



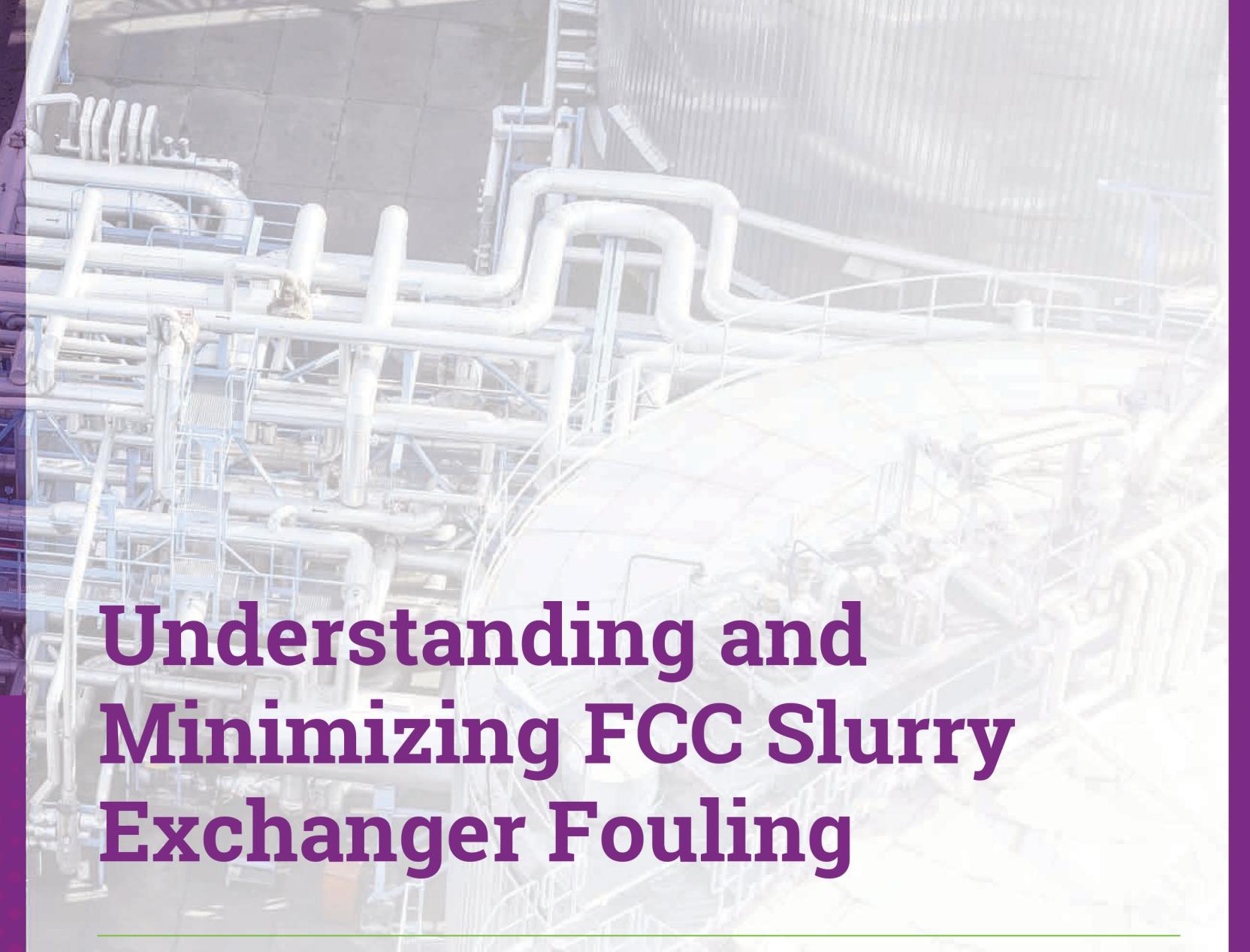
"Understanding and Minimizing FCC Slurry Exchanger Fouling" was published by Grace in *Catalagram 101* in 2007. Slurry exchanger fouling was a frequent problem our customers faced early in my career at Grace as a technical service representative. With limited experience of my own, I turned to Grace's wider expertise and the insights and advice of industry publications along with NPRA Q/A responses on the topic to assist our customers.

