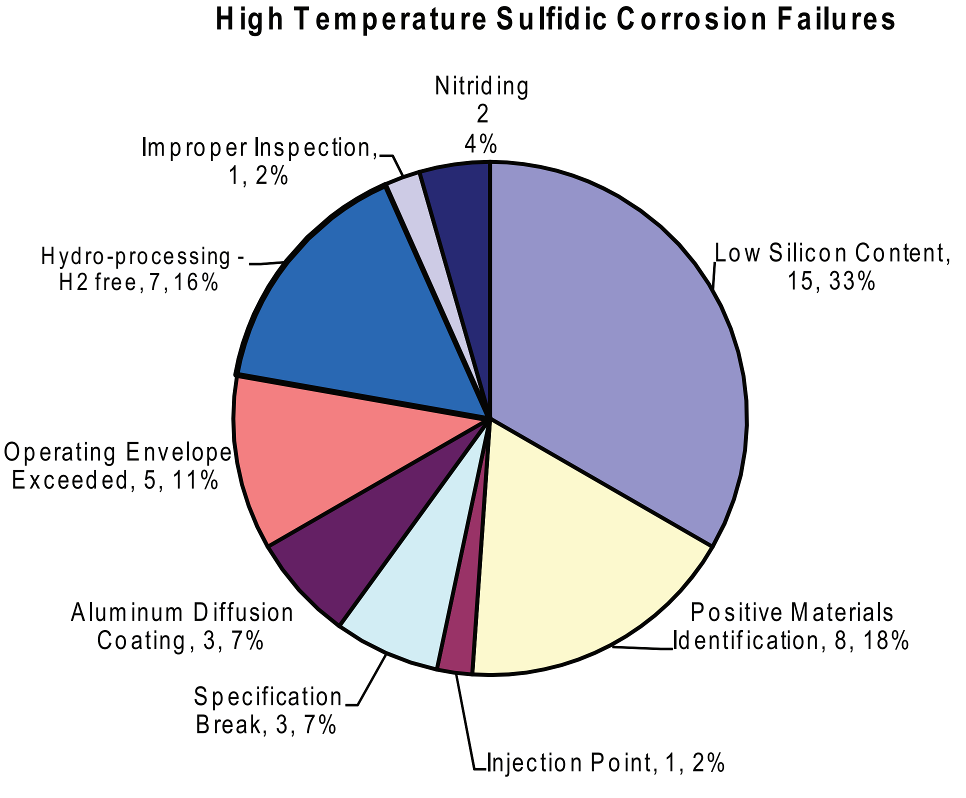
[2] This term is used as an example only, and does not constitute an endorsement of this product by API.

However, older ASTM A53 piping may have lower Si content. This situation creates a major inspection challenge, because small piping sections (pups) or fittings with low Si may corrode at rates 2 to 10 times faster than surrounding higher Si piping. Unless the refinery is fortunate enough to have located an inspection point on that particular section of pipe or fitting, it is very difficult to detect the thinning component. Although the corrosion rate may not be extremely high for any year, many units contain piping that is over 30 years old. Even a low corrosion rate, such as 2 mils/yr to 3 mils/yr (0.05 to 0.08 mm/year), can result in using up the corrosion allowance and leading to perforation of the wall over many years. Section 7 discusses inspection practices specific to low-Si-containing carbon steels.

The chart also highlights the importance of PMI. API 578 was published in 1999, providing guidance for effective PMI. Since the document was issued, many more refineries have instituted both retrospective inspections for proper materials and programs to ensure that the correct material is present when new or replacement components are installed. Some companies have reported retroactive PMI results indicating that the incorrect materials were installed at a rate of about 3 % for piping components and welds and as high as 10 % for items such as drain plugs.



(1963-2003, NACE/API/Owner-Operator Citations)

Figure 5—Summary of Reported Failures by Type, Number of Reported Instances, and Percentage of the Total

Annex A
(informative)

Failure Experience Summary

Section 9 of this RP mentions that the refinery industry has experienced numerous failures and near misses as a result of sulfidation corrosion. Figure 5 is a pie chart that summarized the root cause of failures as reported in NACE Refin-Cor™ 7.0 [15], API Minutes [16], and a survey conducted as part of the drafting of this RP. The following provides more explanation on some of the failures and defines the categories in the pie chart in Figure 5.

— *Low-Si Content*. Carbon steel with low-Si content (Si content < 0.10 wt %) has been shown to corrode at a rate that is as much as 2 to 10 times faster than similar carbon steel with higher Si content. The Si is believed to help form a more adherent and stable scale on the steel surface, which reduces the metal loss rate in comparison to steels with low-Si content. Numerous fires have occurred in crude and coker units due to low-Si content steel piping components. See also Annex C.

— *PMI*. The incorrect (lesser alloy) component was inadvertently present in a system that was intended to have a more highly alloy steel installed. This typically results in the lower alloy material corroding at an accelerated rate vs other "correct" alloy components within the system.

— *Poor Materials Selection and Specification Breaks*. In a process, there are points at which different materials are used adjacent to each other. The specification break should be located so that the material with the lower corrosion resistance does not suffer severe corrosion. Specification breaks can be present at major or at more subtle changes in the operating conditions i.e. upstream and downstream of heat exchangers, at valve locations, at bypasses, etc. Specification breaks need to be inspected carefully, because the more corrosion resistant material may not show any evidence of sulfidation corrosion, but the adjacent less corrosion resistant material may exhibit severe wall loss, particularly if the operating conditions have changed or become more severe.

— *Improper Inspection*. An appropriate inspection technique and coverage at a proper interval should have detected the corrosion condition. For example, sulfidation corrosion can be hard to detect with visual inspection, because it typically results in uniform wall loss, whereas it is readily detected with UT.

— *Aluminum Diffusion Coating Breakdown*. Aluminum is very resistant to sulfidation corrosion at normal refinery temperatures. In the 1950s and 1960s, some refiners used an aluminum diffusion coating on the ID of carbon steel or low-alloy steels to provide an aluminum rich coating that is generally resistant to sulfidation corrosion. However, after many years and operating cycles, these coatings have a propensity for cracking or spalling. This then exposes the less resistant base metal to sulfidation corrosion and results in localized corrosion that is very difficult to detect. Especially failure-prone areas are welds and crevices that could not be coated to the same extent as the smooth bore of piping.

— *Nitriding of Valve and Piping Components*. Nitriding is a process for hardening a surface by diffusing nitrogen into the material for wear, erosion, or abrasion resistance. When used on low-alloy steels, this process forms Cr nitrides that effectively lower the beneficial Cr content of the steel allowing it to corrode at a faster rate than non-nitrided components.

— *Injection or Mix Points*. These are locations where process streams are mixed or a stream is injected into another. For example, hydrogen may be injected into a gas oil stream ahead of the reactor feed heater in a hydrotreater. The turbulence and/or chemical reactions that occur can result in accelerated corrosion at these locations. Guidelines for mixpoint and injection point inspections are outlined in API 570 and in NACE Technical Committee Report 34101 [17].

— *Operating Envelopes*. This is a term used to define the boundary conditions by which a process unit can be safely operated. If operation is "outside of the envelope" it implies that the unit has experienced more severe conditions than appropriate. An example may be running sour crude (high-S crude) in a unit or system designed for sweet (low-S crude). This operating scenario has the potential of altering key sulfidation corrosion variables that may impact equipment reliability.

- *Hydrotreater H_2-free Corrosion*. As reported in NACE Publication 34103 [9], carbon steel and chrome alloy piping and equipment in the furnace feed system, reboiler and hot equipment in the distillation section of hydroprocessing units began exhibiting higher than expected corrosion rates in the 1990s. Despite a significant amount of industry focus and review, at this time there is no generally accepted theory or explanation for the higher-than-anticipated corrosion rates at the very low sulfur levels.

Annex B
(informative)

Sulfidation Corrosion Prediction Tools

Sulfidation corrosion is defined as a degradation mechanism, which forms sulfide corrosion products, leads to metal loss and occurs upon exposure of metals to temperatures above approximately 450 °F (230 °C) in liquids and gases containing H_2S at concentrations greater than 1 ppm. With H_2-free sulfidation, other types of sulfur compounds (i.e. elemental sulfur, polysulfides, aliphatic sulfides and aliphatic disulfides, and mercaptans) are considered to have an impact on the overall sulfidation rate. Hydrogen sulfide is generally regarded to be the most active from a corrosion standpoint; however, mercaptans may be more active at lower temperatures [8]. In theory, the corrosion mechanism proceeds by the conversion of the individual sulfur compounds into hydrogen sulfide, followed by the reaction of the H_2S with the iron in steel alloys. Typically, the sulfur speciation described above is not conducted on crude oils or process streams on a regular basis. Instead, weight % total sulfur is provided. Since the total sulfur content is comprised of many different sulfur-containing compounds which can react at varying rates, corrosion prediction based upon weight % sulfur alone can be misleading. The other primary parameter needed for predicting the relative corrosivity of a process stream is temperature. In general, high-temperature sulfidation corrosion is considered to be a concern from 450 °F to 800 °F (230 °C to 425 °C). Plant experience indicates that corrosion rates begin to decrease above 800 °F (425 °C).

There are two distinct and separate sets of curves that the industry uses to predict high-temperature sulfidation corrosion.

— The first for use in H_2-free streams are the modified McConomy curves. These curves were first published in Gutzeit's paper [3]. The original McConomy curves were based upon an industry survey conducted in 1963 by the API Subcommittee on Corrosion and reflect high-temperature sulfidation corrosion rates in H_2-free environments. Over the years, plant data indicated that the corrosion rates predicted by these curves were excessive. The end result was a reduction of the curves by a factor of roughly 2.5 and renaming them the "modified McConomy curves." These are reproduced in this annex.

