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

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Introduction

Sulfidation corrosion, also often referred to as “sulfidic corrosion,” continues to be a significant cause of leaks in piping and equipment within the refining industry. The objective of this recommended practice (RP) is to provide a better understanding of sulfidation corrosion characteristics and give practical guidance to inspectors and maintenance, reliability, project, operations, and corrosion personnel on how to address sulfidation corrosion in petroleum refining operations. Examples of failures are discussed to highlight the common causes. The methods used to control and inspect for sulfidation corrosion are summarized. The data herein are 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.

There are two separate and distinct mechanisms of sulfidation corrosion. One occurs where H_2 is present in addition to the sulfidation-causing sulfur species, as is common in many refining processes, such as hydrotreating and hydrocracking. The other occurs in the absence of H_2 (hydrogen free) in processing units that do not employ H_2 as a component of the process. They both are non-aqueous, diffusion-based corrosion mechanisms that occur at elevated temperature. There is considerable debate in the industry as to the correct threshold temperature for hydrogen-free sulfidation, and in a change in this edition, the API 571 threshold of 500 °F (260 °C) for hydrogen-free services is adopted herein. Experience has shown that little significant corrosion will occur at operating temperatures below 500 °F for hydrogen-ree sulfidation services without the influence of naphthenic acid corrosion.

Common refinery units in which essentially H_2-free sulfidation corrosion can occur are the crude/vacuum, fluid catalytic cracker, coker, and visbreaker units. Hydroprocessing and hydrocracking units can experience H_2-free sulfidation corrosion in their feed sections before the hydrogen is introduced, and in their distillation sections downstream of where the hydrogen is removed. 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” and the minimum temperature is 450 °F (230 °C).

Included in this RP are:

— background to damage mechanisms,

— the most common types of damage observed,

— root causes of sulfidation corrosion,

— methods to predict and monitor the corrosivity of systems,

— materials selection for new and revamped processes, and

— 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 recommended practice.

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

1 Scope

This recommended practice (RP) is applicable to hydrocarbon process streams with sulfur-containing compounds, without the presence of hydrogen (H_2), which operate at temperatures above approximately 500 °F (260 °C) up to about 1000 °F (540 °C). There is considerable debate in the industry as to the correct threshold temperature for H_2-free sulfidation, and in a change in this edition, the API 571 threshold of 500 °F (260 °C) is adopted herein. Experience has shown that little significant corrosion will occur at operating temperatures below 500 °F (260 °C) for H_2-free sulfidation services without the influence of naphthenic acid corrosion. Mercaptan corrosion, particularly in condensate service, has been reported below this temperature but is not explicitly covered in the Second Edition of API 939-C. For H_2-containing services, the threshold temperature is set at 450 °F (230 °C).

A lower threshold limit for sulfur content is not provided because significant corrosion has occurred in the reboiler/fractionator sections of some hydroprocessing units (which do not contain H_2) at measured sulfur or hydrogen sulfide (H_2S) levels as low as 1 ppm.

Corrosion of nickel (Ni) base alloys in hot H_2S environments is excluded from the scope of this document. In addition, 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 documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any addenda) applies.

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

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

API Recommended Practice 578, *Guidelines for a Material Verification Program (MVP) for New and Existing Assets*

API 579-1/ASME [1] FFS-1, *Fitness-For-Service*, June 2007, Second Edition

API Recommended Practice 584, *Integrity Operating Windows*

ASME SA-516, *Specification for Pressure Vessel Plates, Carbon Steel, for Moderate- and Lower-Temperature Service*

ASTM A106/A106M [2], *Standard Specification for Seamless Carbon Steel Pipe for High-Temperature Service*

3 Terms, Definitions, Abbreviations, and Acronyms

3.1 Terms and Definitions

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

[1] ASME International, 2 Park Avenue, New York, New York, 10016, www.asme.org.
[2] ASTM International, 100 Barr Harbor Drive, West Conshohocken, Pennsylvania 19428, www.astm.org.

3.1.1
common corrosion system and circuits
Typically, the piping and equipment that is organized into corrosion systems, sometimes referred to as loops, that have similar expected damage mechanisms. A system may be the overhead system of a tower. A circuit is a subset of a system, and the term “common corrosion circuit” indicates that corrosion rates and other damage would be expected to have similar likelihood and would have similar process conditions.

3.1.2
hydrogen free
H_2 free
Processes where H_2 is not intentionally added. There may be trace amounts of H_2 present but are in services such as crude/vacuum units, fluidized catalytic cracking (FCC), cokers, etc.

3.1.3
integrity operating window
IOW
Established limits for process variables (parameters) that can affect the integrity of the equipment if the process operation deviates from the established limits for a predetermined amount of time. This documentation describes 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 IOW can also define process monitoring tasks to ensure that operating conditions are maintained within the established parameters.

NOTE Guidance on setting and using IOWs is given in API 584.

3.1.4
killed steel
Steel that has been completely deoxidized by the addition of an agent, such as Si or aluminum (or other methods such as vacuum treatment), before casting, so that there is practically no evolution of gas during solidification. Killed steels are characterized by a high degree of chemical homogeneity and freedom from porosity.

3.1.5
low-alloy (Cr-Mo) steels
Steels that contain 1 % to 9 % chromium (Cr) and 0.5 % to 1 % Mo (molybdenum).

3.1.6
low-silicon (Si) carbon steels
Carbon steels that contain less than 0.10 weight (wt) % Si.

3.1.7
material spec break or specification break
A change in metallurgy where carbon steel or alloys with lower alloy content are joined or mated up to a higher alloy content.

3.1.8
mils/yr or mpy
Corrosion rate expressed as thickness loss over a period of time. 1 mil/yr = 0.001 in./yr (40 mils = 1 mm). Often expressed as “mpy.”

3.1.9
reactive sulfur
Crude oil and fractions contain various sulfur compounds. Some are reactive and can cause corrosion, whereas others are not very reactive and do not cause corrosion. It is not the total sulfur content that is most critical in predicting corrosion, but the amount of reactive sulfur present.

3.1.10
sulfidation
Corrosion of metal resulting from reaction with H_2S, sulfur compounds, and/or sulfur-containing hydrocarbon molecules in high-temperature environments such that a surface sulfide scale forms. The term "sulfidic corrosion" is consistent with this definition.

3.2 Abbreviations and Acronyms

For the purposes of this document, the following abbreviations and acronyms apply.

AUT	automated ultrasonic testing
CDU	crude distillation unit
Cl^- SCC	chloride stress corrosion cracking
CML	corrosion monitoring location; formerly known as "TML" (thickness measurement location)
Cr	chromium
ERW	electric resistance welded
FCC	fluidized catalytic cracking
FCCU	fluid catalytic cracking unit
GWUT	guided wave ultrasonic testing
H_2	hydrogen
H_2S	hydrogen sulfide
IOW	integrity operating window
Mo	molybdenum
NDE	nondestructive examination
Ni	nickel
PMI	positive material identification
PTASCC	polythionic acid stress corrosion cracking
RT	radiographic testing (inspection), a.k.a. gamma ray or X-ray inspection
Si	silicon
SS	stainless steel
UT	ultrasonic testing (inspection)
VDU	vacuum distillation unit
XRF	X-ray fluorescence

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-containing organic compounds found in crude oil. When heated for separation, the various fractions separated from the crude were found to cause corrosion of the steel equipment as a result of reaction with the sulfur-containing compounds. With the advent of FCC and coking processes, 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 that typically involve the presence of H_2.

Empirical industry data as well as laboratory research indicate that the sulfidation corrosion rate is a function of a variety of factors, including temperature, the total sulfur concentration, the types of sulfur-containing compounds present, the type of process stream (e.g. light gas or heavy oil), the velocity, heat transfer conditions, the presence or absence of H_2, and the material of construction.

In the absence of H_2, corrosion due to sulfur-containing compounds typically is thought to occur at temperatures above 500 °F (260 °C). As discussed below, a set of curves called the “modified McConomy curves” [3] can be used to help predict corrosion rates in the absence of H_2. These curves show that at a given temperature and total sulfur level, steels with increasing Cr content [from carbon steel to 5Cr-0.5Mo to 9Cr-1Mo to stainless steel (SS)] will experience lower corrosion rates.

In the presence of H_2, i.e. H_2/H_2S corrosion, corrosion rate starts to increase above about 450 °F (230 °C). A different set of curves, known as “the Couper-Gorman curves,” [4] can be used to help predict the corrosion rate in this environment. These curves relate the amount of H_2S present with temperature to estimate the corrosion rate. While in H_2-free sulfidation, 5Cr-0.5Mo and 9Cr-1Mo have useful resistance, in H_2/H_2S sulfidation, there is little improvement in alloy performance until the Cr level reaches 12 wt %. In addition, materials such as 18Cr-8Ni stainless achieve a significant improvement in corrosion resistance over and above 12Cr wt % SS. Each crude oil or crude blend has its own characteristic chemistry, sulfur-containing organic 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 sulfidation corrosion rate experienced while processing a specific crude oil is very difficult.

In both H_2-free sulfidation and H_2/H_2S corrosion, the metal surface will form sulfide scales. These metal sulfide scales tend to slow down the sulfidation corrosion rate, since their formation tends to protect the underlying metal surface. In plain carbon steel, these will be iron sulfides, and in Cr-Mo steels, these will be chromium-iron sulfides. The Cr-based sulfides are more robust and protective than the plain iron sulfides, and the Cr sulfides will maintain their protection to higher temperatures and fluid velocities than iron sulfides.

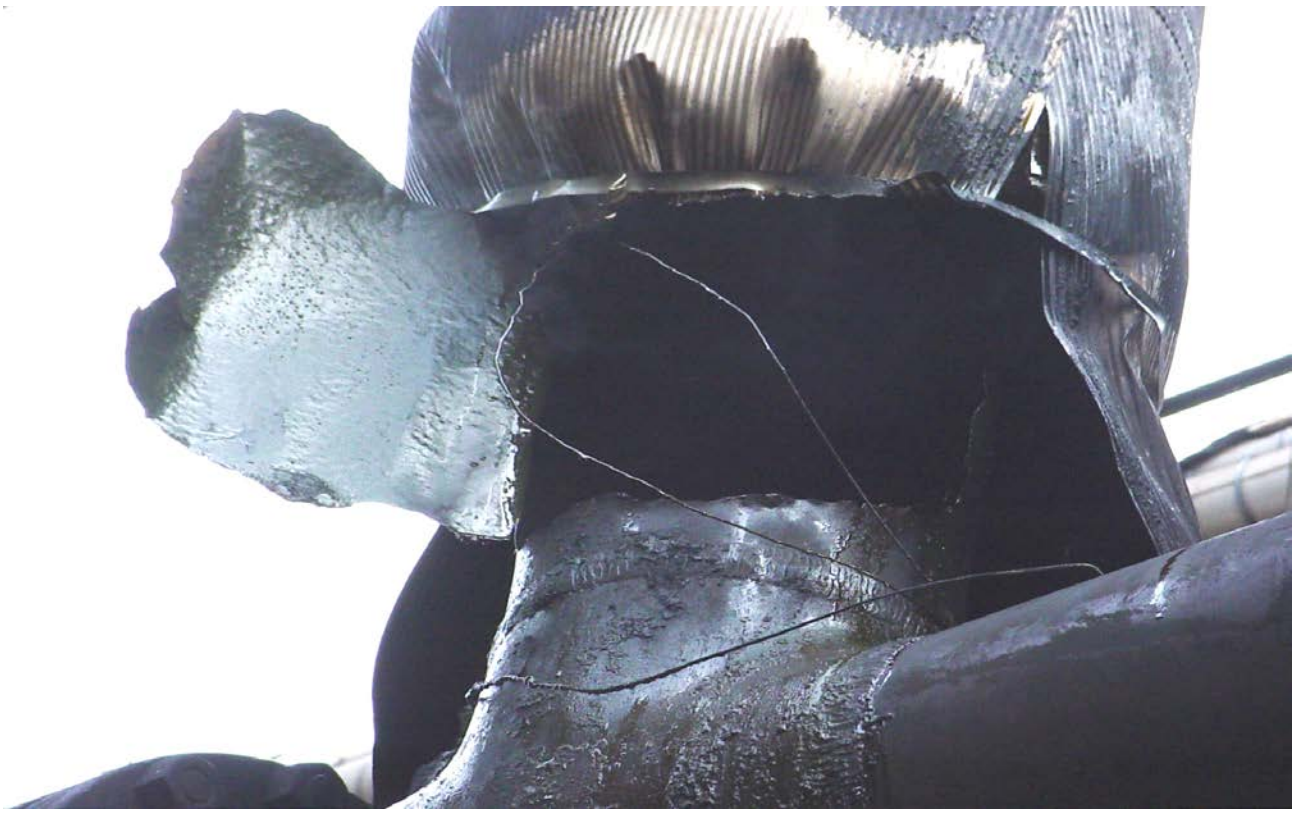
Sulfidation results in wastage of steel, resulting in loss of wall thickness of piping and components, heater tubes, and pressure vessels. Most industry sulfidation incidents have occurred in piping components, due to their thinner overall wall thicknesses and their higher population density vs other equipment types. Although sulfidation corrosion under certain circumstances can be isolated or 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 differences between local conditions and bulk conditions. As a result, because the nature of the corrosion is commonly general thinning, ruptures are possible instead of a pinhole leak. Ruptures can lead to the potential release of large quantities of hydrocarbons. Figure 1 to Figure 4 depict piping components that experienced H_2-free sulfidation corrosion.

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)

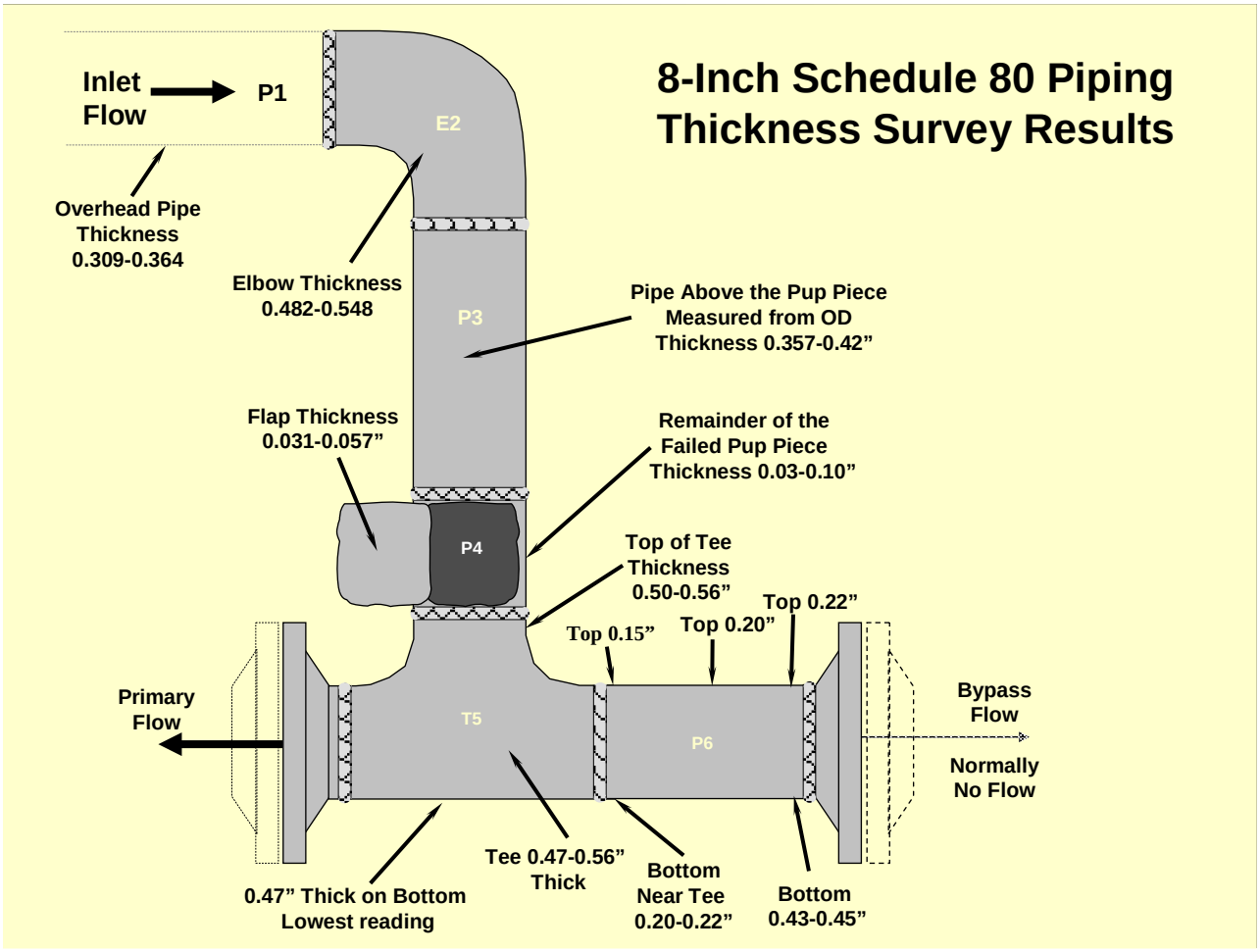
NOTE The carbon steel nipple (on right) corroded severely in 2 years in a crude unit (original thickness on left). It was specified as 9Cr-1Mo.

