
Question 79: What procedures do you use to overcome chloride fouling problems in FCC fractionators? What is the contribution of chloride from the catalyst?

Matthew Meyers (Western Refining)

Overcoming or preventing chloride fouling problems in FCC fractionators is a primary responsibility of the unit engineer. There are several tools that can be used to monitor an operating unit. However, the actions that may be taken depend on available resources. There are also some relevant guidelines to follow to avoid chloride fouling as well as design considerations to be implemented during the engineering phase of the project. Several means of prevention include desalting, maintaining a high main column overhead temperature, continual overhead water washing with an amine filmer and dispersant additive use if required. Once salt deposits have been formed there are some procedures that may be used to mitigate the problem including sublimation, tower water washing and chemical additives.

Prevention:

1. Crude or VGO Desalting

The crude desalter is the first line of defense for preventing high chloride levels in the gas oil intermediates. In most crude, more than 90% of the total salt is found in the bottom sediment. Inorganic salts remaining in the crude downstream of the desalter will concentrate in the intermediate bottoms products such as residue and gas oils. At the FCC, the chloride salts will hydrolyse to HCl and follow the cracked gas to the main column overhead. Therefore, good desalting of the crude oil will minimize the chloride contamination of the FCC feed. At a minimum, weekly analysis of the sodium ppm levels in HVGO is an effective way to monitor relative chloride contamination of the FCC feed. If the levels increase dramatically, main column overhead wash water and fresh cat additions may be increased to protect the FCC against a temporary upset at the desalter. Once the problem is resolved and the amount of contamination is determined, the cat additions and wash water may be modified as needed. But it's best to err on the conservative side, given the potential yield loss due to metals poisoning and damage from chloride attack.

“Some refiners operate FCC feed desalters, especially when processing imported feeds which can be contaminated with seawater. “ – P. Fearnside, Nalco

2. Maintain High Main Column Overhead Temperature

The most effective way to minimize the risk of overhead salting is by maintaining a high main column overhead temperature. The salt deposition temperature of ammonium chloride at the overhead of the main column is a function of the partial pressures of HCl and ammonia. The theoretical salt deposition temperature can be determined based on the amounts of chloride and nitrogen in the FCC feed divided by the mass flow of main column overhead vapor. The resulting NH₃ and HCl ppm in the overhead can

then be compared to the NH_4Cl salt formation isotherms to determine the deposition temperature. The minimum acceptable operating temperature is at least 25 F above the theoretical salt deposition temperature. For example, a typical refinery processing VGO might have a theoretical salt deposition temperature of 242 deg F. In this case, the main column should be normally operated above 267 F. This is not a problem unless there is a heavy naphtha draw off the main column. In this case, other measures may be required to guard against salt formation, such as the continual use of salt dispersant additives injected into the top reflux and HCN pumparound.

3. Overhead Water Washing

A majority of the chloride salts can be removed in the main column overhead with a good continual water wash system. Water washing provides three functions. First it dilutes strong HCl as the acid first concentrates in the condensing water. Second, the ammonium chloride salts are washed out as soon as they precipitate at the salt deposition temperature, preventing the formation of under deposits. Third, a majority of the salts are removed to minimize their impact on downstream equipment in the gas plant. A good water wash system is designed to provide a minimum of 10% free water at the point of injection. Some designs target 30% free water with good results. The pH of the water boot outlet should be monitored and maintained between 8 and 9, which is typically not an issue due to the abundance of ammonia in the water. A filming amine may also be added to the water wash upstream of the injection point for further protection of the carbon steel against the anode-cathode corrosion mechanism.

Mitigation Procedures (Provided by P. Fearnside, Nalco):

1. Sublimation

Main column tray and exchanger fouling can be monitored by trending the column delta P's or loss of exchanger heat transfer. Tower scans may also be used to identify the precise location of fouling so that a dispersant may be added, or a tower water wash procedure may be implemented. Some refiners have tried to drive the salts overhead by temporarily increasing the column overhead temperature. The goal of this is to cause sublimation of the existing solid salts and prevent the deposition of additional solid salts. This approach has been used with mixed success.

2. Tower Water Washing

Tower washing is commonly carried out to remove water soluble salts. This is done by either injecting water into the top reflux or by lowering the column overhead temperature enough to condense liquid water on the trays. The water and dissolved salts are then removed through the naphtha or LCO product draws. It is important to remove all of the liquid water from the tower. Normal duration of the tower washings is between several hours and over one day. Tower water washing imposes significant costs on FCC operations. During water washing the unit feed rates must normally be cut by as much as 20-30%. During water washing, naphtha and possibly LCO, goes off-specification and must be sent to slop with

potentially significant reprocessing costs. In addition, water added to the column may cause damage to the tower internals.

