3.61 Sulfidation

3.61.1 Description of Damage

Corrosion of carbon steel and other alloys resulting from their reaction with sulfur compounds in high-temperature environments. Corrosion in the presence of hydrogen is discussed in 3.35, *High-temperature H_2/H_2S Corrosion*. In this discussion, sulfidation will refer to high-temperature sulfidic environments without hydrogen. This mechanism is also known as sulfidic corrosion. Because of the smooth, large, relatively uniformly corroded surface produced by sulfidation, it can lead to rupture type failure rather than a localized or pinhole leak. Both types of sulfidation, with and without hydrogen present, are covered in much more detail in Reference 6 (API 939-C).

3.61.2 Affected Materials

a) All iron-based materials including carbon steel and low-alloy steels, 400 series SS, and 300 series SS, in that order from most susceptible to less susceptible.

b) Nickel-based alloys are also affected to varying degrees depending on composition, especially chromium content. Above 1193 °F (645 °C), alloys containing high nickel contents can suffer a form of sulfidation and metal loss associated with the formation of nickel sulfides beneath the metal surface. This has also been referred to as hot corrosion. Susceptibility to this form of sulfidation increases with increasing nickel content.

c) Copper-based alloys form sulfide corrosion product at lower temperatures than carbon steel.

3.61.3 Critical Factors

a) Major factors affecting sulfidation are chemical composition of the metal, temperature, and concentration of corrosive (reactive) sulfur compounds. Flow conditions can also affect the rate of damage.

b) In general, the resistance of iron-based and nickel-based alloys is determined by the chromium content of the material. Increasing the chromium content significantly increases resistance to sulfidation. 300 series SS, such as Types 304, 316, 321, and 347, are highly resistant in most refining high-temperature sulfidation process environments. Nickel-based alloys are similar to stainless steels in that similar levels of chromium provide similar resistance to sulfidation; however, nickel alloys with little or no chromium can have poor resistance to these environments.

c) Figure 3-61-1 and Figure 3-61-2 show the typical effects of increasing chromium content, temperature, and sulfur content on metal loss. These curves only indicate the general trends in the effects of chemical composition, temperature, and sulfur content on corrosion rates. They are used in design for estimating the corrosion rate for a particular service but should be regarded as only showing trends, as actual observed rates can often vary substantially. In many cases the predictions are conservative, i.e. they overstate the actual corrosion rates found in service. The references at the end of this section provide additional background on the development of these curves.

d) The silicon content of carbon steel can significantly affect its susceptibility to sulfidation. Carbon steels with Si content less than 0.10 % have been found to suffer variable and often higher sulfidation corrosion rates than carbon steel with silicon content above this level. (Higher-Si carbon steels are still susceptible to sulfidation, but steel with low Si content may suffer higher rates.) Silicon-killed steel has greater than 0.10 % Si, while non-killed steels generally do not. There have been a number of incidents in the refining industry where lower-Si ASTM Grade A53 piping suffered significantly more metal loss than ASTM Grade A106 piping or standard carbon steel pipe fittings or flanges welded to the A53 pipe.

e) The amount of metal loss suffered in a particular service is greatly affected by the material's ability to form a protective sulfide scale. While sulfide scale invariably forms as a corrosion product on the metal surface, the degree to which it is protective depends on its thickness, density, adherence, and completeness of coverage, which depend on its chemical composition and the severity of the process stream, including flow regime.

f)   Sulfidation (H_2-free) of iron-based alloys begins at metal temperatures above 450 °F (230 °C) but normally
     only becomes a practical concern above 500 °F (260 °C). Experience has shown 500 °F (260 °C) to be the
     most useful service temperature above which to focus inspection, monitoring, and corrosion mitigation efforts.

g)   Crude oils and other hydrocarbon streams contain sulfur compounds at various concentrations. Total sulfur
     content is made up of many different sulfur or sulfide species.

h)   Sulfidation is primarily caused by H_2S and other reactive sulfide species formed by the thermal decomposition
     of sulfur compounds at high temperatures. Some sulfur compounds react more readily to form H_2S.
     Therefore, it can be misleading to predict corrosion rates based on weight percent of sulfur alone. Knowing
     the total "reactive sulfur" in the process stream is key to predicting or assessing its actual corrosivity.