— The second for use in H_2/H_2S-containing streams are the Couper-Gorman curves [4]. These curves are based upon an industry survey conducted by the NACE Committee on Refining Industry Corrosion in 1971 and differ from the McConomy curves in that they reflect the influence of hydrogen on the sulfidation rate. They are also reproduced in this annex. Of note is the region where no corrosion is predicted; this region corresponds to a combination of temperature and H_2S concentration where an iron sulfide scale is not thermodynamically stable.

Other Tools

1) ASSET [3] [13] is a commercially-available database and prediction tool that contains information on sulfidation but is not targeted to the refining industry. It contains data on approximately 15 alloys exposed to temperatures ranging from 575 °F to 1650 °F (300 °C to 900 °C) with exposure times up to 6000 hours. Some of the key findings derived from this tool are:

    — the sulfidation rate appears to follow a parabolic model provided the sulfide scale on the alloy surface remains undisturbed and sufficient time has passed (i.e. in excess of 1000 hours);

    — the corrosion rate will approximately double with a temperature increase of 122 °F (68 °C), assuming all other conditions remain constant;

    — the corrosion rate will approximately double with a factor of 10 increase in H_2S concentration, assuming all other conditions remain constant.

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[3] This term is used as an example only, and does not constitute an endorsement of this product by API.

2) Some companies have devised proprietary models that are based on sulfur specification analysis of crudes and streams and calibrated with field experience. This requires a large amount of analytical work.

3) One company has reported using H_2S evolution when heating a sample of crude oil in an autoclave and subsequently correlating the amount of H_2S released to an expected corrosion rate.

4) One refiner believes that with all other factors being equal, the corrosion rate can be up to six times higher for vapor vs liquid phase corrosion (Figure B.11 and Figure B.12 show that all vapor H_2/H_2S corrosion is more aggressive than with a liquid phase present). This refiner also believes that at low-H_2 content, the S activity due to H_2S is much greater and has shifted the high-pressure curves in Figure B.4 to lower partial pressures, i.e. the corrosion rate predicted is higher at the same H_2S partial pressure for a low-partial-pressure H_2 stream than a high-partial-pressure hydrogen stream (compare Figure B.13 with Figure B.11).

5) Another method to evaluate a crude oil is to conduct corrosion studies in a flow loop, where a crude fraction is pumped around and impacts a target coupon material for a few days. The most difficult step is to fractionate the crude into fractions. The corrosion rates measured in a short term flow loop test will be higher than long term rates, because sulfidation corrosion has a parabolic rate, where with time the rate slows, unless the scale is removed. Nonetheless, relative behavior of crudes can be determined by comparing to benchmark crude fractions where field data is available.

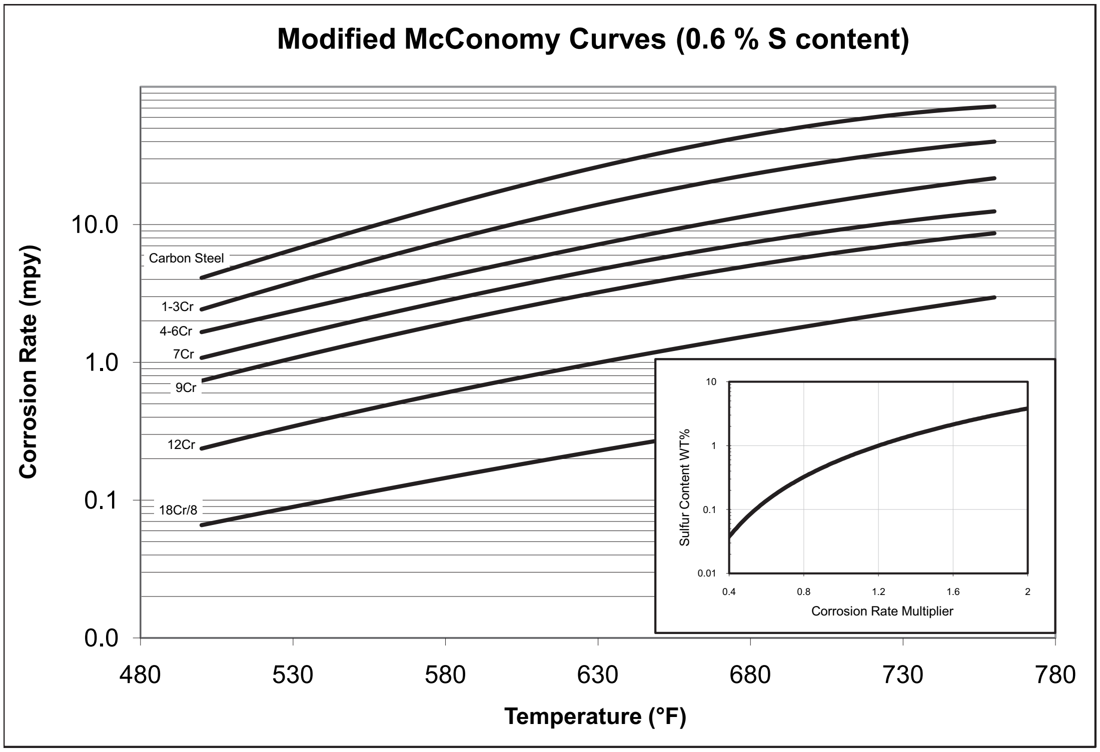


Figure B.1—Modified McConomy Curves

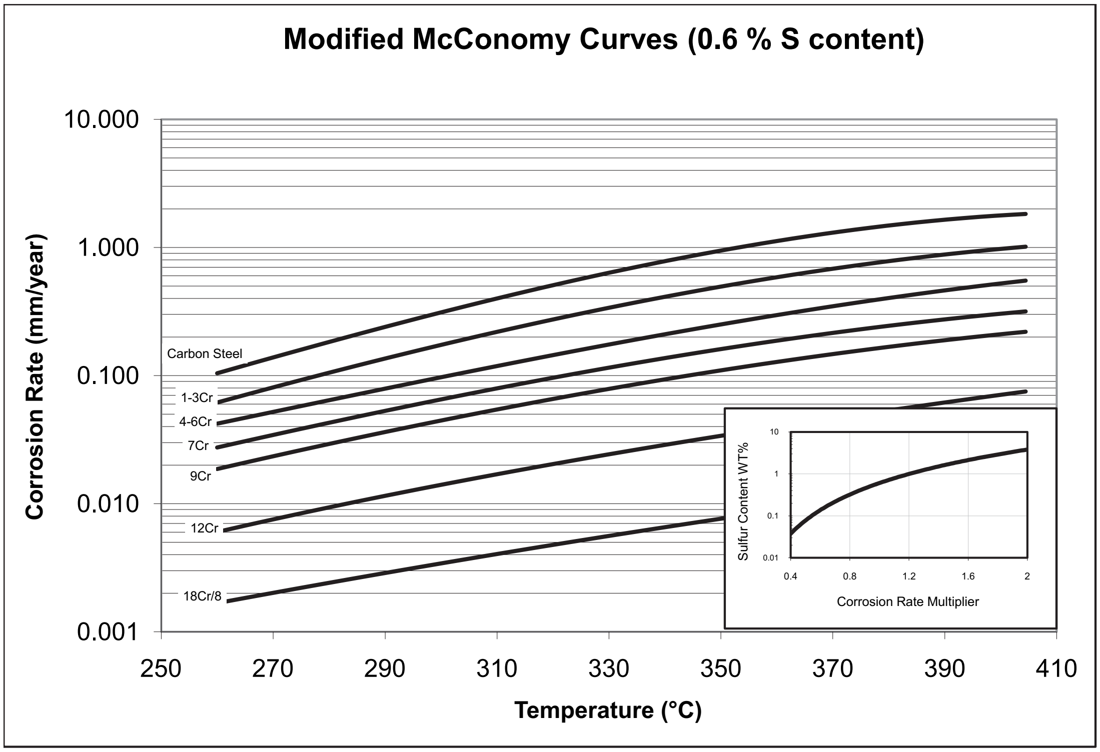
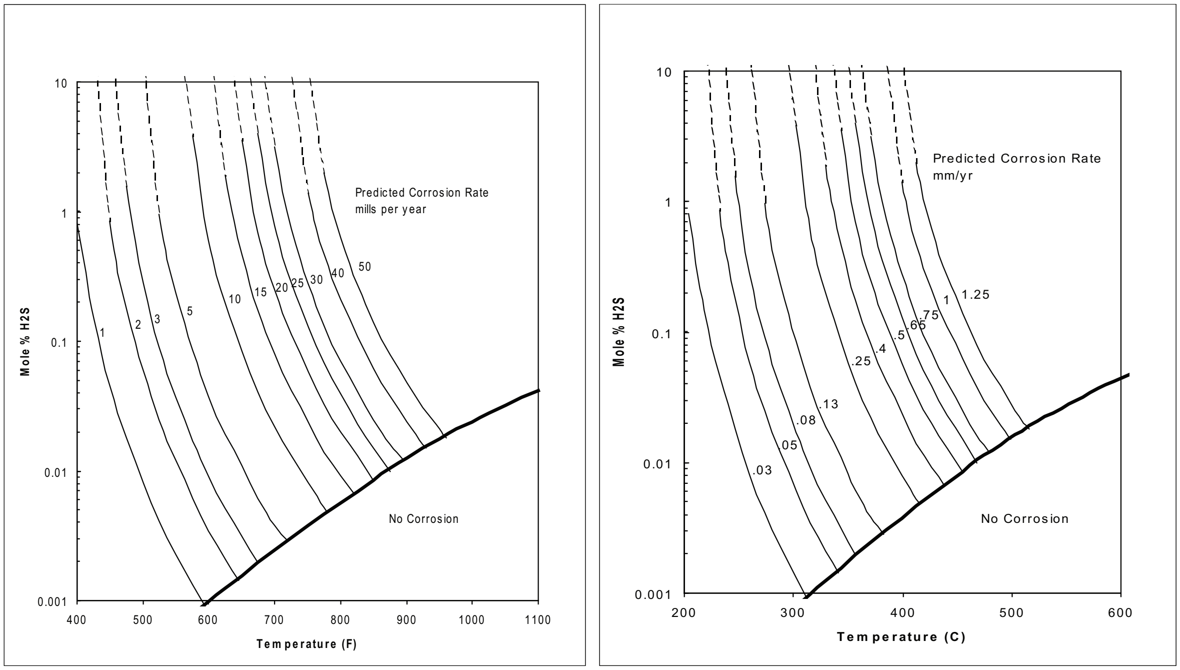
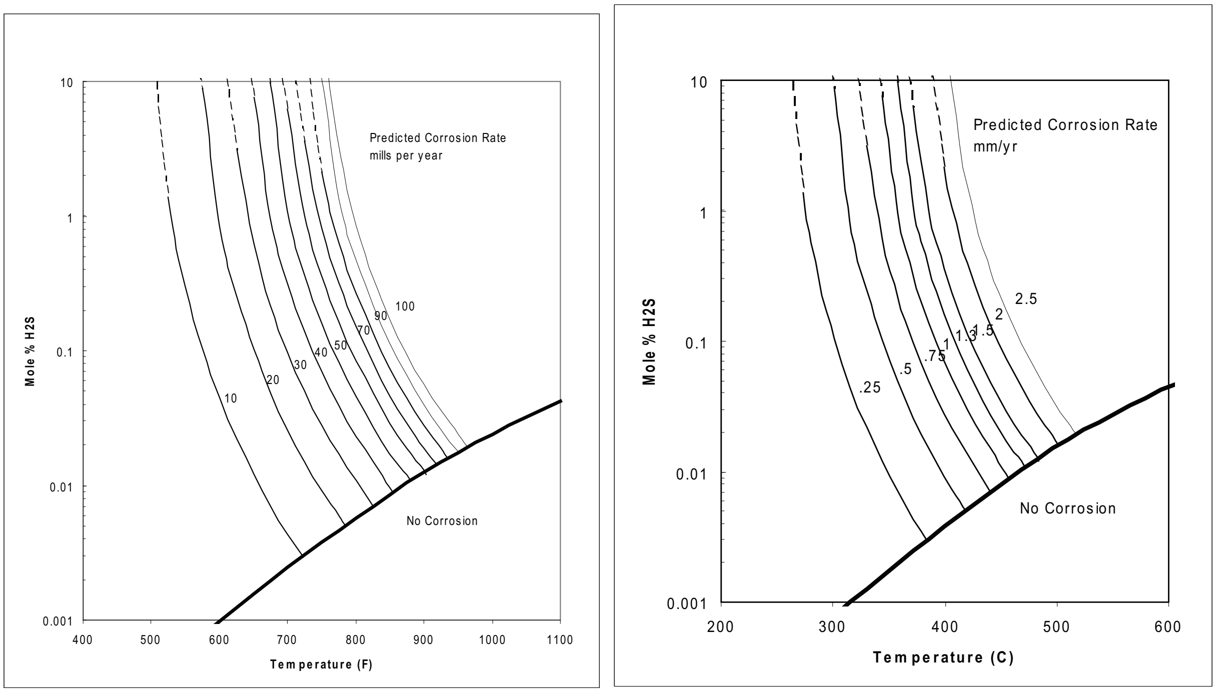


