A GOLDEN OPPORTUNITY

Nigel Hilton, Dorf Ketal, USA, explains why it is difficult to predict a desalter's ability to handle a change in crude slate and offers a new solution to combat the problem.

Operating flexibility to process opportunity crudes is fundamental to refinery competitiveness. One of the risks of processing opportunity crudes is increased risk of overhead corrosion in the crude column. This can occur if the change in crude slate results in an increase in the salt or amine content of the desalted crude.

In this situation, the short-term financial benefit of reducing cost of crude has to be compared to the delayed and less certain cost of increased overhead corrosion, including the possible risk of an unplanned outage or safety problem. The analysis begins by trying to predict if the desalter is capable of handling the new crude slate without any deterioration in performance. If there is a risk to a deterioration in performance, the next step is to assess what can be done to improve performance and reduce risk.

Predicting desalter readiness to handle a change in crude slate is difficult to do. This article explains why this is the case and offers new tools to help the refiner answer this question more efficiently and accurately. These new tools also have the potential to increase the ability of the existing equipment to handle more difficult desalting challenges and protect the overhead system from increased risk of corrosion.

Comparing short-term gain with potential long-term risk is a difficult risk management challenge. Refiners who are better prepared to improve desalter readiness to capture short-term gains without risking long-term damage from corrosion will be more competitive over the longer term.

The largest threat

The single largest threat to obtaining an accurate prediction of desalter readiness is the potential for rag layer formation. Rag is a complex mixture of water, oil, and solids forming a stable oil/water emulsion (Figure 1). Rag in a desalter is analogous to fouling of a heat transfer surface or column tray, it slows the process. It is also analogous to other risks of fouling in that once rag gets into the system, it is difficult to get it out.

Engineers use fouling factor to predict the impact of fouling on heat transfer and monitor pressure drop to assess the impact of column fouling. However, there is no comparable metric for quantifying the impact of rag in the desalter. Accumulating material in the desalter will have a significant impact on the ability of the oil to rise and the water and solids to sink in the desalter. It would be great to avoid rag entirely, but zero tolerance for the risk of rag is not economically viable. The opportunity to save in the acquisition cost of crude is too significant.

How is rag formed?

Rag contains solids, oil, and water. A key driver of rag is the presence of inorganics such as sand, silt, clay, and corrosion

byproducts in the crude. Smaller inorganic particles are more of a problem than larger particles. Oil coating of the inorganic particles reduces the specific gravity of the particle such that they can float on water and settle in oil, accumulating at the oil-water interface of the desalter. Precipitated organics from incompatible blending also contribute to rag formation.

Total solids in the crude are measured as filterable solids, reported as lbs per thousand bbl. The quantity of filterable solids in different crudes is highly variable; levels of solids as low as 50 lbs per thousand bbl can cause rag. Therefore, given the average weight of 1000 bbl of crude is about 300 000 lbs, this means a concentration as low as 160 ppm of solids in the crude can cause rag. Many crudes have significantly higher solids content and proportionately more potential to form rag.

Figure 1. Sample of rag from desalter.

Figure 2. Oil-water emulsion without rag.

When taking a sample of crude containing solids and conducting a laboratory scale desalting test to measure the rate of oil-water separation, the quantity of solids accumulating at the surface is typically imperceptible to the eye. The test may show the rate of emulsion breaking is acceptable, while the risk of rag formation can be hidden. Rag accumulation is localised at the oil-water surface; it is not typically a phenomenon observable in the bulk fluids. The stability of the rag emulsion and the rate of accumulation of rag at the oil-water surface are highly variable. Stability refers to the time required for the rag emulsion to separate into oil and water with solids in either the water or oil phase. The rate of accumulation of rag at the oil-water interface is like any material balance, i.e. rate of accumulation of rag equals rate of rag formation minus rate at which the rag emulsion is resolving.

If the opportunity crude has other contaminants that are slowing the rate of the emulsion breaking process of the bulk liquid, these other contaminants can also increase the rate of accumulation of rag. For example, high total acid number (TAN) crudes are more difficult to desalt because they may contain calcium naphthenate (or other naphthenates such as sodium) with surfactant properties that can create difficult to break emulsions. Sometimes crude oil producers add surfactants to the oil. Amines in the crude or wash water can raise desalter pH and slow the emulsion breaking process.

Figure 2 shows a microscopic view of an oil-water emulsion at the interface without rag. Oil is the continuous phase of the emulsion and water droplets are dispersed in the oil.

Figure 3 shows the presence of clay, iron-sulfide, titanium, and salt in the emulsion. These particles interfere with the ability of the finely dispersed water droplets to coalesce. Depending on the amount and thickness of the accumulated rag, the interference of the rag on emulsion breaking can be seen in tryline samples. Tryline samples are samples of liquid in the desalter taken over the height of the desalter.

