

Removing contaminants from crude oil

Natural and introduced contaminants limit crude desalting effectiveness, increasing fouling and corrosion risks in downstream units

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Crude oil contains millions of components. Most components are natural, resulting from millions of years forming beneath the surface of the earth. Among these, saturates are carbon atoms linked together by single bonds. These can be long or short chains. The short chain saturates become lighter products produced from crude oil, such as butane, heptane, and octane. Longer chain saturates form wax, which can serve as a useful product but also contributes to both corrosion and fouling. Aromatics are benzene derivatives that are useful in boosting octane numbers in gasoline, but are limited due to their harmful effects on health and the environment. Resins are high molecular weight molecules that are readily soluble in oil, unlike asphaltenes, which exist in crude oil as a colloidal suspension.¹ Asphaltenes are polyaromatic materials in heavy residues, characterised by not being soluble in aromatic-free, low boiling point solvents (such as heptane). They are soluble in carbon

disulphide.² This loose definition exists due to the complex nature of the asphaltene molecule. Asphaltenes are particularly problematic in regards to corrosion and fouling.

From first production to the refinery, crude oil is being contaminated. Many contaminants are naturally occurring, such as rock fragments, naphthenic acid, and salt water. Production fluids, H₂S scavengers, and corrosion inhibitors, while necessary in the upstream and midstream, can be troublesome for refiners. Organic chlorides are sometimes used as a solvent in oil production sites and can contribute to corrosion and fouling at the refinery. Iron corrosion products picked up by crude oil in pipelines can lead to fouling problems. Zinc compounds found in reclaimed lubricants can create tight emulsions. Many of these contaminants can upset desalter operations, creating corrosion and fouling risks.³

Once crude oil arrives at refineries, the contaminants must be contended with by the

plant. The quality of crude can vary shipment to shipment. If refineries are not prepared to deal with the contaminants in the crude, they can face serious consequences resulting from fouling and corrosion of process equipment. NACE International defines corrosion as “the deterioration of a material, usually a metal, because of a reaction with its environment”.⁴ Deteriorated equipment can cost a refinery a lot of money in replacement, reduced throughput, and shutdown time. A process leak can result in fire and chemical hazards, posing a catastrophic threat to personnel. Fouling’s consequences are similar to those of corrosion with costs including equipment cleaning and increased energy costs.⁵

Dealing with corrosion and fouling early in the refining process

Good desalting practices are important for corrosion and fouling control. There are several strategies to address crude contaminants before the desalter that also aid the desalting process.

Tank farm management

The tank farm is the first stop for crude oil once it reaches the refinery via rail, ship, truck, or pipeline. Crude oil in the tank farm will likely contain water with dissolved salts and solids. Crude tanks should be drained of water before the crude is charged to the unit. This addresses several problems: it reduces the salt contents in the raw crude charge, and it helps avoid slugs of water to the desalter. Water slugs will cause loss of level control and potentially send excess water containing salts into the crude tower. Too much water can increase tower pressure, usually resulting in backing out crude charge and sometimes blowing out trays and causing a forced shutdown. Crude tank switches should be feathered in over a couple of hours if possible and operated to minimise abrupt changes in feed quality.

Slop oil management

Often, refineries will blend slop oil waste into fresh crude charge to reprocess it. This practice should be limited because the waste and slop are laden with surfactants from around the refinery. The premise of desalting is to wash crude oil with water to remove contaminants and then separate the contaminated water from the dry, clean oil. A surfactant will reduce the surface tension between two fluids. By lowering the surface tension between two fluids (in the case of desalting – oil and water), they are allowed to mix together and become difficult to separate.

