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## **Question 21: We are observing fouling of our feed/effluent exchangers that has impacted heat transfer and restricted feed. What are potential contributing causes and how can we mitigate?**

### **ROBERT STEINBERG (Motiva Enterprises)**

There are many things that can contribute to fouling of feed/effluent exchangers. Fouling can occur on either the feed or product side of the exchangers.

Possibilities sources of fouling on the feed side include:

- Dissolved O<sub>2</sub>. Oxygen can get into feeds if they come from a tank that is not N<sub>2</sub> blanketed, this is especially likely if feeds have been imported from another site via a barge. Oxygen can also be present if a feed come from a vacuum tower with an air leak. Corrosion inhibitors or oxygen scavengers injected into the feed as far upstream as possible may help. The best method to remove oxygen is to add an O<sub>2</sub> Stripper on the stream that contains oxyg

en.

- Caustic. Small amounts of caustic that was not water washed can lead to severe fouling.
- Particulates, scale, corrosion particles. FeS scale is often found in refinery streams. If the source is known, corrosion inhibitors may be able to reduce the amount of scale. Good feed filters may be able to remove some of the scale but FeS particulates can be small enough to pass through most feed filters.
- Dirty feed. Cracked feeds, especially coker gasoils, tend to be dirty and have small coke particles. Good filtering is essential. If not done at the upstream unit it needs to be done on the hydroprocessing unit. It is often a good practice to filter both places in case one of the filters is bypassed.
- Salt in Feeds. If crude oil is not properly desalted there can be salts left in heavy feeds. Salts from other sources can also be present at times. A water wash or a desalter can remove salts.
- High temperatures. High skin temperatures tend to increase fouling. High temperatures may be unavoidable when exchanged against reactor effluent, especially in the hotter shells. An exchanger design that increases velocity and promotes turbulence on the feed side will increase the heat transfer coefficient and reduce skin temperatures. Injecting hydrogen upstream of the exchanger will help.
- Low velocities. Lower velocities in the exchanger reduce pressure drop but lead to higher skin temperatures, make it easier for particulates to stick to tube surfaces and increase fouling. Injecting hydrogen upstream of the exchanger will help. Recycling hydrotreated product when the unit is turned down will maintain higher velocities in the exchangers.
- Cracked feeds. Cracked feeds have olefins and sometimes di-olefins which can polymerize and are more prone to fouling. Cracked feeds can be a particularly severe problem if dissolved oxygen is present. A selective hydrogenation unit or reactor can be used to saturate di-olefins at a relatively low

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temperature upstream of the main reactor before the feed gets hot enough for severe fouling to occur.

- Asphaltene precipitation. This is normally only an issue with resid units. Mixing different feeds, especially a lighter more paraffinic feed with resid, can create incompatible mixtures and cause asphaltene precipitation.

Reactor effluent is normally cleaner than reactor feed. Olefins get saturated and dissolved oxygen gets converted to water in the reactor. The reactor effluent will always have hydrogen which tends to keep velocities high. However, there are some possible sources of fouling on the reactor effluent side:

- Salt precipitation. H<sub>2</sub>S, NH<sub>3</sub> and HCl are normally present. These form ammonium chloride (NH<sub>4</sub>Cl) and ammonium bisulfide (NH<sub>4</sub>HS) salts when temperatures fall below the salt formation point. The salt point is dependent on the operating pressure and concentration of H<sub>2</sub>S, NH<sub>3</sub> and HCl. Salt point curves can be found in API Recommended Practice RP-932B Design, Materials, Fabrication, Operation, and Inspection Guidelines for Corrosion Control in Hydroprocessing Reactor Effluent Air Cooler (REAC) Systems. Typical precipitation temperatures are in the 300-400°F range for NH<sub>4</sub>Cl and around 100°F for NH<sub>4</sub>HS. In addition to fouling, these salts can be extremely corrosive if water is present. Dry salts are not corrosive but an intermittent water wash may be needed to remove them once fouling occurs.
- Polynuclear aromatics. This is normally only an issue with hydrocrackers, especially the 2nd stage of a two-stage recycle unit. If conversion is too high the PNA concentration can get high enough that they become insoluble in the oil. The lighter cracked products can cause PNA's to precipitate in exchangers as the effluent cools and more of the naphtha range material condenses.