This *Catalagram* article pools the insights of 15 references to holistically review all aspects of FCC slurry exchanger fouling together with solutions in a single source. Increased understanding together with improved bottoms cracking catalyst like Grace's MIDAS® technology, introduced in 2002, allowed many of our customers to reduce or eliminate slurry exchanger fouling from their operations.

Today, it maintains its relevance as slurry exchanger fouling continues to be a risk due to increasing contaminant iron levels in FCC feedstocks around the globe. Along with the insights offered, recent Grace FCC technology advancements such as MIDAS® Pro and Grace MILLE™ catalyst increases bottoms cracking despite higher levels of contaminant iron, ensuring excellent slurry exchanger performance and improved profitability for our customers.



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Understanding and Minimizing FCC Slurry Exchanger Fouling



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Slurry exchanger fouling is often considered the worst fouling service in the FCC process.⁽¹⁾ The primary problem that results from slurry exchanger fouling is reduced heat exchanger duty in the slurry/FCC feed preheat exchanger or the steam generators. The reduction in feed preheat temperature that can result from just mild fouling of the FCC slurry/feedstock exchangers can result in reduced unit feed rate or conversion.* Additionally, excessive pressure drop or inability to cool the slurry to the necessary rundown temperature can also require reducing the feed rate. Certainly excessive slurry exchanger fouling can be very costly to the refinery in

terms of lost feed rate, lower conversion and higher maintenance expenses.

The purpose of this article is to present potential sources of slurry exchanger fouling and suggestions on how to prevent or minimize fouling. We Understanding and Minimizing FCC Slurry Exchanger Fouling will draw on industry experience from several sources to present a broad review of the subject. Our readers may consider this information and case study experience as they work to understand and minimize slurry exchanger fouling at their refinery.

*For those FCC units that do not have a fired feed heater and are air blower limited.

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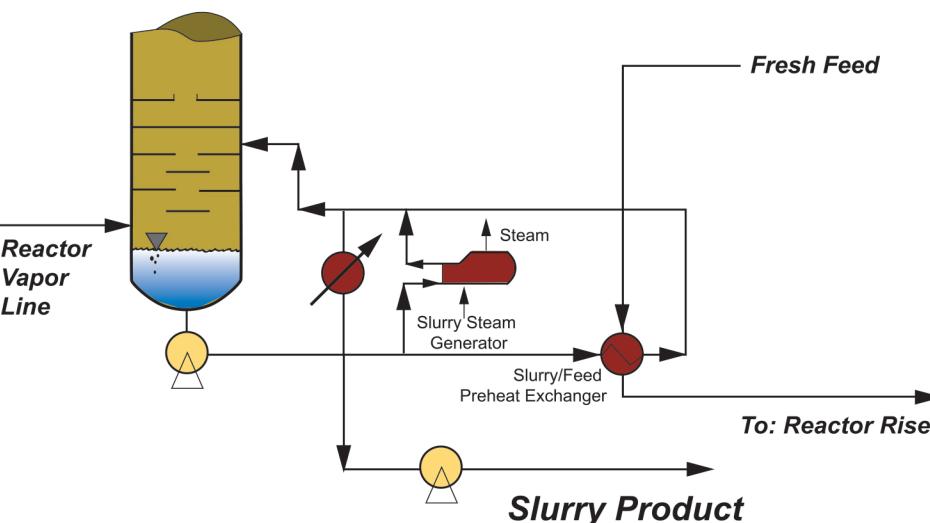


