

Managing ammonium salts corrosion and fouling

An additive overcame corrosion and fouling issues in a FCC unit, avoiding costs arising from water wash

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Fluid catalytic cracker (FCC) and residue fluid catalytic cracking (RFCC) are important parts of modern refineries and are used for converting lower value petroleum fractions to valuable components. Feedstock to FCC is becoming increasingly heavy with the processing of atmospheric residue, which increases the potential for formation of ammonium salts.

Ammonium salts and their management

Fractionators in a FCC unit are prone to corrosion and fouling by ammonium chloride (NH_4Cl) and ammonium bisulphide (NH_4HS) salts. Corrosion and fouling are observed in the fractionator overhead, top section, and pumparound circuits. Depending on the partial pressure of the reactants, and conditions in the tower, salts can deposit and accumulate at temperatures above the water dew point. The consequences of ammonium salts formation in FCC units are:

- High corrosion in the overhead line, top section and pumparound circuit due to absorption of moisture by ammonium salts
- High delta pressure due to fouling of trays in the top section which can result in flooding and loss of tower efficiency
- Reduced heat exchange across pumparound circuits due to exchanger fouling resulting in reduced heat removal from the tower

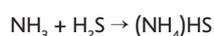
Ammonium chloride formation is a function of localised conditions: temperature, concentration of HCl, and concentration of NH_3 :



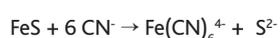
As the partial pressures of NH_3 and HCl increase and the temperature decreases, the potential for ammonium chloride fouling increases. Under-deposit pitting corrosion is predominantly caused by ammonium chloride salt due to its hygroscopic nature. Chloride ions react with iron to form iron chloride which results in severe localised corrosion. In the presence of H_2S , iron chloride reacts to form iron sulphide, and chloride ion is released again to continue the process of corrosion.

Refineries sometimes also face the problem of amine chloride salt formation (RNH_3Cl) due to overdosing of amine to meet the pH of overhead condensed water which, like NH_4Cl , results in localised under-deposit corrosion.

Ammonium bisulphide is formed by the reaction of ammonia and hydrogen sulphide:



Ammonium bisulphide is also corrosive towards steel and forms hydrogen gas and iron sulphide in the corrosion process. Normally, the iron sulphide formed coats the surface of the metal to stop further corrosion and the corrosion mechanism is terminated. But if cyanide is present then it will react with iron sulphide to form a soluble ferrocyanide complex which will remove the protective iron sulphide layer so that the corrosion reaction of ammonium bisulphide with the metal surface can continue:



If corrosion due to ammonium bisulphide continues then this can

lead to hydrogen blistering in the system due to the formation of hydrogen atoms that penetrate the metal surface.

Refineries often use oil soluble filming amines to mitigate corrosion. At higher concentrations they act as salt dispersants to stop fouling problems due to ammonium salt formation. These products just transport salts from one location to another and hence the problem is shifted to another downstream location and is not completely resolved. They work by chemically binding to salts, and if sufficient free water is not present to solubilise the salts then it can be found in product streams as well. Filming amines are surface active products and can stabilise emulsions.

Refineries also use continuous or intermittent wash water to remove ammonium salt deposits and thus minimise under-deposit corrosion and fouling. These water wash systems can be counter-productive in a refinery because the choice of wash water quality is defined by availability of water, and the right quality of water is not always available in abundance. The best source for water wash is either steam condensate or properly stripped water from the sour water stripper unit. Generally, water wash is 6-7 vol% on fresh feed to the FCC unit.

An insufficient or poorly designed wash water system can lead to increased corrosion as ammonium salts form acidic solutions when dissolved in water. Dead areas, bends, and low flow areas are prone to acidic under-deposit corrosion if the wash water is not sufficient; this leads to formation of highly concentrated thick and viscous salt solu-



Figure 1 Dried ACF-Cl salts convert from solid to liquid form on exposure to atmospheric humidity inside the laboratory, illustrating the highly hygroscopic nature of ACF-Cl salt

tions. Wash water can also lead to reduced productivity due to off-spec product, thus increasing reprocessing costs.

Ammonium Chloride Free (ACF) technology

Kurita's ACF technology is a solution which can eliminate problems related to ammonium and amine salts in various refinery units including the FCC unit. Features of ACF technology include:

1. Liquid formulation of a very strong organic base. The pKb value of ACF product is close to zero which indicates a very strong base.
2. Instantaneous reaction with HCl and ammonium salt deposits, hence quick results can be achieved.
3. Water soluble and does not react with hydrocarbons, hence no contamination of hydrocarbon product streams.
4. A single product can be used to handle ammonium chloride, organic

amine chloride, and ammonium bisulphide related corrosion and deposition problems.

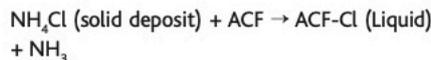
5. The reaction product with salts is ACF-Cl, which has neutral pH, unlike ammonium salts which form acidic reaction products.

6. ACF-Cl salts are highly hygroscopic and are easily removed from the system with free water in the system (see **Figure 1**).

