A FLEXIBLE DIET

Ralph Navarrete and George Duggan, Baker Hughes Inc., USA, explain how desalter pH management can help to increase crude diet flexibility.

Refiners have always sought to boost their profitability by improving their crude diet flexibility. Such flexibility allows refiners to control how much of a discounted, opportunity crude to include in their feed slate, after weighing the financial benefits of running the crude against the processing problems it is likely to create. As crude oil quality declines globally and refiners face additional pressure to boost margins, they will have to process greater volumes of opportunity crudes on a more frequent basis if they are to remain profitable and, ultimately, operational.

Processing problems can begin as soon as the opportunity crude enters the crude unit's desalter and are often exacerbated by uncontrolled desalter pH. The pH of the brine in desalters can vary widely, ranging from 5 to as high as 10. For most desalters, controlling brine pH at the lower end of this range benefits the overall refining process by improving oil/water separation; lowering salt, basic sediment, and water in the crude; and reducing oil undercarry, which decreases chemical oxygen demand (COD) of the brine sent to the wastewater treatment plant.

Additionally, managing brine pH also offers other significant advantages when processing challenging crudes. Crude oils are often treated with H_2S scavengers prior to transportation. The most common scavengers produce sizeable quantities of undesirable amine that remain in the crude oil. Amines can also be re-introduced through the desalter wash water stream or in slop oils that are

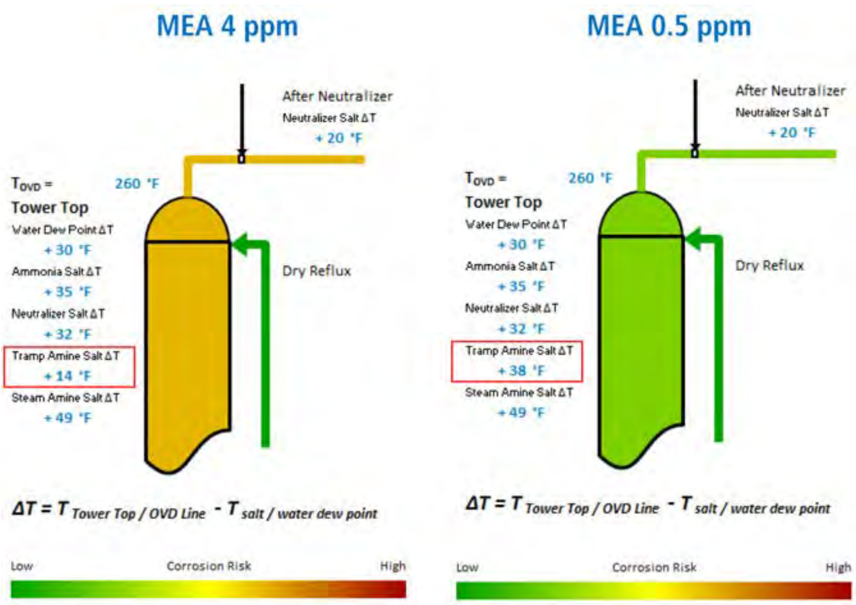

Figure 1. Screenshots of the CRM output depict the reduced corrosion risk to the top of the tower by reducing MEA from 4 ppm to 0.5 ppm in the desalted crude.

reprocessed through the crude unit. Regardless of their source, amines will increase the desalter brine pH. In the simplest case, the increased pH can negatively impact desalter efficiency. However, at higher pH, the amines preferentially partition into the crude oil and are carried downstream, where reaction with hydrochloric acid (HCl) can form corrosive salts that cause damage in the atmospheric tower and overhead system.

In addition to amines, calcium naphthenate presents several well-known processing challenges in the refinery. A salt present in calcium-contaminated crudes with a high total acid number (TAN), calcium naphthenate stabilises emulsions in the desalter. This causes upsets and undermines the performance of downstream units such as the wastewater treatment plant. Past the desalter, calcium naphthenate can form a sludge that causes fouling in towers, drums, heat exchangers, and furnaces.

Calcium can carry through into the atmospheric and vacuum residue streams and feed into the fluidised catalytic cracking (FCC) unit, where it reduces the activity of the zeolite catalyst. Calcium can also end up in the heavy fuel oil and coke products at the refinery, where it degrades product value by increasing ash content.

