



Away with the salts

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discuss ammonium salt removal management.

Ammonium salt fouling and corrosion are common problems in petroleum refining plants, which cause great damage and costs every year. Ammonium chloride (NH_4Cl) and ammonium bisulfide (NH_4HS) are corrosive, as a gas, solid, or in solution. Therefore, corrosion protection is one of the major concerns in refinery operations, where these salts are generated through the process itself or are imported from other process units with the feedstock. To avoid stress corrosion cracking, distillation equipment being exposed to ammonium chloride fouling has to be thoroughly washed with an alkaline solution. Ammonium bisulfides are depositing at far higher temperatures compared to ammonium chloride salts and they are more difficult to remove by water washing. Good wash water system designs are required, but sometimes an uncontrollable outlet temperature still causes problems. This is the case when the fluid velocity in condensers is low enough for ammonium salts to settle down in the tubes, causing pitting and under-deposit corrosion.

Typical areas for ammonium salt fouling and corrosion are CDU or FCC distillation column top sections, hydrocrackers, feed-effluent exchangers from hydrotreater or catalytic reformer reactors, recycle gas compressors, stabiliser columns, reboilers and overhead sections. When neutralising amines are used for corrosion protection of the overhead section, there is always a risk that some amine-HCl salts may enter the distillation column with the reflux stream again. Amine chloride salts dissociate to amine and hydrochloric acid by thermal decomposition or evaporate as a form of amine-HCl by heating and then may deposit in the overhead system at lower temperatures, causing corrosion problems.

Sometimes oil-soluble additives are also used as anti-foulants. Film-forming amines (such as imidazolines) have a dispersing effect at higher treat rates and can therefore mobilise some of the deposited

ammonium salts. Imidazolines belong to the chemical group of heterocyclic compounds. They have surface-active properties, which limits their use as anti-foulants, as they may tend to form emulsions at higher dosing rates. Being high-boiling active substances, they can also be transported downwards with the condensing product streams. This can negatively affect the product qualities of the side streams.

Technology

The ACF technology is a strong-base chemistry that reacts directly with ammonium chloride, hydrochloric acid, and amine salts. It has three very important properties: high ammonium salt replacement action, high moisture absorption and very low corrosiveness. The strong base ACF displaces the weaker base ammonium from its salts to form liquid ACF salts with neutral pH and very low corrosiveness. Fouled neutralising amine salts in distillation columns or overhead systems can also be removed by forming liquid ACF salts.

The ACF reaction product is a quaternary salt compound with a very low corrosion potential. In comparison, reaction products of primary, secondary or tertiary neutralising amine salts show a much higher corrosion potential. The organic base ACF directly reacts with strong acids such as HCl or its salts, where already deposited salts are immediately dissolved into liquid salts.

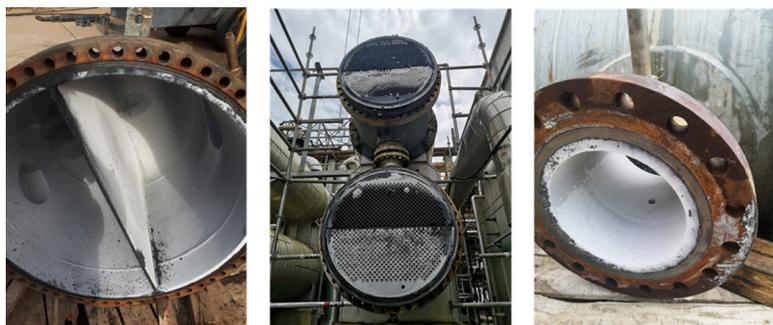


Figure 1. Fouled naphtha hydrotreater effluent exchangers.

