COVER STORY

# KEEP OIL IN THE UNIT

**Troy Davis, Athlon, USA,** offers refiners an overview of the challenges and potential solutions to keeping hydrocarbons in processing units in order to increase production.

Twenty years ago, it was standard to have no oil in the desalter effluent. In fact, many refiners established 'clean water' as an important key performance indicator (KPI). However, somewhere along the way refiners found bigger priorities or lost sight of the costly impact of oily water on wastewater treatment operations.

Today, more time and money is spent cleaning the brine at the wastewater treatment plant than is necessary. Moreover, the removed oil goes to slop rather than a crude unit, which means even more money is spent on reprocessing costs instead of gaining additional revenue from processing crude that should have never left the refinery's processing units in the first place.

The economics of oil production can influence refinery action. When refinery margins are low, there are cost-driven reasons to keep oil out of the effluent. When refinery margins are high, some refiners may feel they can absorb the costs of managing hydrocarbons if treating oily effluent does not cut the revenue generated from high throughput.

However, profitable refineries know it is optimal to keep oil in their processing units and out of the wastewater treatment plant – all the time. It cuts down on the costs to manage oily water and maximises the amount of crude that can be produced.

Prevention is key through best practices and chemical treatment programmes, but remediation might be necessary too. Whatever state a refinery's process to wastewater plant relationship is in, there is a solution.

## Prevention and using built-in advantages

Understanding how processing units work and the types of crude going into them will help operators put in place preventative measures and programmes to limit

**Table 1. Production chemistry's impact**

| Functional chemistry | Potential impact | Water or oil? |
|---|---|---|
| Alkyl phenol resins | Desalter emulsion stability | Oil |
| Calcium stearate | Crude unit fouling | Both |
| Carboxylic acid | Crude unit corrosion | Water |
| Ethylene glycol | Wastewater plant | Water |
| Fatty amines/amides | Desalter emulsion stability | Oil |
| Fluorosilicones | Silicone poisoning of catalyst | Water |
| Gluteraldehyde | Wastewater plant | Water |
| Metal salts | Desalter emulsion stability/ downstream poison | Water |
| Methanol | Wastewater plant | Water |
| Mineral acids | Corrosion in crude unit | Water |
| Organic chlorides (carbon tet) | Significantly limited in 1994 (boil, do not hydrolyse) | Oil |
| Phosphate esters | Fouling in crude tower | Oil |
| Phosphonates | Fouling in crude tower | Water |
| Polyacrylates | Fouling and emulsion stability | Water |
| Polydimethylsiloxane | Silicone poisoning of catalyst | Oil |
| Polyether alcohols | Wastewater plant | Water |
| Polymers | Desalter emulsion stability | Both |
| Quatemary amine salts | Corrosion and fouling | Water |
| Solvents | Phase separation potential fouling | Both |
| Sulfonates | Desalter emulsion stability | Both |
| Surfactants | Desalter emulsion stability | Both |
| Triazines | Crude tower fouling/ corrosion wastewater | Both |
| THPS (tetrakis hydroxymethyl phosphonium sulfate) | Wastewater plant | Water |
| Vinyl acetate copolymers | Fouling potential | Oil |

hydrocarbons from remaining in the effluent and entering the wastewater treatment plant.

From a preventative standpoint, the following best practices are used by many refineries:

- Drain the water from storage vessels in the tank farm, where crude is stored on arrival. This reduces the amount of water mixing with the hydrocarbons, resulting in less salt content and potential water slugs going into the desalter.
- Do not blend (or limit) slop oil waste into fresh crude to reprocess it. The recovered oil will contain surfactants used around the refinery. This will lower the surface tension of oil and water during desalting, enabling them to mix together and become tougher (requiring more energy and money) to separate.
- Modelling to predict potential asphaltene precipitation when crudes are mixed together. This allows refiners and chemical solutions providers to better select a chemical treatment programme, including antifoulants (preheat exchangers), demulsifiers (desalting), water clarifier (remove oil from effluent), and even caustic to reduce corrosion and aid in demulsification among other benefits.

There are also several advantages present in processing units to help separate oil from water. They include using:

- Heat to decrease the viscosity and density of the oil, allowing for more rapid and complete separation of water from the oil.
- Electricity, which may be unique to crude units and desalters, to generate powerful electric fields to assist and facilitate water coagulation and further improve separation of water from the oil.
- Emulsion-breaking chemistry to aid in the separation of oil and water.
- Residence time to ensure that a desalter can fully perform its function – remove water, salt and solids from the oil.
- Low shear and mixing forces (after the initial mixing of crude oil and wash water) to minimise tight emulsions formed by transporting oil and water mixtures through additional piping, pumps, and valves.

