Reﬁnery Process Fouling Control

Abstract

Fouling of reﬁnery process equipment is a common problem resulting in severe economic penalties, as well as signiﬁcant safety and environmental concerns.

GE has developed the technology, the applications expertise, and the global industry experience to effectively treat and minimize fouling throughout the reﬁnery. Typical problem areas include crude preheat exchangers and furnaces, hydrotreater exchangers and reactor beds, FCCU slurry exchangers, and thermal cracking process exchangers and furnaces.

This paper will cover the following topics related to reﬁnery process fouling:

- Fouling mechanisms
- Exchangers – cleaning, bypassing, pretreating
- Economic penalties
- Environmental and safety impact
- Antifoulant chemistries
- Crude (crude blends) quality
- Analytical tools
- Monitoring tools and techniques
- Value of a comprehensive treatment program

Background

Since the early 1980’s, chemicals have been used to help reduce fouling. Early on, the beneﬁts of chemical treatment were difﬁcult to demonstrate due to limitations in monitoring and program justiﬁcation, combined with a developing understanding of fouling mechanisms.

Modern reﬁneries strive for reliability and processing ﬂexibility, with longer run lengths and minimal equipment fouling, to allow the processing of lower quality feedstocks, which offer favorable economic incentives.

For more than 30 years, GE Water & Process Technologies has invested extensively in the identiﬁcation and understanding of fouling mechanisms, as well as how to minimize the fouling in process equipment. The result of these efforts has been the development of proven chemical treatment programs that are unique to each application.

Multiple factors impact fouling including equipment design; ﬂow rates; temperatures; cracking units operational severity; ﬂuid characteristics; caustic addition, can impact crude preheat fouling and coker furnace fouling; and upstream processes, such as desalter operation. Consequently, each process unit and fouling control program is unique. GE has developed state-of-the-art analytical tools and sophisticated monitoring techniques to identify and track process fouling, as well as quantify the impact and economic beneﬁts of a chemical treatment program.

Heat exchangers are used to recover heat from product streams to preheat the feedstock, minimizing the furnace fuel needed to raise the feed to the required process temperature. Fouling in the exchanger train and the related reduction of heat transfer can cause signiﬁcant energy loss and increase operating costs. Fouling can also become so severe that unit capacity and production limits are reached.

In a crude preheat exchanger system, the hot preheat section is usually the area of greatest concern. The hottest exchangers or exchangers with the highest heat ﬂux typically show the high-
est fouling rates. This is also the case for the hydrotreater feed/effluent exchangers and the slurry exchangers.

Intermediate cleanings can be applied, although throughput reductions are typically required if an online clean is carried out or even a shutdown is necessary to clean an exchanger that cannot be isolated and bypassed. This represents significant economic penalties, if not planned in the normal refinery operation.

Mechanical changes and spiral metal inserts, which vibrate as fluid flows through the tube have been used to control the fouling rate. However, other problems such as hydraulic limitations have been encountered.

**Introduction**

Heat exchangers are used to recover sensible heat from process streams leaving reactors, distillation columns etc. to preheat the feedstock and minimize the external energy demand to provide the required heat for the process. Of the total processing cost, energy is a major part, particularly in distillation processes, which can directly influence refinery profitability. Controlling, or minimizing, heat exchanger fouling can dramatically lower overall operating costs.

Typically, refiners acknowledge and accept the gradual diminishing performance from their heat transfer equipment, as fouling inevitably builds. However, when fouling becomes so severe that throughput restrictions occur, the economic penalty is no longer acceptable. Units are then shutdown, or the equipment is by-passed for cleaning, incurring high maintenance costs and production losses, as well as increased environmental and safety concerns.

**Economic Impact of Fouling**

Fouling of refinery process heat exchange systems can cause significant economic penalties. Minimizing operating costs, sustaining throughput, and maintaining equipment reliability are primary goals in today’s difficult economic climate, with more difficult crude slates and blends, stringent regulatory mandates, and greater environmental and safety focus than ever before.

Many factors contribute to the economic impact of refinery process fouling, including those described below. A correctly designed and applied chemical treatment program can help significantly reduce costs and penalties related to equipment fouling.

**Energy Cost:** Fouling in exchanger networks will reduce the amount of heat recovered from product streams. This in turn, requires more heat to be supplied by the furnace to compensate for the lower feed temperature. Also, the higher loading of the furnace often reduces furnace efficiency and increases the fouling or coking tendency of the furnace. Both effects further increase fuel demand and energy costs.

