

3.35 High-temperature H₂/H₂S Corrosion

3.35.1 Description of Damage

The presence of hydrogen in H₂S-containing hydrocarbon streams increases the severity of high-temperature sulfidation (sulfidic) corrosion at temperatures above about 450 °F (230 °C). Because of the smooth, large, relatively uniformly corroded surface produced by high-temperature H₂/H₂S corrosion, it can lead to rupture-type failure rather than a localized or pinhole leak. This subject is covered in much greater detail in Reference 3 (API 939-C).

3.35.2 Affected Materials

For the materials typically used in this service, the order of increasing resistance is carbon steel, low-alloy steels, 400 series SS, and 300 series SS. However, for a practical, useful improvement over carbon steel, the alloy content of at least 9Cr-1Mo is normally needed.

3.35.3 Critical Factors

- a) The critical factors for high-temperature H₂/H₂S corrosion are the temperature, the presence of hydrogen, the concentration and partial pressure of H₂S, the vapor/liquid ratio, and the chemical composition of the alloy.
- b) Depending on the quantity of hydrogen present, corrosion rates may be significantly different than those associated with high-temperature sulfidation in the absence of hydrogen. (See 3.61.)
- c) Sulfidation rates increase with increasing H₂S content and especially increasing temperature. Figure 3-35-1 shows the effect of temperature and H₂S content on the corrosion rate of carbon steel.
- d) Increasing chromium content of the alloy improves resistance. However, there is little improvement with increasing chromium content until about 7 % to 9 % Cr as shown by the relative rate reduction factors in Table 3-35-1. The benefit of higher chromium levels is shown in Figure 3-35-2.
- e) Chromium-containing nickel-based alloys have resistance similar to stainless steel. Similar levels of chromium provide similar corrosion resistance.
- f) Primarily due to the higher partial pressure of H₂S, corrosion rates in higher-pressure units, e.g. hydrocrackers and gas oil hydrotreaters (desulfurizers), are generally higher than those in lower-pressure naphtha hydrotreaters.

3.35.4 Affected Units or Equipment

- a) This form of corrosion occurs in piping and equipment in units where high-temperature H₂/H₂S streams are found, which is primarily hydroprocessing units (hydrotreaters and hydrocrackers).
- b) Noticeable increases in corrosion rates may be found downstream of the hydrogen injection point where the mechanism changes from sulfidation (3.61) to high-temperature H₂/H₂S corrosion. The addition of hydrogen promotes cracking of the reactive sulfur species into H₂S prior to the reactor, increasing the rate of corrosion in comparison to corrosion from the reactive sulfur alone.

3.35.5 Appearance or Morphology of Damage

- a) Corrosion will appear as a uniform loss in thickness from the process side and is accompanied by the formation of an iron sulfide scale.
- b) Scale is about five times the volume of lost metal and may be in multiple layers.
- c) The tightly adherent shiny gray scale attached to the surface may be mistaken for unaffected metal.

3.35.6 Prevention/Mitigation

- a) The corrosion damage is minimized by using alloys with sufficiently high chromium content.
- b) The 300 series SS such as Types 304L, 316L, 321, and 347 are highly resistant at typical service temperatures.
- c) Aluminum diffusion treatment is sometimes used to reduce corrosion rates and prolong the life of thin components such as 300 series SS catalyst support screens in hydroprocessing reactors.
- d) Process simulations should be checked periodically to confirm that H₂S levels have not significantly increased.

3.35.7 Inspection and Monitoring

- a) Thinning in piping and tubing can be detected and measured using UT thickness measurement or RT. Thinning in pressure vessels can be detected by internal VT and measured 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 a more thorough examination and may find thinning missed by spot UT testing.
- 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.

3.35.8 Related Mechanisms

High-temperature sulfidation in the absence of hydrogen is discussed in [3.61](#).

3.35.9 References

1. 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.
2. *Corrosion Control in the Refining Industry*, NACE Course Book, NACE International, Houston, TX, 1999.
3. API Recommended Practice 939-C, *Guidelines for Avoiding Sulfidation (Sulfidic) Corrosion Failures in Oil Refineries*, American Petroleum Institute, Washington, DC.