Figure 1. Typical Main Fractionator Slurry Circuit

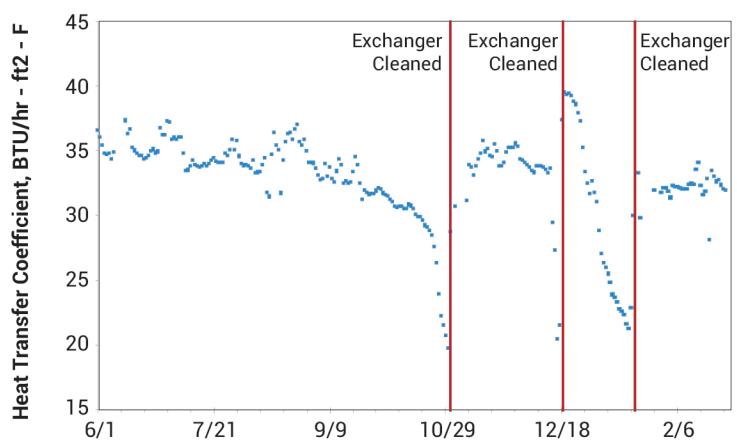


Figure 2. FCC Slurry Exchanger Heat Transfer Coefficient Deterioration

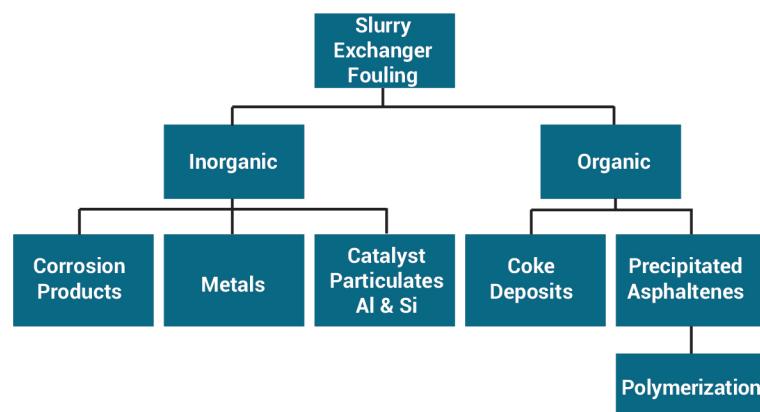


Figure 3. Root Causes of Slurry Exchanger Fouling

Figure 1 illustrates a typical FCC Main Fractionator Slurry circuit. Superheated FCC product vapor is quenched as it enters the main fractionator using the reflux from the slurry pumparound circuit. Slurry exchangers, which recover this energy by heating the feedstock and generating steam, are often subject to fouling through a number of mechanisms. When slurry exchangers foul, feed rate or reactor temperature must often be reduced.

Figure 2 shows how quickly a slurry/feed exchanger heat transfer coefficient can deteriorate. Over a ten-week period, this refiner needed to clean their FCC slurry exchanger three times. During each cleaning cycle they were forced to significantly reduce feed rate.

Potential causes of FCC slurry exchanger fouling are shown in Figure 3. Fouling can be generally classified as either "organic" or "inorganic" based. Several organic or inorganic slurry fouling mechanisms are possible. Each of these possible fouling sources will be discussed and suggestions to prevent or reduce each type will be presented.

Organic Based Fouling

Organic based fouling is the most common fouling type. The potential causes of organic based fouling are very broad. It is helpful to classify organic fouling into two general sub-types: "hard" and "soft" coke fouling.

Hard Coke Fouling

Solid coke fragments circulating to the slurry exchanger tubes that restrict the flow through the exchanger is an example of hard coke fouling. This type of fouling results in excessive pressure drop and a loss of heat transfer duty. These shiny coke fragments generally accumulate on the exchanger tube sheets at the inlet to the tubes. Figure 4 shows how pieces of coke can block the exchanger tubes, increasing exchanger pressure drop.



Figure 4. Hard Coke Deposits

These coke fragments can originate in the reactor overhead line or the main fractionator. The coke often becomes dislodged following an FCC shutdown because of the thermal cycling of the surface that the coke is adhered to. If the coke fragments are small enough to pass through the suction strainers on the slurry pumparound pumps, they can eventually foul the first slurry exchanger in the pumparound loop. Another scenario that can result is excessive hard coke accumulation in the bottom head of the main column that restricts the suction of the circulating slurry pumps.

Smaller coke fragments that pass through the exchanger tubes can still be problematic. These coke particles are either smaller coke particles from the main fractionator or are formed by polymerization reactions in the slurry pumparound circuit at high main fractionator bottoms temperatures. Small coke fragments can settle onto the tube surface and further polymerize, resulting in a barrier to heat transfer and slurry flow.

In some cases, formation of a very thin, hard layer of deposit has been observed on the tube walls. This type of deposit has a hard, shiny appearance similar to varnish. These deposits are formed by polymerization reactions on the tube surface. This type of fouling can reduce the heat transfer coefficient.

