FQE® Chemicals

WHITE PAPER

Online / In-Service Exchanger Cleaning

New high-intensity treatment application for heavy hydrocarbon fouled exchangers

REFINERY PROFILE
Crude Unit - Texas Refinery

CRUDE CAPACITY
310,000 Barrels per day

In-Process Asphaltene Anti-Fouling

Process equipment fouling in oil refineries and petrochemical industries is an on-going, severe and costly problem. Fouling of equipment results in costly operational problems that include:

- Reduced reliability and processing flexibility
- Inefficient heat transfer & subsequent increases in energy costs
- Excessive maintenance requirements
- Potential safety and environmental concerns
- Equipment damage
- Reduced throughput

Fouling can take many forms. Besides dissolved salts that can form scales, there is organic and biological materials that can foul filters, piping, heat exchangers, distillation towers, storage vessels among other processing equipment.

Control of fouling is dependent on understanding the type of fouling and the mechanism that initiates the fouling process. For example, for polymerization fouling the following can be utilized; caustic scrubbing to remove sulfur compounds, anti-oxidation additives to inhibit the polymerization reaction initiator, or desalting to remove metal initiators. Corrosion fouling can be controlled by the use of surface coatings either as anti-foulant paints or as filming amine products designed to protect the surface against the accumulation of corrosion byproducts. For asphaltene fouling, reducing shear and minimizing mixing of high paraffin content streams with asphaltenic crude oil streams reduces the fouling.

Crude Oil Composition and Asphaltene Fouling

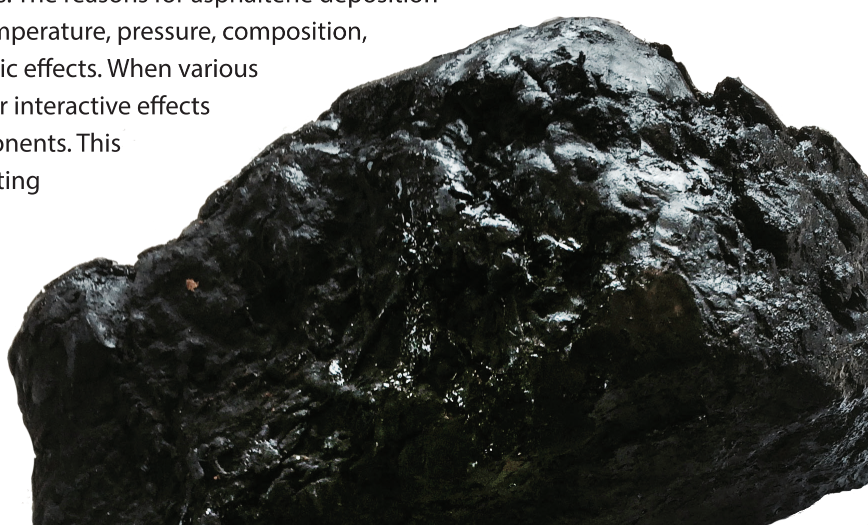
Crude oils are composed of two major organic components; a low molecular weight oil fraction (aromatic and paraffinic saturates) and high molecular weight fraction insoluble in paraffinic liquids. The insoluble portion is often referred to as asphaltenes. Asphaltenes are characterized by a high molecular weight and a broad molecular weight distribution and have a high coking tendency. Asphaltene fouling refers to asphaltenic compounds precipitating out in pipelines, storage vessels, transport vessels and especially in process equipment (heat exchangers, reboilers, etc.) operating at elevated temperatures.

Typical fouled exchanger pulled prior to hydro-blasting operations

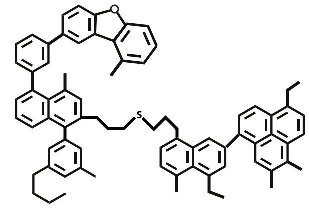
Crude oil low in aromatics content frequently results in equipment fouling during transportation/storage and subsequent processing as the aromatic fraction is separated from the crude oil during the distillation process. The separation is normally carried out at temperatures ranging from 100 to 400°F (38-204°C) and more usually above 500°F (260°C). The presence of even a small quantity of asphaltenes in the crude oil causes fouling in the heat exchangers and distillation equipment such as the reboilers. Additionally, as lighter hydrocarbon components of the crude oil, such as propane, butane, ethane, LPG and condensate range hydrocarbons are removed during distillation, the balance in light ends to heavier hydrocarbon concentration is changed and the tendency for asphaltene fouling is accelerated.

In general, solids in crude oil fall into two classes: "basic sediment" and "filterable solids". These particulates have an economic impact on the petroleum industry. Carried along with the oil, they can cause fouling, foaming, erosion, corrosion and other undesirable problems. Depending on the case, coagulants or flocculants might provide some aid in solids removal. Coagulants are molecules with strong polar charge that act to disrupt charges on the surface of the oil droplets that otherwise prevent coalescence. Flocculants act to agglomerate small particle size inorganic solids into larger particles that can then precipitate based on density.

Depositions of the heavy organics present in oil can happen due to various causes depending on their molecular nature. Diamondoids and paraffin/wax may cause deposition due to lowering of the crude oil temperature and the formation of crystalline solids. Resins are not known to deposit on their own, but they deposit with asphaltenes. The reasons for asphaltene deposition vary on many factors including variations of temperature, pressure, composition, flow, vessel wall imperfections and electrokinetic effects. When various heavy organics are present in the crude oil, their interactive effects can change the behavior of the majority components. This is especially important when one of the interacting heavy organic species is an asphaltene. For example, a regular waxy crude containing minute amounts of asphaltenes will behave differently at low temperatures (below the wax cloud point) compared with a clean waxy crude with no other heavy organics present.



