

### 3.46 Naphthenic Acid Corrosion

#### 3.46.1 Description of Damage

A form of high-temperature corrosion that occurs primarily in crude and vacuum units caused by organic naphthenic acids in the crude oil, as well as downstream units that process certain fractions or cuts that contain naphthenic acids.

#### 3.46.2 Affected Materials

Carbon steel, low-alloy steels, 400 series SS, 300 series SS, and nickel-based alloys. See [Table 3-46-1](#).

#### 3.46.3 Critical Factors

- a) Naphthenic acid corrosion (NAC) is a function of the naphthenic acid content, temperature, sulfur content, velocity (wall shear stress), and alloy composition.
- b) Severity of corrosion increases with increasing acidity of the hydrocarbon phase.
- c) Neutralization number or TAN is a measure of the acidity (organic acid content) as determined by various test methods such as ASTM D664. However, NAC occurs in hot dry hydrocarbon streams that do not contain a free water phase.
- d) The TAN of the crude may be misleading, because the correlation between whole crude TAN and corrosion rate is poor, especially when comparing different crudes. A high TAN crude may be less corrosive than a moderate or low TAN crude. This is because this family of organic acids that together are referred to as naphthenic acid, has a range of boiling points and tends to concentrate in various cuts. Therefore, the occurrence and severity of NAC are determined by the naphthenic acids present in the actual stream, not the crude charge. Additional factors are the following.
  1. TAN is a measure of the total amount of all acids in the crude, not just naphthenic acids.
  2. The various acids that comprise the naphthenic acid family can have distinctly different corrosivity.
  3. The structure and molecular weight of the specific naphthenic acids present have a strong impact on corrosivity, but they are not determined by TAN measurements.
- e) No widely accepted prediction methods have been developed to correlate corrosion rate with the various factors influencing it.
- f) Sulfur promotes iron sulfide formation and has an inhibiting effect on NAC, up to a point.
- g) Naphthenic acids remove protective iron sulfide scales on the surface of metals.
- h) NAC can be a particular problem with very low sulfur crudes. While a crude TAN threshold of 0.30 is typically cited as the TAN level below which NAC is not expected, some NAC cases have been reported with low sulfur and crude TAN as low as 0.10.
- i) NAC primarily occurs in hot streams above 425 °F (220 °C) but has been reported as low as 350 °F (175 °C). Severity increases with temperature up to about 750 °F (400 °C); however, NAC has been observed in hot coker gas oil streams up to 800 °F (425 °C).
- j) Naphthenic acids are destroyed by catalytic reactions in downstream hydroprocessing and FCC units. NAC of 300 series SS is also inhibited by injection of hydrogen in the feed to hydroprocessing units.
- k) Alloys containing increasing amounts of molybdenum show improved resistance to NAC. While alloys with a minimum of 2 % Mo, e.g. Types 316 and 316L SS, have demonstrated adequate resistance in some applications, it is generally agreed based on industry experience that alloys with a minimum of 3 % Mo, e.g.

Types 317 and 317L SS, are needed avoid NAC. To provide a greater degree of assurance, alloys with a minimum of 4 % Mo, e.g. Type 317LM, are sometimes selected. Under severe conditions or for components with nil corrosion allowance, 6 % Mo stainless steels and Alloy 625 have been used.

- l) Corrosion is most severe in two-phase (liquid and vapor) flow, in areas of high velocity or turbulence, and in distillation towers where hot vapors condense to form liquid phase droplets.
  - 1. For piping, NAC typically occurs in high-velocity and turbulent areas. The vapor space may be more susceptible to corrosion when flow is two phase due to acid condensation.

#### 3.46.4 Affected Units or Equipment

- a) Crude and vacuum heater tubes, crude and vacuum heater transfer lines, vacuum bottoms piping, atmospheric gas oil (AGO) circuits, and heavy vacuum gas oil (HVGO) and sometimes light vacuum gas oil (LVGO) circuits. NAC has also been found in resid transfer lines from the vacuum unit to the coker. Although thermal cracking in the delayed coker is thought to break down naphthenic acids, making NAC uncommon in coker units, NAC has been reported in the light coker gas oil (LCGO) and heavy coker gas oil (HCGO) streams in delayed coking units processing high TAN feed.
- b) Piping systems are particularly susceptible in areas of high velocity, turbulence, or change of flow direction. Examples include pump internals, valves, elbows, tees, and reducers as well as areas of flow disturbance such as weld beads and thermowells.
- c) Crude and vacuum tower internals may also be corroded in the flash zones and packing and internals may corrode where high-acid streams condense or high-velocity droplets impinge.
- d) NAC may be found in hot hydrocarbon streams in units downstream of the crude and vacuum units, upstream of any hydrogen mix points.