Preventing Hard Coke Fouling

Poor feed/catalyst contacting can be a significant source of hard coke formation in the vapor line. This is particularly true in units that process resid feeds. Feed /catalyst contacting can be improved in several ways:

- Improve feed atomization;
- Increase feed dispersion steam within the limits of the feed distributor design;

- Repair damaged feed distributors or replace with a more modern design;
- Increase the feed temperature to avoid high feed viscosity at the injection distributors. This is particularly applicable to resid operations.
- Increase the catalyst/oil mix zone temperature. This is most critical in resid or low reactor temperature operations where incomplete vaporization of the feed is more likely. Mix zone temperature can be increased using Mix Zone Temperature Control (MTC)⁽²⁾ and/or higher reactor and regenerator temperatures;
- Optimal catalyst matrix design can improve feedstock vaporization.⁽³⁾

A hot wall reactor vapor line must be properly insulated to reduce the likelihood of liquid condensation at cool spots. Insulation must be properly anchored and should be watertight. Once oil droplets form, they eventually dehydrogenate to form coke. The reactor vapor line blind flange and all the vapor line pipe supports should also be insulated if the designs allow, as coke can accumulate at these locations. Do not insulate the bolts of the blind flange, however, as this can result in the flange opening due to bolt creep.

Reactor vapor line vapor velocities less than 100 fps should be avoided to minimize coke formation. The exception to this is the velocity right at the inlet nozzle to the main column, where lower velocities are permitted.⁽⁴⁾ Higher velocities will reduce the likelihood of un-vaporized oil accumulating along the wall of the vapor line and eventually forming coke. Vapor line velocities between 100 to 120 fps are a good compromise to minimize both coke formation and pressure drop.⁽⁴⁾ Self-draining reactor overhead lines are a design feature often used to minimize coke formation and subsequent slurry exchanger fouling.

The maximum main fractionator bottoms temperature is typically between 680°F and 700°F to avoid coke formation and slurry exchanger fouling. The maximum safe bottoms temperature for any unit is unit and feedstock specific. It is also important to note that the bottoms temperature is often based a single temperature indicator (TI) at the outlet line of the main fractionator. Poor pumparound distribution and liquid mixing may result in locally hotter temperatures than what is actually measured in the bottoms outlet line, increasing the likelihood of coking. This can be particularly true in operations where quench is used to cool the bottom of the main column.

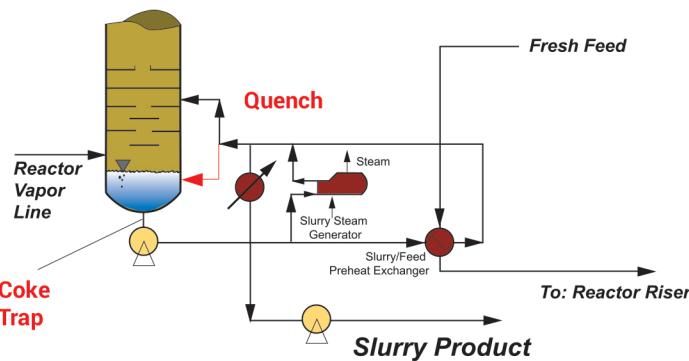
Long liquid residence time in the slurry circuit will also influence coking. Reducing bottoms liquid level can minimize slurry residence time. Also note that increasing main fractionator bottoms temperature and slurry pumparound rate both increase the liquid residence time.⁽⁵⁾

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FCC feedstock, particularly feed containing resid, can form coke at typical main fractionator bottom temperatures. As a result, refiners should ensure that no feedstock is leaking into the slurry pumparound circuit through an emergency feed by-pass valve or slurry/feed exchanger.⁽⁵⁾

The slurry pumparound return should be properly distributed to minimize hot spots. The pumparound rate should be sufficient to ensure the grid zone is well wetted. Local areas devoid of liquid flow will allow hard coke to form. A minimum flux rate of 6 gpm/ft² has been recommended.⁽⁶⁾ A slurry pumparound rate of 1.2 to 1.5 times the feed rate is a rule of thumb that has also been suggested to ensure good liquid distribution in the bottom of the main fractionator.⁽⁷⁾

Slurry quench, as shown in Figure 5, can be used to sub-cool the main fractionator bottoms temperature and reduce hard coke formulation.⁽⁶⁾ A quench distributor should be used to minimize hot spots. Slurry quench, however, is commonly injected from a nozzle that terminates near the wall of the fractionator. As a result, the returning quench liquid is often not well distributed. Therefore, do not rely on perfect mixing of the slurry quench, as zones of high temperature could still be present. The refiner may consider monitoring bottoms temperature on a quench-free basis to account for potential high temperature zones.⁽⁶⁾