Figure 2—Corroded Carbon Steel Sight Glass Nipple



NOTE Also see the sketch in Figure 4.

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)



NOTE 1 1 in. = 25.4 mm.

NOTE 2 There may be a flow regime effect.

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)

5 Location of Sulfidation Corrosion

Sulfidation corrosion can occur wherever sulfur-containing compounds are present in a hydrocarbon stream and the temperature exceeds approximately 500 °F (260 °C). H_2/H_2S corrosion can occur above 450 °F (230 °C) 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 typically occur.

H_2-free sulfidation most frequently 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 H_2 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 several degrees of complexity in this section. First, the fundamentals are covered. Then the basic variables to consider in estimating corrosion rates and complicating factors that can, at times, cause high variability in corrosion rates are covered.

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.” It is often difficult to isolate the individual effects of naphthenic acids and sulfidation. A detailed discussion of the effects of naphthenic acids is 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. Naphthenic acid generally accelerates corrosion rates.

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-containing species with the metal surface. H_2-free services are defined as those in which H_2 is not intentionally added as part of the process.

Carbon steels and some low-alloy steels can corrode in H_2-free process streams in the presence of reactive sulfur-containing hydrocarbon compounds above about 500 °F (260 °C). Corrosion rates can be highly variable and difficult to predict. The basic and complicating variables below affect the ability to predict corrosion rates.

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. Between 450 °F (230 °C) and 500 °F (260 °C), experience has shown that sulfidation rates are extremely low (<1 mpy). The corrosion rate increases with temperature from 500 °F (260 °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 species, and formation of more stable iron sulfide scales. (See 7.3 regarding materials selection and this peak.)

In 1961, McConomy [6] developed corrosion rate vs temperature plots for several alloys. These curves represented average corrosion rates from industry data collected in the 1960s from non-desulfurizing and desulfurizing processes before H_2 addition, including fired heater tubes. In subsequent years, these curves were modified (lowered) by a factor of 2.5 because it was found that they were, in most cases, too conservative [3]. These newer curves are referred to as the “modified McConomy curves,” which are reproduced in Figure B.1 and Figure B.2. These curves have an adjustment for sulfur content. There is significant scatter in the data and other variables influence rates; thus, 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 Cr as an alloying element; the higher the Cr content of the steel, the lower the sulfidation rate, i.e. 9Cr-1Mo will corrode less than 5Cr-0.5Mo, 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 corrosion product scales formed on the surface of the metal.

While the McConomy curves cannot precisely predict corrosion rates, the curves are often successfully used to compare and predict the relative rates of corrosion for different steels, using the ratio of the rates predicted by the curves at a given temperature and sulfur content for the alloys of interest.

6.2.2.2 Sulfur Content and Speciation

The modified McConomy curves are based on a 0.6 % total sulfur 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 sulfur 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-containing species, including H_2S, mercaptans, polysulfides, thiophenes, aliphatic sulfides, and aliphatic disulfides, as well as elemental sulfur, [7] [8] and each has a different reactivity or effect 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 corrosivity 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 steel components and welds with low Si (<0.10 %) content can corrode at an accelerated rate when exposed to high-temperature sulfidation corrosion conditions. Refer to Annex C for data showing the relative corrosion rates of high- and low-Si-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-Si component. Figure 3 and Figure 4 relate to a failure where there were differences in Si content among the various components and welds. The lower-Si-content steel components corroded at a greater rate.

Commonly used grades of carbon steel seamless pipe and fittings used today (including ASTM A106 pipe, ASTM A234 fittings, and ASTM A105 forgings) all have a minimum required Si content of 0.10 wt %. Older forging specifications including ASTM A105 and ASTM A181 had no such requirements until 1995, and ASTM A53 piping still has no minimum Si requirement. In addition, ASTM A234 fittings do not require a minimum Si content if they are made from forgings. Since the advent of dual certification in the mid-1980s, most seamless carbon steel piping has been dual stamped “A53/A106,” meaning that it has 0.10 wt % Si required to meet the ASTM A106 specification. ASTM A53 piping that is longitudinally welded [electric resistance welded (ERW)] pipe is never dual certified, and even today it may be low Si.

There have been reports of accelerated corrosion of low-Si weld metal. These cases are rare and, with a few exceptions, have occurred mostly in non-U.S. refineries. This could be due to different welding practices and electrodes used in other countries. However, none of the 45 incidents reported in Section 9 were attributed to this phenomenon.

Although the case histories and test data to date on the effect of low Si content on carbon steel corrosion rates have been only in H_2-free environments, some users are including H_2/H_2S services in their special inspection programs, as discussed in 7.2.6. This is based on the theories on the corrosion reactions and protective scales, showing a possibility that the two mechanisms could be similarly affected by the Si content.

6.2.3.3 Velocity

Carbon and low-alloy steels form a sulfide scale in high-temperature 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), or the scale that is formed will be thinner and less protective, 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 is immediately eroded away, resulting in bare metal, which then encourages more scale to re-form and erode away further, thus resulting in severe metal loss. 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 in column bottoms, low velocity or long residence time can allow more H_2S to evolve. Long chain sulfur species could thermally crack to create H_2S that can increase the corrosivity of the bulk fluid. In relatively long, normally blocked-in lines, such as recirculation lines or start-up lines, thermal syphons can also occur, which can raise the temperature locally and exacerbate the corrosion. In addition to the long residence time possibly allowing more H_2S to evolve, the thermal syphon creates flow off the main line that can replenish the corrosive sulfur species in the thermal syphon zone, leading to higher-than-expected corrosion rates, particularly along the top of horizontal runs.

Another key factor appears to be whether the surface is liquid wetted or not, with higher rates expected if the surface is in contact with a vapor phase rather than a liquid phase (perhaps six times higher, see 6.3.3.1).

On typical liquid-filled lines with flow velocities of about 3 fps to 10 fps (1m/s to 3 m/s), corrosion rates will be somewhat higher at elbows, but corrosion will also be found on the straight runs.

6.2.3.4 Coking

Coke forming on the walls of piping and other equipment in general will reduce the rate of corrosion in non-heat-transfer components by isolating the steel or alloy surface from the sulfur compounds in the hydrocarbon fluid stream. An example of this is found in coke drums where in lower sections 12Cr cladding has cracked and or spalled off, but the shell did not corrode as severely as expected due to coke formation on the surface. Another example is in FCC reactor cyclones where corrosion is minimal in areas covered with coke. 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 Hydroprocessing Distillation Sections

6.2.3.7.1 General

This mechanism can occur with as low as 1 ppm H_2S and is not well understood. NACE Publication 34103 [9], published in 2002 and updated in 2014, 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).

6.2.3.7.2 Temperature and Alloy Content

The higher the temperature, the more corrosive the stream will be subject to a peak discussed in 6.2.2.1. NACE Publication 34103 [9] shows corrosion rates have approached or exceeded those found in H_2-containing

environments as depicted in the Couper-Gorman curves for various alloys. Depending on temperature, alloying to a minimum of 300 Series SS was needed to be resistant.

6.2.3.7.3 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.

6.2.3.7.4 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-0.5Mo, and 9Cr-1Mo 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. Carbon steels and low-alloy steels will corrode in the presence of H_2 and H_2S above about 450 °F (230 °C). An essential 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 SSs are the most commonly used alloys to obtain increased corrosion resistance in high-temperature H_2/H_2S sulfidation applications such as hydroprocessing units.

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 (230 °C). Corrosion rate increases with temperature. The 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 corrosion rates were different in gas oil and naphtha streams, and because of this, there are two sets of curves for each of these environments. 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 curves when estimating or trying to predict corrosion rates.

There is little useful improvement in corrosion resistance resulting from the use of higher-Cr alloy steels up through 9Cr-1Mo. Carbon steel through 9Cr-1Mo all can be expected to have similar corrosion rates. A useful improvement is obtained with 12Cr SS; however, the improvement is very sensitive to the Cr content, and if it is at the low end of the specified range, the benefit may be minimal. Also, the use of 12Cr is generally limited to non-pressure-containing components, such as vessel cladding, because of the risk of 885 °F (475 °C) embrittlement in 12Cr. The 300 Series SSs and higher alloys offer substantially improved resistance to high-temperature H_2/H_2S corrosion and are typically used in these services.

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 significantly affected 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 based on the curves when the metal surface is exposed to vapor instead of mixed phase (see Figure B.11 and Figure B.12) [10].

6.3.3.2 Effect of H_2 Partial Pressure

For H_2/H_2S systems, increasing H_2 concentration reduces the sulfur activity and tends to reduce corrosion rates [10].

This effect is not readily apparent when there are large levels of H_2 and H_2S present such as in the reaction section of hydroprocessing units. However, there is one theory of why increased corrosion rates are observed in the distillation sections of hydroprocessing units once the majority of the H_2 is removed, which is that H_2 actually reduces the corrosion rate, and without H_2 or with only small amounts of H_2, the reaction is greater. Another credible theory is known as “mercaptan reversion,” typically in the last catalyst bed in the hydroprocessing reactor.

6.3.3.3 Coking

Coke forming on the walls of piping and other equipment is not much of an issue in regard to H_2/H_2S 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, due to restricting the process fluid contacting the metal wall. However, several operators have reported increased corrosion rates after fired heater tubes experienced coking, which could be the result of increased temperatures.

6.3.3.4 Stripping Steam

Steam stripping and reboiling have the benefit of removing H_2S from a liquid stream, which minimizes downstream corrosion issues for the liquid stream in hydrotreater fractionator sections.

6.3.3.5 Velocity Steam

Velocity steam is often injected in to fired heaters to help avoid flow stratification and, in that regard, would be expected to be beneficial. The injection point itself would be an area for frequent thickness monitoring.

7 Practical Guidelines for Avoiding Sulfidation Corrosion Failures

7.1 General

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.

7.2 Existing Units and Components

7.2.1 General

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

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

Equipment operating at conditions under which H_2-free sulfidation or H_2/H_2S corrosion can occur must first be identified. Based on factors such as the anticipated corrosion rate, previous inspection results, and the consequences of a potential failure, an inspection plan should be developed consisting of an inspection date, scope, locations, method, and interval for follow-up inspection. A simplified inspection checklist is included in a new Annex E to help in guiding the inspection plan development. The following are some issues that may need to be considered when planning inspections.

— Increases in operating temperatures and operating severity in terms of H_2S levels, reactive sulfur levels, or increased vaporization over many years can lead to increases in corrosion rates.

— Sulfur-containing compounds can preferentially partition into certain streams from distillation columns; heavier streams may contain more sulfur than light streams, but these often contain less reactive sulfur species.

— Stratification in horizontal piping can cause uneven corrosion between the top and the bottom of the pipe. The top of the pipe may corrode more because of H_2S concentrating in the vapor. Low flow rate lines such as dead-legs to pressure-relief devices, bypasses of filters, heat exchangers, and control valves and lines thought to have no flow, such as blocked-in unit warm-up or heater recirculation lines, may be subject to thermal syphoning. They can suffer nonuniform corrosion, typically with the top of the line corroding at a faster rate than the bottom in horizontal runs off the main line. In these cases, a contributing factor to higher-than-expected corrosion rates may be the long residence time of the oil in the line allowing more H_2S to evolve. Also, if these lines are heat traced where temperature can exceed 500 °F (260 °C), this could contribute to unexpected high corrosion.

— In heater tubes, the tops of horizontal tubes may corrode more because of H_2S vapor liberation resulting from high heater box temperatures. 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. Finned tubes may operate hotter and corrode more than adjacent unfinned tubes.

— Vertical dead-legs can also be prone to higher corrosion rates due to chimney effects, leading to accumulation of higher concentrations of sulfidation corrosion causing species.

— 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 H_2 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 well above 800 °F (425 °C), where the sulfidation rate is relatively low (e.g. where the McConomy curves flatten and sulfidation rates decrease), the support can act as a cooling fin, bring the metal temperature back below 800 °F (425 °C), and increase sulfidation rates locally. The most common example has been in FCC reactor overhead lines.

— Specification breaks, i.e. where a higher alloy adjoins a lower alloy or carbon steel, can be a location of high corrosion rates. There is no “galvanic” effect, but if the spec break is not located appropriately, these locations can be areas where the lower alloy may be marginal with respect to corrosion resistance. This can be especially important in units where incremental process changes have increased operating temperatures to the point that the spec break is no longer in the proper location.

7.2.3 Perform Inspections

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

a) Conventional Methods

Straight-beam Ultrasonic Testing (UT). Straight-beam UT is a common nondestructive testing method used to measure wall thickness. Straight-beam UT thickness measurement applied at corrosion monitoring locations (CMLs) can be a highly effective technique to determine the rate of wall loss, provided repeat measurements are taken at exactly the same recording points with each CML and if the corrosion is relatively uniform, i.e. the localized examples highlighted above are not present. CMLs should be chosen taking into account the actual metal temperatures and other variables affecting sulfidation corrosion rate. Where localized corrosion is suspected, line or area scanning (corrosion mapping) UT, profile radiography (RT), or other nondestructive examination (NDE) scanning techniques should be used.

If UT wall thickness measurements are taken on equipment at elevated temperatures, special probes, couplants, and calibration techniques should be used to optimize UT accuracy. Ultrasonic sound velocity decreases as the temperature increases; therefore, compensation in UT thickness measurements is needed to ensure accuracy of wall measurement. Properly qualified procedures and technicians are required if UT thickness measurements are to be taken at elevated temperatures. 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 operating temperature right after start-up, to improve the accuracy of temperature correction factors and so that subsequent in-service readings can have a better basis for comparison.

Some UT instruments used for thickness measurement provide temperature compensation. This feature allows the operator to dial in the surface temperature where the wall thickness measurement will occur. The material velocity value in the UT instrument is automatically compensated for, based on the temperature entered, resulting in temperature compensated thickness measurement.

Some database software used for storing and managing thickness measurements have temperature compensation features. Caution should be taken to prevent double compensation, e.g. by the thickness measurement UT instrument and within the database software.

Permanently installed UT monitoring systems (PIMS) use a fixed UT probe that sends real-time frequent measurements. They can be very useful in detecting changes in corrosion rates as a result of process changes, including feedstocks.

Radiography (RT). RT is a very common nondestructive technique and is highly effective for detecting wall loss. RT can provide a cross-sectional view of pipe thickness, which is commonly referred to as “profile RT.” Profile RT can be used on insulated and non-insulated components. Although not a major concern, RT is the preferred method to detect weld root preferential corrosion.

b) Other Methods

Other commercially available techniques that can and are being used to detect sulfidation include the following listed below. Each technique has its advantages and disadvantages. Hence each application should be used advisedly with input from NDE subject matter experts.

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, i.e. 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 handheld devices can also be effective for measuring the local wall thickness.

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 field and measuring perturbations in the field to derive a wall thickness. Some companies apply the pulsed eddy current tool more for screening than for precise measurements and then follow up with other techniques like UT straight-beam or profile RT. Similar to RT scanners, an advantage is that insulation does not need to be removed in order to perform this inspection.

UT Mapping or Automated Ultrasonic Testing (AUT). UT wall thickness measurement can be performed by mechanized scanners. Such scanners use encoders to track the UT transducer's position and wall thickness measurements. The wall thickness measurements are illustrated as a map (C-Scan Plot View) using coordinates of the UT probe position and wall thickness illustrated in color. Using mechanized UT scanners on elevated and freezing surface temperatures can be challenging.

Guided Wave Ultrasonic Testing (GWUT). There are several types of GWUT methods available. In some cases, detection of anomalies up to 150 ft (46 m) away from the UT sensor ring can be achieved. GWUT sensors must have direct contact with the pipe. If piping is insulated, a small area must be stripped of insulation to attach the sensors. GWUT is affected by coating condition, OD surface scale, numbers of elbows and welds, etc. Inspection surface temperatures are limited for some GWUT equipment. Given the uniform nature of sulfidation corrosion, GWUT inspection techniques are not recommended because GWUT relies on sudden volumetric changes to provide an indication (reflection). This method is primarily used to detect welds for positive material identification (PMI) and low Si inspection programs.