3.61.4   Affected Units or Equipment

a)   Sulfidation occurs in piping and equipment in high-temperature environments where sulfur-containing liquid,
     vapor, or mixed streams are processed.

b)   Crude, vacuum, FCC, coker, and visbreaker units, as well as the feed sections of hydroprocessing units
     upstream of hydrogen injection [at which point high-temperature H_2/H_2S corrosion (3.35) begins to govern],
     commonly process these high-temperature, sulfur-containing streams without, or prior to, intentionally added
     hydrogen.

c)   Coker heaters fabricated from higher-nickel alloys such as Alloy 800H have shown accelerated sulfidation
     corrosion rates in the lower radiant sections operating with tube metal temperatures exceeding 1193 °F
     (645 °C) as compared to similar tubes operating below this temperature.

d)   Heaters fired with oil, gas, coke, and most other sources of fuel may be affected depending on sulfur levels
     in the fuel; it is now uncommon for heaters to be fired with anything but gas, usually low-sulfur gas to meet
     environmental restrictions, especially in the United States.

3.61.5   Appearance or Morphology of Damage

a)   Depending on service conditions, corrosion is most often in the form of uniform thinning but can also occur
     as localized corrosion or high-velocity erosion-corrosion damage. (Figure 3-61-3 to Figure 3-61-7)

b)   While generally having a uniform thinning morphology, the amount of thinning can vary at different locations
     in the system or at different locations along the length of a piping run.

     1.   The difference in the degree of thinning between low-Si (<0.10 % Si) pipe and higher-Si (≥0.10 Si) pipe
          in the same system can be large, with a marked step change in remaining wall thickness at the transition.
          See Figure 3-61-4 and Figure 3-61-5.

c)   A sulfide scale will usually cover the surface of components. Deposits may be thick or thin depending on the
     alloy, corrosiveness of the stream, and fluid flow regime and velocity.

3.61.6   Prevention/Mitigation

a)   Resistance to sulfidation is generally achieved by upgrading to a higher-chromium steel such as 9Cr-1Mo.

b)   Piping and equipment constructed from solid or clad (or overlaid) 300 series SS should provide significant
     resistance to corrosion. 400 series SS cladding should also provide significant improvement over carbon
     steel. Solid 400 series SS is generally not selected for piping or other pressure-containing equipment
     because of embrittlement and fracture toughness concerns.

c)   Aluminum diffusion treatment of carbon steel and low-alloy steel components is sometimes used to reduce
     sulfidation rates and minimize scale formation; however, it may not offer complete protection.

d) For operation above 1193 °F (645 °C), sulfidation rates of higher-nickel alloys can be reduced by selecting an alloy with a lower Ni content.

3.61.7 Inspection and Monitoring

a) Thinning in piping, tubing, and other equipment can be detected and measured using UT thickness measurement or RT. Thinning in pressure vessels and large-diameter piping where internal inspection is possible can be detected by internal VT, typically followed up with UT.

b) Permanently mounted thickness monitoring sensors can be used.

c) Thinning in heater tubes can be detected using UT or by smart pigging. Smart pigging provides significantly more coverage than spot UT and may find thinning missed by spot UT.

d) Actual operating temperatures should be verified and compared against design. Temperatures and sulfur levels should be monitored for increases above design.

e) Temperatures can be monitored using tube-skin thermocouples and/or infrared thermography.

f) Proactive and retroactive MVPs (materials verification programs) can be used for alloy verification and to check for alloy mix-ups in services where sulfidation is anticipated. (API 578 provides guidance on MVPs.) See Figure 3-61-6.

g) Most refiners have instituted programs to identify low-Si carbon steel piping or components in sulfidation service by measuring the thickness of components in vulnerable piping systems. A small number of refiners have followed a PMI-type approach to measuring or otherwise determining the Si content of piping components.

3.61.8 Related Mechanisms

Sulfidation is also known as sulfidic corrosion. High-temperature sulfidation in the presence of hydrogen is covered in 3.35.

3.61.9 References

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

2. J. Gutzeit, "High Temperature Sulfidic Corrosion of Steels," *Process Industries Corrosion—The Theory and Practice*," NACE International, Houston, TX, 1986, pp. 171–189.

3. J. Gutzeit, R.D. Merrick, and L.R. Scharfstein, "Corrosion in Petroleum Refining and Petrochemical Operations," *Metals Handbook*, Volume 13, ASM International, Materials Park, OH, 1987, pp. 1262–1287.

4. E.B. Backenstow et al., "High Temperature Hydrogen Sulfide Corrosion," *CORROSION*, Vol. 12, No. 1, 1956, pp. 6t–16t.

5. NACE Task Group 176 Draft Report, "Overview of Sulfidic Corrosion in Petroleum Refining," NACE International, Houston, TX, 2003.

6. API Recommended Practice 939-C, *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*, American Petroleum Institute, Washington, DC.

