Question 13: Severe fouling of diesel and gas oil hydrotreating preheat exchangers has been a growing problem. In your experience, what are the causes and how can these be prevented? Have you tried antifoulant injection in this service?

Dan Webb (Western Refining)

Fouling of the heat exchanger train is sometimes a problem particularly when processing cracked feed stocks. The fouling is often caused by polymer like compounds (gums) that form when petroleum distillates come in contact with air. When heated olefinic compounds react with absorbed oxygen to form gums that deposit in the preheat train.Iron scale and other particulates in the feed often adhere to these gums to produce severe fouling that restricts unit capacity and accelerates heat exchanger corrosion rates. Typically, every effort is made to avoid air ingress into any of the unit feed stocks. Fouling precursors may also be present in straight run feed stocks in the form of certain chemical contaminants that may be present in the crude or inadvertently introduced in an upstream process unit. Some precursors such as amines, carboxylic acids, and carbonyls form gums without air ingress into the feed. Antifoulants have been used successfully to mitigate fouling caused by these compounds in addition to mitigated fouling caused by oxygen contaminate cracked feed stocks.

Michael Chuba (Sunoco)

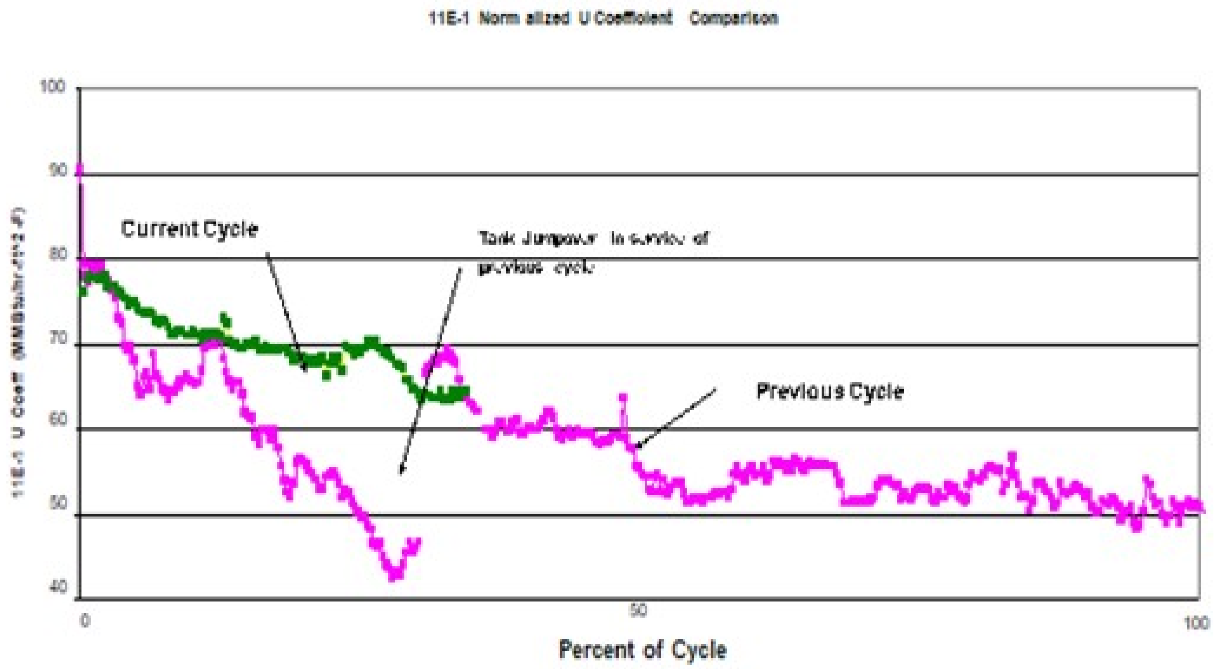
Typically distillate hydrotreaters exchanger fouling has been associated with cracked stocks that contain olefinic material and trace amounts of O2 coming in with the feed from tankage. In addition to oxygen-initiated polymerization, other impurities can lead to free radical formations that can promote polymerization reactions. These impurities include certain nitrogen and sulfur compounds well as some metal ions including iron, calcium, and magnesium.

In addition to free radial polymerization, condensation polymerization reactions can also result in fouling. In this route, two radicals can react to form a larger molecule. The new compound can continue to react and grow until it precipitates out of solution forming deposits.

What I would like to present here is an example of fouling we had on one of our units and how we have significantly reduce fouling via a simple jump over line.