Smart Pigs for Heater Tubes and Piping. There are several types of pigs that can be used to measure wall thickness of heater tubes. Such pigs travel through the tube while taking continuous UT thickness readings. Tubes typically need to be cleaned prior to the inspection, and there are limitations on bend radius.

7.2.4 Evaluate Thickness Readings

Thickness readings should be grouped by common corrosion circuits (per the method indicated in API 570) and evaluated for trends in corrosion rates. Additional readings may be needed if the remaining thickness is approaching the minimum required thickness. Once a component is noted as approaching the minimum required thickness, techniques included in API 570, API 574, and API 579-1/ASME FFS-1 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 ensure that the estimated future corrosion rate is not exceeded.

7.2.5 Perform Retrospective PMI/Verification

Many refineries have instituted retrospective PMI programs (see API 578) for alloy piping systems and equipment. Methods vary, but some programs include stripping all insulation in order to locate every butt weld and, therefore, every piece of pipe. Others have used RT methods or long range GWUT 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 (XRF) types of analyzers. They can be used online or during downtimes to determine alloy content of the outside weld bead and the base metal of the pipe or fitting adjacent to the weld.

If these instruments are to be used to confirm the Si content of carbon steel (see 7.2.6) and low-alloy steels, they should have the sensitivity to determine that the Si meets the ASTM minimum specification limit. The latest generation of handheld XRF analyzers or optical emission spectrometer (OES) is reported to be able to measure light elements (magnesium, aluminum, silicon, phosphorus, and sulfur) to very low limits of detection (LODs) and can provide for field measurement of Si in steel down to a concentration of 0.03 %. Advancements in XRF technology, such as 50KV, X-ray tubes, and silica drift detectors (SDDs), allow the user to detect light elements down to very low concentrations in steel substrates. These advancements allow for accurate, nondestructive measurements to be made. In order to get this near-laboratory-quality measurement, very

careful surface preparation is required in order to eliminate the possibility that any surface contamination that might show up in the analysis as falsely high Si content. Most piping systems and equipment are exposed to the atmosphere and have surface corrosion that interferes with the analysis. Typically, a small area of the surface areas is treated with a portable grinding disk [60 to 80 grit zirconium aluminum oxide 2-in. (51-mm) disposable abrasive disk] to properly clean the sample location prior to analysis.

Refer to API 578 for material verification and PMI recommended practices. 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 installation of carbon steel at temperatures exceeding 500 °F (260 °C) for H_2-free services and 450 °F (230 °C) for H_2/H_2S services without confirmation that carbon steel (base metal and welds) contain 0.10 wt % Si (min). For alloy piping (and associated welds), it should be verified that base metal and weld metal chemistry are the proper alloy. 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.

7.2.6 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 wt %) content can corrode at an unpredictable and often accelerated rate when exposed to sulfidation corrosion conditions in either H_2-free service or H_2/H_2S service. Fittings usually have higher Si content (with the exception of ASTM A234 forged fittings, which have no minimum Si specification), while piping is the most likely component to have low Si content. Typically, carbon steel pipe fittings (elbows and tees) and flanges are manufactured with at least 0.10 % Si.

A potentially low Si system is any carbon steel pipe system where the line class sheets or construction drawings indicate that ASTM A53 or API 5L Grade B piping was allowed (i.e. not specifically disallowed). Before the mid-1980s, it was much more common that ASTM A53 or API 5L Grade B were used. By the mid-1980s, most refineries called for ASTM A106 carbon steel piping (0.10 wt % Si minimum). By the mid-1980s, ASTM A106 carbon steel piping was usually dual certified (usually triple stamped) as “ASTM A106/ASTM A53/API 5LB.” This means that the chemistry of ASTM A106, with minimum 0.10 % Si, was specified; therefore, sulfidation rates will be lower than with ASTM A53 or API 5L (Grade B), which do not specify the minimum 0.10 % Si for welded pipe. Triple-certified material is the common practice now.

It has been reported that in older carbon steel pipe systems (pre-1985) where Si is less than <0.10 wt %, corrosion rates due to sulfidation are highly variable. For piping that has been in service long enough to experience a measurable sulfidation corrosion rate, a thickness check of every component should be performed to identify those that are corroding the fastest. CMLs can then be adjusted to ensure that the locations that are corroding the fastest are being well monitored. Most companies measure thickness and do not try to measure the Si content in older carbon steel piping systems, because it can be difficult to quantify Si content accurately under field conditions.

A few 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 (<0.10 wt %Si) steels were procured and will try to locate the low-Si spools. In such a case, PMI may be considered to confirm that the installed material is what the material test report (MTR) states and identifies. Some field-portable PMI instruments can measure low Si concentrations and can distinguish between high- and low-Si-containing steel; however, because of the difficulties with surface prep and the fact that not all low-Si steels will corrode faster, most companies strongly favor direct thickness measurements instead of chemistry determination.

Insulation (if present) can be completely removed to expose every weld such that each component can be examined 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. If service time is short or if conditions are mild, corrosion may not be observed in any of the inspected components. Under these circumstances, thickness gauging may not reveal low-Si components even if they are present. Thus, future reinspection or confirmation of Si content may be advisable for these systems.

There are some more practical ways to do the baseline thickness checks than stripping all insulation. For example, one could use an X-ray imager to find welds and then cut round holes in the insulation to check each piping segment.

The issue of whether welds need to be inspected for thickness has not been resolved at this time. The ID root pass chemistry cannot be measured in most piping. The number of occurrences of weld preferential corrosion that is not associated with FCC slurry or other erosion services has been few in the industry. Many users have chosen not to inspect for this condition due to the perceived lower risk of failure (likelihood being low and the consequences being less severe with a small leak expected vs the base metal of piping with generally larger thinned areas that could lead to much larger releases).

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 Si 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).

7.2.7 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 sulfur content limits. An IOW [11] also defines sampling and monitoring requirements.

For new units it is advisable to create IOWs per API 584 to guide future operation. For new components in an existing unit, the IOWs should be reviewed and modified if needed. To operate any process unit, a set of operating ranges and limits needs to be established for key process variables, to achieve the desired results (e.g. product within specification, safe operation, reliability). These limits are generally called “operating limits” or “operating envelopes.” IOWs are a specific subset of these key operating limits that focus only on maintaining the integrity or reliability of process equipment. Typically, IOWs address issues that involve process variables that can impact the likelihood and rates of damage mechanisms. [12] For sulfidation services, IOWs are often based on a combination of experience with the crude slate and industry prediction curves.

7.2.8 Institute Corrosion Monitoring and/or Permanently Installed UT Monitoring Systems

Corrosion probes can be used to better understand the sulfidation corrosion behavior of a 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 element probes instead of wire loop element 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 and high-pressure services. Retractable probes require more elaborate access fittings, and there is always a safety concern when retracting or inserting probes during unit operation. Manufacturer’s safety warnings and procedures should be followed.

The probes can be outfitted with local recorders, 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 to obtain reliable data. Ideally, monitoring data are combined with the crude or stream composition and levels and types of sulfur compounds to trend these factors with observed corrosion rates. Although strictly not corrosion probes, permanently installed UT monitoring systems can be very useful in monitoring the effect of process condition and feedstock changes on the corrosion rate [see 7.2.3 a)]. There are also extremely sensitive H_2 probes temporarily attached to the OD that can in some cases detect high-temperature corrosion such as sulfidation and naphthenic acid attack.

7.2.9 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 of carbon steel. At this time, however, inhibitors are not typically used to control sulfidation corrosion.

7.2.10 Replace or Upgrade the Material

If sulfidation corrosion is occurring or future operating conditions will be more severe than in the past, upgrading to a more sulfidation-corrosion-resistant material or replacing the material in-kind (perhaps with a thicker material) should be considered. It is preferable to specify more highly alloyed metals for better corrosion resistance to minimize the reliance on inspection vs doing in-kind replacements (even with a thicker material). In-kind replacements rely on frequent inspections and are, therefore, not considered an optimal solution. Relying on inspection when corrosion rates are predicted to be high is also considered a poor long-term solution.

7.3 New and Replacement Components

7.3.1 Materials Selection Guidance for New and Replacement Equipment

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, the peak in corrosion rate at 800 °F (425 °C) for H_2-free services is rarely taken into consideration to allow lower alloys above this peak. Material selection and replacement materials should also consider any planned future process temperature or severity increases and/or the anticipated duration of potential abnormal operation periods (upsets, IOW exceedances, etc.) if known.

An appropriate corrosion allowance is added for the anticipated sulfidation corrosion rate at the maximum operating temperature. During design, some companies apply conservative measures (e.g. adding safety factor on operating conditions, increasing corrosion allowance) to provide greater confidence that the component will meet its design life 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.

7.3.2 H_2-free Services

Where no prior experience or information is available on a crude or its derived fractions, 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, with 0.6 wt % total sulfur environments. These selections could vary depending on sulfur species, hydrocarbon phase, flow regime, and the other operating variables discussed in 6.2.

— Some users now specify 9Cr-1Mo or higher Cr alloys for sulfidation service above 500 °F (260 °C) when carbon steel is considered to have too high of a corrosion risk. Previously, many would have used carbon steel and 5Cr-0.5Mo, but because of industry incidents with carbon steel, as well as the amounts of Cr trending toward the lower end of the specified limits for more recently manufactured 5Cr-0.5Mo materials, many users no longer specify 5Cr-0.5Mo for new installations. In addition, 9Cr-1Mo generally provides more than double the useful life in high-temperature sulfidation compared to 5Cr-0.5Mo.

— 300 Series SS can also be used to virtually eliminate sulfidation corrosion; however, they are prone to stress corrosion cracking such as polythionic acid stress corrosion cracking and chloride stress corrosion cracking and are more prone to thermal fatigue.

7.3.3 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 450 °F (230 °C), 300 Series SS are typically the preferred choice because of high predicted corrosion rates with lower-alloy steels. 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.

7.3.4 Heater Tubes

For heater tube material selection for corrosion avoidance, the design should assume a metal inner film temperature of at least 100 °F (55 °C) higher than the process outlet temperature. This temperature difference varies based on coking tendency (which is related to the internal tube metal temperature and fluid type) and heater design. If there is a maximum tube metal design temperature, that temperature can be used, but the one needs to remember that a temperature above the peak of about 750 °F to 800 °F (400 °C to 425 °C) may be less corrosive and non-conservative.

7.3.5 Linings or Cladding

Linings or claddings of “higher alloys” are often used in heat exchangers, drums, and towers. Use of linings or claddings is especially advantageous in high-pressure services that require thick wall components.

7.3.6 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 seamless piping today is triple stamped and meets ASTM A106, ASTM A53, and API 5L (Grade B). Most refineries do not allow single-stamped ASTM A53 pipe to be used. Pressure vessels are typically made of ASME SA516 steel, which contains a minimum of 0.15 % Si per heat analysis.

7.3.7 Scaling

Many companies specify materials to limit the corrosion rate to below 10 mils/yr (0.25 mm/yr) 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 small diameter areas, such as reactor beds, instrumentation, etc. Furthermore, iron sulfide deposits can be pyrophoric and prone to catching fire during downtimes.

7.3.8 Material Specification Breaks

Care must be taken to critically examine all material specification breaks. Many of these piping class changes result from sulfidation corrosion concerns. For example, the bypass piping around an exchanger that has carbon steel inlet piping and SS outlet piping will have a piping class change that needs to be carefully designed. Good practice is to use the higher alloy content for the bypass piping.

7.3.9 PMI Program

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

8 Limitations of Current Knowledge Base

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 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 [13], 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 H_2 on the corrosion rate; and

— 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 [15] in the period of 1984 through 2001 involve sulfidation corrosion. To prepare this document, industry sources, such as NACE STG 34 Refining Industry Corrosion Committee meeting minutes and the API Subcommittee on Corrosion and Materials meeting minutes, were reviewed for publicly reported incidents of sulfidation corrosion [16] [17]. In addition, a survey was conducted in 2005 to identify additional incidents to assist in the preparation of this RP.

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 seamless carbon steel piping materials available in North America are typically triple stamped ASTM A106/ASTM A53/API 5L and contain greater than 0.10 % Si. However, older (pre-1985) ASTM A53 seamless piping and modern welded 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 can be 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 mm/yr to 0.08 mm/yr), can result in depletion of the corrosion allowance, with further thinning continuing unrecognized until rupture of the line occurs after many years. Section 7 discusses inspection practices specific to low-Si-containing carbon steels.

The chart also highlights the importance of PMI. API 578, first published in 1999, provides 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 used 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.

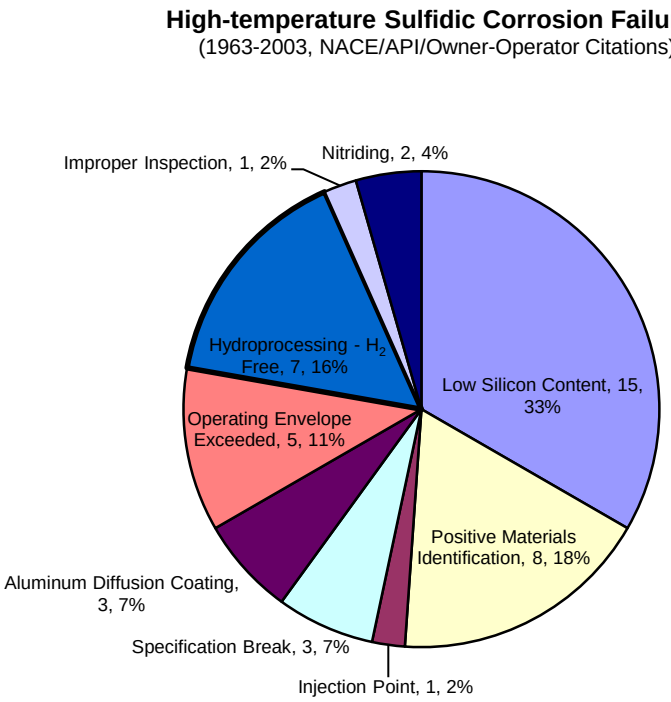


Figure 5—Summary of Reported Failures by Type, Number of Reported Instances, and Percentage of the Total

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 summarizes the root cause of failures, as reported in NACE Refin-Cor™ 7.0 [16], API minutes [17], 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 leaks in 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 alloyed 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, H_2 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 mix point and injection point inspections are outlined in API 570 and in NACE SP0114 [18].

— *Operating Envelopes (IOWs)*. 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. Guidelines for IOWs are found in API 584.

— *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 universally accepted theory or explanation for the higher-than-anticipated corrosion rates at the very low sulfur levels.

Annex B
(informative)

Sulfidation Corrosion Prediction Tools

B.1 General

Sulfidation corrosion is defined as a degradation mechanism that forms sulfide corrosion products, leads to metal loss, and occurs upon exposure of metals to temperatures above approximately 450 °F to 500 °F (230 °C to 260 °C) in liquids and gases containing H_2S or other reactive sulfur species at concentrations greater than 1 ppm. With H_2-free sulfidation, elemental sulfur or sulfur-containing organic compounds (i.e. polysulfides, aliphatic sulfides and aliphatic disulfides, and mercaptans) are considered to have an impact on the overall sulfidation rate. H_2S 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 sulfur in the sulfur-containing molecule into H_2S, followed by the reaction of the H_2S with the iron in steel alloys. Typically, sulfur speciation is not conducted on crude oils or process streams on a regular basis. Instead, wt % total sulfur is provided. Since the total sulfur content is comprised of many different sulfur-containing compounds that can react at varying rates, corrosion prediction based upon wt % 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 (230 °C) (for H_2/H_2S services) and 500 °F (for H_2-free services) to 800 °F (260 °C to 425 °C). Plant experience indicates that corrosion rates begin to decrease above 800 °F (425 °C).

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

— For H_2-free streams, the modified McConomy curves are used. These curves were first published in a paper by Gutzeit [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.

— For H_2/H_2S-containing streams, the Couper-Gorman curves [4] are used. 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 H_2 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.

B.2 Other Tools

1) 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 specialty analytical work.

2) 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.

3) One refiner believes that with all other factors being equal, the corrosion rate can be up to six times higher for vapor vs mixed phase corrosion (Figure B.11 and Figure B.12 show that all vapor H_2/H_2S corrosion is more aggressive than with a mixed vapor/liquid phase present). This refiner also believes that at low H_2 content, the sulfur 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 H_2 stream (compare Figure B.13 with Figure B.11).

4) 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 are available.