### **JOE RYDBERG (CITGO)**

In our recent experience, fouling on the “feed side” of the feed/effluent exchangers in Naphtha units is due to corrosion products (Fe) entering with the feed, and processing recycled Naphtha's particularly from LPG Caustic Disulfide separators. The recycled naphtha's can have higher levels of Sodium and Salts (likely amine degradation products that build up in the caustic).

Other causes can be contamination of cracked stocks into the virgin stocks system. Exposure to oxygen will cause gum formation. Crude supply sources have unknown diluents. Refineries are now collecting more material from various refinery sources and rerunning as slops, for example introduction of flare gas recovery liquids, reprocessed as slop oil; re-processing/chemical cleaning liquids pumped to slop system.

Use of chemical additives (organic dispersant, antipolymerant, oxygen scavengers) can be used and are used within CITGO to mitigate fouling. Proper tracking of heat exchanger fouling is important and can aid in scheduling cleanings (requiring unit shutdowns) outside of turnarounds, during catalyst change-outs, etc. When dealing with especially challenging feeds and / or extending cycle length goals, installation of spare feed/effluent heat exchangers could be value added approach

Effluent side fouling typically is caused by inadequate water wash, presence of NH<sub>4</sub>Cl in addition to FeS. HCl can also react to create additional FeS in the presence of H<sub>2</sub>S.

### **ERIC LIN (Norton Engineering Consultants, Inc.)**

In a hydrocracker with liquid recycle (could be single stage recycle or two-stage recycle), there exists the possibility of HPNA (Heavy Polynuclear Aromatics) buildup at the bottom of the fractionator. Although the overall conversion will decrease, the best solution is to have a dedicated bleed stream out of the unit (FCC is a typical destination) to prevent this buildup. High asphaltenes in the feed are usually a sure

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sign of HPNA production.

In a residue hydrocracker, the existence of sediment can cause similar fouling in these exchangers. Sediment can typically be mitigated with the use of slurry oil as a cutter (much easier to acquire for units that also have an FCC nearby).

### **SAM LORDO (Consultant)**

Fouling in the circuit ahead of the furnace and furnace can be caused by inorganic solids, or polymerization of feed components (organic fouling). Mitigating fouling from inorganic solids, such as iron sulfide and other corrosion byproducts, sand and silt (from imported feedstocks) is primarily done using feed filters. The pore size is best at 1-5 micron. The filter can be cartridge style, sand filters. Some filter arrangement would have backwash capability.

Fouling downstream of the reactor may include ammonium chloride (NH<sub>4</sub>Cl). Typically, a well-designed Waterwash is used. The use of salt dispersants are also applicable where Waterwash is feasible. Organic fouling could be from:

- Stream that contain olefinic/diolefinic components which when exposed to elevated temperatures as found in the hydroprocessing units
- O<sub>2</sub> contamination of feed or feed component streams

Mitigation of this source of fouling can be done using an appropriate chemical additive, such as dispersant and/or anti-polymerant.

### **MICHAEL PEDERSEN (Honeywell UOP)**

Most hydroprocessing catalysts require a conditioning period at start of run to allow the active sites to stabilize. One aspect of this process is the common industry practice to avoid processing cracked feedstocks during the first few days of operation. Prior to conditioning, fresh catalysts have a high tendency to generate excessive coke when operated with reactive feedstocks or at normal unit operating severity. A short period of mild operating conditions can pay big dividends in overall catalyst cycle performance while high severity operation at start of run can have substantial negative impact on apparent catalyst activity and cycle length. In general, catalysts that are claimed not to require conditioning have been artificially inhibited prior to delivery.

Hydroprocessing catalysts encompass a wide variety of formulations, so a general set of conditioning guidelines is not applicable. For a specific catalyst system, instructions from the supplier should be followed.

### **SIMERJEET SINGH and RAJESH SIVADASAN (Honeywell UOP)**

Fouling of feed/effluent exchangers in hydrotreating units is a common problem leading to throughput losses, increased energy consumption, unit downtime and maintenance expenses for exchanger cleaning. Fouling happens due to changes in feedstock quality, exchanger temperature, fluid velocity, degree of vaporization and exchanger configuration leading to formation of hard carbon deposits (coking), deposition of undesirable polymers (polymerization) and corrosion products.