Prior to conversion of this unit to ULSD the unit processed a mix of virgin and cracked distillate stocks. Historically this unit had exchanger fouling that was attributed to the presence of the cracked stocks. When the unit was converted to ULSD the cracked stocks were removed. The resulting feed was a 50:50 mix of direct rundown material from the crude unit and tankage. As a result of this change in operation it was anticipated that the fouling rate would decrease, however, during actual operation the fouling rate actually increased.

An initial program to address the problem included detailed analysis of the various feed stream followed by a targeted antifoulant chemical injection program. Results were somewhat effective but still left significant room for improvement. Continued investigation into the problem targeted O2 contamination coming from the material coming from tankage. The intermediate distillate tanks are cone roof design which would be relatively costly to convert to blanketed tanks. As a first step it was decided to install a jump over from the tank inlet line directly to the suction of the tanks’ transfer pumps. With this simple connection the average volume of material actually drawn from the tanks dropped dramatically.

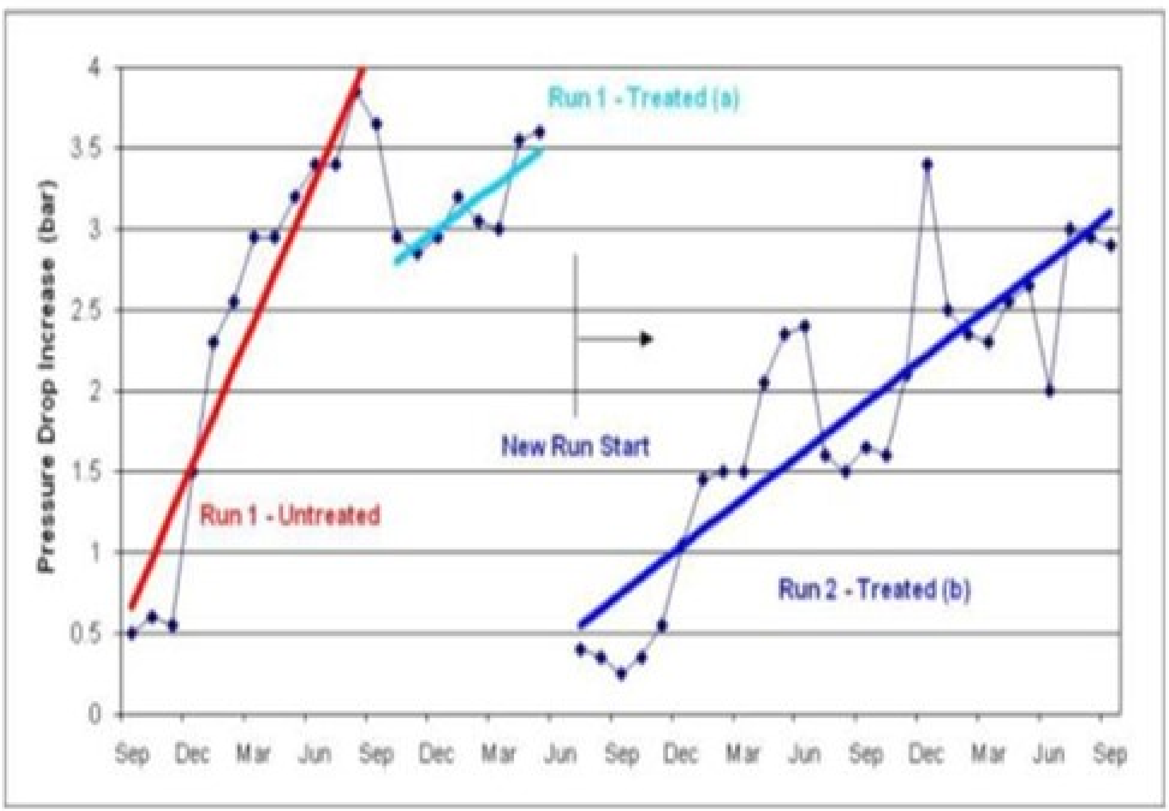


This plot shows the impact on the heat transfer coefficient of the feed effluent exchanger as a result of this simple jump-over. The pink plot represents the previous cycle. At about ¼ of the cycle the jumpover line was installed. At this point significant fouling had already occurred. The discontinuity in heat transfer coefficient a week or two later was the result of a power failure. It is suspected that the rapid depressurization dislodges some of the fouling material thereby improving the heat transfer when the unit is re-streamed. This same response has been seen in previous emergency shutdowns. The green plot represents the current cycle which started with a clean set of exchangers and operation of the jumpover in service from day 1 of the cycle. As can be seen this simple jumpover has significantly reduced the rate of fouling compared to previous cycles. Since the only change was the potential ingress of O2 from the tank, this project confirmed the impact O2 had fouling.