Figure B.2—Modified McConomy Curves

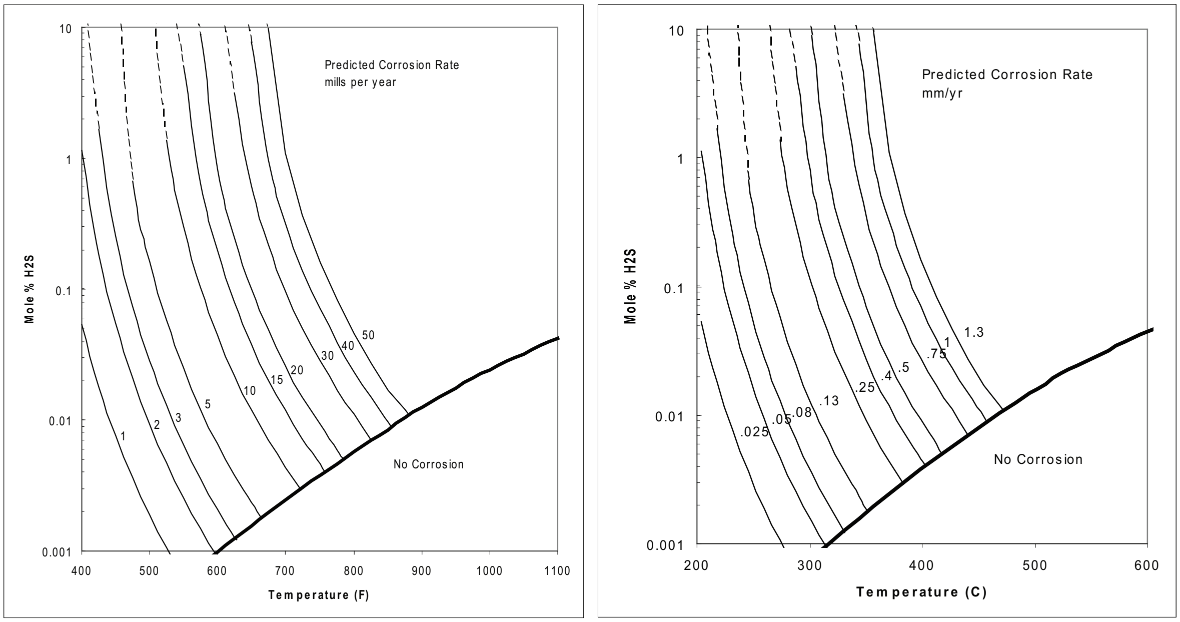


Carbon Steel Naphtha

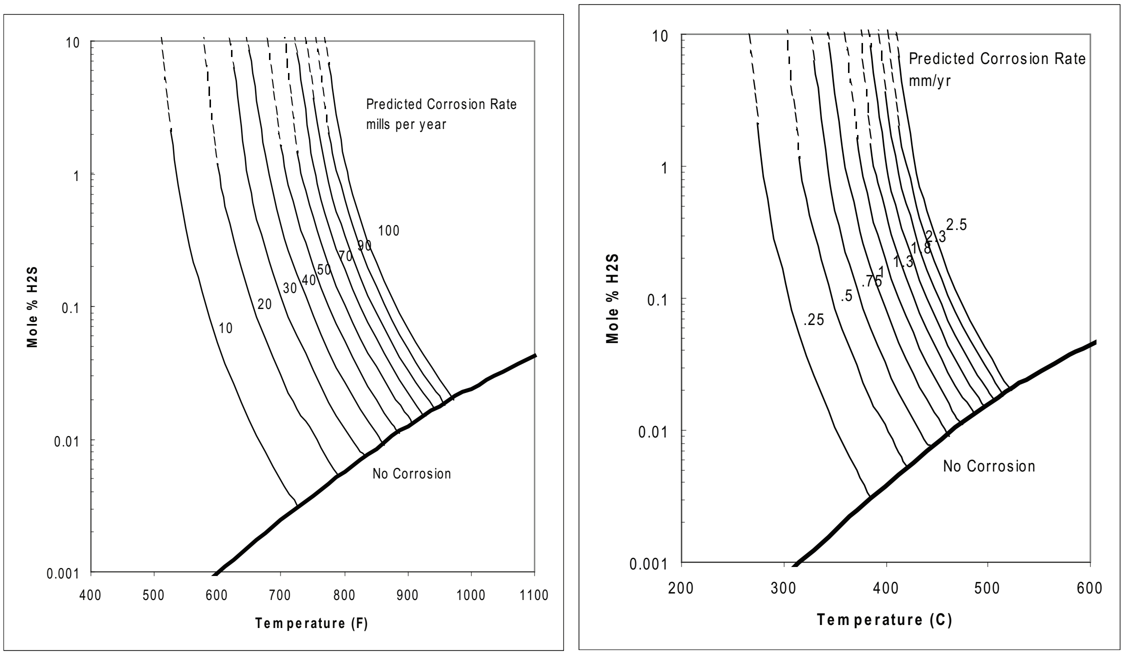


Carbon Steel Gas Oil

Figure B.3—Couper-Gorman H_2/H_2S Curves for Carbon Steel for Both Gas Oil and Naphtha