7. API Recommended Practice 578, *Guidelines for a Material Verification Program (MVP) for New and Existing Assets*, American Petroleum Institute, Washington, DC.
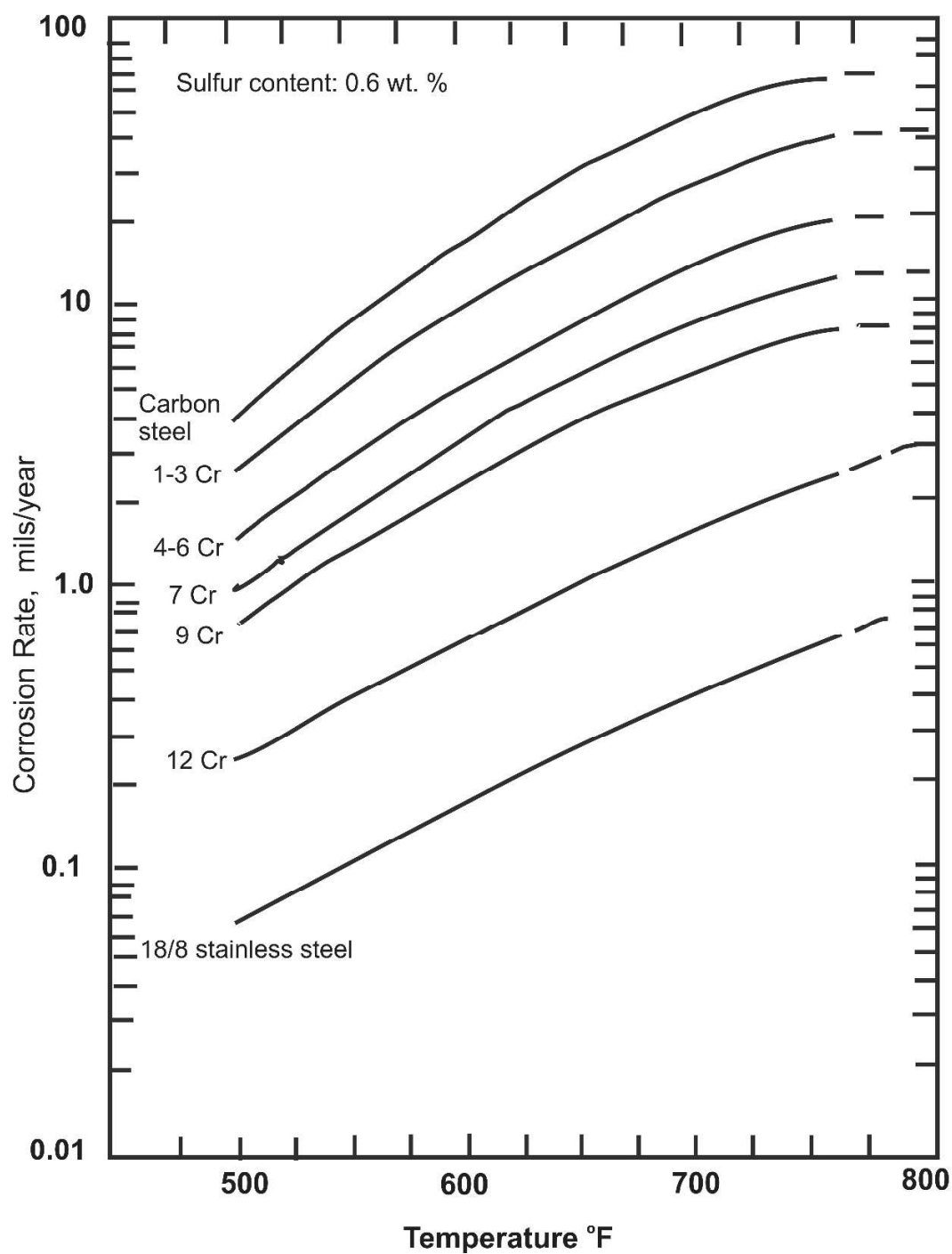
Figure 3-61-1—Modified McConomy curves showing typical effect of temperature on high-temperature sulfidation of steels and stainless steels. (Reference 3)
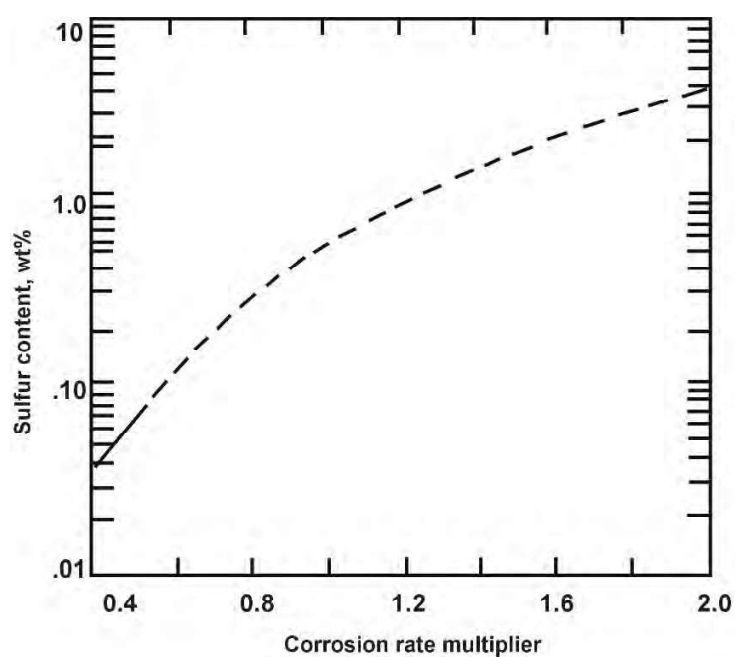
Figure 3-61-2—Multiplier for corrosion rates in Figure 3-61-1 based on the sulfur content of process fluid. (Reference 3)