**Maintenance Cost:** High fouling rates can lead to excessive equipment cleaning requirements and costs. Mechanical cleaning, using high pressure jetting, is typical. It requires equipment opening and often heat exchanger bypassing. In cases where the exchangers cannot be bypassed, a unit shutdown may be required to clean the equipment and a substantial production loss needs to be added to the total cost of cleaning. Opening the equipment also increases the risk of damage and additional repair costs, as well as safety and environmental concerns.

**Throughput Loss:** Fouling of the preheat exchangers will increase the heat duty of the furnace up to the point that the maximum furnace capacity is reached. As that limit is approached, the unit throughput will need to be cut back gradually in order to unload the furnace, and again, significant production losses are incurred.

Process stream fouling can lead to increased pressure drop in the exchangers and furnace. In some cases the fouling is so severe that the hydraulic limits are reached, the throughput is reduced, and significant processing incentives are lost. In the case of a hydrotreater, reactor fouling will also cause pressure drop problems resulting in similar consequences.

**Feed Flexibility:** The fouling rate can be greatly influenced by the crude type or blend. Some crudes contribute to such severe fouling problems that they are not considered for processing in certain refineries. These “opportunity” crudes offer an attractive economic incentive to the refinery that can process them.
**Loss Opportunity:** Modern refinery operation strives to maximize the run-length between shutdowns and plan shutdown activities so as to minimize downtime and production losses. Unit flexibility and equipment reliability are key factors in avoiding unscheduled shutdowns, which might hinder contract fulfillment or the ability to capitalize on “opportunity” crudes.

Equipment fouling in the distillation column, can lead to poor product separation and quality, with dramatic economic consequences.

In a hydrotreater, severe fouling can impact conversion generating off-spec, lower value products, and can also result in throughput reductions.

In an FCCU, severe slurry fouling may force the refinery to run a lower main fractionation tower bottoms temperature, dropping valuable products into the less valuable slurry.

**Safety:** Regular equipment opening for cleaning increases the risk of leakages, specifically during the start-up. Although difficult to quantify, the economic penalties associated with a fire or explosion, and moreover personnel injuries, can be enormously high.

**Fouling Mechanisms**

Fouling deposits can be categorized into two major types, inorganic and organic. To properly control fouling, the differences between these two categories must be thoroughly understood and accounted for when identifying the fouling mechanisms involved and designing an appropriate chemical treatment program.

**Inorganic:** Corrosion of process equipment will form ferrous-based corrosion products, such as FeS (iron sulfide) or Fe₂O₃, (ferric oxide) which will deposit in exchangers, mainly in areas with lower velocities.

Solid, inorganic contaminants in crude oils or reprocessed streams, such as sand and silt, can also deposit in the exchanger and cause hydraulic or thermal obstructions. As the crude is heated in the preheat train, the viscosity of the oil is lowered, and the deposition of solids increases. Although most of the salts in the crude should be removed via the desalting process, some inorganic salts can remain and cause deposition in the preheat train.

A caustic solution is sometimes injected into the desalted crude for distillation tower overhead corrosion control. However, this practice can also enhance the potential for fouling in downstream exchangers and coking in downstream process furnaces.

In an FCC slurry system, catalyst fines can contribute to significant fouling.

Additionally, inorganic salts in the effluent side of the hydrotreater feed/effluent exchangers can become a serious problem.

**Organic:** Organic fouling in a crude unit results from the precipitation of organic components which become insoluble in the system, such as asphaltenes, and high molecular weight hydrocarbons (i.e. paraffins). The asphaltenes can become unstable because of the blending of incompatible crudes and/or the heating of the fluid. The precipitated organic molecules can sit at the metal surface and dehydrogenate, forming coke. The coke formation can also result from thermal degradation of hydrocarbons due to long heating periods.

Organic fouling on the feed side of the hydrotreater feed/effluent exchangers and reactors systems is usually caused by polymerization reactions initiated by fouling precursors that are present in the feed such as unsaturates, carbonyls, highly reactive nitrogen compounds, and metals to name a few. Two polymerization mechanisms have been identified, “free radical” and “non-free radical” reactions.

The most common mechanism is “free radical” polymerization, where unsaturated components, such as olefins and diolefins, react to form longer chain molecules. The molecule chain length increases to the point that solubility is exceeded and deposition occurs. This mechanism is catalyzed by the presence of active metals, like corrosion products, and oxygen, which can form peroxides. These peroxides are unstable molecules requiring only a low level of energy to form peroxy radicals, which act as initiators for further polymerization reactions. Once the initiators are formed, the propagation reaction will be enhanced by higher
levels of unsaturated molecules, temperature, and residence time.