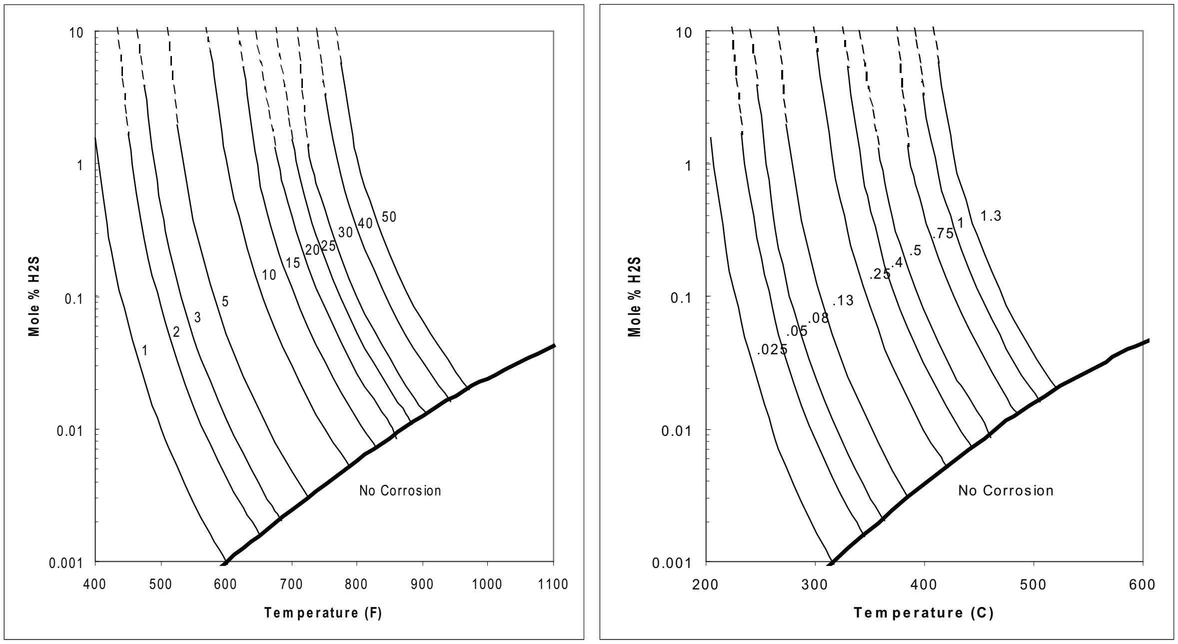


1.25Cr Naphtha

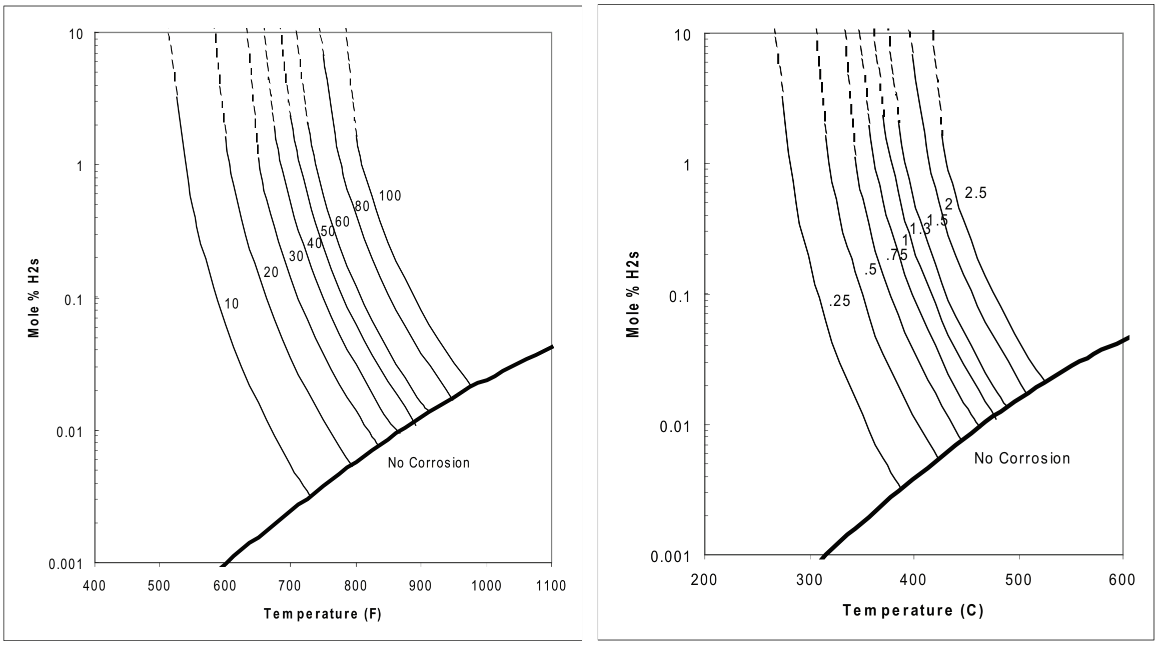


1.25Cr Gas Oil

Figure B.4—Couper-Gorman H_2/H_2S Curves for 1.25Cr Steel for Both Gas Oil and Naphtha

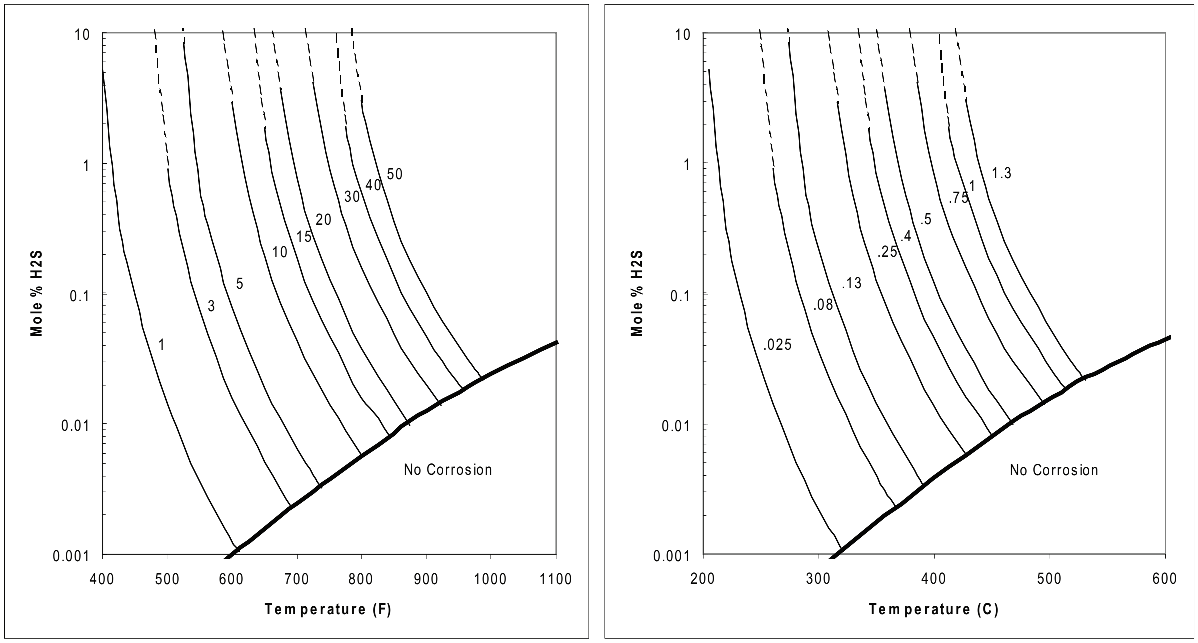


2.25Cr Naphtha

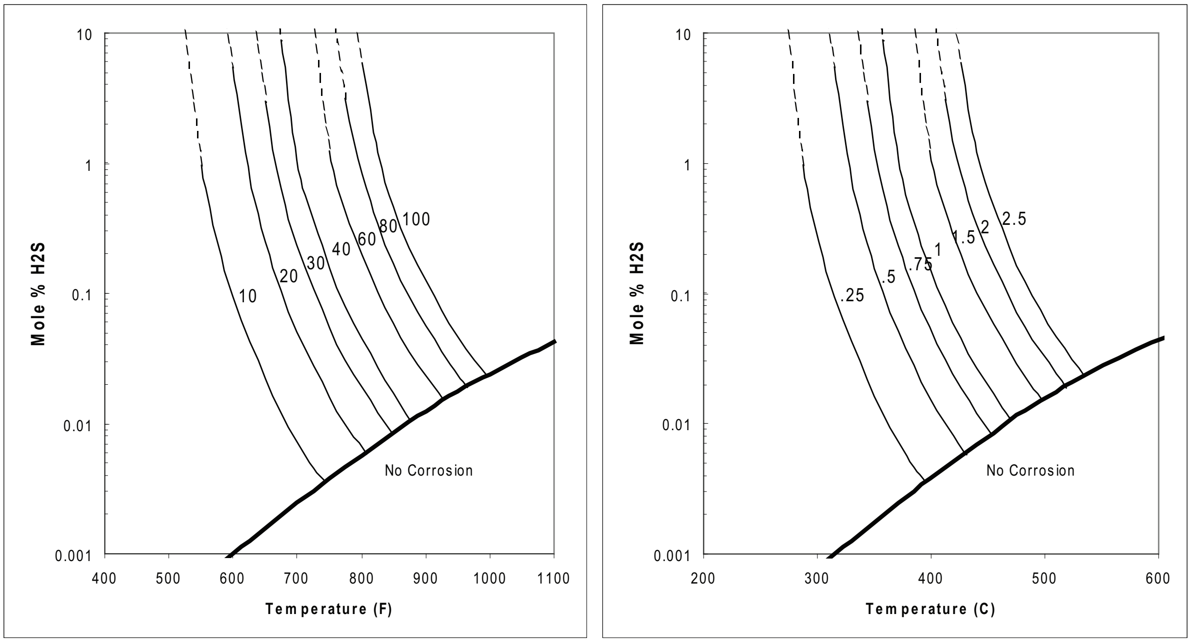


2.25Cr Gas Oil

Figure B.5—Couper-Gorman H_2/H_2S Curves for 2.25Cr Steel for both Gas Oil and Naphtha