7. The corrosion potential of ACF-Cl salts is very low, unlike ammonium salts which are highly corrosive.

Kurita ACF works via two modes (see **Figure 2**):

1. Removal of existing deposits from piping, trays, and heat exchanger surfaces:



2. Reaction with HCl to neutralise it and form non-corrosive ACF-Cl in the column overhead and tower:

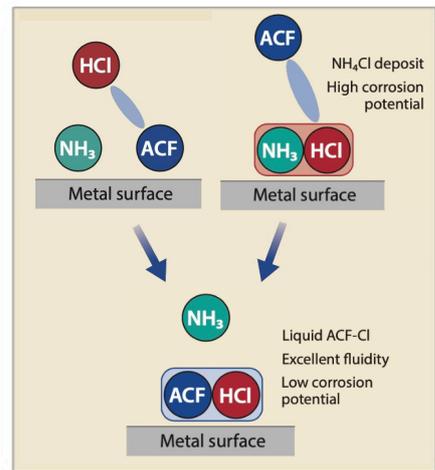


Figure 2 ACF reaction mechanisms



Depending on the application, ACF can be dosed intermittently as an online cleaner for removing existing ammonium salt deposits, or it can be added on a continuous basis to avoid corrosion and deposition due to HCl and ammonium salt formation in the system.

Case study: ammonium chloride fouling removal

Since its commissioning, a refinery experienced ammonium salts deposition in the RFCC fractionator's column top trays and heavy gasoline pumparound circuit (see **Figure 3**).

The plant began a regular water wash to dissolve the ammonium chloride salts, but this resulted in increased corrosion potential and violation of product specification, leading to reduced productivity and high reprocessing costs.

Normally, the chloride content in overhead condensed water are up to approximately 70 ppm, but during water washing they are up to 13 900 ppm, which is a clear indication of a high amount of ammonium chloride salts deposition.

The plant also introduced salt dispersants in the tower reflux and heavy gasoline circuit without much success. In spite of adding high amounts of salt dispersant, water wash was needed to sustain operations.

For this plant there was the possibility to inject ACF in the tower reflux or heavy gasoline pump-around circuit and the latter was selected for dosing. No water wash

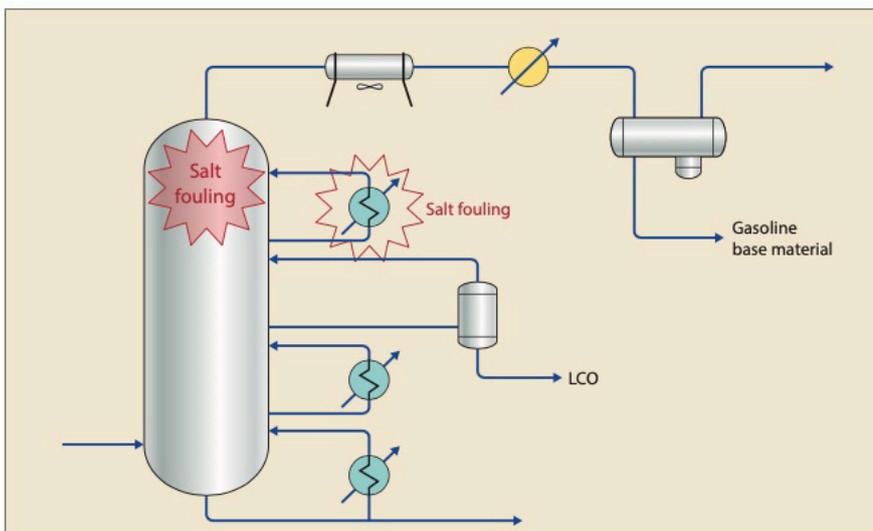


Figure 3 Salts fouling in a RFCC fractionator



Figure 4 Immediate recovery in delta temperature across a heat exchanger after injection of ACF. Recovery in delta temperature was higher than the target value



Figure 5 Immediate reduction in delta pressure across a heat exchanger after starting ACF injection

was done during application of ACF for online removal of ammonium salts from the heavy gasoline pump-around circuit.

The results of online ACF injection are shown in **Figures 4** and **5**.

Other benefits observed were increased depropaniser bottom temperature, reduction in LCO flow, and steam to the depropaniser reboilers.

No water wash during the trial ensured no reduction in unit throughput and no off-spec product for reprocessing.

Conclusions

Ammonium salts formation can lead to unplanned shutdowns and high operating costs if not managed properly in the FCC unit. Kurita's ACF technology is a solution to avoid ammonium salts corrosion and fouling in FCC units. Generally, refin-

eries use oil soluble filming amines or periodic water wash that may increase corrosion potential, reduce productivity, and can shift problems to downstream systems.

ACF technology can completely remove deposited ammonium salts and can also avoid formation of new ammonium salt deposits in the FCC. The reaction of ACF with ammonium salts is instantaneous and immediate results can be achieved. The correct application will eliminate the need for water wash, hence improving plant integrity and productivity.

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