

Preventing ammonium salt fouling and corrosion

Best practices and opportunities to reduce the risk of salt deposition and damage

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Salt deposits and corrosion can lead to damage or high energy losses when crude oils are processed. Usually, these salts are ammonium chloride (NH_4Cl) or ammonium bisulphide (NH_4HS). This article describes a new approach to prevent chloride corrosion or further deposition of ammonium salts in order to avoid or minimise corrosion and fouling potential.

The use of a powerful water washing system is certainly a good step in the right direction to wash out as many salts as possible. Ammonium salts are generally readily soluble in water, but can often not be completely removed in the presence of hydrocarbons. Process units suffering ammonium salt fouling or corrosion are crude distillation units, FCC units, hydrocrackers, hydrotreaters and reformer units.

Higher amounts of chlorides in residue feedstocks or low main fractionator top temperatures to produce low sulphur gasoline are two reasons for salt fouling in FCC units. Sometimes a tower washing programme can be performed

to remove water soluble salts. For this purpose, water is fed into the top reflux, or the overhead temperature is lowered until enough water can condense to the top trays. This usually takes several hours or even days. The feed rate must be significantly reduced by 20-30% during this time. The produced naphtha, sometimes also the light cycle oil (LCO), goes off-specification and has to be reprocessed with increased costs. In addition to the lower throughput, these costs may be particularly high.

The addition of an oil soluble salt dispersant additive can help to prevent salt deposition and keep the salts transportable, but that practice may also lead to several disadvantages. They work by chemically binding to the salt deposits, where the lipophilic functional group keeps microcrystalline salts in the hydrocarbon phase until enough free water is present so that the salts can be solubilised later. The dispersed salts are carried out of the system with the hydrocarbon product flow. Such salt dispersants are often surface active com-

ponents with filming amine properties that can stabilise emulsions. In the event that not all of the bound salts are solubilised in free water later, they may remain in the hydrocarbon phase of the product steam, to be transported to downstream processes.

ACF technology

Kurita's patented ACF technology pursues a completely different approach. Liquid formulations of a very strong organic base called ACF are used. These are water soluble and do not react with hydrocarbons. The organic base ACF has a very low pKb value close to zero, which is an indicator of a very strong base. It reacts preferentially with strong acids such as hydrochloric acid (HCl) or its corresponding ammonium salts (NH_4Cl). The reaction product is ACF-Cl, which is a liquid salt with a neutral pH of 7. ACF salts have very high moisture absorption characteristics (highly hygroscopic) and can be removed easily from the system with free water. One more benefit is that ACF salts have a

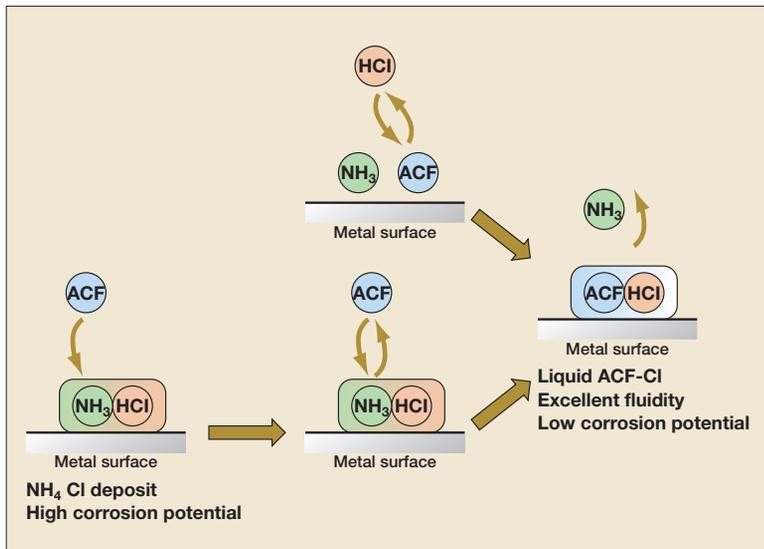


Figure 1 Removal of ammonium salt deposition and corrosion prevention

very low corrosivity. This is a significant difference compared with conventional neutralising amine salt reactions where the formed neutralising amines are almost always very corrosive and require higher amounts of wash water for removal.