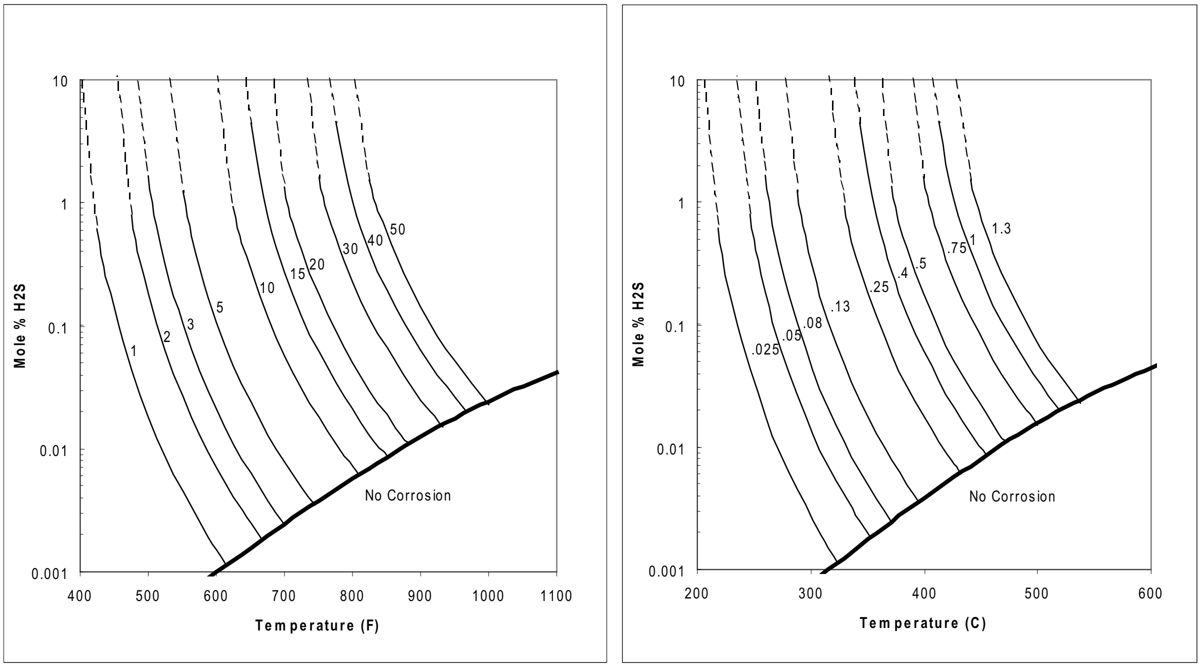


5Cr Naphtha

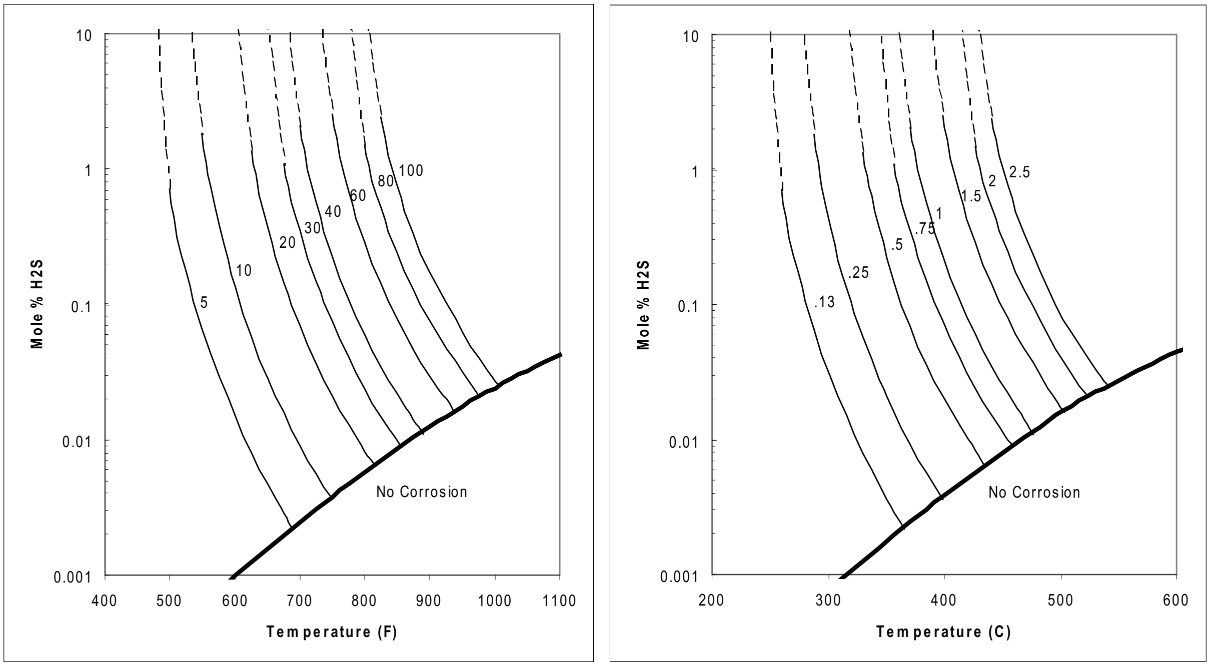


5Cr Gas Oil

Figure B.6—Couper-Gorman H_2/H_2S Curves for 5Cr Steel for Both Gas Oil and Naphtha

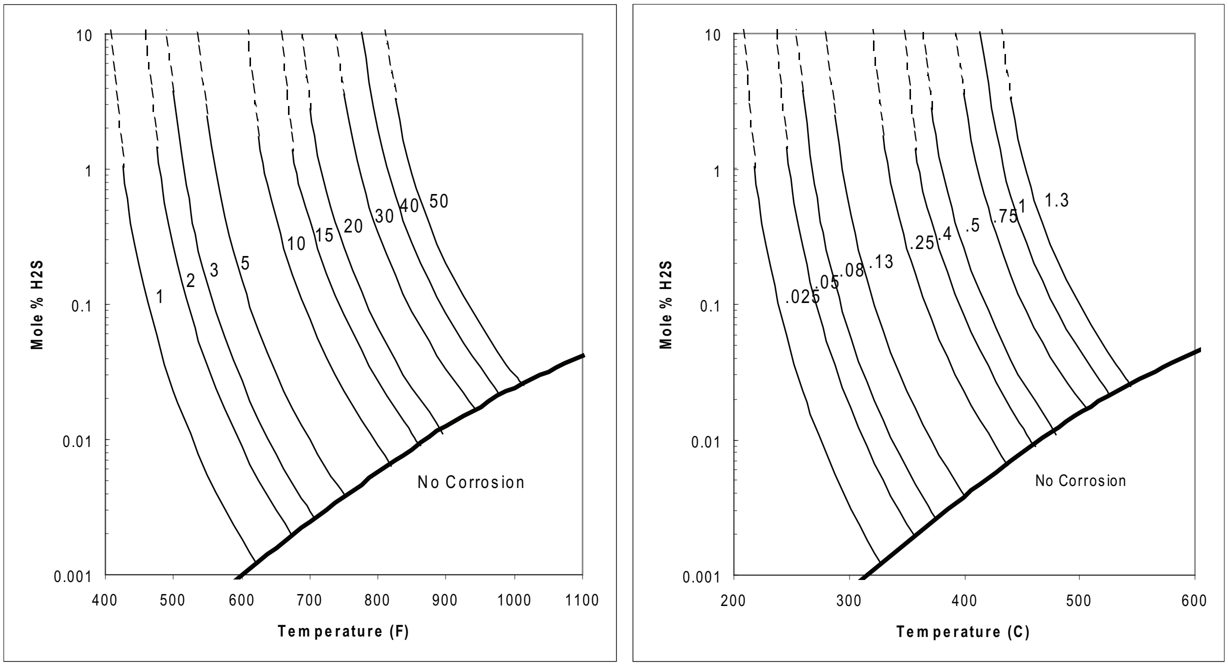


7Cr Naphtha

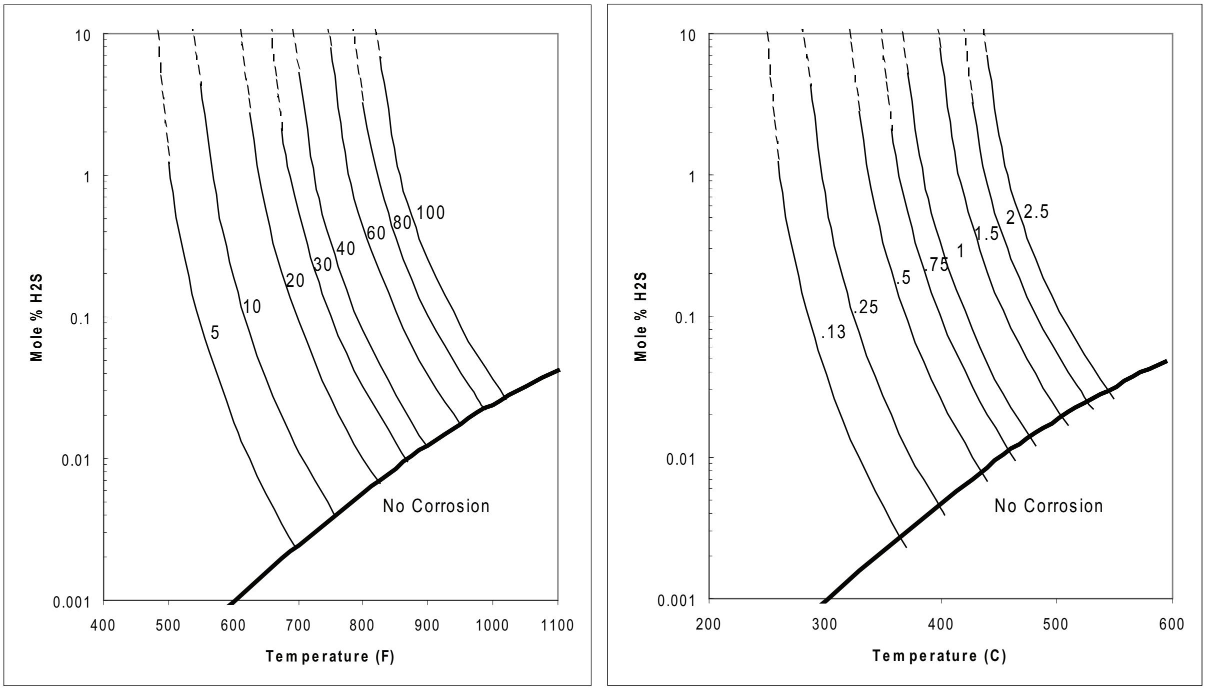


7Cr Gas Oil

Figure B.7—Couper-Gorman H_2/H_2S Curves for 7Cr Steel for Both Gas Oil and Naphtha