5) A joint industry project (NACE paper 2012-0001564) [14] has developed software that gives corrosion rate estimates in hydrocarbon streams due to sulfur and naphthenic acids in H_2-free environments.

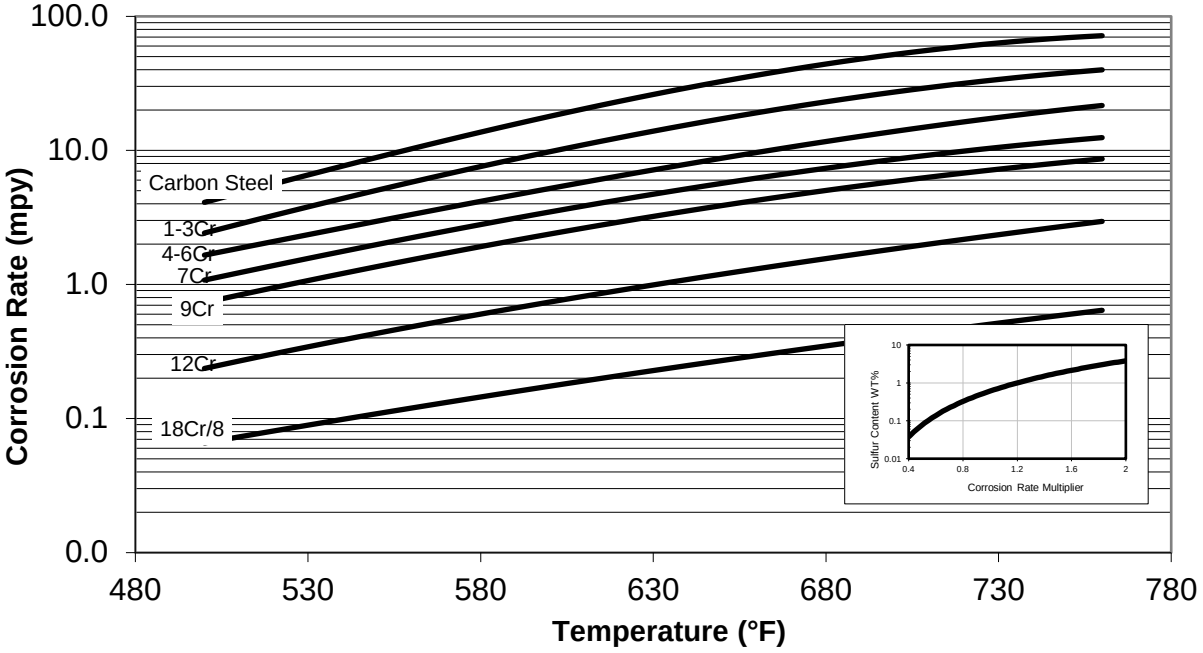


Figure B.1—Modified McConomy Curves (0.6 % Sulfur Content) (USC Units)

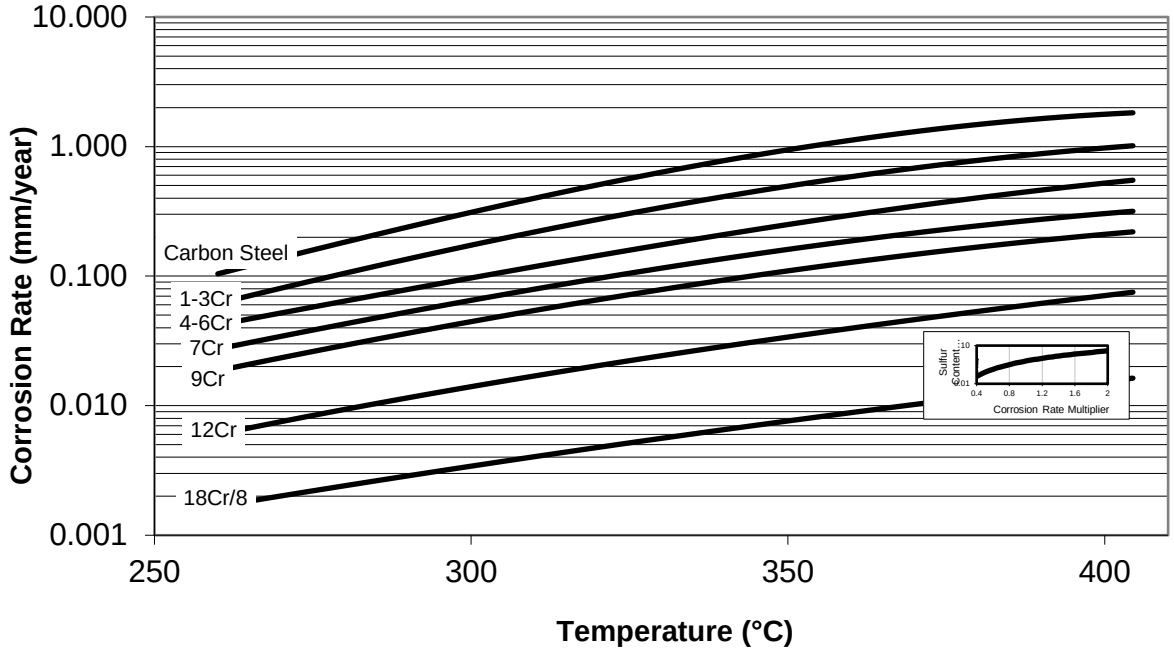
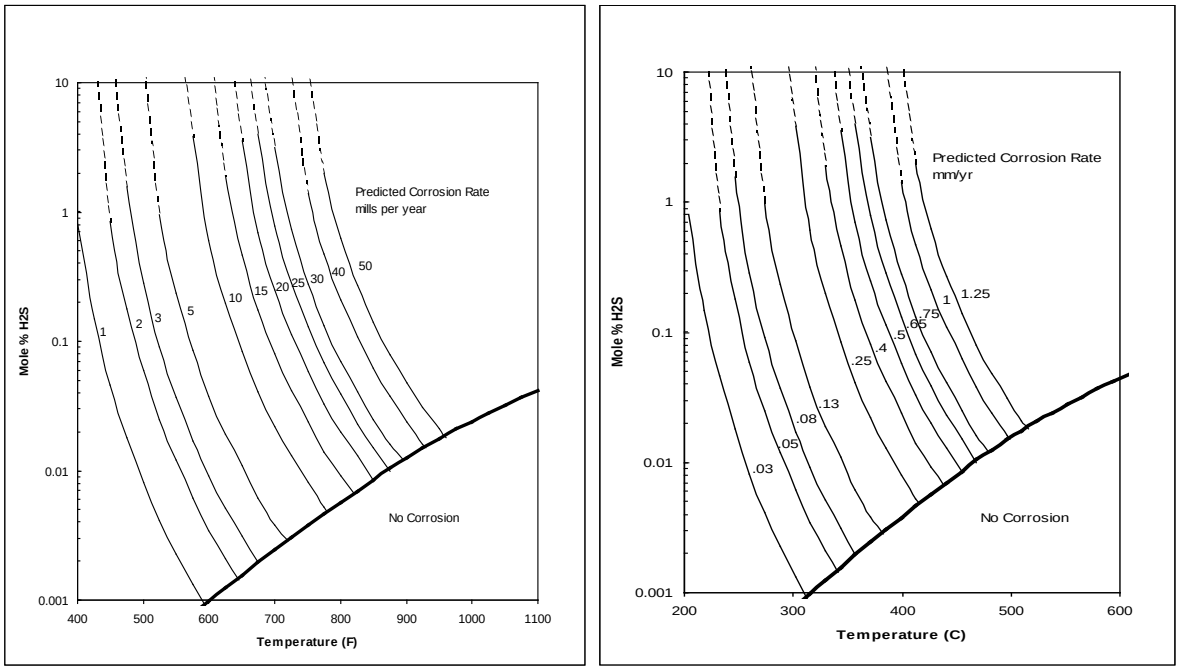
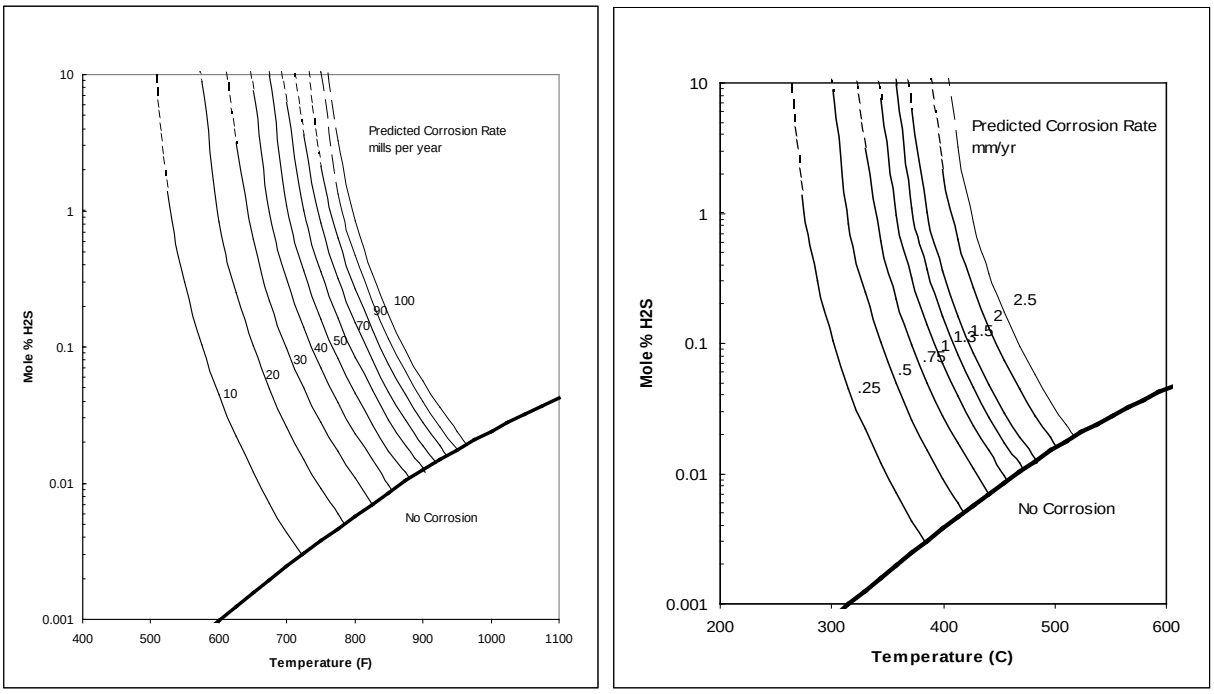


Figure B.2—Modified McConomy Curves (0.6 % Sulfur Content) (SI Units)