The favoured reaction of ACF with HCl is a significant advantage in process units with naturally high H_2S concentra-

tions, such as hydrotreaters or hydrocrackers. Only after the conversion into ACF-Cl can weaker acids like hydrogen sulphide (H_2S) or its salts react with the ACF by forming the corresponding ACF reaction product. The reaction with ACF is shown schematically in Figure 1, which is also valid for other ammonium salts such as NH_4HS or ammonium sul-

phate ($(NH_4)_2SO_4$). In all cases, ACF displaces the weaker base ammonia by forming a liquid salt. In the absence of free water, the salts are transported at temperatures below $180^\circ C$ together with the hydrocarbon stream. When they come into contact with water, the salts can be removed with the aqueous phase. This chemical programme can be applied continuously to prevent fouling and corrosion or it is used at higher dosing rates to remove already formed salt deposits.

Case study 1: FCC main fractionator

Since it is common practice for the top temperature in FCC main fractionator columns to be lowered to produce more low sulphur gasoline, negative impacts are often observed. In most cases, salt fouling is the reason and this can also lead to corrosion if the salts are present on the metal surface as a sticky, highly concentrated and viscous solution.

Negative impacts are:

- Increased pressure drop
- Plugged trays and product draws
- Increased corrosion rates
- Flooding of the main fractionator top section
- Efficiency losses between gasoline and LCO separation
- Wet gas compressor efficiency losses.

During a field trial, the online cleaning performance of ACF was tested in a Western European refinery. Chemical injection into the main fractionator overhead reflux is common to dissolve the deposited salts from the top trays. According to the refiner's experience, naphtha circulation was also

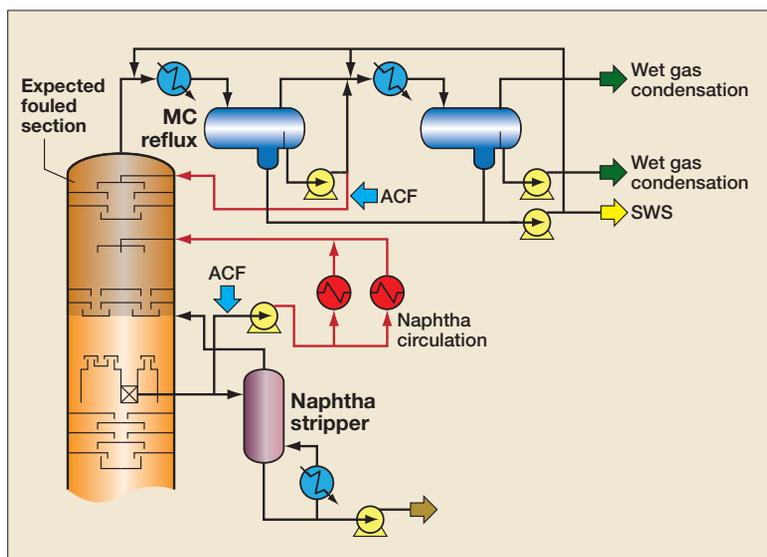


Figure 2 FCC main fractionator top section

affected where salt deposits on the lower trays were assumed to be present. Therefore ACF was additionally injected into the naphtha circulation in order to remove salt deposits from the heat exchangers and from the lower trays of the fractionation column. **Figure 2** shows the two dosing points where ACF was continuously injected during the online cleaning. The reaction with the chloride salts is a stoichiometric balance and, according to the expected high amounts of salt deposits, a few litres per hour of ACF were dosed at both locations to mobilise high amounts of salts.