Amines and calcium naphthenate cannot be easily removed from the crude oil without adjusting the desalter pH – typically achieved by the addition of acids to lower the pH of the brine. However, most commodity acids, while inexpensive, cause substantial secondary processing problems. For example, citric acid reacts to form insoluble calcium salts that can foul desalter internals, reduce desalting efficiency, and lead to unplanned maintenance outages. Sulfuric acid is often considered, but it significantly increases the risk of both corrosion in processing equipment and the deposition of calcium sulfate scale. Acetic acid remains a popular option for handling calcium naphthenates in the oilfield, but the significant volumes required for downstream programmes can introduce several unintended consequences. Not only does acetic acid form emulsion-stabilising salts, it partitions significantly to the crude oil and increases corrosion in the overhead. Additionally, it can cause bulking and settleability issues in the wastewater treatment plant.

A systems-based approach

Baker Hughes developed its EXCALIBUR contaminant removal programme to overcome the negative secondary effects of commodity acids in desalter applications. The programme lets operators manage undesireable amines and process high calcium crude oils without impacting desalter reliability.

The technology includes a water-soluble complexing agent that is injected into the desalter's wash water to lower the pH of the brine and increase the solubility of contaminants in the aqueous phase. The dissolved contaminants are removed from the desalter with the effluent water drained from the bottom of the vessel. The complexing agent formulation avoids many of the processing problems commonly encountered with commodity acids. A corrosion inhibitor in the formulation mitigates corrosion risks in crude unit desalting equipment, and specially formulated emulsion-breaking chemicals help break down stabilised emulsions and maximise crude oil dehydration and salt removal. This minimises the carryover of harmful amines and calcium contaminants into the desalted crude oil stream. A scale inhibitor can be added to the formulation to prevent the deposition of metal carbonates or sulfates in the desalter effluent water removal system.

The programme was designed to provide the aforementioned benefits while having minimal impact on wastewater treatment activities. Improving oil and brine separation in the desalter results in fewer oily solids, phenols, and other organic acid species carried with the brine. Unlike acetic acid, which is broken down by bacteria to increase biomass and cause separation problems in the wastewater treatment system, the technology's components readily biodegrade to release only CO_2 and water.

By providing a lower, more stable pH in the crude unit desalters, the technology allows refiners to improve plant profitability by processing higher volumes of opportunity crude oils, while also reducing operating and maintenance expenses resulting from downstream fouling, corrosion, and catalyst activity losses. It also allows the refiner to produce higher value on-specification coke and heavy fuel oils.

The company's contaminant removal technology has helped refiners around the world successfully process attractively-priced opportunity crude oils. Amine removal has exceeded 90%, allowing management of the corrosion risks associated with amine-contaminated crude oils. Similarly, up to 95% calcium removal has been realised in units processing crudes with high calcium naphthenate content.

Case study 1

A US refiner had experienced significant corrosion to its atmospheric overhead system when processing a shale crude. Baker Hughes completed a comprehensive assessment of the crude unit and suspected that monoethanolamine (MEA) was present in the crude oil as a consequence of H_2S scavenger treatment at the crude oil terminal. Analytical technology confirmed an average of 4 ppm MEA in desalted crude samples.

The MEA measurements, along with other critical, analytical, and operating data, was evaluated with the TOPGUARD corrosion risk monitor (CRM), a proprietary simulation-based technology used to determine the risk of overhead corrosion due to amine and ammonia salt deposition, inadequate pH management, and improper wash water design/operation. The CRM uses a proprietary database of amine thermodynamic data, developed by a major operator and licensed solely to Baker Hughes, to diagnose the causes/risks of corrosion, assess the mitigation options to define a proper operating strategy, and monitor the performance of the corrosion control programme.

The CRM revealed that, with 4 ppm MEA in the desalted crude, MEA-hydrochloride salts were very likely to form and deposit in the tower top and overhead system (Figure 1), confirming the cause of the refiner's corrosion problem. The company recommended a mitigation strategy to promote removal of the MEA at the desalter using EXCALIBUR 7760 contaminant removal additive.

The application of this programme successfully reduced the overhead MEA concentration to 0.5 ppm, which eliminated the salt formation and corrosion risks in the tower top and overhead system (Figure 1). The refiner continued processing high volumes of the shale crude while at the same time avoiding the potential for costly downtime and repairs.

Figure 2. Desalter and crude tower at a US refinery.

