Corrosion in Crude Distillation Unit Overhead Operations: A Comprehensive Review

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ABSTRACT

In the refining industry, the business need to work with opportunity crudes, an essential element of current day reality, has meant that refinery operators face substantial risk of corrosion damage in both the atmospheric unit and the vacuum unit. The atmospheric unit, also called the crude distillation unit (CDU), is often exposed to increased levels of chlorides and sulfur species, leading to substantial corrosion issues related to the species that manifest in crude overhead operations. These corrosion issues include: (a) under deposit corrosion due to sublimating species such as ammonium chloride, (b) aqueous corrosion due to hydrochloric acid (HCl) or acidic sulfur species, and (c) fouling issues related to the build-up of sublimating species. Often, the principal cause for these problems may be correlated to high chloride content in the crude coming out of the desalter or inadequate controls to ensure conditions for fractionation operations above aqueous dew point.

The difficulty in predicting and assessing the contribution and severity of these corrosion / fouling problems stems from the significant complexity of the chemistry involved and the inadequate documented experience correlating speciation of contaminants from the crude feed to the corrosion problem. The purpose of this paper will be to: (a) review published literature to characterize and classify speciation related to the types of impurities encountered in opportunity crudes; and (b) describe and categorize published case studies of corrosion in crude unit overhead operations. In doing so, the authors will attempt to delineate the primary corrosion problems encountered in CDU overhead systems, parametric components or species in the crude that drive corrosion, and gaps in technology that require additional study.

Key words: crude overhead, salt hydrolysis, HCl, ammonium chloride, dew point, salt formation, fouling, neutralizer, ammonia, amine, film-forming inhibitors

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INTRODUCTION

Corrosion in crude overhead systems stems primarily from the presence of hydrogen chloride vapor present from hydrolysis of salts in the atmospheric crude distillation unit. The most common source of HCl is from the hydrolysis of calcium chloride and magnesium chloride salts at temperatures exceeding 250 °F (121 °C) though the HCl may also come from the decomposition of organic chloride species. HCl, being a light volatile gas, moves into the crude unit overhead condensing systems where it is readily absorbed into condensing water.

Various remedies are used to mitigate the acidic attack from condensed water containing HCl, including neutralizing compounds like ammonia and organic amines, film-forming inhibitors, wash water systems, and close control of temperature in the overhead circuit. Care must be taken to implement one or more of these remedies as introduction of the remedies may lead to fouling, under-deposit corrosion, and other problems. Figure 1 presents a schematic of crude overhead circuit and related upstream equipment along with many of the issues related to corrosion and fouling.

Figure 1: Schematic of crude feed, desalter, atmospheric distillation unit, and overhead circuit along with common corrosion and fouling issues.

BACKGROUND

Corrosion in crude distillation overhead systems is a common problem in refineries. The primary mechanism of concern in the overhead system is the acidic attack of unit metallurgy due to the presence of high concentrations of HCl in condensing water. Other corrosion and operational concerns include under-deposit corrosion and fouling usually resulting from unintended consequences of acid neutralization and / or inefficient desalter operations.
Acidic Attack in the CDU Overhead

The presence of acid in the crude overhead system may result in particularly severe attack as the acids easily dissolve in condensing water resulting in local environments with pH values typically as low as pH 1.6-10. While HCl is the most common cause of acidic attack in the CDU overhead, the presence of other acids including sulfur-oxide species and organic acids may also contribute to corrosion. Process upset conditions that result in higher acid content can result in the dissolution of protective iron sulfide/hydroxide scales or film-forming inhibitors9.

HCl Sources. The most common source of HCl vapor in the overhead circuit is from the hydrolysis of chloride salts in the atmospheric distillation unit1-7. The common hydrolysis reactions are:

\[
\begin{align*}
\text{NaCl} + H_2O & \rightarrow \text{NaOH} + 2\text{HCl} \\
\text{MgCl}_2 + 2H_2O & \rightarrow \text{Mg(OH)}_2 + 2\text{HCl} \\
\text{CaCl}_2 + 2H_2O & \rightarrow \text{Ca(OH)}_2 + 2\text{HCl}
\end{align*}
\]

NaCl is more common in desalted crude oil feeds than MgCl2 and CaCl2 but is more resistant to hydrolysis. MgCl2 and CaCl2 start to hydrolyze above 250 °F (121 °C) and 400 °F (204°C) respectively while NaCl is more stable and will not hydrolyze under 450 F (232 °C)1,4-8.