For Coker Naphtha Hydrotreater:

- Feed quality issues:

Coker naphtha (CN), by the nature of thermal cracking reactions, contains free radicals, which react with diolefins and olefins to form oligomers and polymers. By itself CN presents a fouling problem in a NHT, however when combined with stored SRN there exists the potential for significant fouling. Storage of CN

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prior to processing can have disastrous results, as the combination of diolefins, free radicals, and oxygen (peroxides) can lead to rapid fouling on the feed side of the combined feed exchanger (CFE), the NHT charge heater, and the NHT reactor. This fouling can be serious enough to cause premature pressure drop increase along with loss of heat transfer due to fouling in a matter of days if not hours. The downtime associated with addressing this fouling costs the refiner time and money.

The highly reactive diolefins in CN are the four carbon and five carbon species, at the front end of the boiling range. Longer chain diolefins tend to be reactive, but less reactive than the short chain diolefins. Simply increasing the initial boiling point of CN (reducing the quantity of light diolefins) may reduce the tendency of CN to cause fouling. When cracked stocks with significant diolefin concentrations are present, it is UOP's practice to include a diolefin saturation reactor as a first, low temperature reaction stage in a two-stage reactor system. In this reactor, most of the diolefins are saturated. This reactor is located in between CFE shells and its position is selected such that the inlet temperature is in the range of 320-370°F.

- Design considerations:
  - o Feed tank blanketing
  - o Design of feed tanks (Fixed/ floating roof)
  - o Hydrogen Injection to preheat exchangers
  - o "Over-Sized" exchangers for clean duty
  - o Exchanger velocities
  - o Dry Point location

For VGO HDT:

- Feed quality issues:
  - o Fouling is also experienced in units that run straight run feed only, so it is not just a phenomenon that requires cracked olefinic feeds.
  - o Fouling from asphaltene precipitation.
- Design considerations:
  - o Same design considerations as coker naphtha HDT except the dry point location.
  - o Thermal cracking of feed VGO in feed effluent exchanger can be of main issue if separate feed heating is being used as design feature over combined feed heating.

• Fouling Mitigation Strategies:

Many methods exist for managing fouling. The costs of these methods vary, as does their effectiveness. In order to choose the most effective method for managing fouling, an understanding of the source of foulant precursors should be established. Analytical methods are available that can be used to characterize a feed for gums, asphaltene or stability in the presence of oxygen. While these methods may or may not provide a complete solution to exactly where the fouling problem comes from, they may help to characterize the different feeds at a given site and help narrow down the probable root cause.

- Avoid oxygen contamination of feed.

Direct feeding – Supply feedstock to hydrotreater from upstream unit without using intermediate tankage.

Benefits:

- o Eliminates residence time in intermediate tankage, thus minimizing formation of other free radicals.
- o By far the cheapest solution and reduces working capital.

Risks:

- o Lacks flexibility to accommodate swings in feedstock rate and unit outages.

Tank blanketing – If tanks must be used, they should be blanketed. Nitrogen is the best blanketing gas

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owing to its reliably low O<sub>2</sub> content and ease of venting to atmosphere. Gas blanketed internal floating roof tanks are most effective in minimizing oil contact with O<sub>2</sub> and evaporation losses to blanket gas.

Benefits:

- o Commercially just as effective as direct feed and overcomes all the limitations.
- o O<sub>2</sub> cannot react if not in system, therefore should reduce foulant generation.

Risks:

- o Cannot impact O<sub>2</sub> brought in with import through other feeds
- o Choice of correct seal for floating roof and its periodic checking and maintenance.

- Remove Oxygen from Contaminated Feeds.

Oxygen Stripper – Strips out free O<sub>2</sub>, including import O<sub>2</sub> and removes the potential for further formation of peroxides. Common scheme is for ambient temperature hydrogen stripping of the feed to fuel gas system.

Benefits:

- o Only feed streams exposed to O<sub>2</sub> need to be stripped.
- o Maximizing direct feed to the unit in combination with stripping the small O<sub>2</sub> contaminant stream is generally more economical than stripping the complete feed stream.

Risks:

- o Residence time, particularly in imports, may result in some polymer reaction occurring.
- o Expensive option in terms of equipment, and is not so effective if the peroxides/ polymer has already been formed upstream of the stripper.