These are the 'tools' refiners can use within the processing units to help with coagulation and coalescence. Coagulation is when fluid droplets do not repel one another and come into close proximity to each other. Coalescence occurs when, for example, the water droplets come together to form larger ones. When it occurs, the water droplets fall to the bottom of the desalter and exit out.

## Identifying adverse factors

Refiners also need to be aware of the adverse factors outside of processing units and inside wastewater units that can result in increased chemical, energy, equipment, and manpower expenditures. The good news is that they can be prevented or controlled.

Factors to look for include:

- High shear mixing energy.
- Cooler temperatures.
- Varying pHs.
- A substantial increase in volume to be treated – specifically, if oily water joins the rest of the wastewater prior to separation, which is the case in numerous refineries, the volume (compared to the desalter brine flow) increases.

## When oil leaves the unit

There are several factors that cause emulsion stability (or hinder demulsification) and contribute to increased possibility of oil leaving the desalter with the brine.

Upstream chemicals are important to the drilling, production and transportation of hydrocarbons. They protect assets, provide flow assurance and ensure phase separation so that produced hydrocarbons meet pipeline specifications. However, they can also create issues and challenges that have to be met once crude enters a refinery.

Hydrate inhibitors, biocides, amine-based hydrogen sulfide ($H_2S$) scavengers, flocking polymers and paraffin inhibitors are the most common upstream chemistries that create emulsion stability challenges for refiners.

Hydrate inhibitors (e.g. methanol) are a major cause of emulsion stability. They are often used to keep wells workable when temporarily shutting down for events such as hurricanes. Note that emulsion stability is not the worst part of methanol in crude. Methanol is a co-solvent, which allows for an increase in oil-in-water dispersion and also increases total organic carbon (TOC) and chemical oxygen demand (COD) in the water moving to the wastewater treatment plant.

Flocking polymers are also used to compress rags in order to meet the <1% basic sediment and water (BS&W) specifications. Flocking, which is the process of depositing many small particles onto a surface, does not resolve the rag/emulsion layer. The issue is intensified when the emulsion is mixed with water in the desalter, as the emulsion rehydrates and can cause significant issues.

Paraffin inhibitors will generally convert compounds into a sulfonate, which act as surface active agents, and stabilise emulsions by concentrating at the oil/water interface.

Table 1 presents the functional chemistries that impact desalter emulsion stability and phase separation issues. Identifying these chemistries in the incoming hydrocarbon will allow refiners to put in preventative treatment programmes.

## Incompatible crudes due to asphaltene precipitation

Asphaltene precipitation can be disruptive to preheat exchangers and the desalting process. If not managed, refiners will have fouling and corrosion challenges with their process equipment.

Within a desalter, where it is critical to separate salt, solids and water from oil, asphaltenes can work against the desalting process by strengthening the emulsion stability.

### How does it happen?

Asphaltenes precipitate when incompatible crudes are blended in wrong proportions or order. Many crude oils can be blended, but there are a high number of oils that cannot. Some crudes are even self-incompatible and will precipitate asphaltenes by themselves.

To illustrate the challenge of refining hydrocarbons, it is important to note that crude oil is a combination of hydrocarbon molecules, which can aggravate the challenge with the blending of crudes and/or even slop oil into fresh crudes. The blend becomes a mix of several simple and complex molecules and even non-natural contaminants from upstream and midstream processes such as production fluids and metals.

The molecules can be open or straight-chained, single-bonded, saturated molecules (paraffins) or cyclic saturated molecules (naphthenes). Resins and asphaltenes are among the most complex. They both have a high molecular weight, are polar, and are polynuclear aromatic ring molecules.

Unlike resins, though, asphaltenes are not soluble in aromatic-free, low boiling point solvents such as hexane and heptane, keeping the emulsion stability strong. They can also act as surfactants, encapsulating water and