Best practices for treating slop oil are:

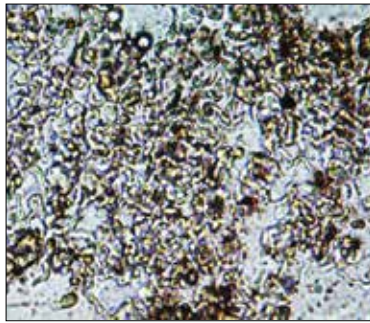


Figure 1 Water and Eagle Ford emulsion (20X magnification)

1. Remove surfactant laden solids via centrifuge before sending slop to the crude tank
2. Break any emulsion that has formed in the slop and separate the oil from the water before sending the oil to crude charge
3. Bypass crude charge and feed slop to another part of the refinery, such as the coker
4. Continuously inject slop directly to the crude charge line at a very low rate, typically <1% of the crude charge rate
5. Have a dedicated slop tank and test the slop for BS&W (basic sediment & water) and filterable solids before charging to the unit.

Crude compatibility

Asphaltene precipitation can be troublesome for both the preheat exchangers and the desalting process. Asphaltene precipitation occurs when incompatible crude oils are blended together. Some crude oils are self-incompatible and will precipitate asphaltenes on their own. There are many crude compatibility models out there, including one developed and patented by Exxon Research & Development.⁶ Refineries can use such models

to predict how different crudes will react when mixed together. Chemical suppliers can use models to predict potential precipitation in crude blends for better optimisation of treatment programmes such as asphaltene dispersants that can help keep asphaltenes in solution. A consequence of asphaltene precipitation is fouling of preheat exchangers, which, as previously mentioned, can be very costly. The application of an antifoulant in the cold preheat exchanger can help reduce the fouling, but can also potentially stabilise an emulsion in the desalter (see **Figure 1**).

Crude unit cold preheat exchangers are usually shell and tube exchangers, with the crude in the tube side and crude unit products on the shell side. These products (naphtha, diesel, kerosene, and so on) are typically at around 200-350°F (90-175°C). The more efficient the heat exchange is between the shell and tubes, the more the crude will be heated before entering the desalter. Heat helps the demulsifying process in the desalter. Heat decreases the viscosity of crude oil and weakens bonds formed by surfactants. This is especially important when running highly paraffinic crudes or highly asphaltenic crudes. Asphaltenes act as surfactants, and paraffinic waxes and asphaltenes can encapsulate water, salts, and solids, carrying them over into the crude unit and creating fouling and corrosion problems.

Desalter operations: mechanical and electrical

A desalter's purpose is to

remove crude oil contaminants that will have harmful effects in downstream equipment and process units. The more desalting is optimised, the more contaminants will be removed. As mentioned previously, feeding the desalter a consistent diet will help in the process as well as keeping the temperature high.

The desalting process is as follows:

1. Water is added to crude oil
2. The mixture passes through a mixing device
3. The mixture enters the desalter and separates
4. Oil exits the top of the desalter
5. Water exits the bottom of the desalter.

Wash water rate, injection location and quality

The amount of water, injection point of the water, and the quality of the water are important. Wash water volume should be between 6-10% of the crude charge volume, and a heavier crude diet may require a higher wash water rate. Higher water rate provides more opportunity for water to contact salts and solids in the crude oil.

Wash water should be injected as far upstream of the desalter as possible. If the crude charge pump has the capacity, it is a best practice to inject at least part of the wash water into the pump suction to maximise contact between the water and contaminants. This should be done with caution, however, because a tighter emulsion can form between the water and oil that may be difficult to break in the desalter. A robust chemical emulsion