Asphaltene particles are believed to exist in oil partly dissolved and partly in colloidal and/or micellar form. Whether the asphaltene particles are dissolved in the crude oil, in steric colloidal form or in micellar form depends to a large extent on the presence of other particles (aromatics, resins) in the crude oil. Small asphaltene molecules can be dissolved in the petroleum fluid, whereas relatively large asphaltene particles may flocculate out of the solution and can then form steric colloids.



Example of various asphaltene compounds are depicted above

Precipitation of the asphaltene in a paraffinic crude oil is known to be irreversible. Due to their large size and their adsorptive affinity to solid surfaces, precipitated asphaltenes can cause irreversible deposition which may not wash away by current remediation techniques. Various investigations have established that asphaltenes can exist as micelles when in the presence of excess aromatic hydrocarbons.

Experimental investigation has shown asphaltenes to be spherical, cylindrical or disk-like forms. All of these studies are indicative of the fact that asphaltene particles self-associate. This is to say, asphaltene molecules are attracted to one another and form yet larger agglomerations of asphaltenic masses.

It has been found that when an asphaltene deposit is in contact with aromatic solvents, an interface with a large increase in viscosity of up to 1000 Poise is formed. This corresponding increase in viscosity obstructs greater penetration of the solvent. Additionally, it is observed that the aromatic solvent systems are not able to keep the asphaltene deposit in suspension when the stirring of the mixture is ceased causing re-deposition of the asphaltenes to the surface.

Off-Line or In-Place Cleaning

Various attempts have been made in the industry to remediate the removal of asphaltenic deposits in petroleum production and refining equipment. In general, the practice is to take the equipment off-line from production and initiate some method to remove the heavy organic deposit accumulation. The circulation of hot aromatic solvents has been used to reduce the heavy organic deposits. A combination of solvent treatment and normal circulation fluid movement with hot oil have been tried with oil wells with mixed results.

The injection of various chemical additives has had inconsistent results where the ratio of asphaltene to resin content is unknown or not high enough to minimize the deposit accumulation. Typically, mechanical methods such a wire scrappers and line moles for downhole tubing and pipeline applications has been the predominant technology for reducing line blockage and improving fluid flow.

In refinery circumstances, the application of high pressure water blasting with pressures approaching 40,000 psig are commonplace for heat exchanger bundle foulant removal. While of some beneficial effect, these methods are costly and result in a large loss of production revenues due to the equipment necessitating being off-line.

CASE HISTORY

Successful Online Asphaltene Remediation of Vacuum Tower Bottoms Heat Exchangers

FQE® Solvent-H

Clean exchangers following shock treatment

Results Achieved

40% Improvement in fluid flow rate

75% Reduction in down time

FQE Chemicals introduced the use of a proprietary chemical formulation for on-line removal of heavy organic deposits wherein the predominant fouling is caused by asphaltene deposition. The intent is to inject the chemical product into an operating system that was heavily contaminated with asphaltenes causing severe fluid flow restrictions and loss of production.

A Texas based refinery processing heavy Canadian crude provided an opportunity to treat heat exchangers from the vacuum tower bottoms circuitry. The intent of the project was to confirm product feasibility to prolong the runtime of the heat exchangers prior to shutdown operations. The exchangers have historically been taken out-of-service, the shell cut-off and the bundles removed and taken to a cleaning location where cleaning was effected by employing high-pressure water blasting. The time required to remove the exchanger bundle for water-blasting has typically been 3-4 days with substantial waste generated.

The refiner decided to try a FQE Chemicals recommended high-intensity treatment where a selected asphaltene anti-foulant chemical product would be injected over a 24-hour period at a dose rate of 1000 ppm based on the crude oil flow rate. The chemical injection was directly into the crude oil stream being processed upstream of the contaminated exchanger bank. The operating temperature of the heat exchangers varied from 530-700°F (277-371°C).

The chemical selected for trial was FQE Solvent-H. This product has been successfully used for asphaltene dissolution and dispersion many times in off-line tower and tank cleaning operations. The product is designed to not negatively impact downstream refinery catalytic operations, cause emulsion stability nor interfere with waste water processing.

Following the injection of FQE Solvent-H over the 24-hour treatment period and pre-turnaround operations, the exchanger bundles were removed without delay and were found to be in a "cleaner" condition than after typical high-pressure water blasting. The Crude Unit management team reported that the exchangers "have never been this clean". As the 24-hour chemical injection proceeded, there was a continual reduction of pressure drop and increase in the fluid flow rate through the exchangers so that after 24 hours of treatment the fluid flow rate had improved by over 40%.

FQE Chemicals has recommended the use of FQE Solvent-H as an anti-foulant additive to the crude oil stream to reduce the occurrence of equipment fouling where it is in downhole petroleum production or refinery operations. A recommended dose rate of 50-100 ppm of FQE Solvent-H into the daily crude production stream can substantially reduce equipment fouling and extend production run times while minimizing maintenance costs.

FQE® Chemicals

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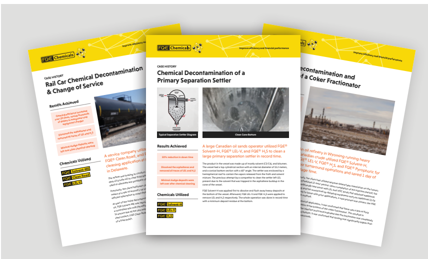

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