The crude desalter is the main defense against the presence of excessive amounts of inorganic chloride salts. The desalter serves to clean the crude of many impurities, especially inorganic chloride salts which are typically removed down to a level of 4 ppm of inorganic chloride species1,9-10. The limitation of inorganic chloride salts entering the crude distillation unit substantially reduces the presence of HCl in the CDU overhead circuit. Experience shows that chloride content of the desalted crude feed to the CDU that exceeds 20 ppm have the potential of leading to significant corrosion and fouling issues in the overhead circuit10.

Caustic injection is also used to control HCl presence and is typically conducted just downstream of desalter operations. One of the primary purposes of caustic injection in the desalted crude is to provide caustic such that HCl generated from salt hydrolysis will react with NaOH to result in NaCl, and is therefore less likely to generate HCl in crude distillation1,5,8.

The processing of crude oils containing high levels of naphthenic acid may exacerbate problems with the presence of salt and hydrolysis. High acid content crude oils often have higher conductivity and emulsion forming tendencies than typical crude oils which can diminish desalter efficiency leading to higher inorganic chloride salt contents in the feed to the CDU. In addition to the presence of additional inorganic salt to hydrolyze, naphthenic acids have been demonstrated in the laboratory to catalyze the hydrolysis of calcium and sodium salts at temperatures similar to those found in the CDU and vacuum distillation unit (VDU)7. The cumulative effect of naphthenic acid content in the crude oil on the resulting HCl in the crude overhead may be substantial when considering the possibility of additional salt content in the crude oil exiting the desalter and a higher proportion of inorganic salts hydrolyzed to HCl in the distillation unit.

Some types of organic chlorides may also serve as a source of HCl in CDU overhead circuits as they decompose at crude distillation unit temperatures1,9-10. While organic chlorides are typically not present in crude feeds in any appreciable amount, feed stocks contaminated with some species of organic chlorides can result in severe attack in the overhead circuit. Organic chlorides are not removed in the desalter operations due to their limited solubility in water1,8-10. As little as 1 ppm organic chlorides in the desalted crude has been found to double the amount of HCl in the overhead circuit9.
While organic chlorides are not a common problem, their unexpected contamination in crude feeds can be troublesome as refineries do not routinely analyze for organic chlorides \(^8\)-\(^9\). Potential sources of organic chloride contamination include\(^9\):

- Organic chloride solvents from oil production fluids,
- Organic chloride solvents used to dissolve wax and tar deposits in midstream equipment,
- Recycled engine lube oil containing additives that form organic chlorides in service or when heated to crude unit temperatures, and
- Spent catalysts and certain by-products of petrochemical processes; these are often referred to as “black oil” or “red oil” and contain large proportion of organic chlorides.

**Sources of Other Acids.** The presence of appreciable amounts of acids other than HCl such as carboxylic and carbonic acid species\(^2\) may result in unforeseen problems in the overhead circuit. The presence of oxygen in desalted crude feed can result in the formation of sulfur oxide species from the reaction of \( \text{H}_2\text{S} + \text{O}_2 \rightarrow \) \( \text{SO}_x \). These sulfur oxide species include sulfates, bisulfates, and thiosulfates that form strong acids in condensing water in the CDU overhead circuit\(^2\).

**Remedies of Acid Attack and Accompanying Issues**

The primary prevention of excessive chloride attack in the CDU overhead circuit is proper desalting operations to remove soluble chloride salts. Even when maintaining a crude feed at or below 4 ppm inorganic chloride with no oxygen and no organic chlorides, acid corrosion in condensing water is still a concern in CDU overhead circuits. Common mitigation strategies to acid attack are neutralization or dilution of the acids with overhead wash water. Typically, target overhead pH levels are 5.5 to 6.5 achieved through the addition of neutralizers (ammonia or proprietary amines\(^1\)-\(^2\)). An alternative method to prevent acid corrosion is to upgrade the metallurgy of the system\(^2\).

