

3.37 Hydrochloric Acid Corrosion

3.37.1 Description of Damage

- a) Hydrochloric acid (aqueous HCl) causes both general and localized corrosion and is very aggressive to most common materials of construction across a wide range of concentrations.
- b) Damage in refineries is most often associated with dew point corrosion in which vapors containing water and hydrogen chloride condense from the overhead stream of a distillation, fractionation, or stripping tower. The first water droplets that condense can be highly acidic (low pH) and promote high corrosion rates.

3.37.2 Affected Materials

All common materials of construction used in refineries.

3.37.3 Critical Factors

- a) HCl acid concentration, temperature, and alloy composition.
- b) The severity of corrosion increases with increasing HCl concentration and increasing temperature.
- c) Aqueous HCl can form beneath deposits of ammonium chloride or amine hydrochloride salts in exchangers and piping. The deposits readily absorb water from the process stream or from injected wash water. Hydrogen chloride gas is normally not corrosive in dry process streams but becomes very corrosive where water is available to form hydrochloric acid.
- d) Carbon steel and low-alloy steels are subject to excessive corrosion when exposed to any concentration of HCl acid that produces a pH below about 4.5
- e) 300 series SS and 400 series SS are not usefully resistant to HCl at any concentration or temperature.
- f) Alloy 400, titanium, and some other nickel-based alloys have good resistance to dilute HCl acid in many refinery applications.
- g) The presence of oxidizing agents (oxygen, ferric and cupric ions) will increase the corrosion rate, particularly for Alloy 400 and Alloy B-2. Titanium performs well in oxidizing conditions but fails rapidly in dry HCl service.

3.37.4 Affected Units or Equipment

HCl corrosion is found in several units, especially crude and vacuum units, hydroprocessing units, and catalytic reformer units.

- a) Crude units.
 - 1. In the atmospheric tower overhead system, corrosion from HCl acid occurs as the first droplets of water condense from the vapor stream off the top of the tower. This water can have a very low pH and can result in high rates of corrosion in piping, as well as exchanger shells, tubes and header boxes, and cold dead-legs.
 - 2. HCl corrosion can also be a problem in the vacuum ejector and condensing equipment off the top of the vacuum tower.
- b) Hydroprocessing units.
 - 1. Chlorides may enter the unit as inorganic or organic chloride in the hydrocarbon feed, or with the recycle hydrogen, and react to form HCl.

2. Ammonium chloride salts can form in various parts of the unit, including the effluent side of the hot feed/effluent exchangers because both NH_3 and HCl are present and they may condense with water in the effluent train.
3. HCl -containing streams can migrate through the fractionation section, resulting in severe acid dew point corrosion at the mixing point where the stream contacts water.

c) Catalytic reforming units.

1. Chlorides may be stripped from the catalyst and react to form HCl that carries through the effluent train, regeneration system, stabilizer tower, debutanizer tower, and feed/preheat exchangers.
2. HCl -containing vapors can migrate through the gas plant fractionation section, resulting in corrosion at mix points where HCl -containing vapor streams mix with streams containing free water. HCl corrosion can also occur in these streams where they cool below the acid dew point and in water boots and lines off the water boots.

3.37.5 Appearance or Morphology of Damage

- a) Carbon steel and low-alloy steels suffer uniform thinning, localized corrosion, or under-deposit attack.
- b) 300 series SS and 400 series SS will often suffer pitting attack, and 300 series SS may experience Cl^- SCC if the temperature is sufficiently high. (See 3.17.)

3.37.6 Prevention/Mitigation

a) Crude units.

1. Optimizing the crude oil tank water separation and withdrawal and crude desalting operation will help reduce chloride content in the feed to the crude tower. A common target is 20 ppm or fewer chlorides in the overhead accumulator water.
2. Upgrading carbon steel to nickel-based alloys or titanium can reduce HCl acid corrosion problems.
3. Water wash can be added to quench the overhead stream and to help dilute the condensing hydrochloric acid concentration.
4. Caustic injection downstream of the desalter is another common method used to reduce the amount of HCl going overhead. Proper design and operating guidelines should be followed to avoid caustic SCC (3.15) and fouling in the feed preheat train.
5. Various combinations of ammonia, neutralizing amines, and filming amines can be injected in the atmospheric tower overhead line before the water dew point.
6. Well-maintained process monitoring locations, e.g. for measuring chloride content, water injection rates, and chemical injection rates, are important for managing HCl corrosion.

b) Hydroprocessing.

1. Carryover of water and chloride salts, including neutralizing amine hydrochloride salts, should be minimized.
2. HCl in H_2 streams should be minimized (e.g. by installing scrubbers or guard beds to remove HCl from hydrogen produced in catalytic reforming units).
3. Corrosion-resistant nickel-based alloys should be used where necessary.
4. Well-maintained process monitoring locations are important for minimizing the effects of HCl corrosion.

c) Catalytic reforming.

1. Same as hydroprocessing, but in addition, water washing the hydrocarbon stream has also been used to remove the highly water-soluble chlorides. Special care in the design and operation of this equipment is needed. Minimizing water and/or oxygenates in the feed will reduce stripping of chlorides from the catalyst.
2. Special adsorbents in chloride beds and chloride treaters can be used to remove chlorides from the recycle hydrogen streams and from liquid hydrocarbon streams.
3. Well-maintained process monitoring locations are important for minimizing the effects of HCl corrosion.

3.37.7 Inspection and Monitoring

- a) Hydrochloric acid causes both general and localized corrosion and is very aggressive to most common materials of construction, especially carbon steel, across a wide range of concentrations.
- b) Where applicable, VT should be performed on all accessible components with the potential for hydrochloric acid corrosion. These areas of concern can be characterized by orange-yellow discoloration of the affected material with scale buildup and various levels of deterioration.
- c) UT thickness mapping, including AUT, can be utilized to determine the extent of localized thinning.
- d) RT can be utilized to find or monitor localized thinning in piping components. RT is often performed at transition components (e.g. elbows, three-way or four-way fittings, and dead-legs).
- e) Strategically placed corrosion probes and/or corrosion coupons can provide additional information on the rate and extent of damage.
- f) Permanently mounted thickness monitoring sensors can be used.
- g) The pH of the water in the boot of the atmospheric tower overhead accumulator should be checked regularly. Other variables including chloride and iron content are typically checked on a less frequent basis but do need to be monitored regularly. The water draws from fractionator and stripper tower overhead drums in hydroprocessing and catalytic reformer units should also be checked regularly.

3.37.8 Related Mechanisms

Ammonium chloride corrosion (3.6), Cl⁻ SCC (3.17), and aqueous organic acid corrosion (3.7).

3.37.9 References

1. *ASM Handbook—Corrosion*, Volume 13, ASM International, Materials Park, OH.
2. A. Bagdasarian et al., "Crude Unit Corrosion and Corrosion Control," Paper No. 615, *Corrosion/96*, NACE International, Houston, TX.
3. NACE Publication 34105, *Effect of Nonextractable Chlorides on Refinery Corrosion and Fouling*, NACE International, Houston, TX.