Main Fractionator Slurry Circuit

Figure 5. Slurry Quench and Coke Trap in the slurry circuit

Maintaining slurry exchanger tube velocities greater than 6 fps will help minimize any settling of small coke fragments or FCC catalyst onto the tube service.⁽⁸⁾ Units often have spillback valves on the slurry product exchangers to help maintain minimum slurry flows during times of turndown operation. Tube velocities should be less than 10 fps to avoid erosion.⁽⁸⁾

Using an elevated slurry exit nozzle can reduce the likelihood of coke being entrained into the slurry pumparound loop.⁽⁸⁾ However, this results in the bottom head of the main column

filling with accumulated coke and catalyst. On units where the liquid draw is on the bottom head, a coke trap should be employed in the bottoms suction nozzle on the column and/or upstream of the slurry exchanger as shown in Figure 5 to trap any entrained coke particles before they can foul the exchanger. G. Walker discussed application of a coke trap and resulting reduction in slurry exchanger fouling.⁽⁹⁾

Soft Coke Fouling

Soft coke fouling is organically based where commonly an insulating barrier is deposited inside the exchanger tubes, reducing the exchanger heat transfer coefficient. The insulating barrier can be found throughout the tube service.⁽¹⁰⁾ Figures 6 and 7 show examples of soft coke fouling. Just a thin layer of material can result in a costly reduction of the exchanger heat transfer coefficient. In some cases, soft coke fouling can also result in increased exchanger pressure drop.⁽¹⁰⁾ Generally, however, reduced heat transfer is apparent before excessive pressure drop with this type of fouling.



Figure 6. Soft Coke Precipitation Fouling



Figure 7. Soft Coke Precipitation Fouling

Precipitated asphaltenes are a common source of soft coke fouling. Asphaltenes are highly condensed polyaromatics typically insoluble in a saturated hydrocarbon such as heptane.⁽¹¹⁾ The concentration of these multiring aromatics in the slurry can be increased by thermal condensation reactions in the slurry circuit.

Asphaltenes can become insoluble in the slurry oil and begin to precipitate onto the tube surface. The tar-like layer on the tube service can also trap coke and catalyst particles that are present in the slurry.⁽¹²⁾ Figure 8, an abbreviated version of Figure 3, illustrates the sequence. Analyzing such tube deposits and slurry for fused aromatics can be insightful. Higher amounts of fused aromatics in the deposit relative to the slurry can confirm asphaltene precipitation.⁽¹³⁾

Slurry viscosities increase at the tube wall due to the locally cooler temperature. The higher viscosity can cause material to adhere to the tubes, resulting in exchanger fouling.⁽¹²⁾ Slurry with a higher paraffinic content may be more prone to fouling due to the inherently higher viscosity.

Preventing Soft Coke Fouling

Two sources suggest minimizing asphaltene content of the slurry in order to minimize fouling.^(5,14) ASTM D3279 can be used to determine asphaltene content. The asphaltene content is defined as those components in the sample that are not soluble in n-heptane. This procedure gives the combined amount of asphaltenes and particulate matter.

Maintaining asphaltenes in solution is key to preventing soft coke fouling. The composition of the slurry will affect the solubility of the asphaltenes. Generally higher aromatic content of the slurry tends to keep asphaltenes in solution. As such, changing the slurry composition by dropping some LCO down the tower can increase the

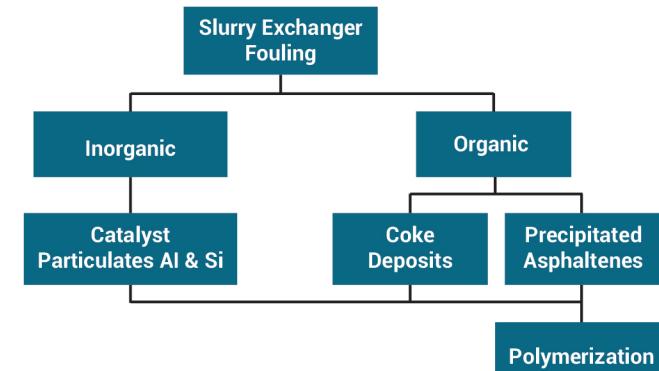


Figure 8. Catalyst and Coke Interaction with Precipitated Asphaltenes

solubility of asphaltenes in the bottoms material. This also has the benefit of reducing the temperature at the bottom of the main column.