**Modeling and Simulation.** Modeling and simulation programs aid the refiner by calculating process parameters and important control variables using thermodynamic and kinetic calculations to diagnose conditions of the overhead circuit and identify the levels of mitigation required. Typical parameters evaluated by these modeling and simulation programs are\(^14\):

- Water dew point temperature at different locations in the circuit
- Vapor-liquid distribution of ionic species as water condenses
- Interaction between acids and bases present in both liquid and vapor phases
- Temperature and kinetics of neutralizer-chloride salting
- Initial water dew point ionic conditions including pH and concentration

Modeling and simulation are particularly important in CDU overhead circuits as many parameters cannot be accurately measured. Sampling points in the circuit may underestimate the level of chloride present as salts may have already formed and deposited ahead of the sampling point\(^14\). Dew point pH can be pH units lower than bulk pH and cannot be directly measured so simulation programs are used to predict the pH at the point of water condensation\(^3\)-\(^4\),\(^14\).

Knowledge of dew point and salt formation temperatures permits strict control of CDU overhead circuit temperatures to identify the locations in the circuit susceptible to strong acid attack, under-deposit corrosion, and fouling\(^3\),\(^13\)-\(^15\).

**Neutralization of Acids.** While the primary cause of corrosion is the presence of HCl, mitigation strategies using neutralization often result in additional problems including under-deposit corrosion and fouling issues due to depositing salts of HCl and neutralizers. Modeling and simulation programs exist
that are used to predict pH along with other parameters and can be used to calculate the appropriate amount and type of neutralizers that can help avoid under-deposit corrosion or fouling issues\textsuperscript{2,3,15}.

Ammonia and basic organic water-soluble amines can be used for neutralization of acids in the CDU overhead circuit. The important parameter for neutralization is the minimum amount of neutralizer for an acceptable dew point pH\textsuperscript{2,4,6,8,11}. Ammonia gas is directly injected into the overhead circuit for neutralization while amines are typically dissolved in water and injected into the circuit. Organic neutralizing amines used include alkyl, alkanol, alkoxy, and cyclic ether types\textsuperscript{4}.

Ammonia was once more commonly used as a neutralizer but the disadvantages of its use have promoted the use of neutralizing amines. Disadvantages of ammonia include a lack of neutralization at the beginning of water condensation, typical salt formation temperatures above the water dew point, and problematic injection rate control\textsuperscript{2,8}. Ammonia does not serve to neutralize acid at the point of water condensation as HCl more readily dissolves in water than ammonia as shown in Figure 2\textsuperscript{2}. Salt formation temperatures above the dew point can result in fouling and under-deposit corrosion.

Neutralizing amines typically have an advantage over ammonia in that they have better control of pH at water condensation and salt formation temperatures\textsuperscript{2,6}. Weaker base amines have lower temperature salt formation with HCl but if they form a salt, the result is more acidic and consequently may be more corrosive\textsuperscript{13}.

The behavior of neutralizers and HCl in a vapor stream can be calculated based on thermodynamic and kinetic behavior dependent on the partial pressure of HCl, the neutralizer and temperature\textsuperscript{1,2,11,14,16-17}. Figure 3 presents a phase diagram for an amine-HCl salt formation from vapor\textsuperscript{3}. The salt formation occurs when the product of the basic neutralizer and HCl is greater than the stability constant at the temperature of the system as shown in Figure 4\textsuperscript{2}. The higher the base strength of the neutralizer, the higher the temperature at which salts of the neutralizer and HCl will form\textsuperscript{1,11,16}. The goal of the neutralization strategy is to achieve an acceptable dew point pH without salt deposition.
Fouling and Under-deposit Corrosion. Fouling and under-deposit corrosion in the CDU overhead circuit is common and is caused by the reaction of vapors that form depositing salts. The salt deposition point is predicted thermodynamically and is a common calculation in models and simulations. Refinery experience indicates that salt deposition is typically not as severe as predicted.