Figure 3-61-3—Sulfidation failure of an 8-in. carbon steel pipe. Note the relatively uniform thinning that resulted in a sizeable rupture.

Figure 3-61-4—Sulfidation failure illustrating the effect of accelerated corrosion due to low silicon content. This 8-in. pipe section in FCC bottoms piping was in service at 150 psig (1 Mpa) at 650 °F to 700 °F (340 °C to 370 °C). The piping sketch in Figure 3-61-5 illustrates the difference in corrosion rate as compared to adjacent high-silicon components.
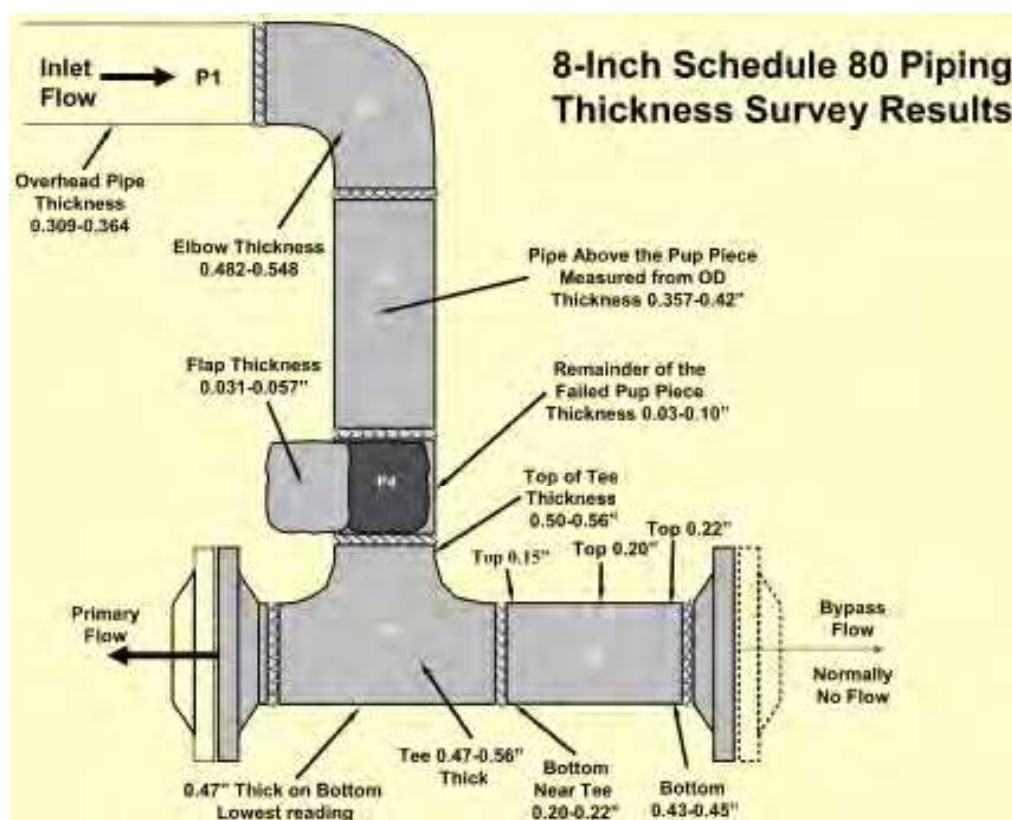

Figure 3-61-5—Thickness survey of 8-in. pipe shown in Figure 3-61-4 above.

Figure 3-61-6—Sulfidation failure of a carbon steel sight glass nipple on the right after 2 years in a crude unit. Original thickness is shown on left for comparison. Material was supposed to be 9Cr-1Mo.

Figure 3-61-7—Sulfidation failure of piping elbow.