Table 3-35-1—Rate Factors vs Chromium Content (Reference 2)

Alloy	Rate Factor
CS, C-0.5Mo	1
1Cr-0.5Mo	0.96
2.25Cr-1Mo	0.91
5Cr-0.5Mo	0.80
7Cr-1Mo	0.74
9Cr-1Mo	0.68

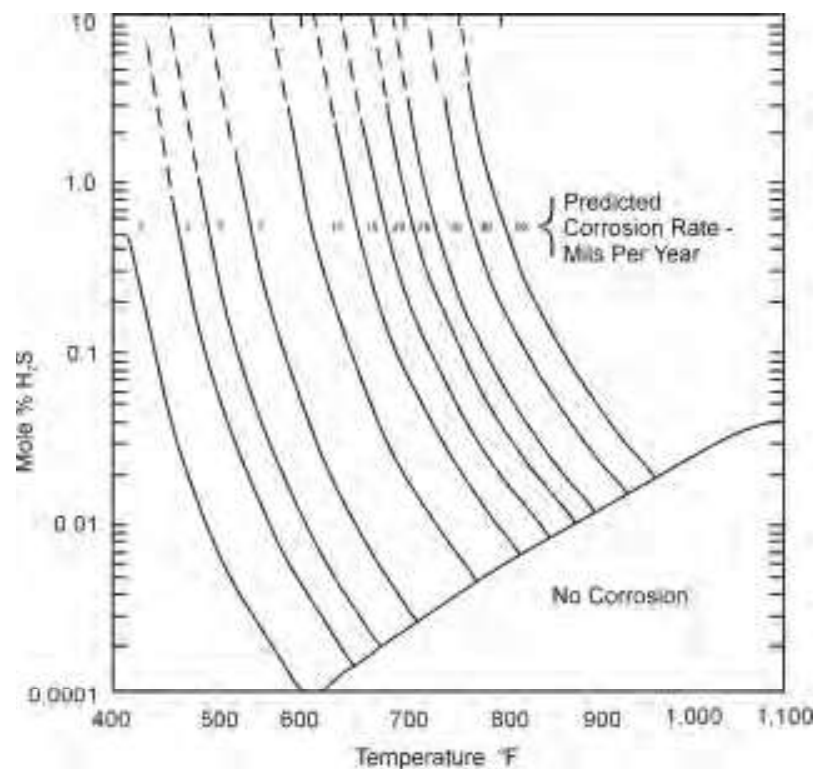


Figure 3-35-1—Corrosion rate of carbon steel in H_2/H_2S service in a naphtha desulfurizer from the modified Couper-Gorman curves. (Reference 1)

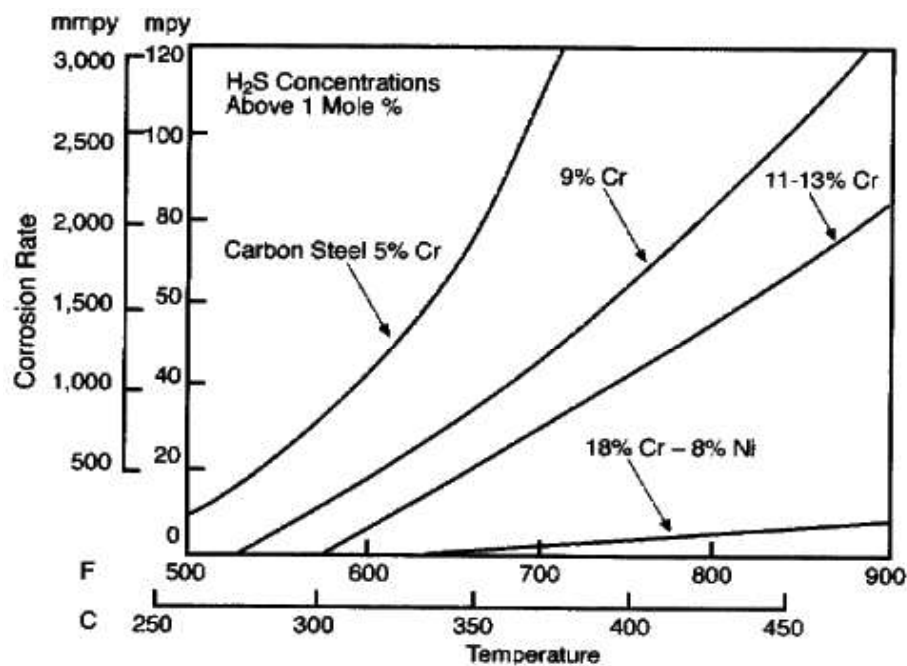


Figure 3-35-2—Corrosion rate curves for Cr-containing alloys in H_2/H_2S service. (Reference 1)