Injection of anti-oxidant chemical – Antioxidant chemicals have been used with a degree of success in some locations.

Benefits:

- o Act as chain stoppers that react preferentially with O<sub>2</sub> and peroxides, making them unavailable to take part in free radical polymerization reactions.

Risks:

- o Although chemical treatment can help, it is not always successful and it tends to be most effective when the antioxidant is dosed into the upstream unit rundown ahead of the storage tank.

- Remove foulant/prevent laydown.

Hydrogen treat gas injection – Inject hydrogen treat gas upstream instead of downstream of preheat exchangers.

Benefits:

- o Hydrogen gas increases turbulence and can also help to reduce polymer formation reactions.
- o For VGO HDT hydrogen injection especially for units with separate heating of VGO will prevent thermal cracking of VGO.
- o Avoid dry point in exchanger areas where the feedstock is completely evaporated towards dryness as severe fouling may happen. Polymer and gum tends to build up on the shell-side behind baffles, because of relatively stagnant zone. Evaporation of feed leaves less liquid solvent for the gums and gums get deposited. Most severe at the liquid dry point.

- Modify exchanger design – Modify exchanger internals, maintain high velocities in exchangers, appropriately oversize exchangers to lower high tube wall temperatures below the critical temperature required for coking or polymerization.

Parallel exchanger – Flexibility for bypassing and cleaning.

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Benefits:

- o Clean all exchangers on-the-run, extra exchangers mean no loss of throughput to clean.

Risks:

- o No reduction in rate of fouling.
- o Additional design features required (such as PRV's) to safely by-pass/isolate exchangers.

- Anti-foulant chemical injection.

Benefits:

- o A reduction in the rate of fouling.

Risks:

- o Fouling mechanisms will still occur, probably downstream.

- Prevent corrosion

Corrosion resistant tube metallurgy – select appropriate tube metallurgy to prevent formation of corrosion products that aid the process of foulant formation such as naphthenic acids or high TAN feeds.

Benefit:

- o Easy to implement for new unit and revamp of existing unit.

Risks:

- o May not be the best solution as metallurgy upgrade is expensive and components other than tubes can still provide corrosion products to aid fouling.

## **IHSAN RAAD (Shell Catalysts & Technologies)**

There are several types of fouling in Hydrotreating feed/effluent exchanger units, the three most common types in the industry are:

1. Inorganic particulates.
2. Organic deposits.
3. Ammonium salts.

Each type of fouling has its own characteristics and deposition locations. Knowledge of the type of fouling and the underlying deposition mechanism is essential to tackle the fouling problem. This can either be done by eliminating the root-cause, or by selecting a fit-for-purpose and cost-effective abatement approach.

1. Inorganic particulates: Inorganic fouling is mainly caused as a result of iron sulfide, sodium or coke fines that can either be carried from upstream units or generated in-situ in the preheat exchanger network. These foulants are:

- Iron Sulphide (FeS) and Iron Oxide (FeO, Fe<sub>2</sub>O<sub>3</sub>): Scales of iron oxide (FeO, Fe<sub>2</sub>O<sub>3</sub>) and iron sulphide (FeS) are generated as corrosion products within the unit itself but can also come from upstream units, intermediate storage and transport from well to refinery. Important corrosion sources are furnace tubes (hot sulphur corrosion), the CDU overhead condenser and the reactor effluent air cooler. Iron corrosion products in VGO's are also associated with processing of naphthenic crudes.
- Sodium (Na): Na can come from brackish or salty cooling water (i.e. leaking heat exchangers) or from processing water-containing slops or imported feeds. Sodium in combination with iron has been known to promote coke formation under conditions of high temperature and low pp H<sub>2</sub>.
- Coke (C): Coke fines can be entrained from VBU's and cokers, which cause mainly fouling of the feed side of the feed/effluent heat exchangers, furnace tubes and the top beds of reactors. VGO

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hydrotreaters might also experience coke formation due to a poor separation in the upstream HVU.