#### 3.46.5 Appearance or Morphology of Damage

- a) NAC is characterized by localized corrosion, pitting corrosion, or flow-induced grooving in high-velocity areas. (Figure 3-46-1 and Figure 3-46-2)
- b) In low-velocity condensing conditions, many alloys including carbon steel, low-alloy steels, and 400 series SS may show uniform loss in thickness and/or pitting.
- c) At temperatures below ~450 °F (230 °C), NAC can have a smoother, more uniform appearance than is typical at higher temperatures.

#### 3.46.6 Prevention/Mitigation

- a) For units and/or components of systems that have not been designed for resistance to NAC, the options are to change or blend crudes, upgrade to a resistant alloy, utilize chemical inhibitors, or some combination thereof.
  - 1. NAC can be reduced by blending crude to reduce the TAN and/or increase the sulfur content.
- b) Monitor TAN and sulfur content of the crude charge and side streams to determine the distribution of acids in the various cuts.
- c) Use alloys with higher molybdenum content for improved resistance. Type 317L SS or other alloys with higher molybdenum content may be required.
- d) High-temperature NAC inhibitors have been used with moderate success in reducing corrosion rates. However, their potential detrimental effects on downstream catalyst activity must be considered. Phosphorus-based inhibitors tend to be more effective but have more detrimental effect on downstream catalyst than sulfur-based inhibitors. Inhibitors effectiveness needs to be monitored carefully.

### 3.46.7 Inspection and Monitoring

Localized wall loss due to NAC is difficult to predict and find.

- a) VT can be used where access is available.
- b) RT can be used to look for and identify the extent of localized wall loss.
- c) Close-grid UT thickness examination or UT thickness scanning can also be used, either as an alternative to RT, e.g. when RT is not practical due to piping size or configuration, or as a follow-up to RT.
- d) Permanently mounted thickness monitoring sensors can be used.
- e) Electrical resistance corrosion probes, hydrogen probes, and corrosion coupon racks can be used if properly located. However, caution needs to be exercised with intrusive devices such as ER probes and coupons since they may create the turbulence that results in corrosion not only of the measuring device but of the adjacent pipe wall.
- f) Streams can be monitored for Fe and Ni content to assess corrosion in the system.

### 3.46.8 Related Mechanisms

Sulfidation (3.61) is a competing and complimentary mechanism that must be considered in most situations with NAC. In cases where thinning is occurring, it may be difficult to distinguish between NAC and sulfidation, and both may be contributing to wall loss, but pitting damage is attributable to NAC.

### 3.46.9 References

1. W.A. Derungs, "Naphthenic Acid Corrosion—An Old Enemy of the Petroleum Industry," *CORROSION*, Vol. 12, No. 12, NACE International, Houston, TX, pp. 41–46.
2. J. Gutzeit, "Naphthenic Acid Corrosion," Paper No. 156, *Corrosion/76*, NACE International, Houston, TX.
3. R.L. Piehl, "Naphthenic Acid Corrosion in Crude Distillation Units," *Materials Performance*, January 1988.
4. B.E. Hopkinson and L.E. Penuela, "Naphthenic Acid Corrosion by Venezuelan Crudes," Paper No. 97502, *Corrosion/97*, NACE International, Houston, TX.
5. M.J. Nugent and J.D. Dobis, "Experience with Naphthenic Acid Corrosion in Low TAN Crudes," Paper No. 98577, *Corrosion/98*, NACE International, Houston, TX.
6. API Recommended Practice 581, *Risk-Based Inspection Methodology*, American Petroleum Institute, Washington, DC.
7. C. Shargay et al., "Survey of Materials in Hydrotreater Units Processing High Tan Feeds," Paper No. 07573, *Corrosion/2007*, NACE International, Houston, TX.

**Table 3-46-1—Alloys Listed in Approximate Order of Increasing Resistance to NAC**

CS, 1¼Cr-½Mo, 2¼Cr-1Mo, 5Cr-½Mo 9Cr-1Mo, 410 SS, 304L SS, 321 SS, 347 SS 316 SS (2 % to 3 % Mo) 317 SS (3 % to 4 % Mo) 6 % Mo alloys Alloy 625, Alloy 276
NOTE Alloys listed above 316 SS in the table are not considered NAC-resistant materials.



Figure 3-46-1—Erosion-corrosion damage due to NAC in a 10-in. 5Cr- $\frac{1}{2}$ Mo elbow in the outlet of a vacuum heater in a vacuum distillation unit.



Figure 3-46-2—Severe NAC of 410 SS trays and bubble caps in the HVGO section of the vacuum tower fed by the vacuum heater referred to in Figure 3-44-1.