3. Use of Salt Dispersant Chemical Additives

The first additives developed for dispersing solid salt deposits were introduced over 30 years ago. Since then, chemical salt dispersants have been applied to numerous FCC towers worldwide. The additives remove ammonia chloride, ammonium bisulfide and iron sulfide salts. They will also inhibit the build-up of these deposits when used on a continuous maintenance basis.

When applied to an already fouled tower, a relatively high injection rate of chemical is used to disperse and remove the deposits. The dosage required depends in part on how well the chemical is distributed across the trays and how much salt is physically deposited. The high injection rate is maintained for 30-48 hours or until a decrease in tower delta P has been observed. The heavy naphtha and LCO pump suction screens should be monitored for signs of solids dispersed out of the tower.

In a relatively clean system, a low dosage of salt dispersant is normally applied in the top reflux and pump around circuits to keep salts from building up. Some refiners monitor the feed sodium content on the assumption that the majority of the chlorides are entering the unit as sodium chloride. Adjustments to the chemical injection rate are then made according to the changes in the feed sodium content.

The payout for using the chemical additives can be quite large. Benefits related to better unit operations, less reprocessing of off-specification product, improved reliability, and lower corrosion potential are possible. The use of the additives in most cases provides a cost-effective alternative to water washing.”

Design Considerations

The wash water pumps, water boot and control valve hydraulics should be designed for a flow to allow at least 10% free water at the injection point. More flow is most likely better. The wash water injection point should be in a turbulent flow path but nozzles may be required for good vapor liquid contact especially in larger pipes. Redundant wash water pumps should be provided to ensure against HCl attack at the first drop of water condensation. If the unit is to be used in Resid processing, a makeup water source should be considered to maintain high wash water flow rates, steam condensate or stripped sour water are good sources.

Our special thanks to Paul Fearnside with Nalco for his numerous contributions to this answer.

Ray Fletcher (Intercat)

Salt fouling can be a serious problem in FCC fractionators. The salt deposits are primarily ammonium chloride although some ammonium bisulfide may be present. If not removed, these salts will accumulate

and cause a number of significant problems. Ammonium salt deposition occurs when the temperature drops below the salt dew point (~250°F or 120°C). Fouling typically occurs in the mid-to-upper section of the main fractionator column. Delta pressure increase and heavy cracked naphtha end point specification problems are indicators of salt deposition.

Typical sources for ammonium chlorides include high acidic feedstocks (it is not at all uncommon for FCC units to contain chloride feedstocks), poor desalter operations or bypassing the desalter with imported feedstocks, low main fractionator top temperatures due to quenching from naphtha pump around streams, reprocessing of slops in the main fractionator, etc.

Solutions include:

- 1) Maintain the fractionator overhead temperature above the salt dew point (250°F or 120°C)
- 2) Continuous water washing in the main fractionator overhead with typical rates in the range of 6-7 vol% water on fresh feed basis for the elimination of ammonium chloride deposition
- 3) Addition of antifouling additive in the reflux stream can prevent the formation of ammonium chloride deposits on the trays and packing realizing that this approach is most effective when initiated with a clean fractionator
- 4) Consider use of Kurita's ACF technology to inhibit or remove salts. ACF is a liquid strong organic base belonging to the "Lecithin group". ACF reacts with HCL &/or NH₄Cl forming a liquid neutral, noncorrosive water-soluble salt. This reaction is spontaneous and occurs both in the paper and liquid phases.
- 5) Water washing the main fractionator overhead achieved via water injection in the reflux stream while the main fractionator top temperature is reduced to approximately 175°F (80°C). This water is typically separated from the heavy cracked naphtha stream
- 6) Consider revamping the main fractionator for producing low end point naphtha and 6) the addition of an FCC feed desalter for imported feedstocks. It is recommended that the fractionator overhead temperature be maintained at a minimum of 250°F (120°C).

The second half of this question asks, "what is the specific contribution of chlorides from FCC catalyst". Chlorides are used in the alumina sol binding system utilized by at least one supplier. The chloride content remaining on the finished catalyst will be very low since these catalysts are washed, ion exchanged and calcined. Any remaining residual chlorides remaining on the FCC catalyst will likely be released as HCl within the FCC. We believe that the decomposition of chloride is not instantaneous and therefore most is released on the regenerator side where residence times and hydrothermal conditions are favored. Some, however, will be released on the reactor side, in our experience up to 5%. Our expectation regarding chloride contribution from the catalyst is as follows: residue operations - very small, VGO operations - more but still likely to be negligible, very clean or highly hydrotreated feedstocks - the main cause.