Figure 4 gives four examples of desalter tryline samples. Figure 4a is an example of a desalter free of rag. There is a sharp break between the oil and water phase. Figure 4d is an example of a desalter that has lost control of the rag. Rag has accumulated to the point where oil and rag are exiting with the brine.

Methods for controlling rag

Other than limiting crude selection, improving the speed of emulsion breaking by changing emulsion breaker is the easiest option for reducing rag. If this option is not sufficient, adjunct chemistry should be considered. Adjuncts are additives to supplement the emulsion breaker such as acid, reverse emulsion breaker, and solids wetting agent.

Acid addition reduces the desalter pH and can increase the speed of emulsion breaking if desalter pH is above 7.5. Acid can also react with metals in the rag to disperse the metals. Acid is not commonly used because of the:

- Safety risk.
- Downstream risk of overhead corrosion from carryover of acid.
- Cost of trialling the acid.

- High chemical consumption.
- Lack of consistency in results.

A reverse emulsion breaker tries to reduce the oil content in the water phase of a desalter. The term 'reverse' refers to the fact that this chemical works on water as the continuous phase. A solids wetting agent is a chemical that works to water wet the solids, allowing them to release and break the rag, ultimately settling in the water phase and exiting with the brine.

A fourth class of adjunct is called 'reactive adjunct'. Reactive adjuncts are chemicals that react with contaminants in the desalter in ways other than an acid-base reaction. Dorf Ketal has developed a non-acid adjunct that works synergistically with emulsion breakers to increase the speed of emulsion breaking. Since rag is a slow to resolve emulsion, faster emulsion breaking resolves rag faster. The reactive adjunct chemical also reacts with amines to form water soluble imines, reducing the pH impact of tramp amines and the impact of pH on rate of emulsion breaking. It also reacts with hydrogen sulfide (H_2S) to form a non-volatile H_2S adduct, quenching the release of H_2S gas and the upward force this can create in the desalter. Finally, the chemistry reacts with inorganic components in rag, dispersing the forming components and helping it resolve. The combination of these mechanisms generated by the reactive adjunct dramatically improves rag management. The reactive adjunct is non-acid, this makes it safer and easier to trial.

Predicting the impact of crude slate changes on risk of corrosion

Returning to the corrosion engineer's fundamental question on the risk of corrosion with opportunity crudes, operators should ask desalting experts if the crude being considered has rag precursors and if the supplier has experience desalting the opportunity crude. The historical records for the desalter should be reviewed, with focus on salt removal, oil content in brine, and tryline pictures. If the salt removal has been excellent and the trylines consistently look similar to Figure 4a and 4b, the desalter has some excess capacity that may allow operating with higher levels of rag precursors.

If rag is a concern with the opportunity crude and the trylines appear the same as Figure 4c and 4d, it is prudent to improve desalter readiness before bringing the opportunity crude into the refinery.

Improving desalter readiness with reactive adjunct

Figure 5 shows a picture of brine from a desalter before use of reactive adjunct and 24 hours later. This improvement is the result of reactive adjunct resolving the rag layer in the desalter, allowing the oil to float up, cleaning up the brine.

Ammonia and amine removal using reactive adjunct

Reactive adjuncts can reduce concentrations of ammonia and amines in the desalted crude. This can be important to the corrosion engineer as they can react with chlorides to form corrosive salts. A refinery processing a blend of opportunity crude was experiencing high pH in the desalter and

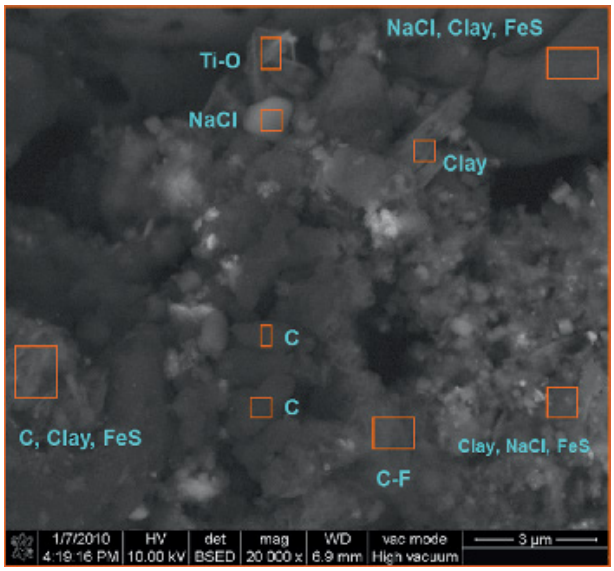

Figure 3. SEM EDAX analysis of rag layer.

