

3.6 Ammonium Chloride and Amine Hydrochloride Corrosion

3.6.1 Description of Damage

Localized corrosion, often pitting, normally occurring under ammonium chloride or amine salt deposits, often in the absence of a free water phase.

3.6.2 Affected Materials

All commonly used materials are susceptible. In order of increasing resistance: carbon steel and low-alloy steels; 300 series SS; duplex stainless steel and Alloys 400, 800, and 825; Alloys 625 and C276; and titanium.

3.6.3 Critical Factors

- a) Concentrations of NH_3 , hydrochloric acid (HCl), and amine salts; temperature; and water availability are the critical factors.
- b) Ammonium chloride salts may precipitate from high-temperature streams as they are cooled, depending upon the concentration of NH_3 and HCl, and may corrode piping and equipment at temperatures well above the water dew point. Salting has been observed up to approximately 400 °F (205 °C).
- c) Ammonium chloride salts are hygroscopic and readily absorb water. A small amount of water can lead to very aggressive corrosion [>100 mpy (>2.5 mm/yr)].
- d) Ammonium chloride is highly water soluble, highly corrosive, and forms an acidic solution when mixed with water. Neutralizing amines can also react with hydrogen chloride to form amine hydrochlorides that can act in a similar fashion.
- e) Corrosion rates increase with increasing temperature.
- f) When the salts deposit above the water dew point, a water wash injection may be required to dissolve them.

3.6.4 Affected Units or Equipment

- a) Crude tower overheads.
 1. Tower top, top trays, and overhead piping and exchangers may be subject to fouling and corrosion. Deposits may occur in low-flow zones due to ammonia and/or amine chloride salts condensing from the vapor phase.
 2. Top pumparound streams may be affected if ammonia or amine chloride salts are present.
- b) Hydroprocessing.
 1. Reactor effluent streams are subject to ammonium chloride salt fouling and corrosion. Water washing may be required if exchanger fouling or loss in duty occurs.
- c) Catalytic reforming.
- d) Reactor effluent streams and the H_2 recycle system are subject to ammonium chloride salting and corrosion.
- e) FCC unit and coker fractionator overheads.
 1. Overhead systems and top pumparounds are subject to ammonium chloride corrosion and salting.

3.6.5 Appearance or Morphology of Damage

- a) The salts have a whitish, greenish, or brownish appearance. Water washing and/or steam out will remove deposits so that evidence of fouling may not be evident during an internal VT.
- b) Corrosion underneath the salts is typically very localized and can result in pitting.
- c) Corrosion rates can be extremely high.

3.6.6 Prevention/Mitigation

Alloys that are more pitting resistant will have improved resistance to ammonium chloride salts, but even the most corrosion-resistant nickel-based alloys and titanium alloys may suffer pitting corrosion.

- a) Crude unit.
 - 1. Limit salts by limiting chlorides in the tower feed through desalting and/or the addition of caustic to the desalted crude.
 - 2. A water wash may be required in the crude tower overhead line to flush the salt deposits.
 - 3. Filming amine inhibitors are often added to control corrosion but may not reach metal surfaces under deposits that have already formed.
- b) Hydroprocessing.
 - 1. Limit chlorides in the hydrocarbon feed to the reactor.
 - 2. Limit chlorides in the make-up hydrogen supply.
 - 3. A continuous or intermittent water wash may be required in the reactor effluent stream to flush out the salt deposits or, preferably, prevent them from forming.
 - 4. Monitoring of the feed streams and effluent waters will give an indication of the amount of ammonia and chlorides present; however, process simulation may be required to determine the concentrations and dew point temperatures. If the ammonium chloride salt deposition temperature has been calculated, temperature monitoring and control may be effective for maintaining metal temperatures above the salt deposition temperature.
- c) Catalytic reforming.
 - 1. Net hydrogen produced can be treated in alumina bed chloride traps to remove chlorides.
 - 2. Water washing has been used in some cases, but the system must be carefully designed.
 - 3. Some tower overheads may require neutralizing or filming amines.
- d) FCC and coker units.
 - 1. Continuous water wash in overheads is usually used to dissolve salts as they form.
 - 2. Intermittent water wash can be used to remove salt deposits from fractionator trays. This usually requires "slumping" the column and re-running of affected cuts.

3.6.7 Inspection and Monitoring

- a) Ammonium chloride corrosion can be highly localized and difficult to locate. Salts are often mobile, depending on size of accumulation and hydration, causing them to flow with hydraulic traffic and gravity.

- b) RT or UT scanning methods [automated ultrasonic testing (AUT), manual close-grid, scanning UT] can be used to determine remaining wall thickness. These methods are preferred over typical spot UT thickness monitoring because the corrosion is so highly localized.
- c) GWT can be used as a screening tool.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) 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 distortion or other damage.
- f) The presence of deposits is often detected when the pressure drop increases or the thermal performance of exchangers has deteriorated.
- g) Corrosion probes or coupons can be useful, but the salt must deposit on the corrosion probe element to detect the corrosion.
- h) For steel (magnetic material) air cooler tubes (which are normally finned), IRIS, MFL, NFT, and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material air cooler tubes.
- i) For steel (magnetic material) exchanger bundle tubes, IRIS, MFL, RFT, and other electromagnetic techniques can be used. ECT and IRIS can be used to inspect nonmagnetic material exchanger bundle tubes.

3.6.8 Related Mechanisms

Hydrochloric acid corrosion (3.37), Cl^- SCC (3.17), aqueous organic acid corrosion (3.7), and concentration cell corrosion (3.19).

3.6.9 References

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3. NACE Publication 34101, *Refinery Injection and Process Mixing Points*, NACE International, Houston, TX, March 2001.
4. J. Turner, "Control Corrosion in Washwater Systems," *Hydrocarbon Processing*, June 1997, pp. 87–95.
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