2. Organic deposits: The organic foulants are primarily gums formed as a result of processing cracked material and accelerated if the material is exposed to oxygen at any time. The types of foulants are:

- High di-olefin Content: Di-olefins (molecules containing (multiple) double bonds) are mainly found in product streams from (thermal) cracker units but can be present in other streams as well. At the right temperature level (~400-500°F) they polymerize readily to form gum-like substances often showing up as greyish flakes on the FEHXers. The rate of this reaction increases at higher temperatures, making the FEHX especially vulnerable. Elimination of feed streams with high di-olefin content is an easy way to reduce fouling but may not be preferred economically. If long periods of operation with high di-olefins content are expected, an option to avoid high fouling rates could be the installation of a low temperature di-olefin saturation reactor.

- Oxygen in Feed: Oxygen can form a range of different molecules when it is dissolved in a hydrocarbon stream (e.g. peroxides, carboxylic acids, aldehydes and other oxygenated compounds). Amongst other problems, these molecules can initiate polymerization reactions to form gums. Oxygen can enter a feed stream in several ways, including but not limited to air-breathing storage tanks, marine or surface transport vessels, leaks in equipment operating in sub-atmospheric pressure or faulty pump seals. One common point for oxygen to enter feedstock is during storage. Feed streams can be routed directly from unit to unit to avoid intermediate tank storage. Another option is to put in a bypass jump-over on the tank such that only the extra feed goes to tankage and the rest will bypass and go directly to the hydrotreater. All tanks used for storing hydrotreater feed should be nitrogen blanketed, also for straight-run feed. If this is not done, gum formation and other side reaction might happen in the tank itself. Other mitigation is to run it through a stripper, fractionator or distillation unit before introducing it to the unit in order to strip away both dissolved oxygen and the oxygenated compounds, like peroxides. A last option that is used to avoid oxygen related fouling is by injecting anti-oxidants into the feedstock. These compounds are only effective when they are injected prior to the feed stream coming into first contact with the oxygen. So, it should be ideally be injected at the source prior to transportation to site or send to storage. Also, good mixing of the anti-oxidant with the hydrocarbon streams is essential. Only then can they prevent gum formation during storage.

3. Ammonium salts: There are several types of salts that can formed in the effluent exchanger.

- If ammonia and HCl are present, ammonium chloride may deposit directly from the gas phase. The sublimation point in the process depends on the operating conditions (pressure and temperature profile) but also on the concentrations of ammonia (generated from hydrogenation of nitrogen compounds) and chlorides. Main locations of deposition are the feed/effluent heat exchangers (effluent side), the air cooler and recycle gas compressor valves. In the dry state this salt is not corrosive, but in areas where the water dew point is approached, the deposited  $\text{NH}_4\text{Cl}$  salt will become moist and can be very corrosive ( $\text{NH}_4\text{Cl}$  salts are hygroscopic, therefore the stream temperature must be maintained 15-20 C above the water dew point to assure dryness). Furthermore, apart from the danger of excessive corrosion,  $\text{NH}_4\text{Cl}$  deposition can drastically increase the pressure drop and to decrease the effective duty of feed-effluent heat exchangers.

- Like Chloride, organic bromide will convert to hydrogen bromide after hydrotreating and then react with ammonia to form ammonia bromide salt in the exchanger.

- Ammonium bisulphide ( $\text{NH}_4\text{HS}$ ) hydroprocessing reactors convert sulphur and nitrogen compounds in the feed to  $\text{H}_2\text{S}$  and  $\text{NH}_3$ . On cooling, these two compounds react to form  $\text{NH}_4\text{HS}$ . In the absence of water,  $\text{NH}_4\text{HS}$  deposits to form a crystalline solid that can cause plugging of the reactor effluent air cooler. This will occur at relatively low temperatures, 10-30°C. If the dew point of water is reached in the

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effluent air cooler (or water cooler) or if insufficient wash water is injected.

In summary, foulants are typically found on the feed side of the preheat exchangers include various gums or polymers, iron sulfide, and salts. The organic fouling due to gums and polymers results from the polymerization of unstable species in the unit feed. Therefore, in order to determine the risk of organic fouling for a particular feed stream, detailed analysis of the feed is required to determine the problematic species in order to evaluate the fouling propensity and mitigation strategies. Another key factor to consider is the oxygen content of the feed stream as this can promote the polymerization of various unstable compounds, particularly olefins. Therefore, it is a good practice to exclude oxygen from feed storage tanks using a nitrogen blanket. However, this method is ineffective with streams already exposed to oxygen. The inorganic fouling is mainly caused as a result of iron sulfide that can either be carried from upstream units or generated in-situ in the preheat exchanger network. Identifications of the contaminants source and mitigations are key to eliminate the inorganic foulants.