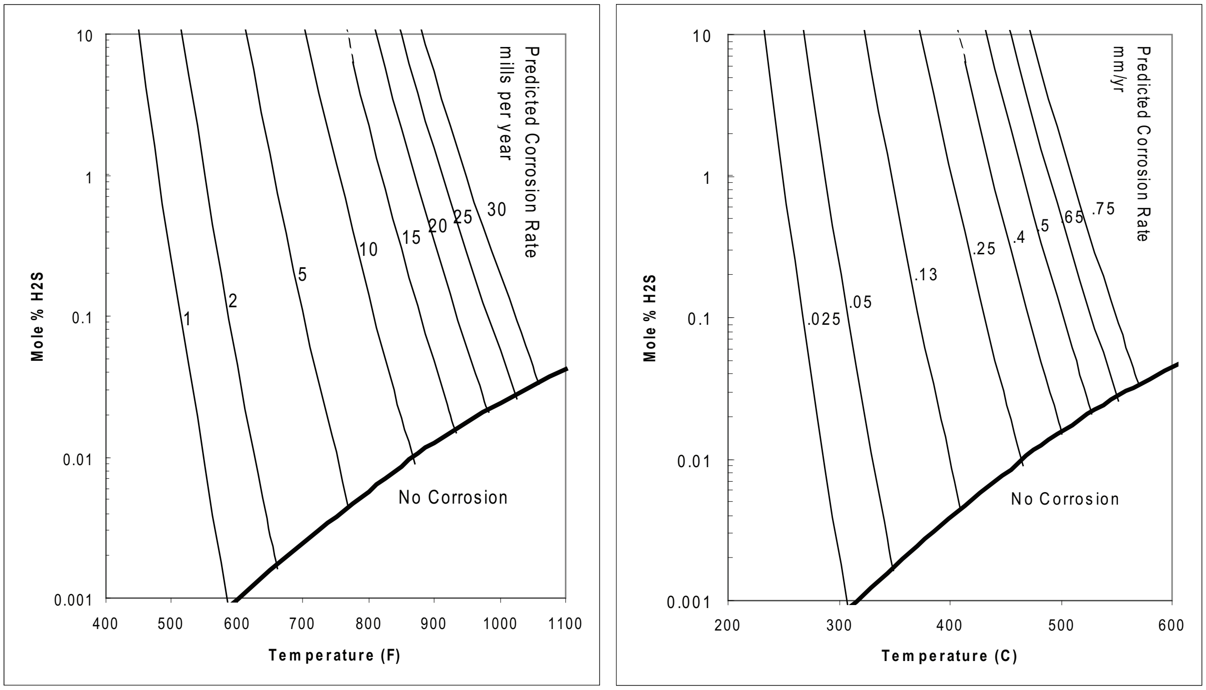


9Cr Naphtha



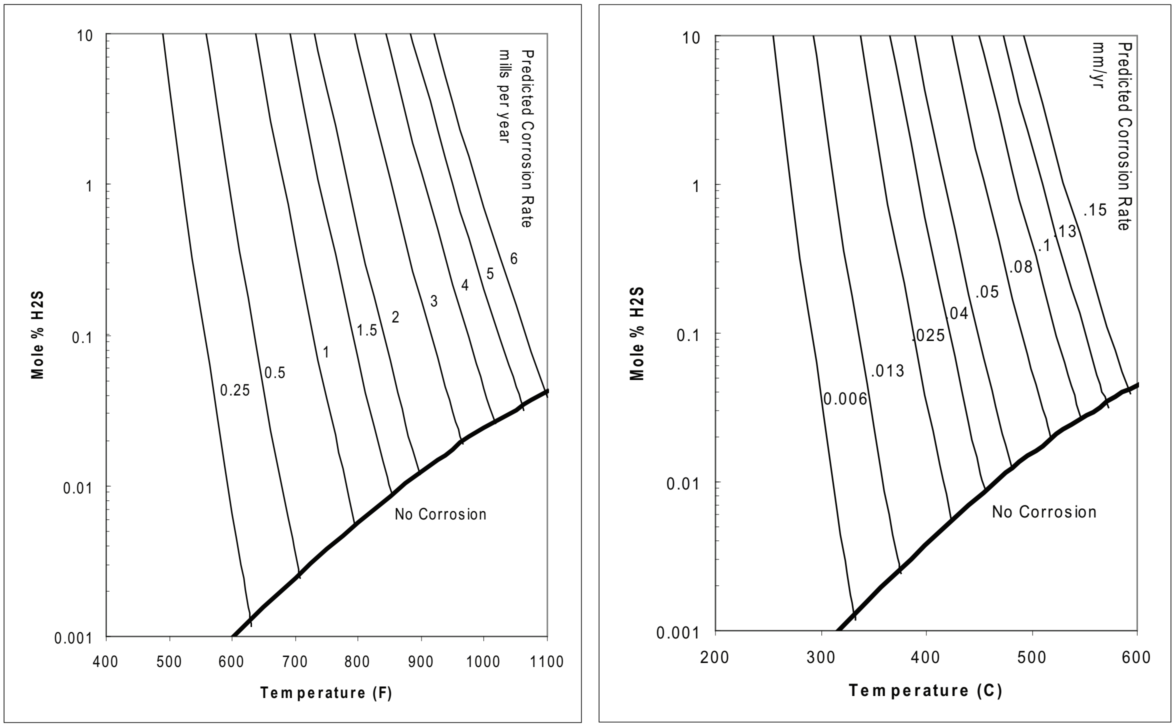
9Cr Gas Oil

Figure B.8—Couper-Gorman H_2/H_2S Curves for 9Cr Steel for Both Gas Oil and Naphtha



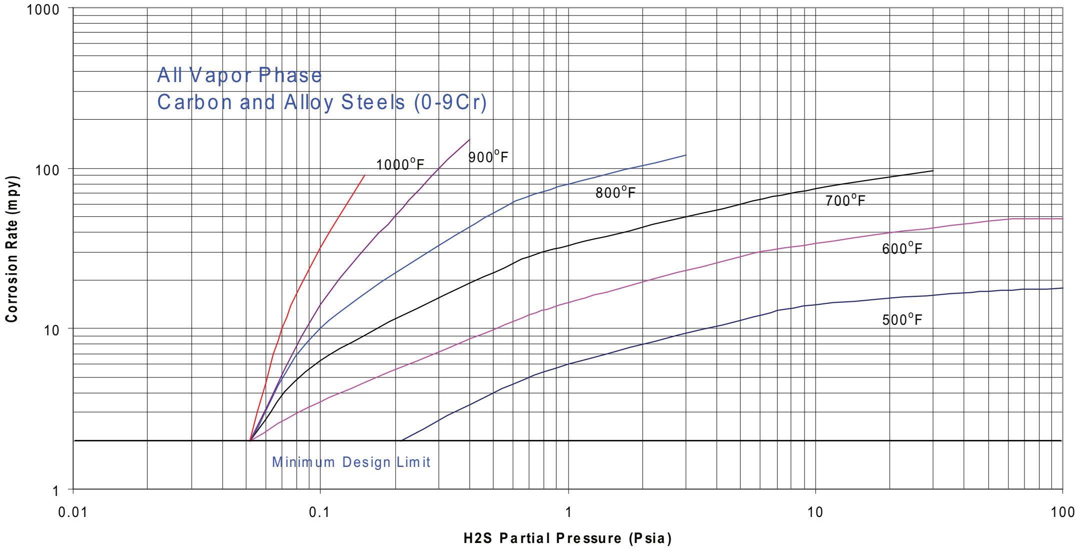
12Cr

Figure B.9—Couper-Gorman H_2/H_2S Curves for 12Cr Steel (Same for Both Gas Oil and Naphtha)