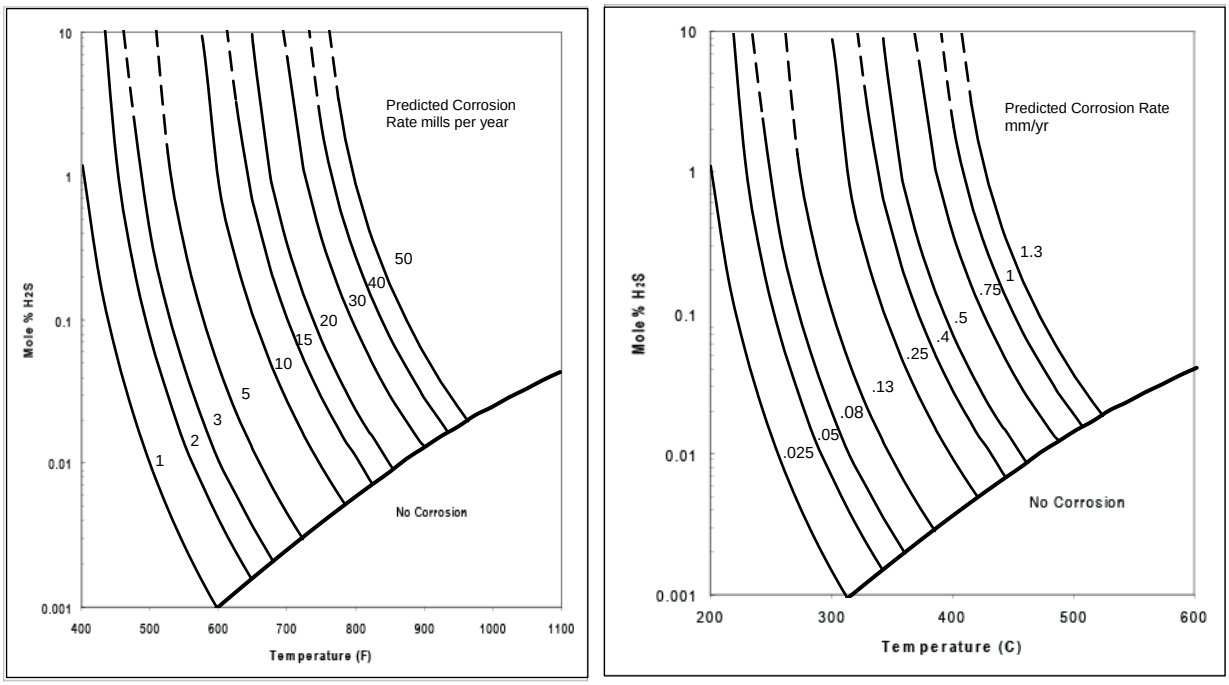


Carbon Steel Naphtha

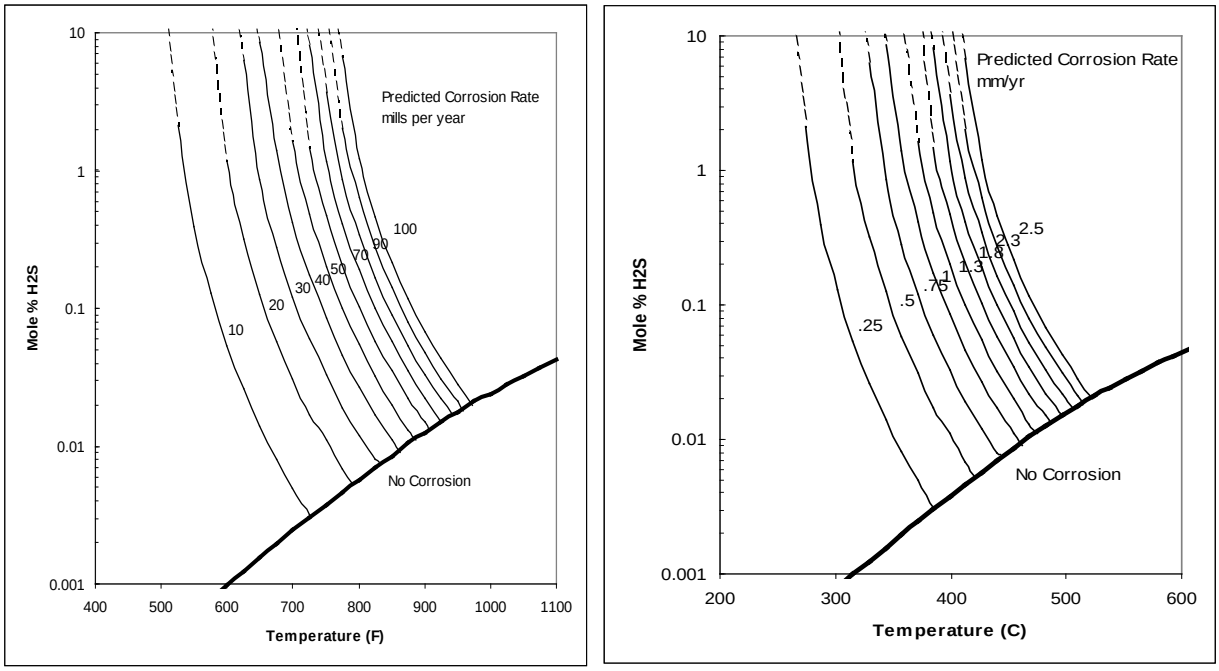


Carbon Steel Gas Oil

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

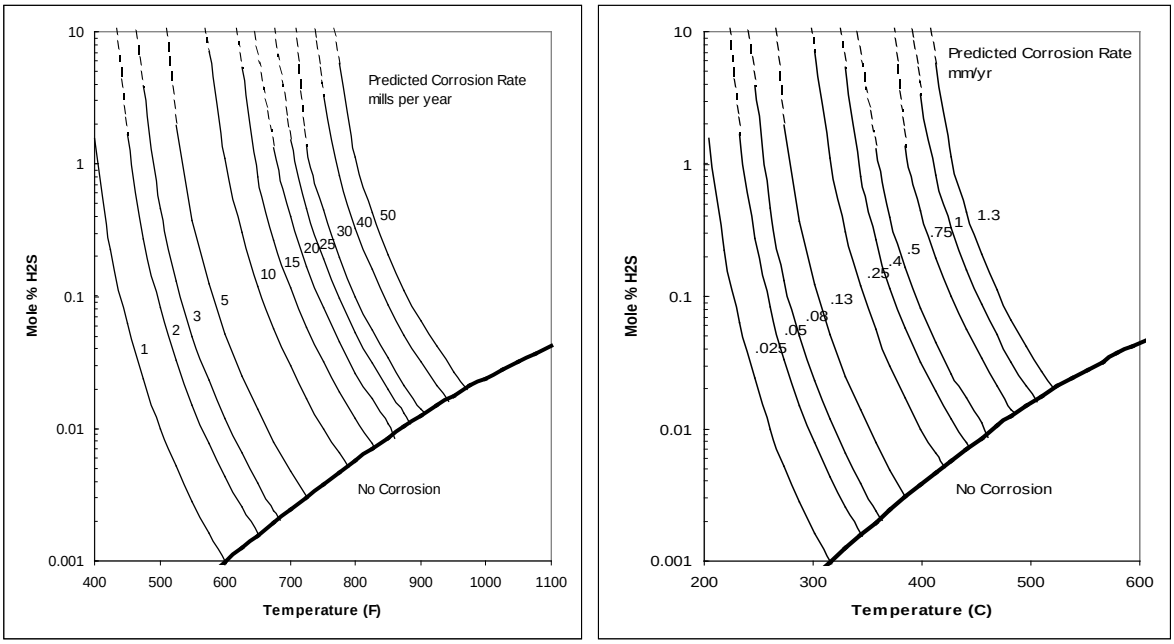


1.25Cr-0.5Mo Naphtha

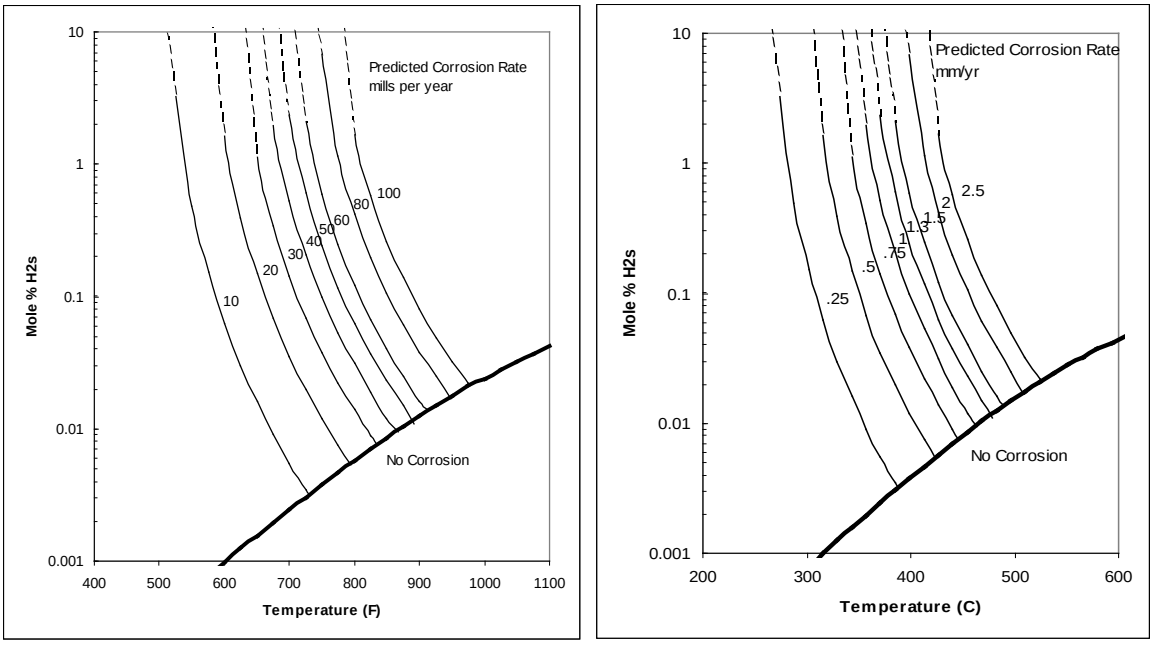


1.25Cr-0.5Mo Gas Oil

Figure B.4—Couper-Gorman H_2/H_2S Curves for 1.25Cr-0.5Mo Steel for Both Naphtha and Gas Oil

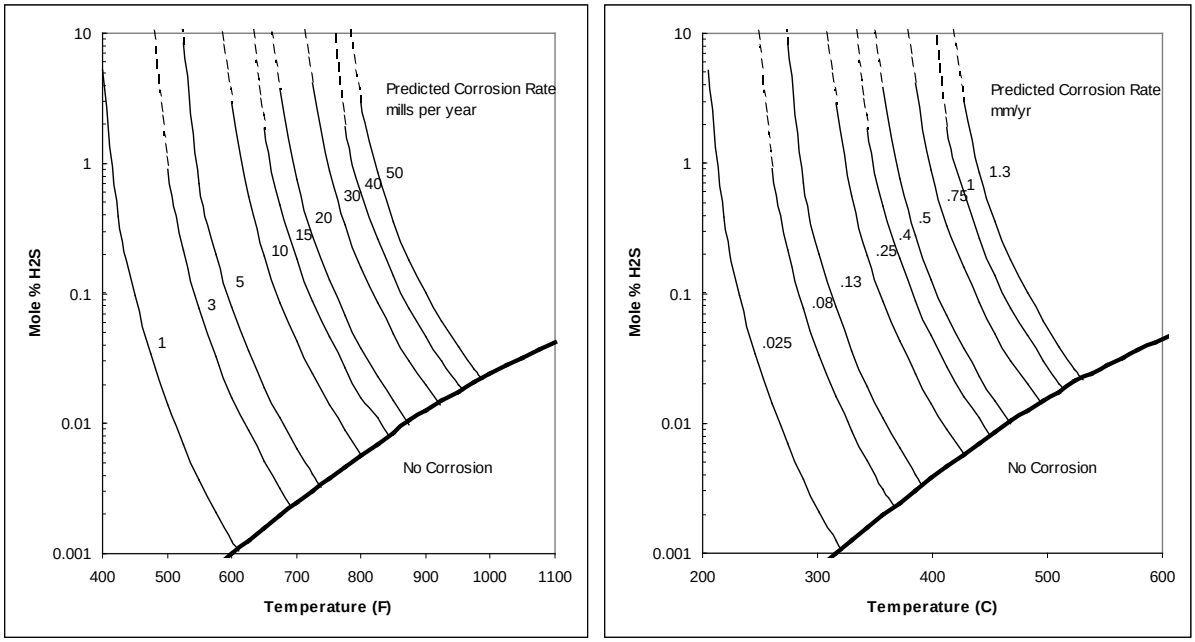


2.25Cr-1Mo Naphtha

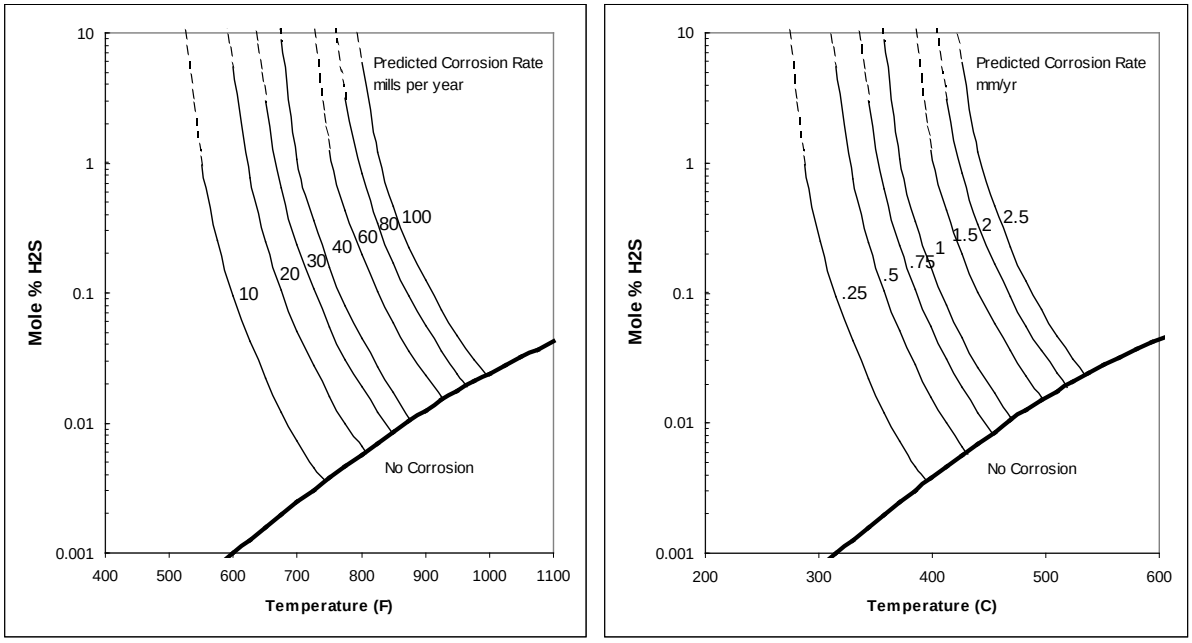


2.25Cr-1Mo Gas Oil

Figure B.5—Couper-Gorman H_2/H_2S Curves for 2.25Cr-1Mo Steel for Both Naphtha and Gas Oil

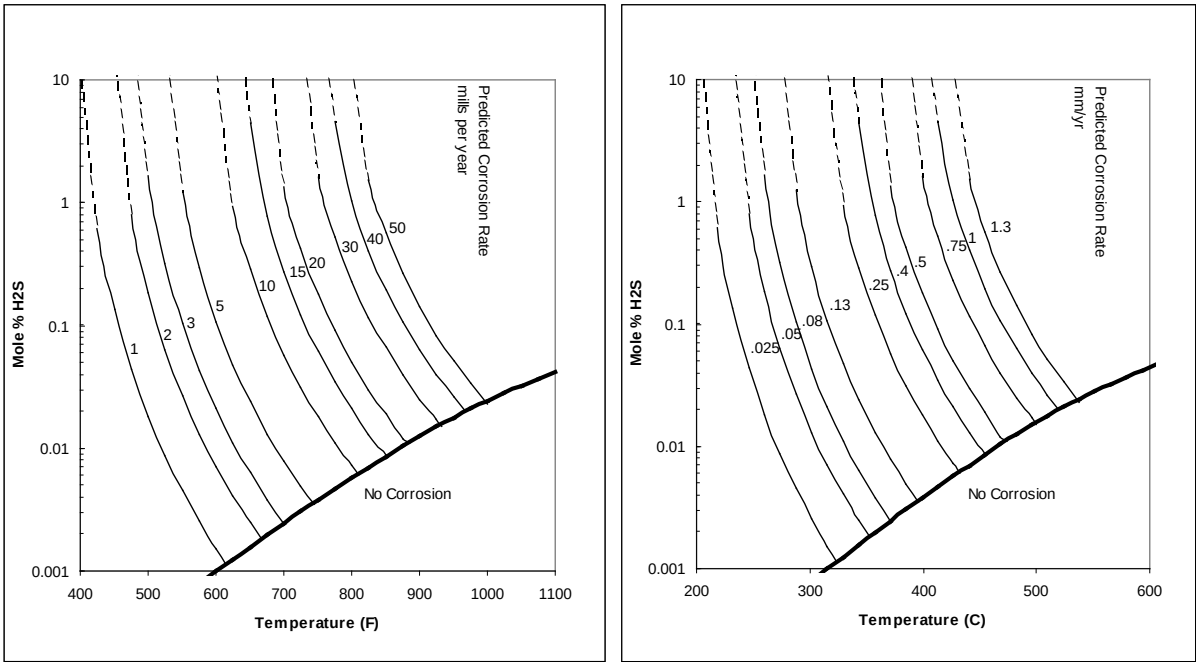


5Cr-0.5Mo Naphtha

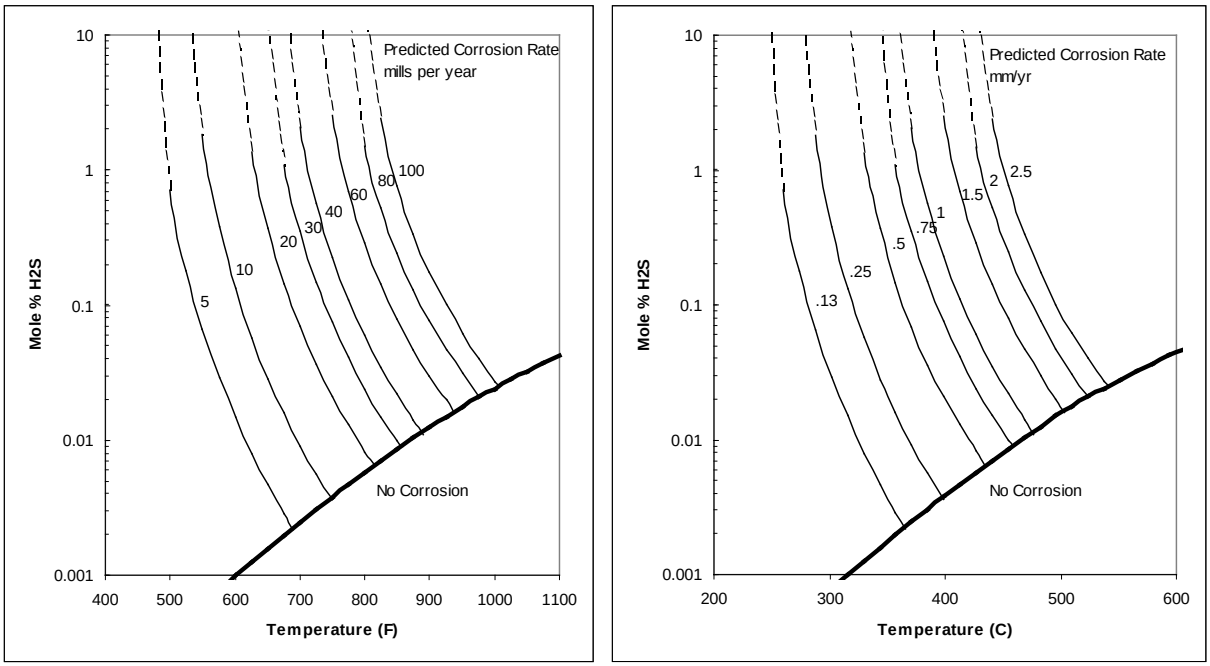


5Cr-0.5Mo Gas Oil

Figure B.6—Couper-Gorman H_2/H_2S Curves for 5Cr-0.5Mo Steel for Both Naphtha and Gas Oil