“Non-free radical” polymerization mechanism occur mainly as a result of condensation reactions involving components such as carboxylic acid and pyrolle nitrogen.

In an FCCU slurry system, similar polymerization reactions can take place. Furthermore, heavy molecular weight polynuclear aromatics (PNA) can agglomerate and further degrade on the tube surface and contribute to fouling. These heavy aromatic compounds result from the cleaving of aliphatic side chains off of naturally occurring asphaltenes compounds and from recombination reactions of high molecular weight cracked hydrocarbons within the transfer line and in the quench zone of the main fractionator.

Chemical Treatment Capabilities

Following the identification and accessing the relative importance of each fouling mechanism occurring in a heat exchanger system, the chemical treatment program can be designed to obtain maximum inhibition efficiency.

Dispersants: Dispersants are designed to limit the particle size of solids in the system. Various dispersants have different efficacies, depending on the components to be dispersed. Dispersant chemistries are available that address deposition problems such as coke particles, asphaltene precipitation, organic or inorganic deposition. Dispersants will prevent smaller particles from agglomerating to form larger particles which deposit more easily. Similarly, they also prevent the small particles from being attracted to already existing deposits in the system. Maintaining a high fluid velocity also helps to keep small particles from settling onto the process equipment. Some dispersants can also be surface active providing a surface which hinders a particle’s ability to lay down on the metal surface.

Corrosion Inhibitors: Corrosion inhibitors are designed to minimize the contact between the metal surface and the corrosive fluid in order to minimize the formation and deposition of corrosion products in the system.

Metal Coordinator: A metal coordinator (deactivator) will modify the metal ions by complexing, thus reducing the catalytic activity of the metal, so that initiation of polymerization reactions is minimized. The GE metal coordinator is unique and proven to be very effective on both iron and copper.

Polymerization Inhibitors: “Free radical” polymerization inhibitors are designed to react immediately with any radical formed in the system to form a new “stable” molecule which will no longer contribute to the propagation reactions. These inhibitors will reduce the free radical polymerization of olefins and some of the sulfur compounds and stabilize unstable feedstocks.

“Non free radical” polymerization inhibitors reduce the condensation polymerization reactions of carboxylic acids and some of the nitrogen compounds.

The most effective and economical treatment program is one that addresses only those mechanisms that cause the fouling problems and at the same time provide sufficient flexibility to handle the typical processing variations.

Tools Used to Design the Chemical Treatment Program

The selection and design of a successful chemical treatment program relies on tools specifically developed to identify the root cause and quantify the impact of the fouling problem.

Deposit Analysis: Deposit samples are taken from the unit during equipment opening, prior to high pressure jetting.

Sampling should be done to ensure an average composition is obtained, unless the local differences are intentionally analyzed. The shutdown procedure prior to equipment opening should be clearly described, such as rinsing, steam-out etc. in order to provide the correct interpretation to the analytical results.

A thermographic analysis is performed to define the organic and volatile inorganic part of the deposit as well as the ash level remaining. A methylene chloride extraction is typically applied to identify the entrained hydrocarbon and degraded oil fraction in the sample. The non-extractables represent mainly the coke and inorganic fraction of the sample. Besides metal analy-
sis (Fe, Na, Ca, Mg, Cu, etc.) elemental analysis for C, H, N and S is also conducted. The deposit analysis can give an indication if the major mechanism is inorganic, organic or a combination.

**Feedstock Characterization:**

A feedstock can be analyzed to identify specific concern levels for components that reflect a specific fouling mechanism.

Besides the physical property data, analysis of salts, filterable solids, asphaltenes, sulfur, mercaptans, basic nitrogen, neutralization No., bromine No. and metal levels are performed to characterize the feedstocks.

**Pressurized Hot Wire Test:** A relatively rapid method to evaluate the efficacy of different anti-foulant products and combinations is the Pressurized Hot Wire Test. The feedstock sample is first equally divided into several sample cells. An electrical resistance wire is then submerged in the fluid. The sample cells are the pressurized and the wire is then electrically charged for a specified period (Figure 1), depending on the fouling tendency of the fluid.

![Figure 1: Pressurized Hot Wire Tester](image)

Four tests can be conducted simultaneously under the same conditions including the blank. Both the wire deposit and the solids formed in the fluid are compared relative to each other for quantity and nature. Figure 2 shows a picture of the wires after the test, and clearly illustrates the efficacy differences between the treatment programs in comparison with a blank.