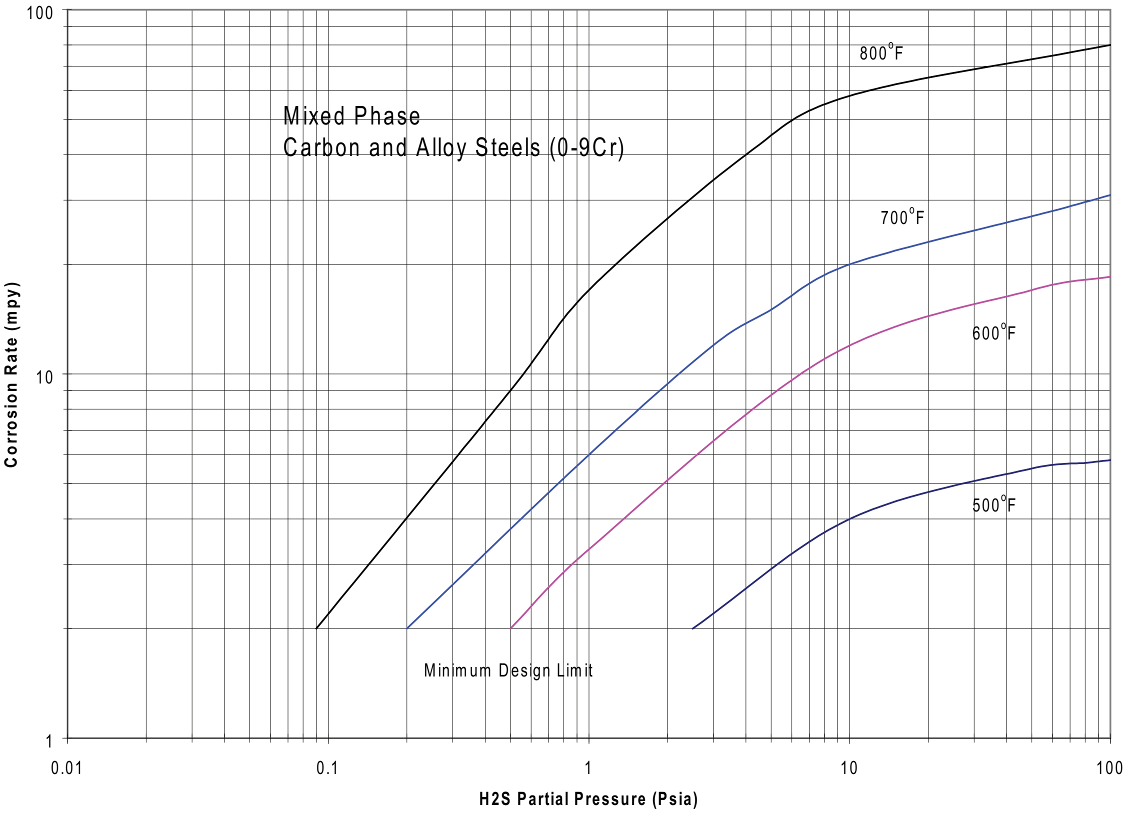
18Cr

Figure B.10—Couper-Gorman H_2/H_2S Curves for 18Cr Steel (Same for Both Gas Oil and Naphtha)



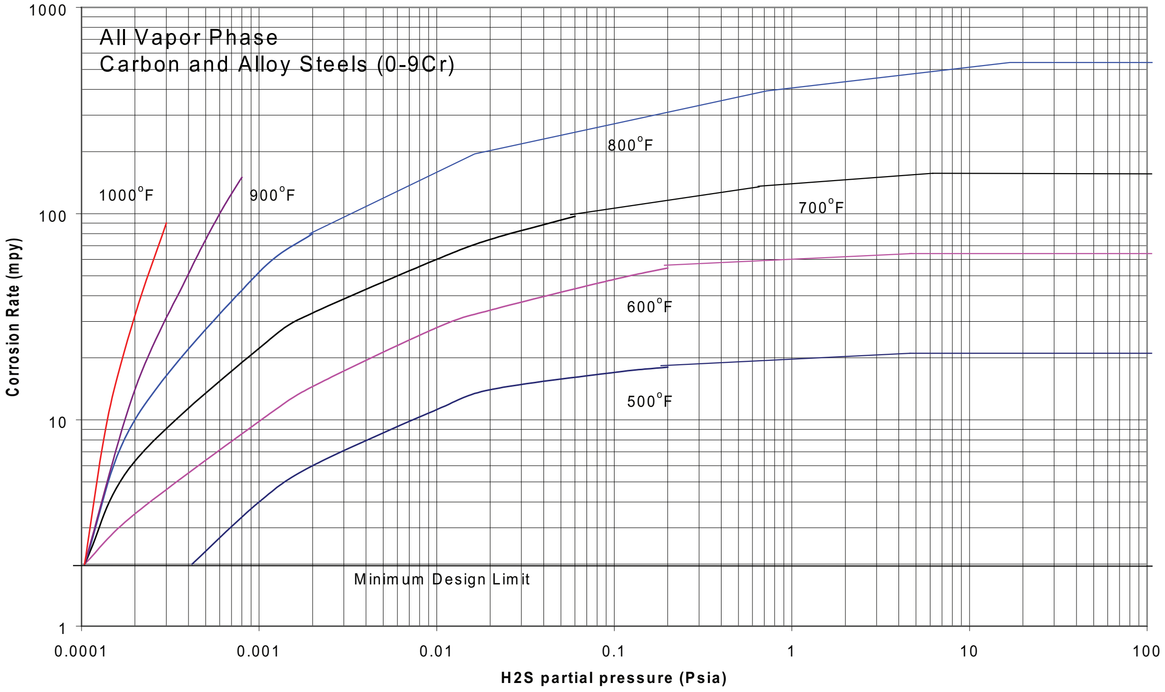
(Data from NACE Publication 59-10, 1958)

Figure B.11—Corrosion Rate in H_2S/High H_2 Partial Pressure—All Vapor



(Data from NACE Publication 59-10, 1958)

**Figure B.12—Corrosion Rate in H_2S/High H_2 Partial Pressure—
Liquid Shifted by a Factor of 6 Lower vs Vapor**



(from the *API Roundtable on Sulfidation*)

Figure B.13—Corrosion Rate in H_2S/H_2 Vapor—Low H_2 Partial Pressure (High H_2 Partial Pressure—All Vapor Curves Adjusted by Experience)

Annex C
(informative)

Corrosion Data for Carbon Steel Piping with Higher and Lower Si Contents

As explained in Section 9 and Annex A, there have been numerous incidents and investigations that have shown that low-Si carbon steels can corrode faster than higher Si containing carbon steels in the same environment. Figure C-1 is a curve plotting corrosion rate vs Si content for the failure shown in Figure 3 and Figure 4 in an FCC slurry piping system.

Figure C.3 and Fighre C.4 were created from several references listed below. Components were in service for many years in crude units, cokers, and FCC units. Many of the references did not provide quantitative corrosion rates, just a description of the corrosion: severe or minor. To generate the plot "Severe" was equated to 10 mils/year (0.25 mm/yr) and "Minor" was equated to 1 mil/yr (0.025 mm/yr).

Sources

1) Refin Cor™ [4] 94F5.17-01
2) Refin Cor™ [4] April 1966 T-8 Minutes—Fred Hame
3) Refin Cor™ [4] 2000C5.3-01:
4) N. Niccolls, 2005 Spring API Meeting Roundtable on Sulfidic Corrosion