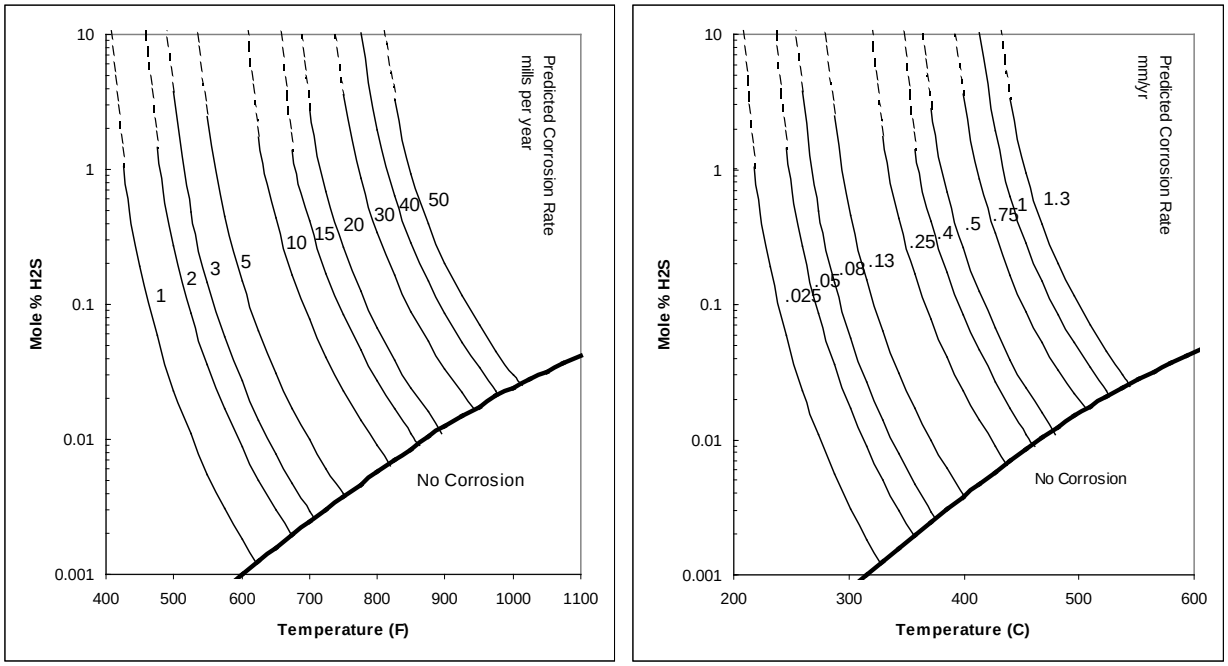


7Cr-0.5Mo Naphtha

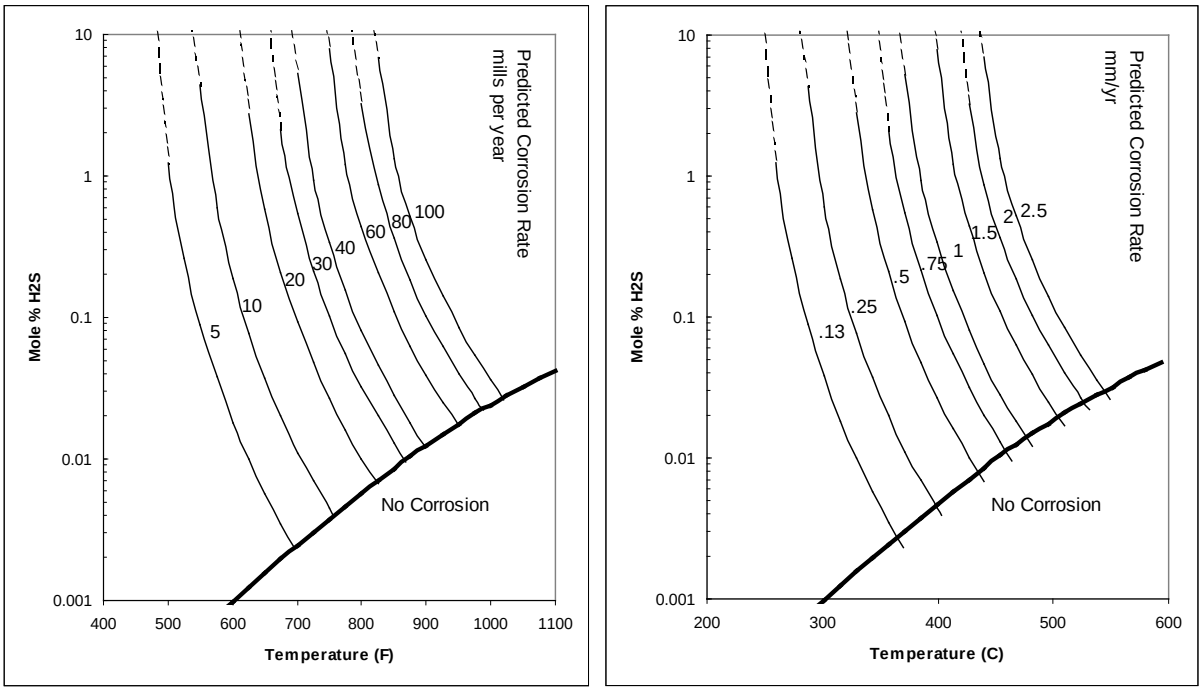


7Cr-0.5Mo Gas Oil

Figure B.7—Couper-Gorman H_2/H_2S Curves for 7Cr-0.5Mo Steel for Both Naphtha and Gas Oil

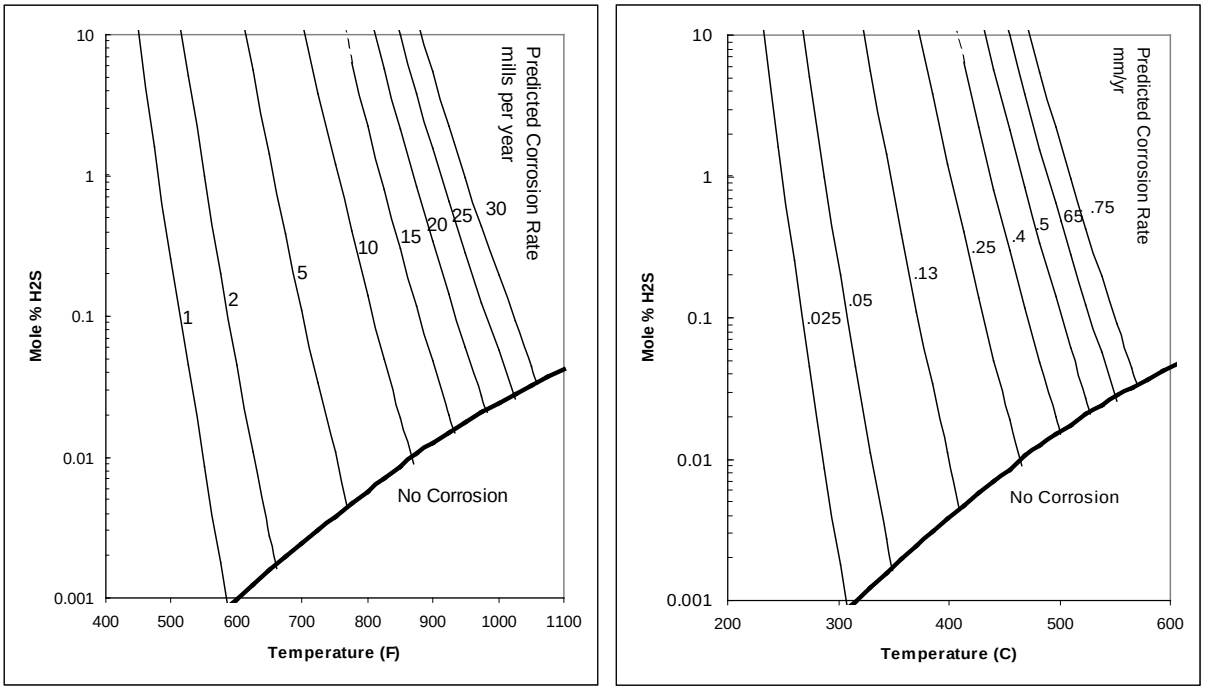


9Cr-1Mo Naphtha



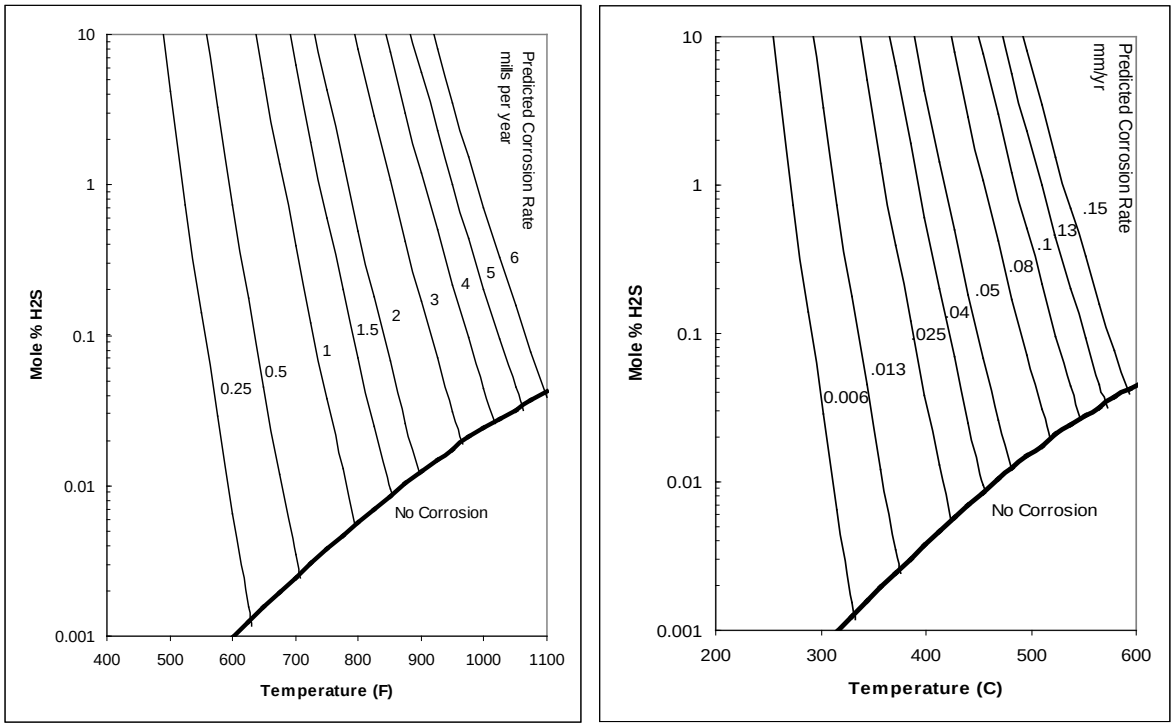
9Cr-1Mo Gas Oil

Figure B.8—Couper-Gorman H_2/H_2S Curves for 9Cr-1Mo Steel for Both Naphtha and Gas Oil



12Cr

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



18Cr

Figure B.10—Couper-Gorman H_2/H_2S Curves for 18Cr 8 Ni Steel (Same for Both Naphtha and Gas Oil)

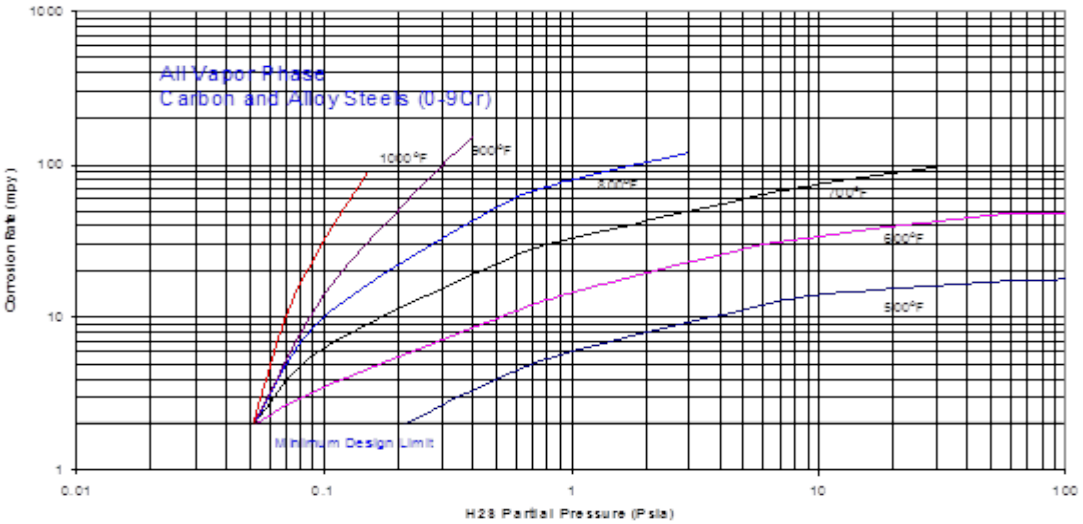


Figure B.11—Corrosion Rate in H_2S/High H_2 Partial Pressure—All Vapor
(Data from NACE Publication 59-10, 1958)

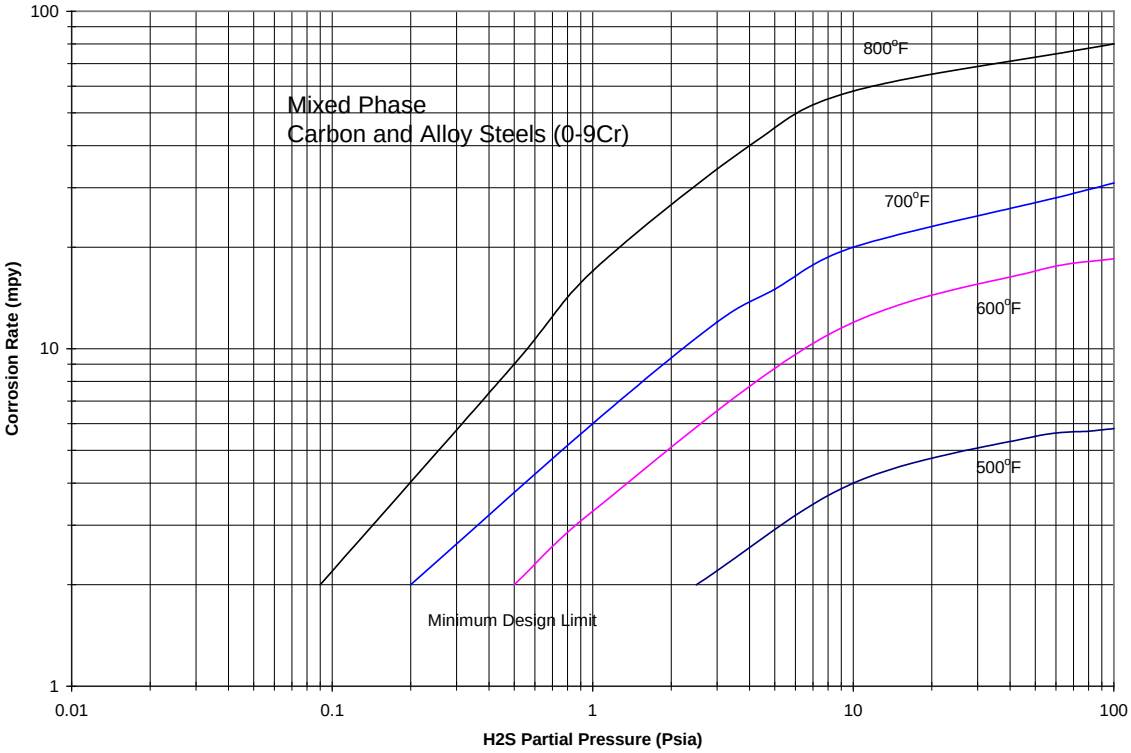


Figure B.12—Corrosion Rate in H_2S/High H_2 Partial Pressure—Liquid Shifted by a Factor of 6 Lower vs Vapor
(Data from NACE Publication 59-10, 1958)

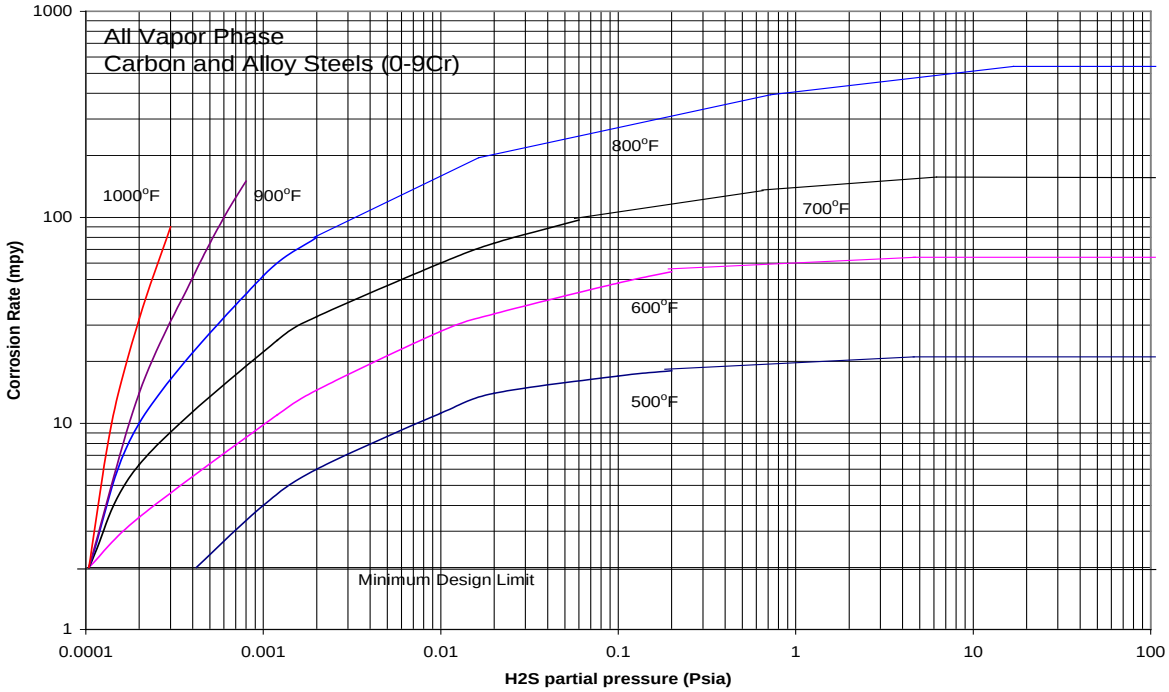


Figure B.13—Corrosion Rate in H_2S/H_2 Vapor—Low H_2 Partial Pressure (High H_2 Partial Pressure—All Vapor Curves Adjusted by Experience)
(from the API Roundtable on Sulfidation)

Annex C
(informative)

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

C.1 General

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 (in USC units) and Figure C.2 (in SI units) are curves 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 Figure 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).