![Figure 2](image)

**Hot Liquid Process Simulator:** The Hot Liquid Process Simulator (HLPS) is a dynamic simulation test device which can be used in different operation modes, simulating a heat exchanger, a furnace or even a hydrotreater reactor pressure drop problem. This simulation method is much more time consuming than the Pressurized Hot Wire Test. A schematic is shown in Figure 3.

![Figure 3: H.L.P.S. - Simulator Schematic](image)

The fluid is circulated at a controlled flowrate via an electrically heated core, which provides the required heat to simulate the process. The inlet temperature is maintained constant and depending if the core or outlet temperature is controlled, the outlet or core temperature respectively is monitored to evaluate the fouling rate. Again, different treatment programs can be evaluated as shown in Figure 4. Figure 5 illustrates two cores shown with different deposits.
Monitoring Techniques

The development and selection of the appropriate monitoring technique for each heat exchanger system is crucial in order to be able to evaluate the performance of the chemical treatment program and quantify the benefits achieved. Monitoring should not only define the actual state of a treated system, but also compare the data with that obtained during an untreated processing period. The selected techniques depend on the accuracy and availability of process data.

Three direct indicators of heat exchanger train performance are the furnace inlet temperature (FIT), throughput, and pressure drop. The process conditions change so often that comparing the actual measured furnace inlet temperatures is not possible and a normalization technique is required to evaluate the performance of a treatment program.

A unit survey is required to collect the necessary basic information to define the appropriate monitoring and calculation methods. This survey should provide the correct system configuration and exchanger mechanical data with indications of the available flow and temperature measurements and their locations.

Techniques such as regression analysis and statistical programs are used to evaluate the overall train performance without detailing each individual exchanger. The same techniques can be used to evaluate the pressure drop over the exchanger train or reactor bed. Furthermore, simple heat transfer calculations (Q and U) can be done on exchangers where phase change is not a factor.

Additionally, GE has developed a rigorous PC-based calculation program, called “Heat-Rate Pro™”, which calculates the actual status of each individual exchanger and recalculates the furnace inlet temperature under standardized conditions (NFIT). In addition, the program also performs simulation calculations in order to define the optimum cleaning program and calculate the impact on the whole train if selective exchanger cleaning was applied. The program uses the actual plant data to check the heat balance per exchanger and over the whole train. Data corrections can be applied to ensure the adiabatic nature of heat transfer in heat exchangers is respected and consistent, accurate data is used for the calculations. The fouling factors and heat transfer coefficients are also calculated per exchanger. Comparing the normalized furnace inlet temperature for a treated and untreated run period will quantify the performance of the chemical treatment, where the fouling rate or slope of the NFIT curve is compared during both runs (Figure 6).
All parameters measured and calculated are regularly evaluated versus the preset objectives.

**Treatment Evaluation and Economical Justifications**

The methods applied to evaluate the treatment program and the parameters used to quantify the benefits are dependent on the original treatment objectives and monitoring methods selected when the treatment program was designed. Some of the benefits can be quantified quite easily; however, others are not but still offer significant value. Examples of these benefits are: increased safety, reduced risk of leakage, avoiding unplanned shut-downs, operating stability and flexibility, less cleaning and less toxic waste generation, less supervision required, less outside contracting personnel on-site, built-in engineering support etc.

The return on investment for a treatment program, based on the quantifiable savings is defined as:

\[
R.O.I. = \frac{\text{Total savings} - \text{Treatment cost}}{\text{Treatment cost}}
\]

Typical ROI's of 50 to 300% are obtained and some even exceed 1000%.

The quantification of the obtained total savings is based on one or more of the following savings:

**Energy cost:** The energy cost associated with fouling can be one of the major driving forces to initiate energy saving projects. In order to calculate the energy cost, either the normalized duty across the exchanger network or normalized furnace inlet temperatures at the start of run (SOR) and at the end of run (EOR) must be used.

Using an MRA, a normalized duty or FIT can be easily obtained at the beginning and end of run. The following is an example on how to calculate the energy lost due to fouling.