It is reasonable to conclude that chlorides from the FCC catalyst are causing main fractionator overhead fouling If a refiner has been utilizing a zero-chloride containing catalyst and has been operating stably

without fouling who then begins to experience salt fouling after switching to a chloride containing catalyst. Conversely, a refiner which has been operating stably without fouling while using a chloride containing catalyst which then begins to "mysteriously" experience fouling cannot reasonably expect this problem to be caused by the catalyst. In general, the FCC catalyst suppliers provide top quality catalyst to the refining industry. It is prudent for the FCC operator to first thoroughly review their own operation before reaching the conclusion that the chlorides are entering the unit with the FCC catalyst.

Rosann Schiller (Grace Davison Refining Technologies)

The question as to whether chloride from catalyst can contribute to fouling problems is occasionally raised and, in this context, the following facts are relevant. The majority of FCC suppliers utilize rare-earth chloride to exchange with sodium, stabilizing the zeolite and determining product selectivity's. Chloride is also an integral feature of the Grace Davison Al-sol binder system. The Al-sol binder system provides the basis for formulation flexibility, as well as best-in-industry attrition resistance. Several other suppliers also utilize similar chloride-based binders. Chloride binder chemistry was selected by Grace for its performance benefits; however, it has the additional advantage of being a green process to manufacture catalyst.

During the FCC catalyst manufacturing process, the Al-sol binder is "set" using a high temperature calcination; this step also removes most (>80%) of the chloride from the catalyst. Additional processing steps can be used to further reduce the fresh catalyst chloride content. At the end of the process, residual chlorides are treated, and the resulting effluent can be safely discharged into the saltwater estuaries where our manufacturing facilities are located. At Grace we seek to minimize any environmental risk associated with our manufacturing processes. Alternate materials can be used, such as nitrates; however, release of nitrates into waterways can cause algal blooms that can negatively impact the local eco-system. We are dedicated to the highest standards of health and safety practices and realize our corporate responsibility to the environment.

In use, the fresh catalyst is added to the FCCU via the regenerator, where the typical temperatures are significantly higher than those used during the calcination in the standard catalyst manufacturing process, which in turn are higher than typical reactor temperatures in the FCCU. In consequence, and accelerated by the steam which is also present, any remaining chloride on the fresh FCC catalyst is quickly removed in the regenerator before the catalyst makes its first transit to the reactor section. Typically 80-95% of the fresh catalyst chloride is therefore removed in the FCCU flue gas, depending on the regenerator design. It is therefore recommended to avoid adding the fresh catalyst to a zone where it can bypass the regenerator bed and travel directly to the riser/stripper.

Salt deposition in FCC gas concentration units can lead to various operational problems if it is addressed. It is important for refiners to be aware of the main causes of salt deposition so that the correct procedures can be applied to manage this phenomenon. The salt that is deposited most in FCC gas concentration units is ammonium chloride (NH_4Cl), but deposits can also occur of the salts ammonium hydrosulphide (NH_4SH) and iron sulphide (FeS), although they are less common. Grace Davison's Refining Technologies technical service team has helped various refiners manage the issue of salt deposition and the experience gained has been previously published (PTQ, Q4 2009, Grace Catalagram® No. 107, 2010).

There are several causes of salt deposition, but the two primary reasons are an increase in resid processing and the shift to low sulfur gasoline due to environmental regulation. Resid feedstocks typically have higher chloride content than traditional VGO streams. Some refiners also bypass the desalter with imported atmospheric resid, which contributes to higher feed chloride levels. To produce low sulfur gasoline, a gasoline side cut is extracted from the main fractionator (MF) and subsequently hydrotreated. This leads to MF top temperatures as low as 212 °F, compared to previous temperatures in the range of 275-293 °F.

To prevent ammonium chloride deposition in the overhead line, water is usually added, with typical quantities in the range of 6-7 vol.% water on a fresh feed basis. Addition of an anti-fouling additive in the reflux stream can prevent the formation of NH₄Cl deposits on the trays and packing. The salt is carried instead with the gasoline stream, in which it is insoluble. These additives have been successfully used in many refineries around the world and are said to protect against corrosion.

Another recommendation is to water wash the MF. Water is injected periodically in the reflux stream, and the MF top temperature is reduced to approximately 176°F using the reflux rate or the tip top pumparound, to allow water to condense inside the column to dissolve the salt. The water is preferably removed on a dedicated tray, where it is separated from the heavy cracked naphtha. Alternatively the MF top temperature can be increased (for instance, to above 275°F) for a given period of time to enable dissociation of the salt. This will result in full-range gasoline leaving overhead during the time period.

Hardware modifications may also be considered to mitigate salting. These can include redesign of the MF's reflux distributor to avoid cold spots at the top of the column or installation of a water boot in one of the trays to allow water (and the dissolved salt) to be removed without contaminating the heavy cracked naphtha. A two-stage desalter could optimize the operation at the crude unit. Lastly, a feed hydrotreater could also be considered; this will remove most of the feed chloride and significantly improve the FCC yield structure. However, this requires a large capital investment.

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