3.5 Ammonium Bisulfide Corrosion (Alkaline Sour Water)

3.5.1 Description of Damage

Aggressive corrosion occurring in hydroprocessing reactor effluent streams and in units handling alkaline sour water (SW), especially in areas of high turbulence.

3.5.2 Affected Materials

a) Carbon steel and low-alloy steels.

b) 300 series SS, duplex stainless steel, nickel-based alloys, and titanium and its alloys are more resistant, depending on ammonium bisulfide (NH_4HS) concentration and velocity.

   1. Aluminum has been used for NH_4HS corrosion resistance in air coolers, but can suffer high corrosion rates in high-velocity or turbulent locations.

   2. Titanium and its alloys have been used for NH_4HS corrosion resistance in air coolers but can suffer embrittlement from hydriding in these services. (See 3.66.)

   3. Welds in duplex stainless steel can be susceptible to SSC. (See 3.67 and API 582.)

c) NH_4HS rapidly corrodes admiralty brass tubes and other copper alloys.

3.5.3 Critical Factors

a) NH_4HS concentration, H_2S partial pressure, velocity (i.e. wall shear stress), and/or localized turbulence, pH, temperature, alloy composition, and flow distribution are all critical factors to consider.

b) Corrosion increases with increasing NH_4HS concentration and increasing velocity (i.e. wall shear stress). For carbon steel, solutions below 2 wt % NH_4HS are not generally corrosive. Above 2 wt %, solutions are increasingly corrosive.

c) In hydroprocessing reactors, nitrogen in the feed is converted to ammonia and reacts with H_2S to form NH_4HS. NH_4HS precipitates out of the gas phase in the reactor effluent stream when temperatures drop to within the range of 120 °F to 150 °F (50 °C to 65 °C), depending on the concentration of NH_3 and H_2S, and may cause fouling and plugging unless flushed away with wash water. A similar reaction between NH_3 and H_2S occurs in FCC and coker units, leading to precipitation in the associated fractionator overheads.

d) NH_4HS salt deposits can lead to under-deposit corrosion and fouling. The salts are not corrosive unless they become hydrated at which point they become corrosive.

e) Oxygen and iron in the wash water injected into hydroprocessing reactor effluent can lead to increased corrosion and fouling.

f) The presence of cyanides increases the severity of corrosion in FCC gas plants, coker gas plants, and sour water stripper (SWS) overheads by diminishing the protection afforded by the normally protective sulfide film.

3.5.4 Affected Units or Equipment

a) Hydroprocessing units.

   1. Several major failures have occurred in hydroprocessing reactor effluent systems due to localized corrosion.

   2. Fouling and/or velocity accelerated corrosion may be found at:

      — air cooler header boxes;

— inlet and outlet piping of air coolers;

— exchanger tubes, especially at the inlet and outlet;

— effluent separators and piping into and out of the reactor effluent separators;

— SW draw piping from reactor effluent separators, especially downstream of control valves where flashing may cause severe erosion-corrosion (Figure 3-5-1);

— vapor lines from the high-pressure separator due to entrained or condensed SW;

— hydrocarbon lines from reactor effluent separators due to entrained SW; and

— stripper column overheads containing SW.

b) FCC units.

NH_4HS concentrations are usually less than 2 wt %, but high velocities and/or the presence of cyanides can damage protective iron sulfide scales.

c) SWSs.

High concentrations of NH_4HS and the possible presence of cyanides can lead to corrosion in stripper overhead piping, condensers, and accumulator and reflux piping.

d) Amine units.

High concentrations of NH_4HS may be found in regenerator overheads and reflux piping depending on unit operation.

e) Delayed cokers.

High concentrations of NH_4HS may be found in the gas concentration plant downstream of the fractionator tower.

3.5.5 Appearance or Morphology of Damage

a) General loss in thickness of carbon steel, with the potential for extremely high localized rates of wall loss at changes in direction or turbulent flow areas above 2 wt % concentration. Generalized corrosion, especially if combined with high unit pressure, can lead to rupture failure.

b) High localized corrosion rates have also been seen in straight runs of piping, so locating the site of the worst corrosion can be a challenge.

c) Low velocities may result in extremely localized under-deposit corrosion if sufficient water is not available to dissolve the NH_4HS salts that precipitated.

d) Heat exchangers may show plugging and loss of duty due to fouling.

3.5.6 Prevention/Mitigation

a) Good design practice includes symmetrical and hydraulically balanced flow in and out of air-cooled exchangers.

b) Carefully review design and localized velocities as process conditions change, particularly as NH_4HS concentrations exceed 2 wt % and begin to approach 8 wt % or higher.

c) Use resistant materials of construction (e.g. duplex stainless steel, Alloy 825) at velocities above 20 fps (6 m/s), depending on NH_4HS concentration.

d) Properly design and maintain water wash injection with low oxygen content; provide sufficient excess water to ensure that an adequate amount of water remains as liquid to dilute the NH_4HS salts. Use proper injection spray nozzles and metallurgy.

e) Titanium and Alloy C276 have been used in overhead condensers in SWS units.

f) Aluminum exchanger tubes are extremely susceptible to erosion-corrosion damage.