Given:

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>( Q_{\text{SOR}} )</td>
<td>7000 MMBTU/D</td>
</tr>
<tr>
<td>( Q_{\text{EOR}} )</td>
<td>5600 MMBTU/D</td>
</tr>
<tr>
<td>Run Length (RL)</td>
<td>365 days</td>
</tr>
<tr>
<td>Furnace Efficiency (FE)</td>
<td>85 %</td>
</tr>
<tr>
<td>Fuel Cost</td>
<td>4 $/MMBTU</td>
</tr>
</tbody>
</table>

Assuming a linear fouling rate the heat transfer loss can be calculated as follows:

\[
Q_{\text{loss}} = \frac{(b^2t_f^2 + 2at_f + b^2t_0^2 + 2at_0)/2}{FE}
\]

\[
a = (Q_{\text{SOR}} - Q_{\text{EOR}}) \quad b = (Q_{\text{EOR}} - Q_{\text{SOR}})/(RL)
\]

\[
a = 1400 \text{ MMBTU/D} \quad b = -3.84 \text{ MMBTU/D}^2
\]

\[
Q_{\text{loss}} = \frac{300,588 \text{ MMBTU/year}}{FE}
\]

**Energy Cost:**

\[
\text{Energy Cost} = Q_{\text{loss}} \times \text{Fuel Cost} = 1.2 \text{ MM$/year}
\]

**Maintenance cost:** The direct cleaning costs are compared for a treated and equivalent untreated period. In the case of online cleaning, the number of exchanger cleanings is multiplied by the cost per exchanger to estimate the cleaning costs. Damage to the heat exchanger can occur during excessive cleaning operations. In particular when the bundles need to be pulled for cleaning, the risk that repair costs may be involved is significantly higher.

**Throughput:** In today’s refinery operation with limited margins on crude oil processing, it is important to maximize the utilization rate of the unit in order to remain profitable. Any throughput restriction can be viewed as a direct profitability restriction. However, the crude processing incentive is directly market related and shows large variations with time.

Throughput restrictions occur for many reasons. Due to hydraulic limitations or capacity limitations of the furnace as more duty is required when the furnace inlet temperature declines, the refinery needs to reduce gradually the throughput in the unit from a certain time during the run in order to maintain column operating parameters.

Example: After six months operation, a 100,000 BPD refinery needed to gradually reduce the throughput. By the end of the year, the refinery averaged 5% in throughput loss for the last 6 months. The refinery operating incentive to process this crude is $10/bbl. The reduction in operating income, due to production loss, is calculated to be:

\[
\text{COF} = 100,000 \text{ BPD} \times 0.05/2 \times 180 \text{ days} \times \$10/bbl \\
\text{COF} = 4.6 \text{ MM$/yr}
\]
Similarly, incentive losses can be calculated in those cases where the throughput needs to be reduced during on-line cleaning or for the period that an extra shutdown is required to clean the equipment.

**Crude quality:** Some refiners are reluctant to process lower quality crudes in view of the anticipated problems, of which crude preheat fouling often is the major problem. These “opportunity” crudes however can offer a significant economic incentive to the refinery. A correctly designed treatment program can cost effectively enable processing of these crudes without significant problems.

Example: Assuming a refinery with a capacity of 100,000 BPD processes a low quality crude equal to 20% of the total capacity. The extra incentive would be $0.5/bbl opportunity crude, after subtracting the cost of chemical treatment and any other additional operating expenses. The operating income for the refinery would increase as follows:

\[
100,000 \text{ BPD} \times 0.2 \times 365 \text{ days} \times $0.5 /\text{bbl} = US\$ 3,650,000/\text{yr}
\]

**Conclusions**

Fouling of refinery process equipment results from a number of different mechanisms; unique fluid characteristics; operating practices; unit configuration; as well as ever changing operational parameters, primarily temperature and pressure. Regardless of the cause, process fouling exacts significant economic and operational penalties. Chemicals, if correctly selected and applied, can cost effectively reduce fouling in several critical areas throughout the refinery. The appropriate tools need to be used to understand and quantify the fouling phenomena and design the most effective treatment program. Clear treatment objectives need to be set prior to the treatment start up based on reliable plant data and an agreed monitoring schedule where key performance parameters are clearly defined. The research efforts have led to the creation of unique treatment chemistries, which allow processing of variable feed quality enabling refiners to increase their margins. Chemical treatment programs have been proven to be very effective, which is supported by real life case histories. Treatment programs are justified based on the preset treatment objectives, which are then closely monitored to evaluate the actual performance. Chemical treatment programs show a return of investment of 50 to 300% of which some even exceed 1000%. A lot of spin-off benefits are also obtained with the treatment programs, which sometimes can be more important than the quantifiable benefits.

A successful antifoulant treatment program is the result of the co-operation of the refinery with an experienced and knowledgeable chemical supplier both striving to achieve mutual goals.

**References**

2. “Predicting Crude Oil Fouling Tendency” by D.E. Fields, R.F. Freeman and B.E. Wright; Betz Process Chemicals, Inc. The Woodlands, Texas Energy Progress (Vol 8, No. 4)