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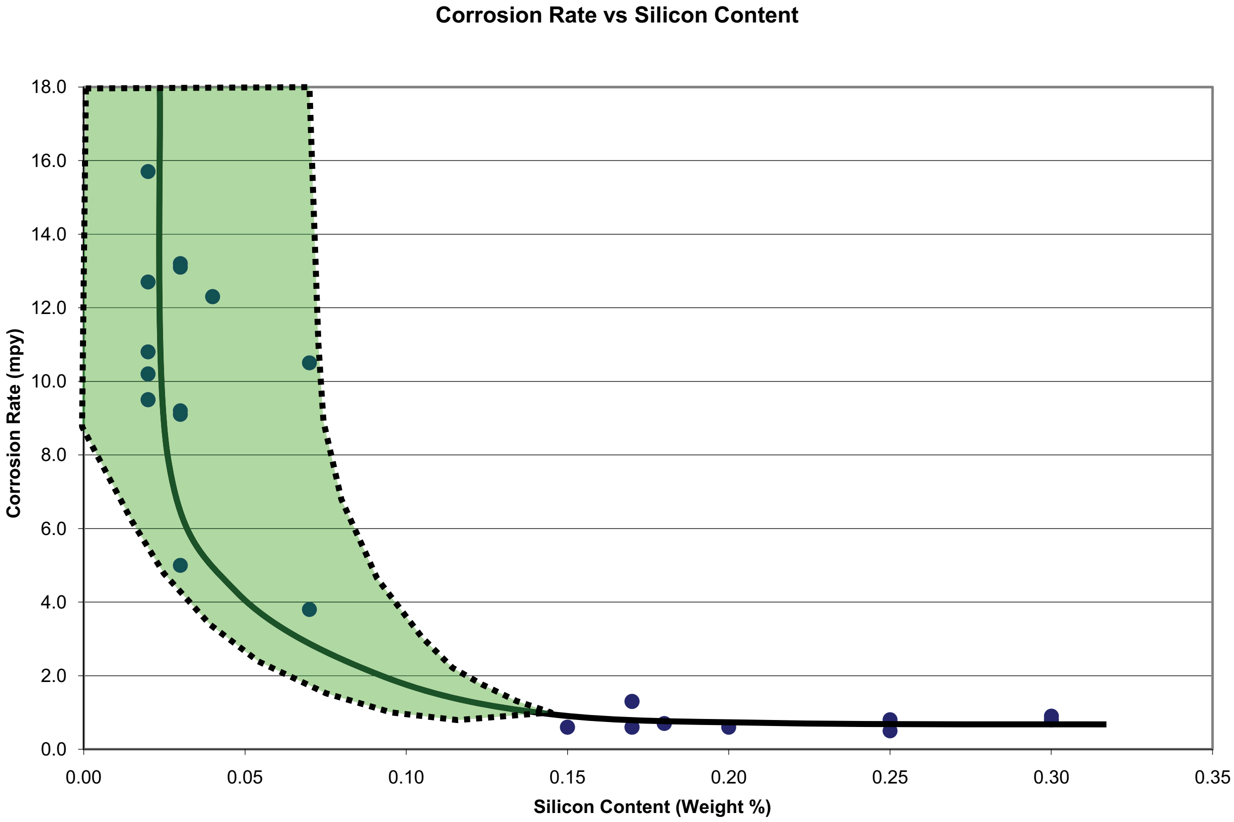
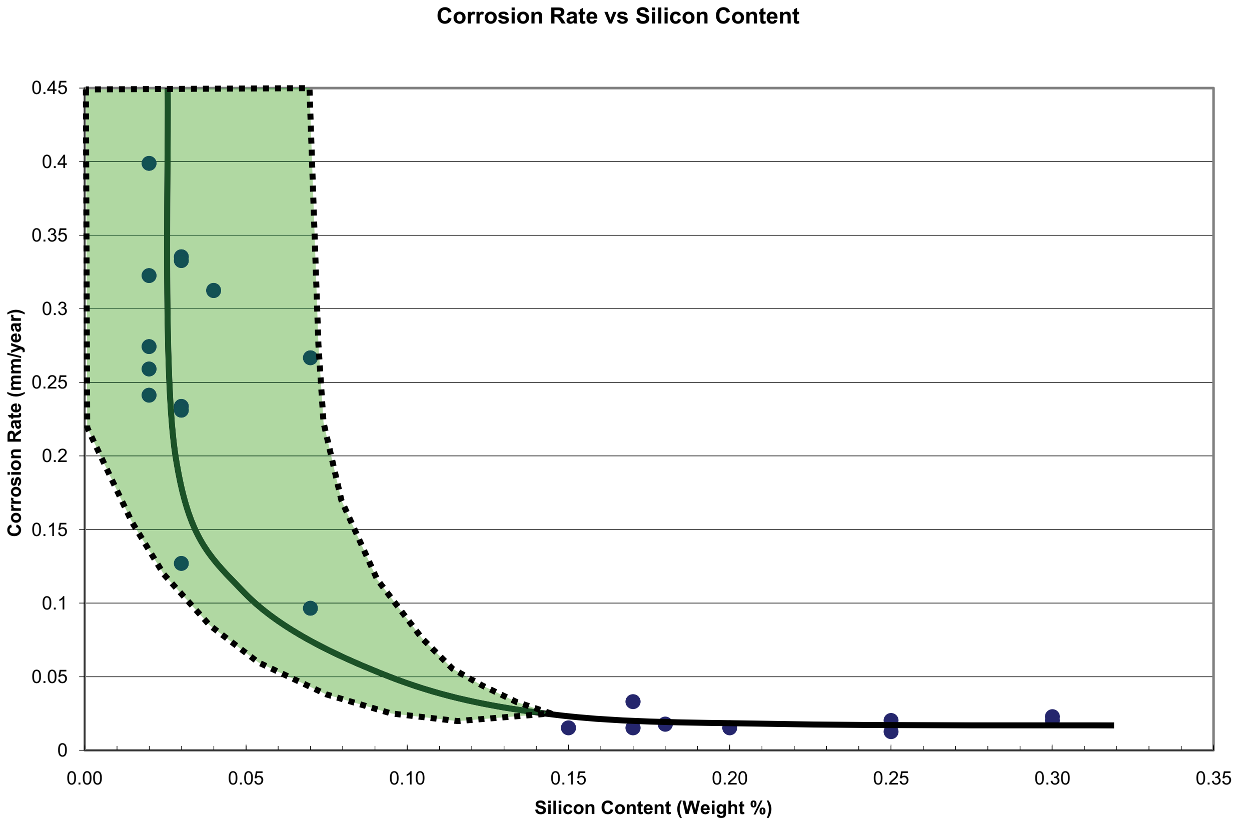
[4] This term is used as an example only, and does not constitute an endorsement of this product by API.



(Courtesy of BP)

Figure C.1—Corrosion Rate vs Si Content for FCC Slurry Carbon Steel Piping Failure
(Shown in Figure 3 and Figure 4),
(Operating Conditions: 150 psig and 650 °F to 700 °F)



(Courtesy of BP)

Figure C.2—Corrosion Rate vs Si Content for FCC Slurry Piping Failure (Shown in Figure 3 and Figure 4), (Operating Conditions: 1 MPa and 340 °C to 370 °C)

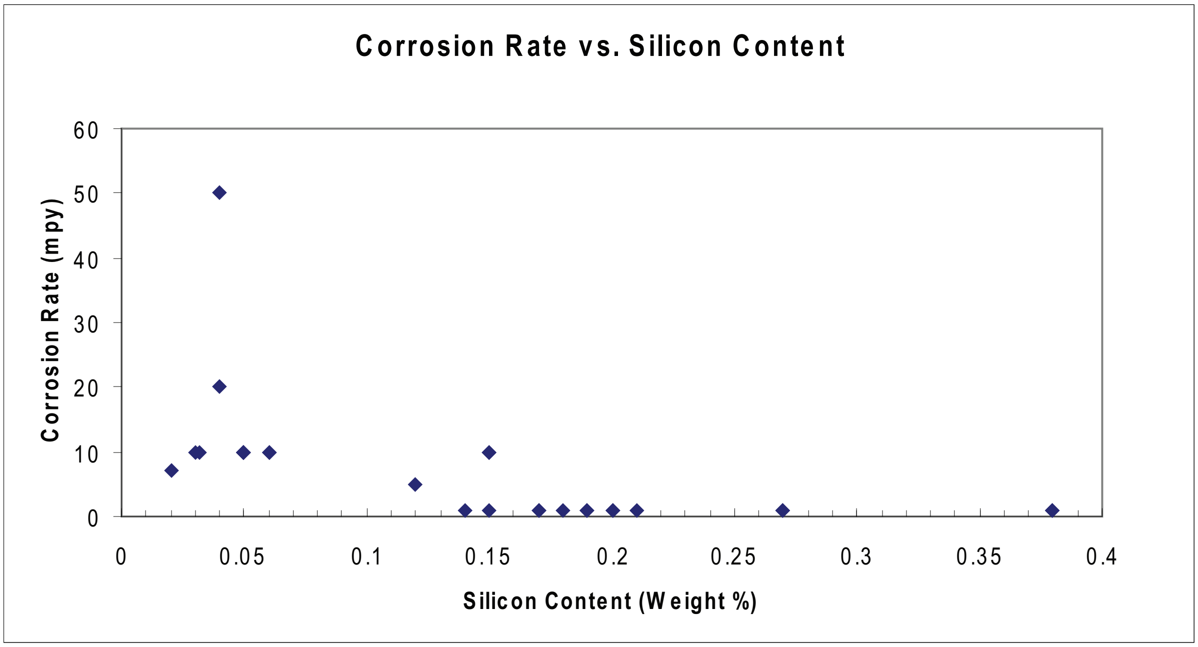
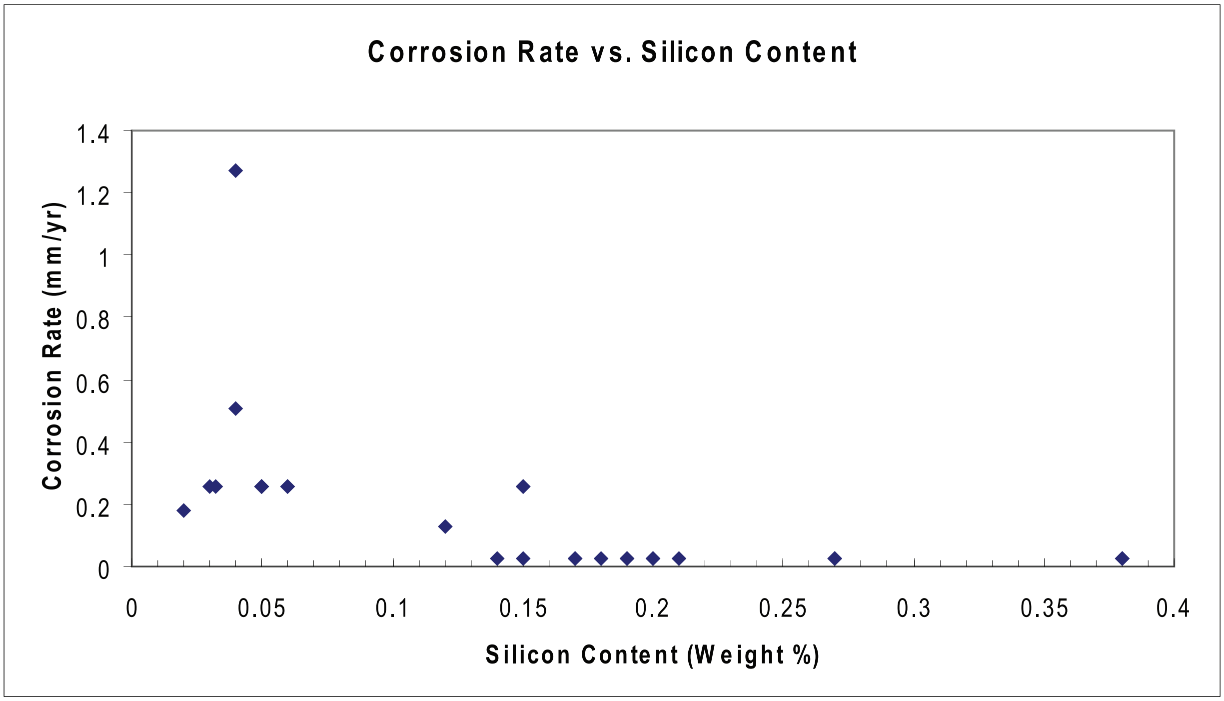


Figure C.3—Corrosion Rate vs Si Content for Various H_2-free Services



NOTE The only data point with the corrosion rate of 10 mils/yr (0.25 mm/yr) or higher at silicon content > 0.1 wt % was in a high velocity stream.

Figure C.4—Corrosion Rate vs Si Content for Various H_2-free Services

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[5] This term is used as an example only, and does not constitute an endorsement of this product by API.

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