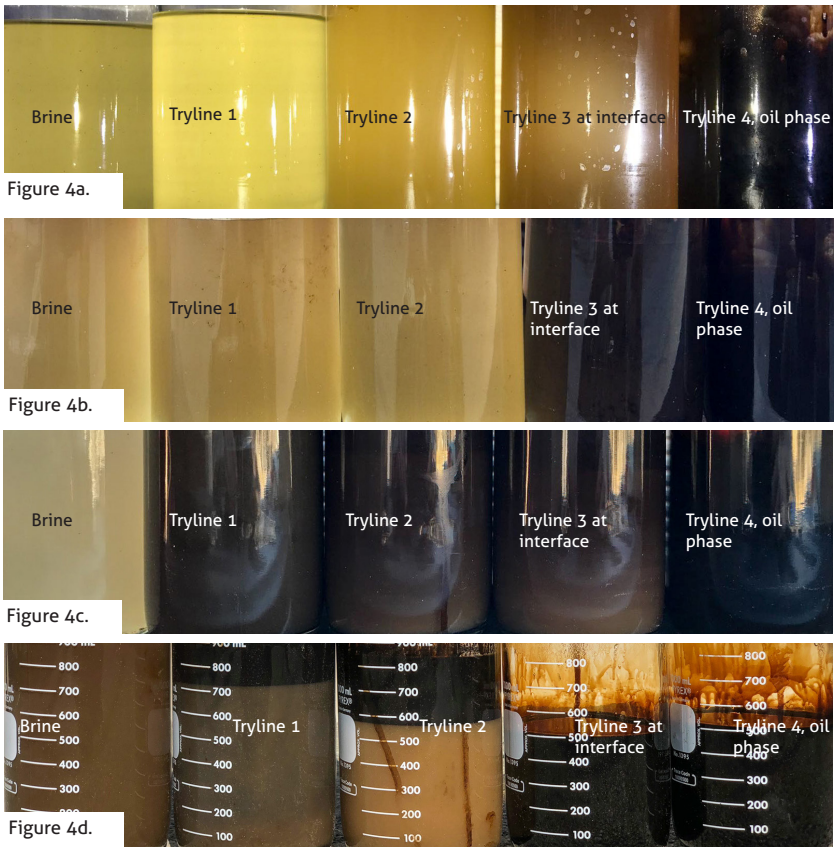

Figure 4. Examples of tryline samples from desalter with varying accumulations of rag.

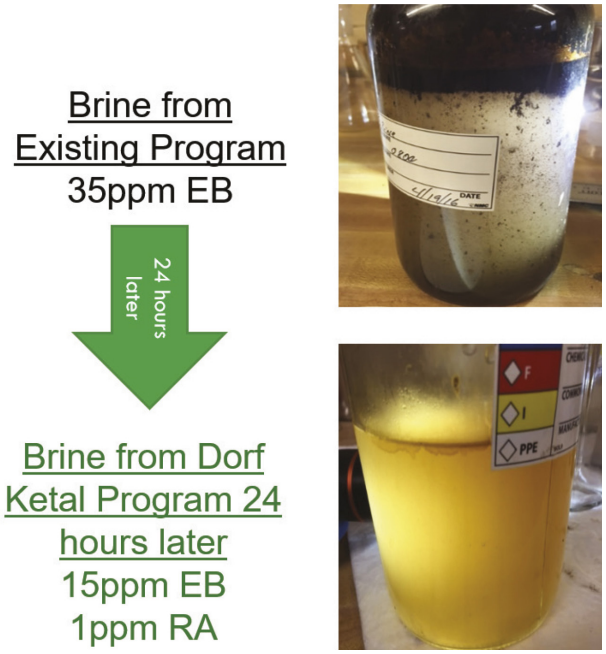

Figure 5. Impact of reactive adjunct on brine quality.

wash water (8+) and the crude was contaminated with tramp amines. Not wanting to deal with acid, the refinery agreed to a reactive adjunct trial. This trial held the dosage of emulsion breaker constant and varied the dosage of reactive adjunct to optimise the cost performance of converting the amines and ammonia to the imine form. The refinery experienced a significant reduction in wash water pH (<7) and the brine pH (7 – 7.5). Table 1 shows the impact on reduction of salt point after 21 days of trial.

Table 1. Reduction in salt point using reactive adjunct

Ammonia/amine salt of	Reduction in salt point (°C)
NH_3	10
MEA	20
MDEA	9
DMEA	10

Conclusion

Protecting against risk of overhead corrosion can conflict with the need to process opportunity crudes and increase refinery competitiveness. To manage these conflicting priorities, the corrosion engineer needs to work with the desalting experts to understand desalter readiness for opportunity crudes. The single biggest threat to obtaining an accurate projection on desalter readiness is the potential for rag formation. Rag is a foulant that slows the desalting process, is difficult to quantify, and difficult to remove. Assessment of the potential for rag formation begins with determination of rag precursors in the opportunity crude and the experience of the emulsion breaker (EB) supplier with the opportunity crude. However, laboratory testing cannot simulate the cycling effect of rag formation, meaning field trials are required to more definitively assess the ability to control rag and the desalter readiness for the opportunity crude under consideration. A new chemistry called reactive adjunct is giving refiners another option for controlling rag, which has been proven in the field and is easy to trial.