A common fouling and under-deposit corrosion species is NH₄Cl which forms by reaction of NH₃ and HCl vapor at the salt formation temperature. NH₃ may be carried into the crude distillation unit from multiple sources including the presence of NH₃ in desalter wash water or from the use of NH₃ as a neutralizer. Figure 5 presents a diagram of NH₄Cl salt formation at various temperatures and concentrations of NH₃ and HCl in an overhead system. The knowledge of the salt formation thermodynamics allows the construction of a figure for injection rates of neutralizer to avoid salt formation, as shown in Figure 6.
Figure 5: NH₄Cl salt formation at various overhead temperatures\(^{14}\).

Figure 6: Neutralizer nomograph\(^3\).

Amine neutralizers may also form fouling and under-deposit corrosion species\(^{2,3,8,9,11-15}\). Figure 7 presents a diagram of amine salt formation for an example amine with HCl concentration at various temperatures\(^{13}\).
Another fouling and under-deposit corrosion species that can result from the presence of ammonia in overhead circuits is NH₄HS. NH₄HS is the product of NH₃ and H₂S gases and like chloride salts, may form salt on equipment directly from the vapor phase. The corrosion from NH₄HS may also be accelerated by the presence of cyanides, oxygen, or chlorides.

Under-deposit corrosion is common in CDU overhead circuits and is often most severe along the bottom of heat-exchanger shells. The under-deposit corrosion may occur at corrosion rates 100 times that of general acid attack in the overhead circuit. Amine hydrochloride salts formed in the CDU overhead circuit are typically hygroscopic, which can result in hydration of the salt and liquid water present above the dew point of water. This local water formation with the salts creates high concentrations of corrosive species and drives the under-deposit corrosion.

Water Washing. Water washing is another mitigation strategy for controlling overhead circuit corrosion issues. Water washing serves both to dilute acid in the overhead circuit as well as to solubilize and/or physically flush salt deposits that can result in fouling and under-deposit corrosion. When using water washing, it is important to maintain a continuous liquid water phase to prevent local corrosion issues. The water wash rate should be sufficient to ensure that the overhead stream condition is at the water dew point and excess water wash should be used to account for process variability. Care should be taken though as excessive water wash rates may result in erosion issues.

Corrosion Inhibitors. Filming amine corrosion inhibitors are commonly used in the CDU overhead circuit to protect metallic surfaces, typically carbon steel, from condensed acidic water and under-deposit corrosion. These amine corrosion inhibitors are injected directly into the overhead system and create a protective film on the equipment surfaces. Process upsets resulting in low dew point pH conditions can result in removal of the filming inhibitor along with the protective scale.
This section presents several case studies on actual CDU overhead system corrosion and operational problems. The common theme of most of these case studies is that the source of the corrosion problem should be identified and addressed rather than fixing the symptoms. For additional details on any of the case studies, the referenced papers should be consulted.

A study by Gutzeit\(^9\) of unexpected failures of carbon steel tubes and stress corrosion cracking (SCC) of 300 series stainless tubes identified organic chloride contamination in the crude feed as the source of the upset condition. A crude oil pipeline had been periodically contaminated with organic chlorides from hydrocarbon waste that had been blended and fed into the refinery. The level of organic chloride contamination of the crude feed entering the refinery was estimated at 50 ppm. This level of organic chloride contamination was estimated to have increased the amount of HCl in the CDU overhead by 50 times the anticipated amount from the typical presence of 4 ppm inorganic chlorides. The higher HCl level resulted in much stronger acid attack in the overhead circuit and significant additional salt formation. The dew point pH was estimated to be as low as pH 0 with the increased level of HCl. The salt formation temperature was estimated to have increased to 270 °F (132 °C), leading to salt deposits throughout the overhead circuit. These deposits led to under-deposit corrosion and fouling along with chloride SCC of 300 series stainless steel tubes.

A study by Braden et al\(^2\) identified a condenser system where pH measurements were 2-3 pH units lower than the pH predicted by modeling and simulation. Chemical analysis of samples from the condenser system found that unexpectedly high concentrations of non-HCl acidic species were present. These acidic species included sulfate, bisulfates, thiosulfates, carbonates, and carboxylic acids. The investigation found that a significant deviation in the oxygen content of the desalter water wash, from 10 ppb to 3.5 ppm, was present. The higher oxygen content had led to the formation of sulfur-oxide species through the reaction of H\(_2\)S with O\(_2\) in the distillation unit. After correcting the desalter water wash oxygen content problem, the measured pH values were much closer to those predicted by the modeling.