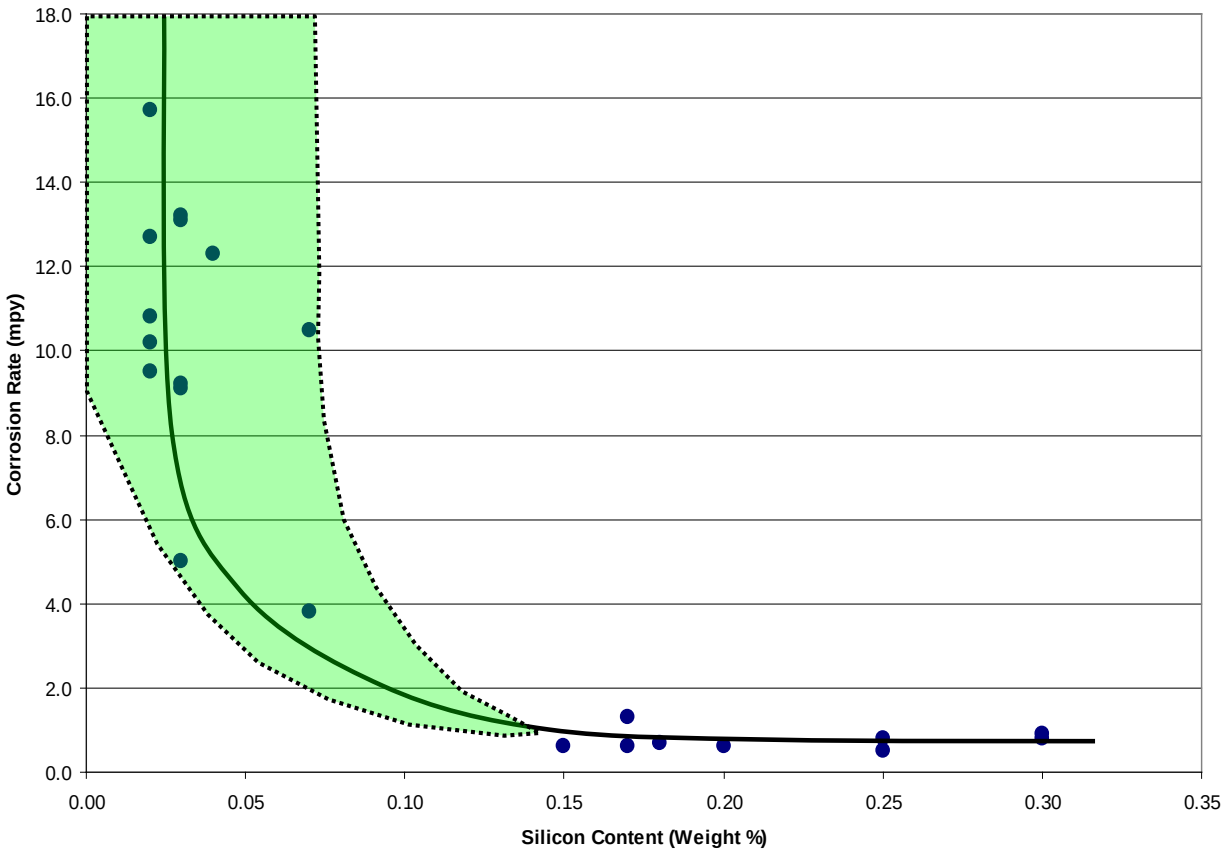
C.2 Sources

— NACE Refin-Cor 94F5.17-01

— NACE Refin-Cor April 1966 T-8 Minutes—Fred Hamel

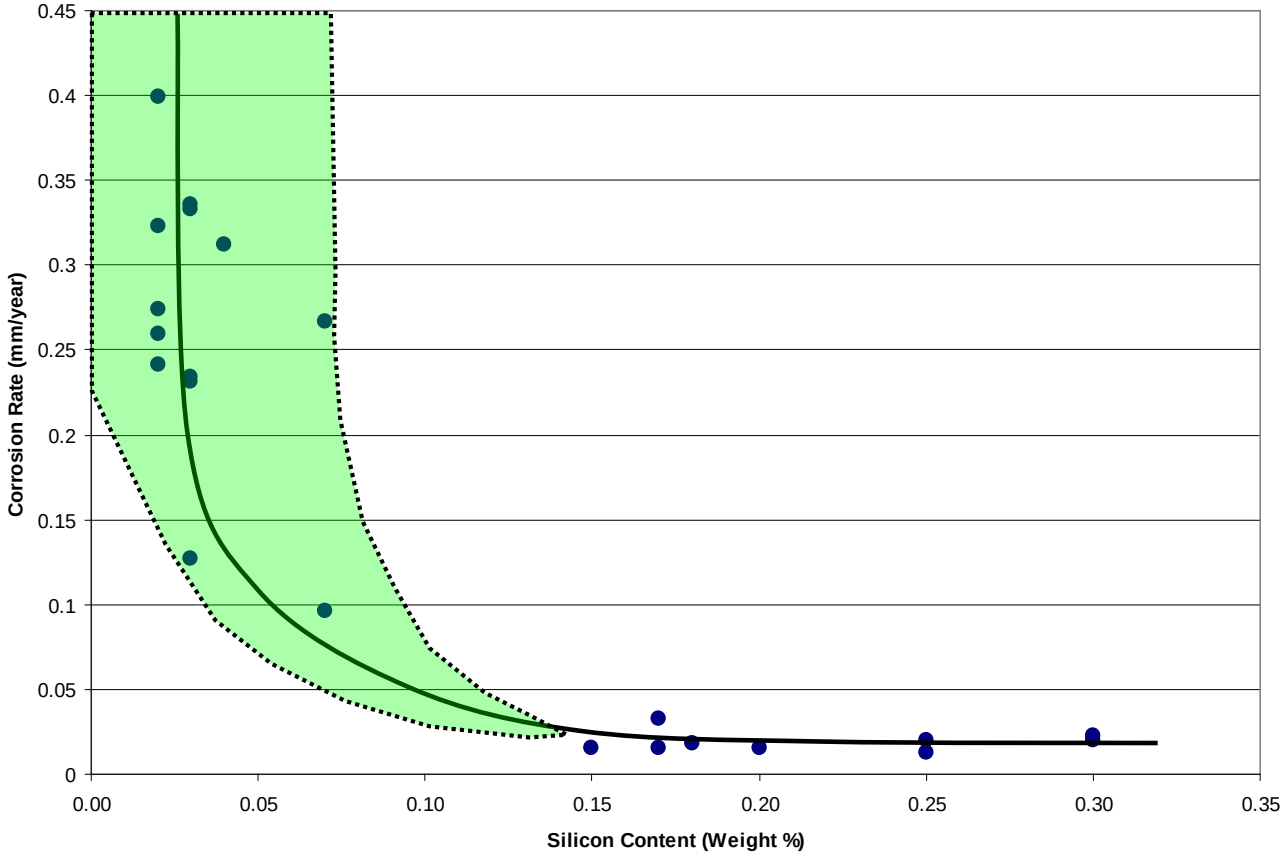
— NACE Refin-Cor 2000C5.3-01

— N. Niccolls, 2005 Spring API Meeting Roundtable on Sulfidic Corrosion



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)

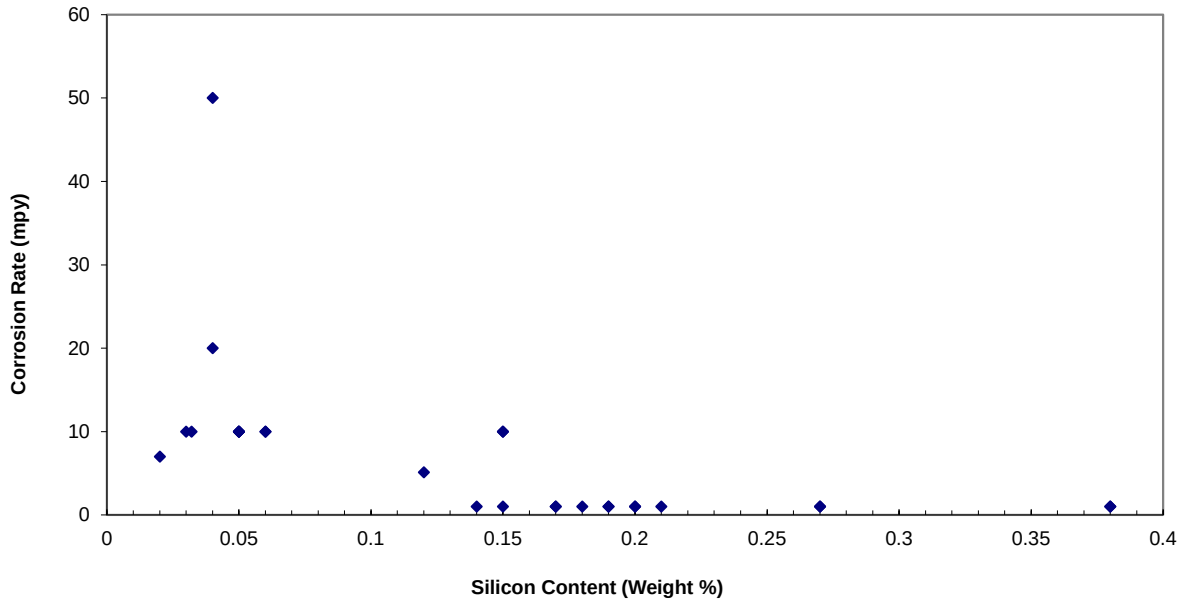
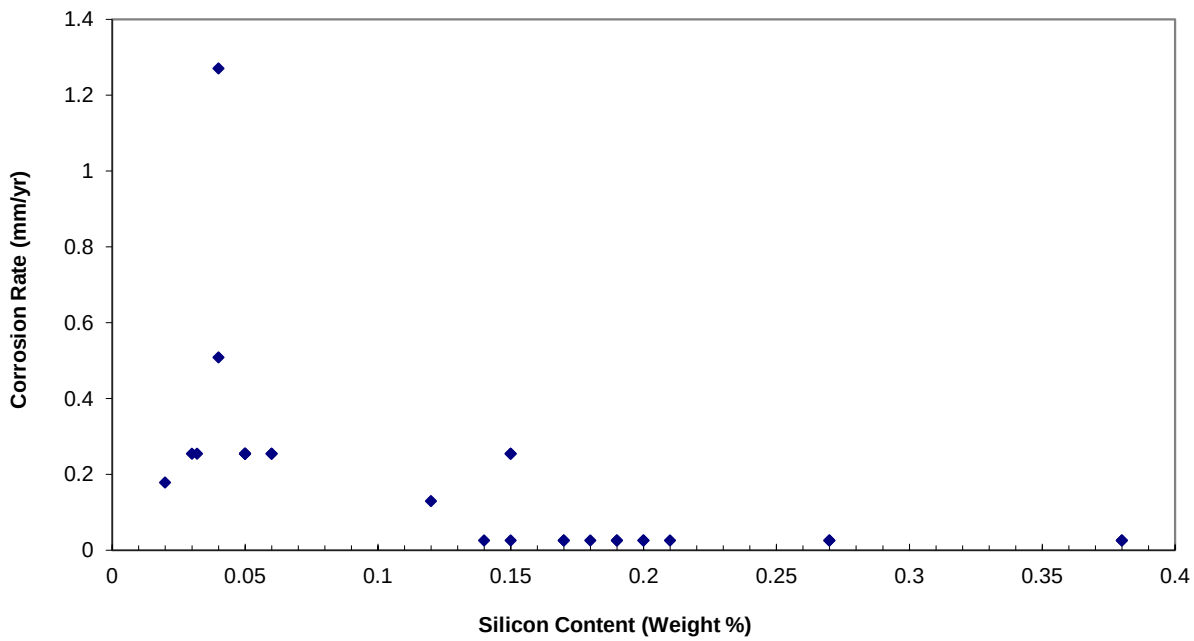


Figure C.3—Corrosion Rate vs Si Content for Various H_2-free Services (USC Units)



NOTE The only data point with the corrosion rate of 10 mils/yr (0.25 mm/yr) or higher at Si content >0.10 wt % was in a high-velocity stream.

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

Annex D
(informative)

Overview of Sulfidation Corrosion Throughout Refinery Units

D.1 General

Annex D provides inspectors and corrosion engineers with a summary of the locations within refinery processing units where the different types of sulfidation corrosion are commonly found. In addition, it includes information on the form (general or localized) of corrosion that may result from the exposure within each section of the plant. Knowledge of the form of corrosion is important, as the scope and type of a thickness monitoring inspection (CML coverage per API 570) should be adjusted to reflect the ability to detect and monitor the different forms of corrosion. The amount of inspection performed will depend on the construction material installed.

D.2 Part A: Types of Sulfidation Corrosion

The types of sulfidation corrosion are characterized as follows and as used in this annex. Considerations for the forms of corrosion found for each type of corrosion are summarized here and would be applicable, regardless of unit.

1) H_2-free Sulfidation (per the Modified McConomy Curves) = H_2-free Sulfidation

   a) General corrosion with sampling CMLs predominantly, but with the following exceptions where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

      i) Fittings, such as elbows, reducers, or tees, may create higher general corrosion losses. CML coverage includes sampling of fittings and pipe.

      ii) Higher local velocity regimes, such as pumps, control valve stations, orifice plates, and warm-up lines, create local corrosion. CML coverage for local corrosion at suspect locations.

      iii) Steam injections, such as used at furnaces, can create local corrosion losses typical of a mix point. CML coverage such as for a mix point.

      iv) Flow combination of two hot streams into a single pipe with higher local flow velocities could create local losses typical of a mix point. CML coverage such as for a mix point.

      v) Stratification of flow could lead to higher vapor region corrosion and H_2S accumulation in upper portion of pipe or horizontal run heater tubes. CML coverage around the diameter of the suspect low flow pipes or heater tubes.

      vi) Extended process dead-legs (start-up piping, bypass piping) that are open to process that could lead local H_2S evolution and vapor stratification could lead to local topside corrosion. Dead-leg CML coverage to include coverage around the diameter of the piping.

2) H_2-free Sulfidation (Low H_2S Content per 6.2.3.7) = H_2-free Sulfidation Low H_2S

   a) General corrosion with sampling CMLs predominantly, but with the following exceptions where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

      i) Fittings, such as elbows, reducers, or tees, may create higher general corrosion losses. CML coverage includes sampling of fittings and pipe.

ii) Higher local velocity regimes, such as pumps, control valve stations, orifice plates, and warm-up lines, create local corrosion. CML coverage for local corrosion at suspect locations.

iii) Stratification of flow could lead to higher vapor region corrosion and H_2S accumulation in upper portion of pipe or horizontal run shock/shield or convection heater tubes. CML coverage around the diameter of the suspect low flow pipes or heater tubes.

iv) Vapor spaces of heat exchangers with hot heating mediums and residual H_2S levels could lead to higher corrosion. CML coverage of vapor zones of tubes/shells.

3) H_2/H_2S Sulfidation (per the Couper-Gorman Curves) = H_2/H_2S Sulfidation

a) General corrosion with sampling CMLs predominantly, but with the following exceptions where local conditions can create local conditions (vapor concentration and shear stresses) that can create potential localized corrosion.

i) Fittings, such as elbows, reducers, or tees, may create higher general corrosion losses. CML coverage includes sampling of fittings and pipe.

ii) Higher local velocity regimes, such as pumps, control valve stations, orifice plates, and warm-up lines, create local corrosion. CML coverage for local corrosion at suspect locations.

iii) High delta thermal mix points, such as exchanger bypasses, can create losses typical of a mix point. CML coverage such as for a mix point.

D.3 Part B: Unit Exposures to Sulfidation Corrosion

The following summarizes unit specific sulfidation exposure types and unit-based problems that have been reported that impact the CML monitoring for sulfidation corrosion for that unit.