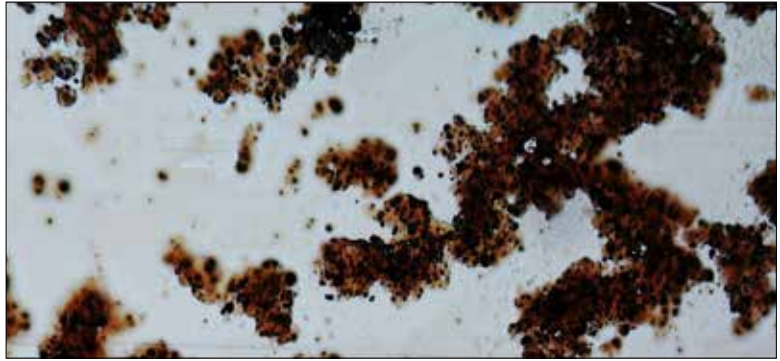


Figure 2 Oil floccing at 20X magnification

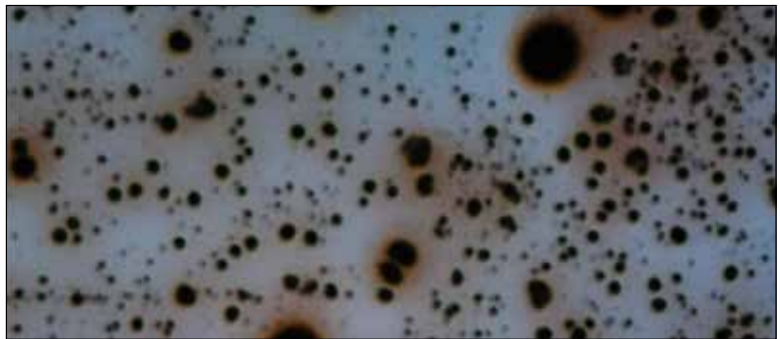


Figure 3 Oil coalescing at 20X magnification

breaker must be used.

Wash water should be O₂ free, low in hardness, salts, solids, sulphides and contain less than 30 ppm of ammonia. Preferred wash water sources are stripped sour water and crude and vacuum unit condensate.

Not only does water help with solids and salt removal, but sufficient water also aids in the separation of water and oil in the desalter. For the water and oil to separate in the desalter, two things must happen: flocculation and coalescence. Flocculation occurs when fluid droplets become attracted to each other.

Coalescence means to come together and form one group or mass. When water droplets combine to form larger water droplets, they coalesce and fall

vertically in the desalter (see **Figures 2 and 3**).

Two equations can explain why more water aids in better flocculation and coalescence:

$$V = \frac{g(\rho_w - \rho_o)d^2}{18\mu} \quad [1]$$

This is Stokes Law where:

V = velocity of water droplet fall

g = gravitational constant

ρ = density of water (w) and oil (o)

d = water drop diameter

μ = viscosity of oil

To achieve maximum water droplet fall velocity (V), the difference between the density of the water and oil should be maximised. Heavier crudes tend to be more difficult to desalt than light crudes and thus require higher tempera-

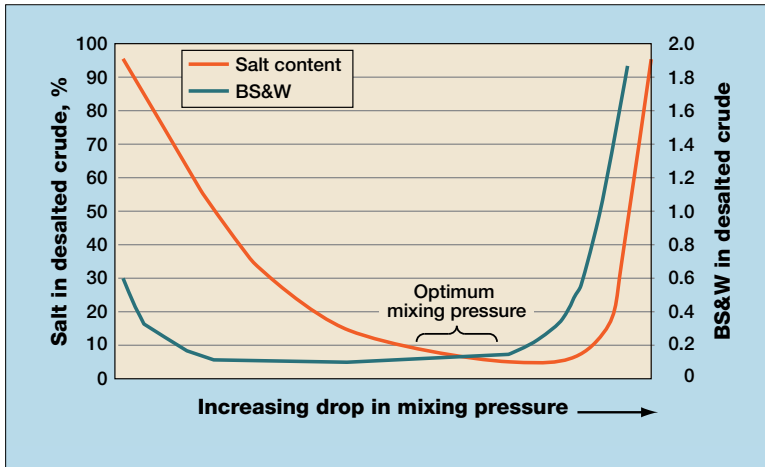


Figure 4 Mix valve pressure drop optimisation

ture to reduce viscosity and higher wash water rate for intimate contact. As mentioned, this is a function of temperature, so hotter is better. The single greatest factor that affects water velocity is the diameter of the water droplet (it is a squared function in the equation). In order to get a large water droplet, a lot of water is needed. Equation 1 applies to a perfect system, but with the presence of surfactants there must be enough force to break tension and allow the flock to coalesce:

$$F = \frac{K(\varepsilon^2)(d)^6}{S^4} \quad [2]$$

F = attractive force between droplets

K = constant

ε = voltage gradient

d = average radius of water droplet

S = average distance between water droplets

To achieve maximum force between water droplets, the average radius of the water droplet should be maximised.