Two studies by Giesbrecht et al\(^12\) identified insufficient and improper water wash systems. The first case study identified the cause of excessive fouling as an improper installation of a water wash nozzle just upstream of a 90 degree elbow such that no wash water reached the back end of a heat-exchanger bundle. The second study identified both a change in neutralizer chemistry and a change in water wash as necessary to fix the fouling issues in the overhead circuit. The change in the neutralizing amine resulted in a lower salt formation temperature while higher flow in the water wash allowed flushing of formed salts from the system.

Case studies by Coble\(^5\) and Duggan et al\(^3\) identified excess use of ammonia as a neutralizer which resulted in significant NH\(_4\)Cl fouling. Modeling was used to determine a lower ammonia dosage that resulted in overhead system temperature that remained above the salt point temperature, preventing salt formation and fouling.

Two studies by Clarida et al\(^11\) identified the need for a change in amine neutralizer chemistry. The first study examined a refinery which after switching crude feed to an opportunity crude employed more neutralizer injection to counteract additional HCl present in the overhead system. The additional neutralizer injection resulted in a salt point temperature that was 20 °F (11 °C) above the dew point temperature leading to under-deposit corrosion and fouling in the system. By reducing the base strength of the amine neutralizer, the salt point temperature was lowered and the fouling and under-deposit corrosion were stopped. The second study was similar in examining corrosion and fouling that was consistently present in overhead heat exchangers. Again, a switch to a lower base strength amine neutralizer minimized fouling and corrosion in the heat exchangers.
A separate case study by Clarida et al.\textsuperscript{11} identified a set of heat exchangers where the use of the standard neutralizing amine was resulting in corrosion rates in excess of 30 mpy (0.8 mm/yr). A water wash system was installed in the system, reducing corrosion to less than 5 mpy (0.1 mm/yr). Though the water wash system was able to reduce fouling and under-deposit corrosion issues, erosion from the water wash became a significant issue.

A study by Lordo\textsuperscript{14} presents a simple case where an overhead system was experiencing fouling issues. Modeling was able to calculate that the troubled area of the overhead system was operating 42 °F (23 °C) below the salt point temperature. By increasing the temperature 25 °F (14 °C) above the salt point temperature, the fouling ceased in this portion of the circuit.

**CONCLUSIONS**

Based on the information provided herein and case studies reviewed from published literature, the following conclusions were made:

1. Significant corrosion problems have been reported in crude unit overhead operations, including those due to chloride and sulfur species in the crude. Most of these problems, such as those due to NH\textsubscript{4}Cl or HCl have been dealt with after the damage has occurred, and continue to be a source of significant material degradation in CDU overhead operations.
2. The main causes of corrosion in crude overhead systems are the presence of HCl from the hydrolysis of inorganic chloride salts in crude feeds and under-deposit corrosion from ammonia or amine hydrochloride salts.
3. Problems with crude feedstock or desalter operations can lead to excessive amounts of HCl being formed in the atmospheric distillation unit causing acid attack in the CDU overhead circuit or formation of salts that lead to fouling and/or under-deposit corrosion.
4. Multiple strategies for mitigation of HCl acid attack in the CDU overhead system include neutralizers, wash water, corrosion inhibitors, and metallurgy upgrades.
5. Neutralizers include ammonia and organic water-soluble amine compounds and are injected to raise the water dew point pH to a suitable level for corrosion control.
6. Reaction of neutralizers with HCl can lead to salt formation that can cause fouling and under-deposit corrosion.
7. Water wash systems act to dilute acid and remove salt deposits in the CDU overhead circuit.
8. Filming amine corrosion inhibitors are often used to provide a protective film on the overhead circuit to mitigate corrosion.
9. Models and simulations using thermodynamic and kinetic calculations of dew point and salt point temperatures along with other variables are useful tools for control of overhead system corrosion.
10. Multiple case studies exist on various overhead corrosion problems and solutions. The common theme of these case studies is to treat the source of the problem and not the symptom.

**REFERENCES**