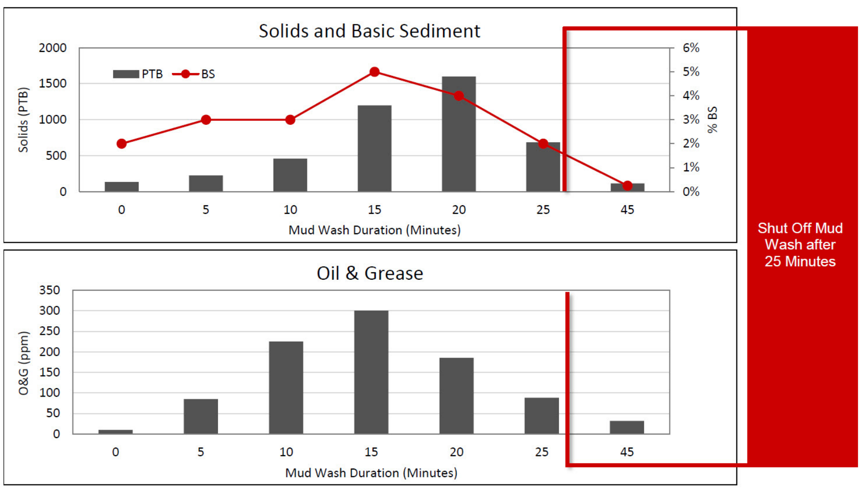


**Figure 1.** Proper mud washing will reduce solids, basic sediment, oil and grease, and produce cleaner water as the oil-coated solids are removed from the desalter.

**Table 2. Mud washing practices**

| | Pros | Cons |
|---|---|---|
| Continuous mud washing | ■ Fewer slugs of solids to the wastewater treatment plant | ■ More constant turbulence in desalter<br>■ More pump maintenance due to prolonged use |
| Periodic mud washing (e.g. 1 hr/d) | ■ Fewer periods of turbulence in desalter<br>■ Less pump maintenance | ■ Intermittent slugs of solids to the wastewater treatment plant |
| Observe mud wash effluent | ■ Do not rely on visual appearance of mud wash effluent exiting a sample tubing. Collect sample and analyse for:<br>▪ Total suspended solids (TSS)<br>▪ Hydrocarbons (oil and gas)<br>▪ Turbidity<br>▪ Microscopic examination<br>■ If performing periodic mud wash, plot the observations and determine if water is cleaning up | |

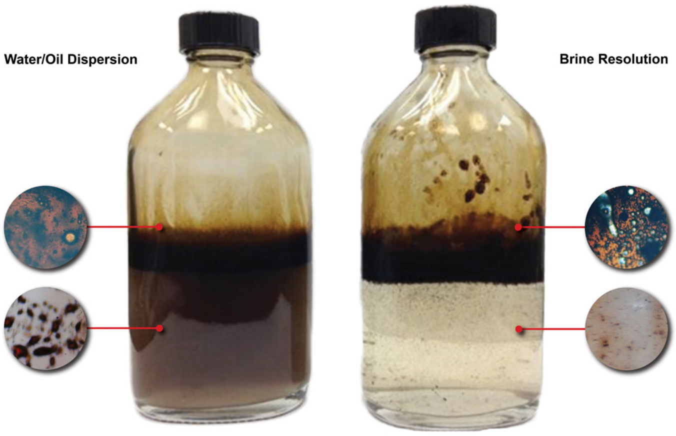


**Figure 2.** Example of treating a growing rag layer with adjunct chemistry to prevent emulsion build-up in the desalter. The bottle on the left is a sample of the growing rag layer untreated. The bottle on the right is a sample of the same rag layer that has been treated with adjunct chemistry. This treatment helped prevent further formation and stabilisation of a rag layer and significantly decreased oil to the wastewater treatment plant.

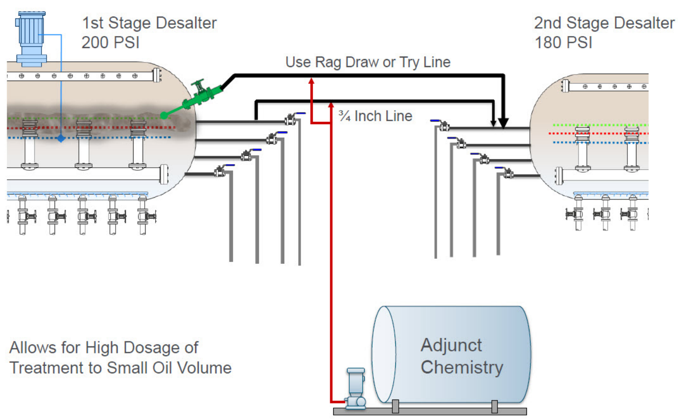


**Figure 3.** Process to reduce rag layer from desalter by transferring and treating small portions of the problematic emulsion.

salts, which strengthen the emulsion and can be problematic when transferred to the crude unit.

Asphaltenes, however, may precipitate out if the concentration of the paraffins in the crude oil or crude oil mixture is right.

### How to manage it

To manage asphaltene precipitation from incompatible crudes, Athlon's experience has been to use (or modify) a crude compatibility model, to predict which single crude, crude blends, and ratio of crude blends will be most likely to precipitate asphaltenes.

The method has provided the company with an extensive crude database, which coupled with onsite compatibility testing makes it possible to predict which crude preheat antifoulant and desalter emulsion breaker technologies and applications to use to prevent upsets.