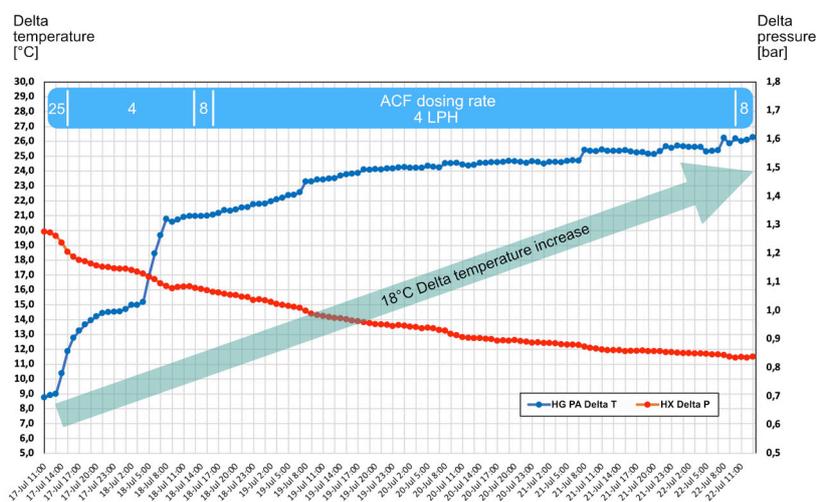


Figure 2. Test results from the heat exchanger of the heavy gasoline loop.

In systems where even small amounts of salt deposits lead to problems with safety and control valves, online cleaning can achieve great success in a few minutes and restore the old condition as with mechanical cleaning. In systems where large salt deposits have built up over a longer period of time, dosing is carried out over a few days and the deposits are continuously removed from the system. Interestingly, there are process plants where regular water washing removes only small amounts of chlorides despite the presence of salt deposits. This can be attributed to the fact that above the salt layer, hydrocarbons probably prevent direct contact with the water. When ACF is added to the wash water, the chloride concentration in the sour water then increases rapidly. Such effects have been observed a few times, where after adding ACF to the wash water, the chloride concentration suddenly increased from <10 ppm to >5000 ppm chlorides in the wash water.

ACF technology is used during online cleaning to remove ammonium chloride, ammonium bisulfide or neutralising amine hydrochloride (e.g. MEA hydrochloride). When large amounts of ammonium salts need to be dissolved and removed, it is particularly important to provide a sufficiently high amount of ACF during cleaning. The deposited salts are chemically converted into water-soluble ACF salts, which can then be easily removed.

There is a stoichiometric ratio of ACF to ammonium salts and one can calculate very precisely how much product is needed for cleaning if the amounts of deposited salts are known. In practice, it has proven useful to apply a ratio of 1:5 or five parts ACF to one part deposited salts as a rule of thumb. When ACF is injected on a continuous basis it prevents the harmful chloride salts from forming and keeps the corrosion potential low. This allows the refinery to operate at low overhead temperatures without fouling or corrosion restrictions. For continuous applications as a preventive measure, dosing is usually realised in the low ppm range. It is possible to combine ACF together with film-forming amines in one product. Salts can then be removed at the same time and the metal surfaces can be effectively protected against direct acid attack.

Case study 1

A refinery observed ammonium salt deposition in the Residue FCC (RFCC) main fractionator column upper trays, overhead system and depropaniser reboiler after commissioning to expand the profitability to crack a wider range of feedstocks.

Up to 70 ppm chlorides are regularly measured in the RFCC main fractionator overhead separator drum. During a 2 – 8 hr online water wash,

which must be carried out every two months, up to 13850 ppm of deposited chlorides can then be dissolved and removed with the wash water. However, the water wash is only partially helpful because during this time production is out of spec and the top pumparound flow must be reduced by 20 – 30%. After the water wash, 10 – 15°C heat recovery on the hot side of the circulating heavy gasoline is observed.