### **SERGIO ROBLEDO (Haldor Topsoe, Inc.)**

To answer this question, we need to differentiate between feed-side fouling and effluent-side fouling. Potential causes and mitigations will depend on which side is experiencing the fouling.

Feed-side fouling in your F/E exchangers can be the result of:

- Olefins
- Oxygen
- Particulates

#### Olefins/Oxygen

Olefins are normally introduced with cracked stocks in the feed. Typically, olefin gumming happens at lower temperatures (300 – 350 °F). Gums formed from peroxides, as a result of oxygen contamination of straight run feed, usually occurs at >400 °F.

In the case of coker naphtha, conjugated diolefins are present which are highly reactive species. In the presence of very small amounts of oxygen, or at elevated temperatures above 450 °F, these molecules will radically polymerize to form gum that can foul exchangers causing poor heat transfer as well as high pressure drop. If the feed contains significant quantity of coker naphtha then these Diolefins must be removed to prevent gum formation.

The coker naphtha should preferentially be sent directly from the coking unit to the hydrotreater to prevent contamination with oxygen. Even straight run stock, which may be part of the feed component, must be prevented from contacting oxygen by storing the feed in a nitrogen blanketed storage tank. Even with strict adherence to avoid feed contact with oxygen, the diolefins in the coker naphtha can polymerize at elevated temperatures. A dedicated saturation reactor operating in the range of 300 °F to 450 F will ensure that these highly reactive species are removed from the feed before polymerization can take place. Once the diolefins are removed from the feed then the feed can be heated to the required temperature for the required operating scenario.

Keep in mind that even though cracked stocks are not fed directly to a unit, there is potential of introducing cracked stock in sites that process slop in their Crude unit.

#### Particulates

Particulates, at high enough concentrations, in conjunction with low tube velocities, can result in these particulates settling out and plating on the surface. If no filter is present, then plans should be made to engineer and install a filter system to reduce the amount of particulates present in the feed. There are also companies that offer tube inserts to reduce the likelihood of particulates settling out and plating on the tube surface, preventing a loss of heat transfer.

Even with filters and tube inserts, if any gumming is taking place in the exchangers, then any small



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amount of particulates present will be picked up by the gums formed.

Examples in industry where fouling occurred on the feed side are:

- Cracked stocks blended with Canadian crude coming down the pipeline. These formed gums with oxygen and fouled the exchangers.
- Crudes from Venezuela blended with cracked stocks.
- Virgin jet was exposed to oxygen and fouled in exchangers operating >400 °F (this happened in multiple units).
- o Similar example with natural gasoline.

As mentioned before, preventing oxygen ingress via direct, hot feed of cracked stocks to the unit, along with floating roof and/or nitrogen blanket on tanks is imperative. Tube inserts are also a viable option to prevent fouling where tube velocities are low enough allowing particulates to drop out in the exchanger. Most importantly, quality control is paramount in preventing this, or reducing further loss in performance.

Examples of actions are:

- Notify the shipper and have the diluent stream changed.
- ? What is the crude source? Are there potential cracked stocks coming down the same line? How about Canadian crudes?
- Notify crude supplier about the poor quality.
  - Install an oxygen stripper.
- ? Done for the virgin jet example.
- Install nitrogen blanket on feed tank or change to floating roof tank.
  - Inject antioxidants into the tanks (mixed results).
  - Bypass tank and go hot (direct) to the unit.

As for effluent side fouling, this is typically the result of  $\text{NH}_3\text{Cl}$  (salts), which are the result of high levels of Cl in the feed. A water wash should be installed to remove these salts, and continuous is recommended versus intermittent.

- A licensor can help calculate where the water should be injected.
  - Need to inject enough water and at the right spot to keep it as a liquid and not vaporize
  - Liquid water will wash out the salts while steam will not
  - Licensor can calculate where the dry point will occur and how much water needs to be injected
- Many examples of where water wash helps
  - If done at the right spot with the correct amount of water and at the right temperature
- Boiler fouling
  - Water treatment company can help with this

There is also a very good P&P this year covering reactor effluent diseases jointly presented by Flint Hills Resources and Marathon. Please plan to attend to learn more.

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