After the dosage had been started, first successes were observed within less than 30 minutes. **Figure 3** shows some recorded results from the control room with basic data before the treatment and significant changes during the online cleaning. The differential pressure of the main fractionator column as a direct key indicator for fouling, the FCC feed rate, and the heat transfer coefficient of the naphtha circulation are displayed graphically in **Figure 3**. The rapid increase in the heat transfer coefficient and the main fractionator differential pressure drop impressively demonstrate that higher amounts of salt deposits were dissolved and mobilised in a short period of time.

Case study 2: hydrotreater feed/effluent exchangers

In a naphtha hydrotreater operating with several feed/effluent heat exchangers, corrosion problems occurred in the space of a few years, mainly due to the formation of ammonium salt deposits. As a correc-

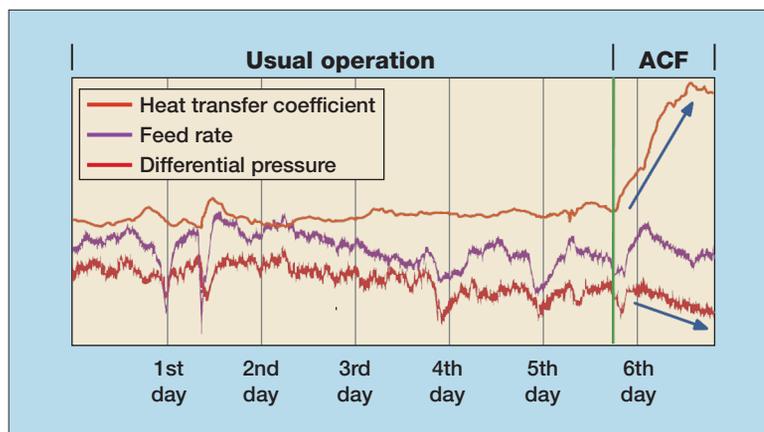


Figure 3 FCC main fractionator online cleaning results

tive action, ACF was injected between the second and third heat exchangers after the reactor with the aim of stopping corrosion in the third feed/effluent exchanger and airline coolers. Since the treatment was started, large amounts of chlorides were collected in the water boot of the accumulator from where they could be frequently removed. Despite the higher chloride concentration in the accumulator, the corrosion potential was significantly lowered since ACF salts have a very low corrosion potential. **Figure 4** shows the location where ACF is continuously dosed with a low ppm injection rate into the effluent product stream.

After some months of operation, when no damage occurred, the ACF programme was

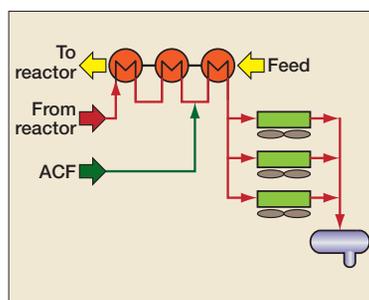


Figure 4 Naphtha hydrotreater feed/effluent exchangers

extended with an additional function of film forming properties. The metal surfaces are thus directly protected from acid attack and, because of the smooth and clean metal surface, any salt deposition is prevented. The result is longer time in operation with clear energy savings. The duty calculations and hot approach temperature (HAT), where the thermodynamics of heat recovery can be determined by superimposing the curves showing heat demand from the reactor feed and heat release from the reactor effluent, are good key performance indicators.

Figure 5 shows the heat exchanger duty trends and calculated energy savings in comparison to the previous operational mode over a period of two years since the application was started. The success of the treatment is demonstrated by the fact that no further corrosion damage has occurred so far, as well as by an improved energy balance of the feed/effluent exchangers.