It is often necessary to adjust the bottoms composition and temperature in this manner during changes in feed composition. For example, slurry produced from paraffinic feedstocks tends to be more prone to fouling and requires lower main fractionator bottoms temperature to minimize fouling.

Many refiners will also adjust bottoms temperature with conversion shifts to minimize fouling. A drop in conversion could result in higher slurry exchanger fouling. Slurry with higher API gravity, generally due to lower conversion, contains more saturated compounds, which can reduce asphaltene solubility and increase soft coke fouling. Slurry with a high API gravity is also more viscous and more prone to fouling.

Feedstock leaking into the slurry circuit can cause asphaltene precipitation. This occurs because the feedstock is more paraffinic than the slurry and reduces the solubility of the slurry asphaltenes. The refiner should take all precautions necessary to ensure that the feed emergency by-pass valve and the slurry/feed preheat exchangers do not leak feedstock into the slurry circuit.

The FCC catalyst can be formulated with features to minimize fouling. Catalyst matrix design can be optimized to improve slurry exchanger fouling by increasing Type III cracking as described by Zhao.⁽³⁾ Minimizing naphthoaromatics and paraffinic content of the slurry by increased Type III cracking may improve asphaltene solubility and reduce slurry exchanger fouling. Using a catalyst with proper tolerance to contaminant metals will help avoid fouling as well. Increased catalyst contaminants that result in a loss of FCC conversion can increase the likelihood of fouling as discussed above.

Hot Cycle Oil Flush at the inlet of the slurry exchangers can help keep asphaltenes in solution and increase tube velocity, both of which will help reduce slurry exchanger fouling.⁽⁵⁾

Inorganic Based Fouling

Inorganic fouling can include fouling prompted from corrosion or iron scale, catalyst or precipitated metals. Catalyst is often found in tube deposits and can be identified by the presence of alumina, silica, and rare earth. Catalyst in the deposits is often a result of organic based fouling, since catalyst generally accumulates onto viscous precipitated asphaltenes or other hydrocarbons already present on the tubes.

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Another inorganic foulant in FCC slurry service is antimony. Antimony present in the slurry has been found on tube deposits. In one instance, 20 wt% antimony was found in a deposit.⁽¹⁵⁾ The antimony source was from antimony injection into the FCC feedstock to passivate equilibrium catalyst nickel.

Preventing Inorganic Based Fouling

Catalyst losses to the main fractionator should be minimized by proper reactor cyclone operation and good reactor cyclone mechanical integrity. The catalyst itself can also be designed to minimize losses to the main fractionator. To maximize catalyst retention, the following catalyst design parameters should be considered:

- Low Attrition Index (Low DI);
- Low 0 to 40 micron content;
- High Particle Density.

Antimony levels in the slurry should be closely monitored to minimize the possibility of antimony depositing onto the tube service. FCC equilibrium catalyst antimony to nickel ratio is generally between 0.10 and 0.60 by weight. The antimony chemical should be injected to maintain the target level on the equilibrium catalyst without significant overfeed.

Proper metallurgy in the main fractionator, slurry piping and slurry exchanger should be used to minimize corrosion. Below is a summary of suggested materials:⁽⁶⁾

- Main fractionator internals TP 410 SS ;
- Exchanger tubes TP 405 or TP 410SS ;
- Slurry Lines 5 Cr - 1/2 Mo with 1/4" CA.

Antifouling

Antifouling agents have been successfully used to prevent FCC slurry exchanger fouling. Antifouling agents can be generally classified as follows:

- **Organic dispersants** – prevent the agglomeration and deposition of asphaltenes;
- **Inorganic dispersants** – prevent the deposition of catalyst fines or other inorganic foulants such as Fe compounds;
- **Coke suppressants** – inhibit condensation reactions, which lead to hard coke-like deposits in exchangers.

A combination of antifouling agents can be used. However, the likely source of the fouling should be identified before a specific antifouling agent is applied.

Note that there can be some downstream effects when using an antifouling agent. For example, in some cases catalyst fines settling in slurry tanks can be impacted if an inorganic dispersant is used.

Additional Design and Operation Considerations

There are many design considerations for exchanges in slurry service that can help to minimize the potential for exchanger fouling.

Slurry exchanger tube velocities should be 6 to 10 fps.⁽⁸⁾ Velocities below six fps can result in catalyst, coke or other particulates settling onto the tube surface, resulting in fouling. The minimum slurry exchanger tube diameter should be one inch.⁽⁵⁾ Smaller tubes can be subject to excessive fouling and are difficult to clean.