In a trial lasting several days, an ACF additive was dosed into the inline tube to the heat exchangers of the heavy gasoline loop. The aim of this test was to dissolve the salts and also to achieve 10 – 15°C heat recovery. Wash water was not added at all. For about two hours, 25 l/hr of ACF additive were dosed to fill the dosing line. After that, the dosing was reduced to 4 l/hr. The results and adjustments to the dosing rates during the trial are shown in Figure 2, where one of the heat exchangers was used for monitoring to evaluate the performance.

With improved 18°C hot side delta temperature and almost 0.45 bar strongly falling differential pressure, the specified success criteria were clearly exceeded. During the ACF trial phase, the unit throughput did not need to be reduced and only heavy gasoline was sent to slop for reprocessing as a precautionary measure. During classical water wash, heavy gasoline and light gasoline are sent to slop for reprocessing. Other positive effects were an increase in the depropaniser bottom temperature and the reflux ratio. The LCO flow rate to the depropaniser reboiler was reduced as well as the steam flow.

Counteracting negative effects

Refineries have some options to increase the middle distillates and propylene production. However, this often has negative consequences or requires additional capital costs. A common strategy is to adjust the cut points between the naphtha and middle distillates draws in the crude distillation unit, coker unit or FCC plant. This is usually done by reducing the fractionator top temperature, which then inevitably increases the ammonium chloride (NH_4Cl) salt potential. FCC units and delayed coker main fractionator towers often show salt fouling. They are particularly sensitive to salt fouling because of the relatively high concentration of ammonia (NH_3) and hydrogen chloride (HCl). A temperature reduction of 3 – 5°C can result in nearly three times the salting potential. An FCC main fractionator temperature decrease of 5 – 10°C or more will inevitably lead to a rapid salt fouling with significant differential pressure increase.

Continuous use of oil-soluble salt-dispersant technologies can help, if the temperature reduction is in the 3 – 5°C range. However, its use is often limited by a certain tendency to emulsify which should be avoided. It has its limits in the case of long-term temperature reductions of more than 5°C, when higher additive dosing rates are necessary and high-boiling hydrocarbon components could enter downstream products (e.g. LCO).

Kurita DMax products are water-soluble formulations and counteract these negative effects. Applied with continuous dosing it will ensure stable process conditions

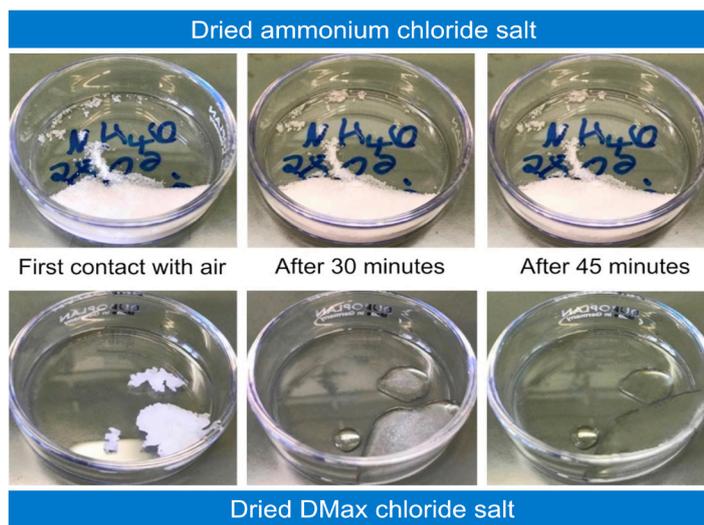


Figure 3. Hygroscopicity test with NH_4Cl and DMax chloride salts.

without significant pressure increase or rising corrosion rates. This achieves higher profits quickly and without extensive conversion work. Kurita DMax products are based on organic hydroxide chemistry. The very strong base provides the full base strength of the hydroxide ion, which is by a factor of 10 – 100 stronger than typical organic amines. Ammonium salt-based deposits are fully dissolved into the process stream. It is a curative treatment, which prevents salt precipitation and corrosion. This chemistry can even be applied at high temperatures.