It is a factor raised to the 6th power and will have a huge impact. The more water available to flock and then coalesce to make large droplets, the better. The distance between water droplets has a fourth root impact on the force. Adding more water decreases the distance between droplets, which has a huge impact on attractive force.

Electrical grids

Equation 2 also shows the benefit of having a voltage gradient. Desalters usually have one to three transformers powering electrical grids. The higher the voltage gradient in the desalter, the better. The opposite is true for current. When too much water gets close to the grids, amps increase and the transformers can potentially trip and shut down to avoid overload. This is yet another reason why water carryover in the desalter is problematic.

Mix valve dP

The water and crude mixture passes through a mixing device, usually a valve with a

controlled pressure drop. The higher the pressure drop, the more the water will be dispersed in the crude, providing more opportunity to contact contaminants. However, at some pressure drops, mixing energy will be too much and the water will become finely entrained in the crude oil. See Figure 4 for a graphical representation.

Mud wash

The more time water and oil can spend in the desalter separating, the better. This residence time is hindered whenever there is a build-up of solids and grease in the bottom of the desalter (referred to as mud). Mud occupies space in the desalter that the water and oil could be occupying, decreasing residence time. Desalters typically have mud wash headers that consist of a brine recycle system. Water is pumped out of the desalter and back in through small nozzles that pressure wash the bottom of the vessel. It is very important to have a mud washing routine, whether it is continuous or scheduled throughout the day.

The ultimate objective of desalting is to have water, salt, and solid-free oil leaving the top of the desalter destined for the crude unit and oil free, and contaminant-laden water exiting the bottom of the desalter to the wastewater plant.

Chemically enhancing desalter performance

There are many philosophies regarding chemical desalting aids, and any can be correct depending on the objective of the program. Crude slates vary

just as much in contaminates as they do properties, so there is no one size fits all program. A primary emulsion breaker is standard for desalting operations, and they are typically injected into the crude oil. Adjunct chemistries can also be used. For example, a water clarifier can help remove oil from effluent water before it is processed at the wastewater plant.

Adding caustic before, at, or after the desalter has a number of benefits, one of which is reducing the corrosion risk in the crude unit overhead. Salts that come in with crude oil include magnesium chloride, calcium chloride, and sodium chloride, and they hydrolyse at varying temperatures. Magnesium and calcium chloride that escape the desalter will hydrolyse at crude unit heater temperatures and create potential for corrosion.⁷ Caustic converts hydrochloric acid formed to sodium chloride, which will not hydrolyse at crude unit temperatures.⁴

Caustic has also shown to be helpful in breaking difficult emulsions. By successfully breaking emulsions, less water (containing contaminants) is carried over into the crude unit and therefore fouling and corrosion potential is reduced. Oil under-carry to the wastewater plant is minimised. See **Figure 5** for a case history example.

Caustic can aid in iron removal at the desalter. Iron partitioning in the desalter can be controlled by pH. With caustic addition, iron is forced from the oil and is removed from the system in the effluent water. Iron removal decreases



Figure 5 From left to right: an emulsion treated with caustic, no chemistry, and a standard emulsion breaker

fouling potential and increases the value of coke.³

Amines that arrive with crude oil can be problematic. These typically originate from triazine based H₂S scavengers added in the upstream and midstream industry to mitigate safety and environmental hazards. If the amines and salts make it through the desalting process, they can form amine chloride salts that can be very corrosive.⁷ Acidifying the desalter can force the amines to partition to the water phase and out of the crude oil.

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