Spill back control can be used on net product exchangers in turndown conditions to keep tube velocities above minimum values.

Slurry should be present only on the exchanger tube side. With slurry on the shell side, it is impossible to prevent catalyst settling in the exchanger because of low local velocities.

Vertical and Spiral slurry pumparound exchanger designs tend to be less prone to slurry exchanger fouling.

Finally, having spare slurry exchangers should be considered to minimize turndown during exchanger cleaning.

Case Study

An FCC unit began observing severe fouling of their Slurry Steam Generator exchangers. The fouling began suddenly and continued for approximately two weeks and then stopped. During that time, it was necessary to clean the exchangers several times. The exchangers exhibited a reduction in heat transfer coefficient. Exchanger pressure drop was not affected.

The FCC was a modern design employing a modern riser termination device and state-of-the-art feed injection nozzles. The reactor temperature operated at 980°F and main fractionator bottoms temperature was typically 690°F. Conversion normally was ~78 vol.% with a slurry API gravity of -2 API.

The feedstock was a vacuum gas oil and resid blend with the following nominal feedstock properties:

- API 22° to 24°;
- K Factor 11.7 to 11.8;
- Conradson Carbon ~1.0 wt%;
- 10% Greater than 1050°F.

A deposit was taken from the fouled exchanger. Analysis of the deposit showed the following:

- 87% Carbon, 94% Organic Based (C, H, N);
- <1% Alumina;
- 1 wt% Antimony;

- <1 wt% Iron;
- 52% of the sample was Asphaltenes.

The refinery does use antimony to passivate nickel. However, antimony had been used for several years without any previous issues. No recent change in antimony injection was made and consequently antimony was likely not the cause of the fouling.

The deposit itself did not contain catalyst, as evident by the low amount of alumina.

The high amount of asphaltenes in the deposit confirmed asphaltene precipitation as the likely fouling mechanism.

A review of feedstock properties showed the feedstock had recently become more paraffinic, as evident by the higher API gravity and K Factor during the same time as the exchanger fouling. Figure 9 shows how feedstock API and K factor shifted. When the refinery changed the feed source the feedstock properties returned to typical values and the fouling stopped.

Many refineries recognize that some feed and crude sources can result in increased FCC slurry exchanger fouling. Those sources are either avoided, the main fractionator temperature is reduced, and/or antifoulants are used to minimize fouling while those feedstocks are processed.

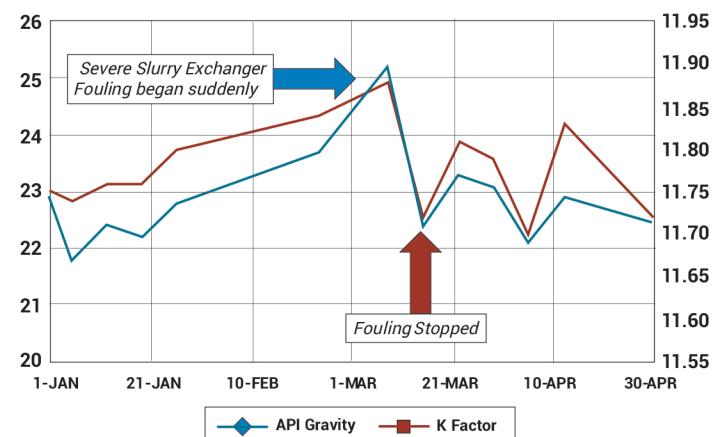


Figure 9. Feed Shift Property Shift Impacts Slurry Exchange Fouling

Final Remarks

Continuous monitoring of the overall heat transfer coefficients is critical to catch a slurry exchanger fouling problem early. Monitoring slurry properties such as API gravity, ash content, asphaltene content, and viscosity can also alert the refiner when the FCC unit may be more susceptible to slurry exchanger fouling. A shift of feedstock properties or unit conversion may also increase slurry exchanger fouling.

Slurry exchanger fouling often occurs during start-up or at turndown conditions when feedstock and operating conditions may be atypical. Special precautions may be considered during these unusual operations.

Reducing slurry exchanger fouling by lower main fractionator bottoms temperature and higher slurry product rate can be costly in terms of lower product value. Grace Davison can work with the refiner to adjust catalyst properties and operating strategy to minimize fouling and any subsequent yield loss.

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