## Solids present in the incoming crude

Solids in the incoming crude act as surfactants, which stabilise emulsions preventing the separation of water and hydrocarbons. Some of the heavier solids can be oil-coated and leave with the brine, increasing slop-oil generation.

It is important to measure solids, in order to learn what potential problems may arise from desalting the crude. When analysing crude oil, it is important to note that basic sediment from the BS&W test is not the same as filterable solids. The 'solids' reported from the two tests will impact the wastewater plant differently. Basic sediment can include unresolved emulsions, asphaltenes and heavy paraffins as well as high molecular weight polymers from the production field. Refiners should refrain from performing only a toluene wash on a filterable solids test. It will leave behind salt crystals and provide a false high value for filterable solids. After completing a toluene wash, a hot water wash should be performed to remove the crystalline salts and provide an accurate value of filterable solids.

## Proper mud washing is a best practice

Solids and grease that settle at the bottom of a desalter vessel can build up to form a mud or a sludge. It occupies space, which decreases the residence time for oil droplets to separate from water (Figure 1).

If not addressed, solids can plug off draws in the effluent water header, which can lead to increased currents and straight line velocities inside the desalter and pull the oil/water interface into the effluent water headed for the wastewater treatment plant.

Mud washing is an excellent way to ensure residence time is not reduced. The practice allows a desalter to fully perform its function – remove water, salt and solids from the oil leaving for the crude unit and oil-free water leaving for the wastewater treatment plant to remove contaminants.

Most desalters include mud wash headers with a brine recycle system. Water is pumped out of a desalter and back in through nozzles, which acts as a power wash on the desalter's bottom surface.

The key questions are the frequency of mud washing and whether the source of water for the mud wash is fresh or effluent.

Periodic and continuous mud washing each have their pros and cons. The use of fresh water, effluent, and even steam, which provides additional heat and can assist in oil dispersion, also have their positives and negatives. However, good observation, sampling and testing will ensure that a refinery benefits from mud washing (Table 2).

## Unconventional ways to keep oil in the unit

When prevention has not been optimally employed or implemented programmes are not achieving the right results, remediation steps might be necessary. A refinery should work with a chemical engineering team to evaluate operations and current conditions from the tank farm through to the wastewater treatment plant. Having a team that understands both process and water treating chemistry is key to an effective programme. Sometimes the solution might be an unconventional one.

## Treating the rag layer

There are a few options to treating the rag layer, which often has high levels of sulfonates that act as surface active agents stabilising emulsions. The goal is to gradually remove the rag layer (Figures 2 and 3).

The first option is to pipe a try line that removes the rag layer from the first stage of desalter and injects it into the second stage of the desalter. If this arrangement is not possible, refiners should inject the rag into the suction of the crude charge pump, then the wash water pump and lastly the mud wash pump (in order of preferred injection locations).

While removing the rag layer through a try line, the emulsion should be treated with some form of adjunct chemistry. Treating it in the try line allows for very high concentrations of treatment chemicals at minimal volumetric usages. Gradually the rag layer will be removed from the interface and back into the treatment zone, where it can be further dehydrated.

Treating the rag layer will break the cycle of oily water generation and back out fresh crude charge, but it could also cause further issues when processing. Consequently, refiners should be sure that the adjunct chemistry is thoroughly screened prior to introduction, especially if caustic is to be used.

## Pipe recovered oil into the desalted crude

Refiners can pipe the recovered oil off a brine deoiler into the desalted crude. This will require a judgment call on whether the salt levels would be acceptable.

To help, refiners can calculate how much salt the recovered oil will add to the desalted crude. Does the amount of salt fit into the range of acceptability? This, like treating the rag layer, breaks the cycle of slop oil generation, which could back out fresh crude charge or cause further emulsion issues when processing.

## Conclusion

There is no shortage of reasons to keep oil in a refinery's processing units. Managing costs in the face of lower refinery margins, asset protection to avoid downtime, and most of all maximising crude oil processing are enough to persuade refiners. At the end of the day, prevention is less expensive than equipment repairs, energy costs and solutions to address oily water at the wastewater plant.

There are several built-in advantages within process units and treatment programmes that refiners can employ. Doing so will lessen the need for unconventional methods.

Unique treatments need to be evaluated on a case-by-case basis with a speciality chemicals solutions provider – preferably one that has a team of onsite representatives and an in-house engineering team that understands process and water-side operations and chemistry.

## Acknowledgement

The author would like to thank Harold Eggert, Wole Olowu and Wesley Teasdale for their contributions and guidance in the preparation of this article.