3.5.7 Inspection and Monitoring

a) Ammonium bisulfide corrosion can be highly localized and difficult to locate.

b) Determine ammonium bisulfide content through sampling or calculation.

c) UT scanning and/or RT thickness measurement should focus on areas of turbulence and areas of high and low velocity.

    1. Special attention should be given to water injection locations in areas of expected water impact (injection point inspection).

    2. UT downstream of control valves that see high NH_4HS concentrations.

d) Permanently mounted thickness monitoring sensors can be used.

e) Guided wave testing (GWT) can be used as a screening tool.

f) For steel (magnetic material) air cooler tubes (which are normally finned), internal rotating inspection system (IRIS), magnetic flux leakage (MFL), near-field testing (NFT), and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material air cooler tubes.

g) For steel (magnetic material) exchanger bundle tubes, IRIS, MFL, remote field testing (RFT), and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material exchanger bundle tubes.

h) Water injection facilities and flow meters should be monitored to ensure proper operation. Spray nozzles should be inspected for proper distribution pattern and evidence of damage or distortion.

3.5.8 Related Mechanisms

Erosion/erosion-corrosion (3.27), ammonium chloride corrosion (3.6), concentration cell corrosion (3.19), titanium hydriding (3.66), and chloride SCC (Cl^- SCC) (3.17).

3.5.9 References

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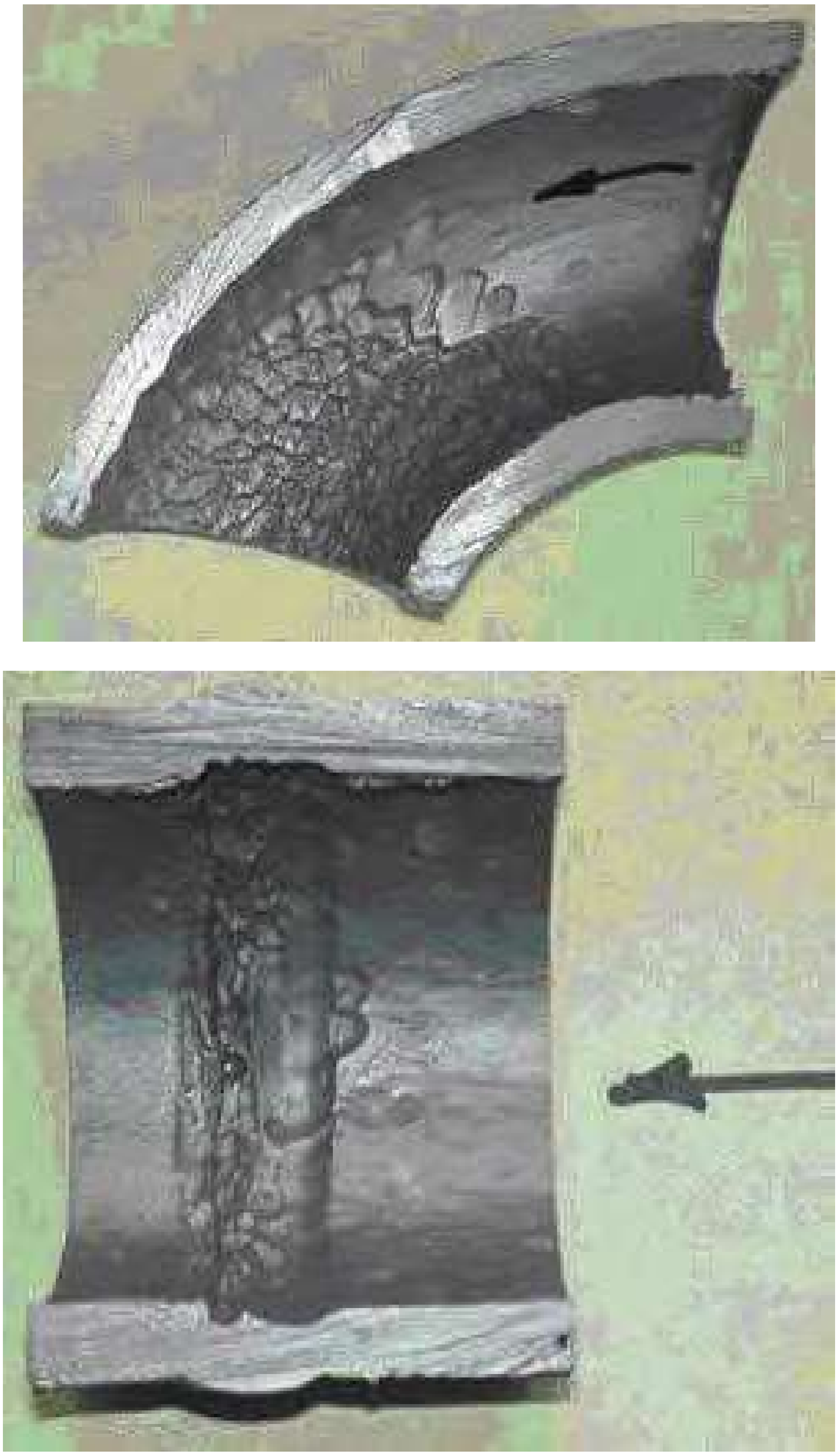

Figure 3-5-1—Ammonium bisulfide corrosion in a 2-in. CS elbow and straight section in a SW line off the cold high-pressure separator (HPS) in an HDT unit.