Formed DMax salts have a very low corrosion potential and are highly soluble in water. As an additional benefit they have a very high tendency to absorb the humidity from air or steam addition. The salts are highly hygroscopic, referring to the property of substances to bind humidity from the environment, if free water is not present. Ammonium chloride salts absorb water, but the damp salts are extremely corrosive and plug fractionator trays, piping, and heat exchanger surfaces. The situation is different where DMax chloride salts remain liquid and leave the system with the condensed steam or sour water phase. Figure 3 shows a laboratory test, where dried ammonium chloride and DMax chloride were in contact with ambient air at room temperature. After about 30 minutes the dried DMax salts started to become liquid again, while ammonium chloride salts stayed solid.

Case study 2

To achieve specifications for low-sulfur gasoline or higher LCO yields, modifications and operational changes may be required. This could include undercutting of FCC naphtha, separation of high sulfur naphtha via the heavy naphtha train. Due to lower temperatures and higher concentrations of NH_3 and HCl , a build-up of salt deposits may then be observed in the upper section of the FCC main fractionator and upper pump-around circuits. Clogged bottoms and product draw, significantly increased corrosion, loss of fractionation and loss of compressor performance are known problems in that case.

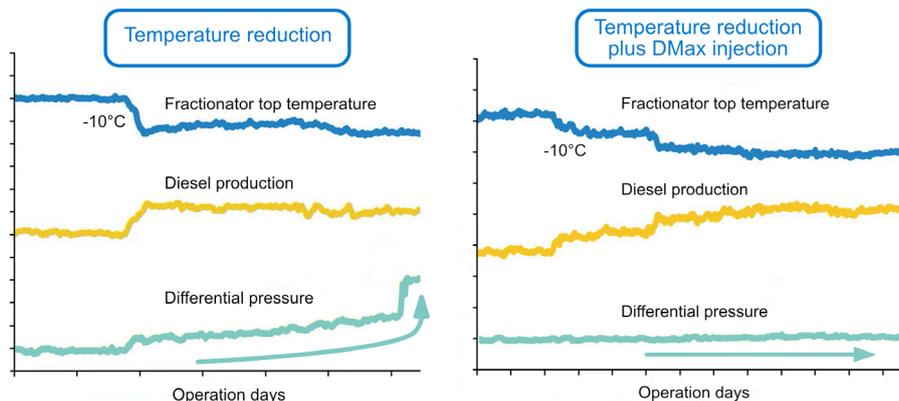


Figure 4. Effects of temperature reduction without and with DMax application.

An FCC plant wanted to increase the LCO yield as blending material for higher diesel production and at the same time significantly increase the profit for the refinery without major conversion work or time-consuming approach. The simplest way was to lower the cut temperature of the gasoline base material in the main fractionator by 10°C. As expected, a higher product yield was achieved. Relatively quickly, an increase of the differential pressure was observed, which was a result of unwanted salt deposits in the column. The differential pressure rose steadily and after a few days a very sharp jump to a much higher critical level was observed. This mode of operation was then stopped in order to remove the salts and restore the previous operation conditions.

When the FCC system was running again under constant conditions at a later time, the temperature was lowered again by 10°C, but at the same time an additive from the DMax series was also dosed with continuous treatment. Compared to the first observations and experiences, the yield of diesel could be increased again, but now the differential pressure remained constant and no increase in corrosion was reported at a later point in time. For the customer this performance means an economic advantage and it has become an important application.

Conclusion

The formation of ammonium salts and their deposits is sometimes difficult to prevent. A well-functioning water wash can help to remove these salts in some cases. The right design then plays a very important role and about 20% of the wash water should not vaporise if possible to avoid acidic dew point corrosion. Deposits in condenser tubes are often difficult to prevent if the fluid velocity is low enough for ammonium salts to settle down, causing pitting and under-deposit corrosion. The use of a chemical treatment programme can help to achieve long run times without the problems discussed in this article. 