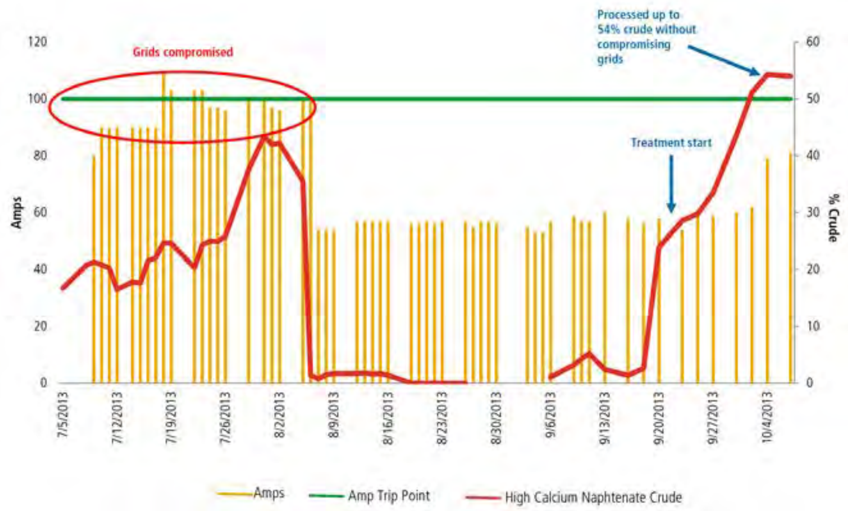

Figure 3. Grid amperage as a function of the percentage of high calcium naphthenate crude sent to the desalter. Prior to the EXCALIBUR treatment, large concentrations of high calcium naphthenate crude resulted in a significant increase in amperage, past the grid's amp trip setting. The refiner stopped processing this crude to maintain the amperage at reasonable levels. After starting the programme, the refiner was able to process a crude slate with 54% of this crude without compromising the grids.

Case study 2

A US refiner was having difficulty processing large percentages of heavy opportunity crudes without causing operational upsets. Multiple attempts to process these crudes showed them significantly increasing the desalter pH, resulting in desalter emulsion growth, poor brine quality, reduced solids removal efficiency, and fouling of downstream equipment. In this specific case, the poor emulsion resolution and poor brine quality negatively impacted the refiner's wastewater treatment capabilities and limited the amount of these crudes that could be processed.

Baker Hughes correctly assessed the high desalter pH as the root cause of the wastewater issues and recommended a mitigation strategy that included its contaminant removal additive to reduce and stabilise the desalter pH. By mitigating the pH swings, the refiner achieved faster resolution of the oil/water emulsion in the desalter and significantly improved the brine quality, eliminating its negative impacts on the wastewater treatment plant.

Solving the brine quality issues allowed the refiner to improve its crude diet flexibility and increase the percentage of this heavy opportunity crude in its crude slate, unlocking US$120 000/d in additional profit.

Case study 3

A refiner along the US Gulf Coast was experiencing desalter reliability issues when processing high calcium, high TAN South American crudes (Figure 2). The high conductivity of these crudes compromised the effectiveness of the desalter's electrical grids, increasing the amperage draw and reducing the voltage differential between the grids.

As a result, the driving force behind water and oil separation was lost. This led to a subsequent decrease in brine quality, which raised the risk of upsetting the downstream waste treatment facilities. It also resulted in an increase in desalted crude basic sediment and water (BS&W) to as much as 1.4%, which increased the risk of downstream fouling and corrosion.

The refiner required a processing solution that would allow it to process a higher volume of calcium naphthenate crudes without compromising desalter reliability. Baker Hughes conducted a system-wide survey to determine the root cause of the problems. Based on the findings, the service provider recommended its contaminant removal additive for calcium removal and emulsion control when processing these South American crudes.

With the new technology applied, the conductivity of the calcium naphthenate crude was reduced and the desalter amps were stabilised. Once the desalter operation was under control, the refiner could process an additional 13 000 bpd of calcium naphthenate crudes without any drop in asset reliability or performance. This increased processing volume translated to a profit gain of US$50 000/d (Figure 3).

Technology for the future

Today's refiners face increasing market pressures, compressed crude differentials, rising crude prices, and product supply gluts. These drivers will only grow in the future, compelling refiners to process higher volumes of opportunity crudes and continue pushing refinery units far beyond their design limits. A dynamic and flexible contaminant removal programme offers a comprehensive treatment solution – one tailored to solve today's processing problems and be easily reconfigured to meet future refinery targets and cost objectives.

Note

EXCALIBUR is a trademark of Baker Hughes Inc.

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Our solution includes a suite of technologies that provide the best feedstock preparation and desalting performance possible to ensure **reliable and profitable refinery operations**.

Find out how you can confidently **increase your crude diet flexibility** and your opportunities at BakerHughes.com/COM or stop by and see us at AFPM, NACE CORROSION, and ARTC.

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