Case study 3: debutaniser cleaning

Severe flooding problems were

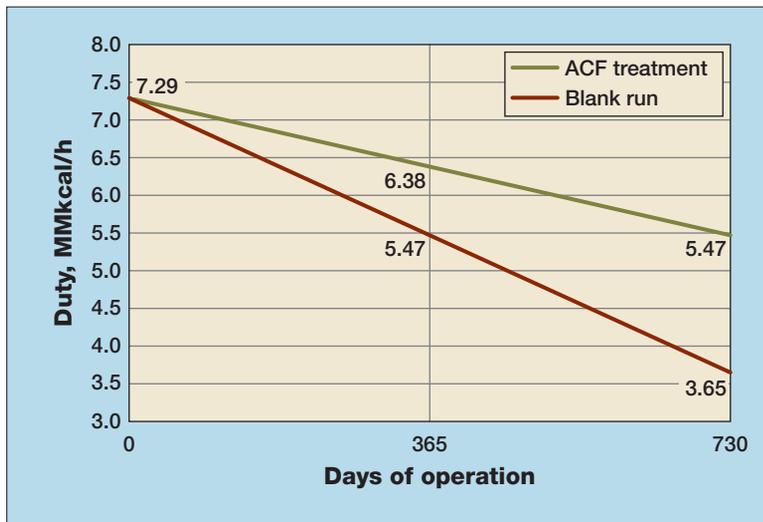


Figure 5 Feed/effluent exchanger energy savings

observed in the debutaniser column of a naphtha hydro-treater unit. The results of a root cause analysis pointed out that mainly ammonium salts and corrosion products such as iron sulphides were the originators. The debutaniser column is equipped with valve trays, where it was expected that many of the top trays were heavily fouled and blocked. This resulted in a high differential pressure increase, excessive liquid return to the bottom section, and a significantly reduced throughput. Clear indicators for flooding were the high levels of C_5 hydrocarbons in the C_4 section, due to a decline in separation (off-spec production), and the high Reid vapour pressure of the isomerate. The debutaniser bottom reboilers had to be stopped to keep the unit running.

Previously, water washing had been carried out with only mediocre success, where not all fouling deposits were removed and the naphtha hydrotreater had to be stopped for one to two days. This was

not an option this time because it would involve a shutdown of the reformer and isomerisation unit. Mechanical cleaning of the debutaniser column would also result in unwanted shutdowns of the reformer and isomerisation unit for three to five days. For these reasons, online cleaning with ACF was selected to put the debutaniser back on track.

High amounts of fouling deposits were expected in the top section of the debutaniser column. To reach that area for direct contact of ACF with the fouled salts, there was only one possible location for the injection, which was the suction side of the overhead reflux pump. While about 80% of the liquid phase returns back to the debutaniser top section, about 20% is passed via a reflux pump to the LPG unit.

Taking this into account, the ACF dosage was started and showed immediate improvements. Over a period of six days, ACF was injected continuously, where water samples were taken several times

per day from the overhead accumulator to report the status of the online cleaning. The pH, conductivity, chloride and ammonium concentrations and total nitrogen content were analysed. During the online cleaning, the pH value stayed relatively stable at the same level of approximately 8.5 because of the presence of NH_3 . Directly after the start of the injection, the conductivity immediately leapt up as a function of dissolved chloride salts. A slight increase in the pH at the end of the online cleaning was a direct indicator that injection could be stopped. This was also confirmed by the fact that the debutaniser was again running under normal operating conditions.

Conclusions

Each oil refinery is aware of the high risks of ammonium salt deposits, which can quickly lead to corrosion damage to plant equipment and represent a ubiquitous risk for the continuous operation of a process unit. Water washing is a first step in the right direction, but sometimes with only mediocre success. Therefore there is great interest in avoiding corrosion attack and in finding powerful opportunities for the removal or prevention of fouling materials such as ammonium salts.

Kurita's ACF technology is a completely new approach, where corrosive HCl or ammonium salts are directly chemically binded. The formed ACF salts have a low corrosivity and can be removed easily with free water. This approach is completely different to technologies where additives with dispersing properties are used that

simply shift the salts to another location. In a refinery, there are many opportunities to use ACF during online cleaning or for continuous corrosion protection and fouling removal treatment. For the operating refinery, this represents significant added value since production losses caused by fouling or corrosion can be reduced to a minimum.

References

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