Gregg McAteer (Nalco Company)

Fouling can be a serious problem in hydro-desulfurization (HDS) units because of their importance in producing fuels that should meet environmental specifications. Fouling can limit a unit's ability to maintain a specific feed rate or meet an extended turnaround date. It can greatly influence product quality as well as energy consumption, and catalyst or equipment life. Stricter limits on sulfur and aromatic content of finished fuels make fouling control even more important today. To achieve today's limits of 0.05 wt.% for diesel, refiners must increase severity of refining operations, which often worsen fouling. Fouling ultimately necessitates shutdown and extensive maintenance, a costly process, both in terms of maintenance expenditures and lost production. Causes of fouling in diesel and gas oil hydrotreaters are both organic and inorganic in nature. 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. Antioxidants and/or antipolymerants are used to reduce the formation of gums and dispersants are used to keep any gums already formed from growing in size.

In one case an antifoulant program utilizing both an antioxidant and a dispersant was applied to a gas oil hydrotreater that normally fouled enough to require a shut down after an average of 440 days. The antifoulant program started on a fouled system and showed



a slight recovery of pressure drop. After a shutdown they started again and achieved a 1300 day run (see graphic below).

"Run 1" is shown in red and light blue. The red trend shows the steep increase in pressure drop during normal operation (without antifoulant program). The light blue trend shows the antifoulant program started, saw a small decrease in pressure drop, and then the unit was brought down for a regeneration. "Run 2" is shown as the dark blue trend and shows a lower fouling rate and longer run length with the antifoulant program. Customer estimated the ROI to be between 400-500%.

Phil Thornthwaite (Nalco Company)

Foulants typically found on the feed side of the preheat exchangers include various gums or polymers, iron sulphide and salts.

The organic fouling due to gums & polymers results from the polymerization of unstable species in the unit feed. The problematic species include olefins (generated in cracking processes), organic acids, mercaptans, ketones, aldehydes, phenols, organo-nitrogen and organo-sulphur compounds. Therefore, in order to determine the risk of organic fouling for a particular feed stream, detailed analysis for the problematic species can be useful guide in evaluating fouling propensity and mitigation strategies.

A typical level for concern for each problematic specie is outlined below:

Feed component	Concern Level
Bromine Number	5 g Br_2/100 g sample
Carbonyl Content	150 ppm wt as C=O
Pyrrole type Nitrogen	10 ppm wt as N
Basic Nitrogen	30 ppm
Total Acid Number	0.25 mg KOH/g
Mercaptan Sulphur	20 ppm as S
Copper	10 ppb wt as Cu
Iron	0.3 ppm wt as Fe

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 good practice to exclude oxygen from feed storage tanks by ensuring tank seals and vents are in good condition and through the use of a nitrogen blanket. However, this method is ineffective with streams already exposed to oxygen since the nitrogen blanket will have no effect on oxygen reaction products such as aldehydes, peroxides and hydroperoxides.

Inorganic fouling is mainly caused as a result of iron sulphide that can either be carried from upstream units or generated in-situ in the preheat exchanger network. However, the latter is not so common since refiners choose the metallurgy to mitigate against sulphidic corrosion in most cases.

In order to mitigate and control fouling in the preheat train, chemical dispersants and antipolymerants are used. The properly selected dispersant will act upon the organic polymers by keeping them finely dispersed within the feed stream thus minimizing the risk of deposition on the exchanger surfaces. Likewise, dispersants can also prevent deposition of FeS by keeping them dispersed in the feed stream.

Antipolymerants act by disrupting the propagation and chain extending stages of the free radical polymerization reactions and by increasing the rate of termination. This will limit the rate of polymer growth within the preheat system. They will also minimize carbonyl formation which will in turn disrupt condensation polymerization reactions.

The key to monitoring the program effectiveness is through accurate monitoring of the preheat exchanger network. If the fouling results in a limitation of heat transfer efficiency, then a temperature survey of the exchanger network is carried out and this data is entered into a rigorous thermodynamic process model, such as Nalco's MONITOR® program. This model will then use the plant data to calculate actual and normalized exchanger duties and heat transfer coefficients plus it will calculate the normalized furnace inlet temperature (NFIT). A successful antifoulant program will limit the decay in the NFIT and will generate significant returns for the refiner by improved energy efficiencies and optimized unit operation.

Robert Wade (ART)

We have not had success reducing fouling effects by adding antifoulants. It is our experience that adding antifoulants at best treats the symptom of the problem, and at worst further contributes to localized and downstream fouling. We recommend that the source of the fouling contaminant be identified through analysis and addressed at the source. If this is not possible then we revisit the basic design of the heat exchanger in question and ensure that it is operating in a shear controlled flow regime so that fouling effects are minimized

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