1) Crude Distillation Unit/Vacuum Distillation Units

a) Liquid streams operating at 500 °F (260 °C) are exposed to H_2-free sulfidation. General corrosion with sampling CMLs predominantly but where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

i) Steam injections, such as used at furnaces, can create local corrosion losses typical of a mix point. CML coverage such as for a mix point.

ii) High-velocity two-phase flow regimes, such as crude distillation unit and vacuum distillation unit heater outlet tubes and outlet transfer piping, can cause local corrosion due to flow velocity and regime impacts. CML local corrosion coverage at two-phase high-velocity points (heater elbows and transfer piping suspect zones).

iii) Hot vapor regimes, such as flash tower overheads or reboiled stripper tower overheads, can create higher general corrosion due to H_2S vapor exposure of the tower top and overhead piping. Expanded general CML coverage.

iv) Tower piping that has stratified flow and causes local corrosion. CML coverage for localized corrosion.

2) Hydroprocessing (Hydrocracking, Hydrodesulfurizing) Units

a) Feed streams operating at >500 °F (260 °C) prior to H_2 injection may be exposed to H_2-free sulfidation. General corrosion with sampling CMLs predominantly but where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

i) Hot vapor regimes in light hydrocarbon (naphtha and kerosene) furnaces can be exposed to light reactive sulfur species and create higher general corrosion at high heat flux regions. Expand CML coverage in high heat flux zones and include band type coverage.

b) Feed streams operating at >450 °F (230 °C) after H_2 injection may be subject to H_2/H_2S sulfidation corrosion (particularly if sour recycle gas is used). General corrosion with sampling CMLs predominantly but where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

i) Injection zone of H_2 in hot feed may create a localized corrosion characteristic of a mix point. CML coverage such as for a mix point.

c) Reactor outlet and downstream to hot separators are exposed to H_2/H_2S sulfidation. General corrosion with sampling CMLs predominantly but where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

i) See D.2.3, H_2/H_2S Sulfidation.

d) Hot sour recycle gas may be exposed to H_2/H_2S corrosion. General corrosion with sampling CMLs predominantly but where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

i) See D.2.3, H_2/H_2S Sulfidation.

e) Hot streams after separation through to fractionation, including hot preheat, hot fractionation bottoms, and reboilers, may be exposed to H_2-free sulfidation low H_2S. General corrosion with sampling CMLs predominantly, but where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

i) Pressure letdown from hot high-pressure separators may cause local flashing of H_2S and turbulence creating local corrosion. Local corrosion CMLs at letdown control valve and downstream.

f) All vapor sections and overhead piping of hot high-pressure separators are exposed to higher H_2/H_2S sulfidation general corrosion rates (see Annex B, Figure B.11). CML coverage for general corrosion.

3) Fluid Catalytic Cracking Units (FCCUs)

a) Liquid feed streams operating at >500 °F (260 °C) are exposed to H_2-free sulfidation. General corrosion with sampling CMLs predominantly but where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

i) Steam injections, such as used at furnaces or riser injection, can cause localized corrosion characteristic of a mix point. CML coverage such as for a mix point.

b) Hot reactor vapor to fractionation may cause a form of H_2-free sulfidation. General experience is that this temperature is high enough, and combined with coking, does not cause a high corrosion rate. General corrosion with sampling CMLs is predominantly used. Local conditions (vapor concentration and shear stresses) can create localized corrosion.

i) Steam injections sometimes found here may cause localized corrosion characteristic of a mix point. CML coverage such as for a mix point.

c) Liquid FCCU fractionator streams operating at 500 °F (260 °C) are exposed to H_2-free sulfidation. General corrosion with sampling CMLs predominantly but where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

i) Fractionator bottoms streams (slurry) may have sulfidation corrosion accelerated locally if solids levels are high in stream. CML coverage for localized corrosion at high-velocity points such as warm-up line orifices, piping at pumps, and control valves, etc.

4) Coking Units

a) Liquid feed streams operating at 500 °F (260 °C) are exposed to H_2-free sulfidation. General corrosion with sampling CMLs predominantly but where local conditions (vapor concentration and shear stresses) create potential localized corrosion:

i) Steam injections, such as used at furnaces, can cause localized corrosion characteristic of a mix point. CML coverage such as for a mix point.

b) Hot coke drums and vapor to fractionation may cause a form of H_2-free sulfidation. General corrosion with sampling CMLs predominantly but where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

i) Coker clad 12Cr or stainless lining does not need to be monitored for sulfidation corrosion, but acidic corrosion can occur.

c) Liquid coker fractionator streams operating at >500 °F (260 °C) are exposed to H_2-free sulfidation. General corrosion with sampling CMLs predominantly but where local conditions (vapor concentration and shear stresses) can create potential localized corrosion.

d) Fluid coker reactor bottoms streams (slurry) are exposed to H_2-free sulfidation. General corrosion with sampling CMLs predominantly, but corrosion accelerated locally if solids levels are high in stream.

i) CML coverage for localized corrosion at high-velocity points such as warm-up line orifices, piping at pumps, and control valves, etc.

5) Light Ends Recovery Units

a) Hotter sour feed light end tower reboiler systems with a high-temperature [>600 °F (315 °C)] heat source can be exposed to H_2-free sulfidation low H_2S.

i) Localized corrosion may occur in hot vapor systems of reboilers such as shells and bundles. Local CML coverage in hot vapor zones.

6) Sulfur Recovery Units

a) Hotter-vapor H_2S-containing streams from the waste heat boiler/condenser through the inline heater and first catalytic bed to condenser may be exposed to a form of H_2-free sulfidation, but as the exposure is to elemental sulfur and H_2S, vapor will not be predicted by H_2-free sulfidation. General corrosion with sampling CML coverage to monitor corrosion rate.

7) Tail Gas Units

a) Hotter-vapor H_2S-containing stream from the hydrogenation reactor to quench tower will be exposed to a form of H_2-free sulfidation but is not well predicted as a hot vapor. General corrosion with sampling CML coverage to monitor corrosion rate.

Annex E
(informative)

Simplified Inspection Checklist for Refinery Piping and Equipment in Sulfidation Service

Inspection Consideration	Complete?
1) IDENTIFY RELEVANT PROCESS ENVIRONMENTS Identify all refinery equipment in sulfidation service. At minimum, sulfidation service should include all process equipment operating above 500 °F (260 °C) in crude, vacuum distillation, FCC, cokers, and thermal crackers and 450 °F (230 °C) for all types of hydroprocessing units containing more than a 5 wt ppm sulfur.	
2) IDENTIFY POTENTIALLY SUSCEPTIBLE MATERIALS In general, the following metallurgy/operating condition combinations should require a thorough thickness inspection program for sulfidation corrosion: — all carbon steel through 2.25 Cr piping and equipment in sulfidation service, as defined in Item 1) above; — all 5 and 7 Cr equipment in the sulfidation process units listed in Item 1), when normal operating temperatures are greater than 650 °F (334 °C); or — all 5, 7, and 9 Cr equipment in hydroprocessing units downstream of the H_2 injection point(s) and operating above 450 °F (230 °C).	

Inspection Consideration	Complete?
3) MAKE SPECIAL PROVISIONS FOR LOW-Si CARBON STEEL "Potentially low Si carbon steel piping" in the sulfidation process units listed in Item 1) and operating above 500 °F (260 °C) or 450 °F (230 °C) in H_2/H_2S services should require extensive thickness inspections. A typical approach should look like the following. — *Identify All Components*. For insulated piping, individual pipe segments (or "pups") must be identified by locating the butt welds. This can be done visually after insulation removal or it can be done via real-time RT or other techniques that can penetrate or interrogate underneath the insulation to locate welds. — *Baseline Inspection*. Measure the thickness of every pipe segment and (whenever practical) measure the thickness of all fittings. For horizontal runs, thickness checks should include the top and bottom of the pipe at a minimum. Welds are not normally thickness gauged in carbon steel piping, although if localized weld attack is suspected it might be prudent. — *Ongoing Inspection*. Establish permanent CMLs on a representative number of pipe segments with higher-than-circuit-average corrosion rates and with the shortest remaining lives and incorporate those CMLs into an inspection program in accordance with API 570. The following is a partial list of carbon steel ASTM specifications that DO NOT have a minimum specified Si content: — ASTM A53 pipe, unless dual stamped as "ASTM A106" (typical by mid-1980s); — API 5L Grade B pipe, unless dual stamped as "ASTM A106" (typical by mid-1980s); — ASTM A234 Grade WPB forged fittings (WPB fittings require Si unless they are forgings); — ASTM A105 forgings prior to 1995; — ASTM A671 and ASTM A672 fusion welded pipe when made from ASTM A285 or ASTM A442 plate; — ASTM A134 fusion welded pipe; and — ASTM A135 ERW pipe.	

Inspection Consideration	Complete?
4) CHECK FOR LOCALIZED CORROSION AT LOCATIONS OF HIGH SHEAR STRESS OR EROSIVE CONDITIONS When inspecting sulfidation service equipment as defined in Item 1) above, special emphasis thickness inspections consisting of either RT, an array of UT points, grid UT, AUT scan, or other techniques should occur for any metallurgy at the following locations where erosive conditions and/or high velocity can aggravate sulfidation corrosion: — pump balance/warm-up lines; — outlet lines from reboilers; — locations just downstream of pressure letdown valves; — reducers and changes of direction just downstream of pump discharges; — downstream of orifice plates, flow restrictors, and metering devices that can introduce turbulence; — steam injection or other high-velocity injection points; — FCC fractionator slurry systems; or — services where there is potential for naphthenic acid corrosion (though distinct from sulfidation corrosion, damage can be collocated with sulfidation).	
5) INSPECT AT FEATURES THAT CAN TRAP H_2S AT HIGH POINTS When inspecting sulfidation service equipment as defined in Item 1) above, special emphasis thickness inspections, well over and above spot ultrasonics (possibly including RT, an array of UT points, grid UT, AUT scan, or other techniques) should occur for any metallurgy at the following locations where mixed phases and/or H_2S evolution can locally aggravate sulfidation corrosion: — vertical dead-legs and high point vents and — the 12 o'clock position on elevated horizontal pipe runs with no/low flow (e.g. possibly subject to thermosyphon effects).	

Inspection Consideration	Complete?
6) CHECK AT MATERIAL SPEC BREAK All material spec breaks (e.g. carbon steel to 5Cr, 5Cr to 9Cr, 5 Cr to 300 Series SS) connecting to sulfidation service equipment, as defined in Item 1) above, should be identified. Once identified, a program to monitor temperatures and/or CMLs on the carbon steel or lower-alloy side of the spec break should be established. Key focus areas should include heat exchanger bypasses and start-up lines that are not normally in service. Clad/overlay terminations in vessels should also be regarded as sulfidation spec breaks.	
7) ADDITIONAL CONSIDERATIONS FOR FIRED HEATERS Due to hot wall effects, furnace tubes should be considered subject to sulfidation corrosion at process temperatures 100 °F (55 °C) below the threshold temperatures provided in Items 1) and 2) above (i.e. consider the tube wall temperature to be at least 100 °F (55 °C) hotter than the process temperature). Focus areas for thickness inspections of furnace tubes subject to sulfidation should include: — the “cold” as well as “hot” sides of heater tubes in coking prone services; — tops of heater tubes in horizontally tubed heaters and tops of return bends in vertically tubed heaters; — finned convection sections (smart pigging typically required since the highest heat flux regions are generally not available for thickness measurement by other means); and — radiant sections (smart pigging sometimes selected to achieve complete coverage).	
8) IMPLEMENT AND MAINTAIN PMI For all sulfidation services as defined in Item 1), retro PMI should be performed on all 1 to 9 Cr piping components in accordance with API 578 and PMI practices maintained in place to ensure the specified materials are used in new construction. Consideration should also be given to recurring checks of removable items, such as blind flanges, bolted valves, and threaded plugs, that can become mixed up during maintenance activities. Threaded plugs that are protected by a closed block valve are usually excluded.	
9) CONSIDER SPECIAL CIRCUMSTANCES Finally, sulfidation inspections should occur at locations where sulfidation corrosion may not have been anticipated in the design such as the following: — breaches in alloy strip lining or weld overlay/clad layer has been compromised; and — heat sink areas near supports and flanges for lines operating above ~800 °F (425 °C), such as FCC reactor overhead piping.	

Bibliography

[1] G. Sorell and W.B. Hoyt, NACE Technical Committee Report, Publication 5B156, pp 213t–234t, 1956

[2] C. Phillips Jr., NACE Technical Committee Report, Publication 5B257, pp 37t–42t, 1957

[3] J. Gutzeit "High-temperature Sulfidic Corrosion of Steels," *National Association of Corrosion Engineers, Process Industries Corrosion—The Theory and Practice,* pp 367–372, 1986

[4] A.S. Couper and J.W. Gorman, "Computer Correlations to Estimate High Temperature H_2S Corrosion in Refinery Streams," *Materials Performance*, Vol. 10, Issue 1, pp 31–37, 1971

[5] API Publication 943, *High-temperature Crude Oil Corrosivity Studies*, September 1974

[6] H.F. McConomy, "High Temperature Sulfidic Corrosion in Hydrogen-free Environments," API Proceedings, Vol. 43(III), pp 78–96, 1963

[7] C. Husen, "High-temperature Corrosion by Organic Sulfur Compounds," *High-temperature Metallic Corrosion of Sulfur and its Compounds*, Z.A. Foroulis, Ed., The Electrochemical Society, 1970

[8] J.P. de Jong et al., "Effect of Mercaptans and Other Organic Sulfur Species on High Temperature Corrosion in Crude and Condensate Distillation Units," *NACE Corrosion* 2007, Paper 07565

[9] NACE Technical Publication 34103, *Overview of Sulfidation (Sulfidic) Corrosion in Petroleum Refining Hydroprocessing Units,* Latest Edition

[10] J.E. McLaughlin, "Sulfidation Corrosion Due to H_2S/H_2: Effect of H_2 Partial Pressure and Effect of Fluid Flow," API Roundtable on Sulfidation Presentation, New Orleans, LA, April 19, 2005

[11] J.I. Danis and A.C. Gysbers, "Creating Materials Envelope Statements for Petroleum Refining Operating Units," *NACE Corrosion* 98, Paper 589

[12] R.A. White, "Materials Selection for Petroleum Refineries and Gathering Facilities," NACE, 1998

[13] M.D. McConnell, G.M. Buchheim, and J. Yoakam, "Is Your Killed Carbon Steel Resistant to High Temperature Sulfidation," *Inspectioneering Journal*, Vol. 20, Issue 2, March/April 2014

[14] NACE Paper 2012-0001564

[15] *The 100 Largest Losses 1972–2001: Large Property Damage Losses in the Hydrocarbon-Chemical Industries*, 20th Ed., Marsh Property Risk Consulting, February 2003

[16] NACE Refin-Cor™ [3], Latest Version

[17] API Subcommittee on Corrosion and Materials Meeting Minutes (Various)

[18] NACE SP0114, *Refinery Injection and Process Mix Points*

[19] API Specification 5L, *Specification for Line Pipe*

[20] API 510, *Pressure Vessel Inspection Code: In-service Inspection, Rating, Repair, and Alteration*

[21] API Recommended Practice 574, *Inspection Practices for Piping System Components*

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

[22] ASTM A53/A53M, *Standard Specification for Pipe, Steel, Black, and Hot-Dipped, Zinc-Coated, Welded, and Seamless*

[23] ASTM A105/A105M, *Standard Specification for Carbon Steel Forgings for Piping Applications*

[24] ASTM A134/A134M, *Standard Specification for Pipe, Steel, Electric-Fusion (Arc)-Welded (Sizes NPS 16 and Over)*

[25] ASTM A135/A135M, *Standard Specification for Electric-Resistance-Welded Steel Pipe*

[26] ASTM A181/A181M, *Standard Specification for Carbon Steel Forgings, for General-Purpose Piping*

[27] ASTM A234/A234M, *Standard Specification for Piping Fittings of Wrought Carbon Steel and Alloy Steel for Moderate and High-Temperature Service*

[28] ASTM A285/A285M, *Standard Specification for Pressure Vessel Plates, Carbon Steel, Low- and Intermediate-Tensile Strength*

[29] ASTM A442/A442M, *Specification for Pressure Vessel Plates, Carbon Steel, Improved Tension Properties*

[30] ASTM A671/A671M, *Standard Specification for Electric-Fusion-Welded Steel Pipe for Atmospheric and Lower Temperatures*

[31] ASTM A672/A672M, *Standard Specification for Electric-Fusion-Welded Steel Pipe for High-Pressure Service at Moderate Temperatures*

[32] NACE Publication 59-10, *Iso-Corrosion Rate Curves for High-Temperature Hydrogen-Hydrogen Sulfide*

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