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The utilisation of opportunity crudes in the refinery processing diet is a key driver of refinery profitability, given that crude oil accounts for more than 85% of a refiner’s cost structure. Opportunity crudes are those that trade at a discount compared to similar crudes in the marketplace. The availability of such opportunity crudes like oilsands, light tight oils and high naphthenic acid containing crudes, continues to be an excellent profit improvement opportunity for those refineries able to process these feedstocks.

**Challenge Nexus**

The production techniques necessary to economically extract oilsands and tight oil add to a refinery’s processing challenges. For example, these crudes typically contain greater levels of solids than conventionally produced crudes, with the distribution of those solids shifted toward smaller particle size, increasing the difficulty of solids management. Tight oils can also contain significant levels of production chemicals, including H₂S scavengers containing amines. Critical characteristics can vary greatly from batch to batch, even within shipments labelled as coming from the same crude oil supply. This high degree of variation adds significant complexity to the processing strategy and puts a premium on the ability to rapidly respond to unexpected, frequent changes in crude blending properties.

**Expanded role of the desalter**

When processing opportunity crudes, refiners often operate the desalter more as an extraction vessel, removing many more contaminants than just salt; for instance, metals, solids, and tramp amines can be dealt with in the desalter. While the individual desalter challenges may not be particularly new, their convergence is.

**Ever tightening wastewater regulations**

As refineries across the globe tackle these operational challenges, they also face tightening regulations. Focusing on water regulations, two key trends can be highlighted. First, stricter wastewater limits and water scarcity are driving more water reuse. Second, while national level water regulations are tightening, local watershed and site based restrictions are increasing as well. Brazil, China and Russia are enforcing strict industrial effluent discharge regulations, including in some cases, the required use of advanced treatment and/or ‘water savings technologies’. In Brazil, the Capuava refinery in São Paulo became the first refinery in Latin America to reuse all its wastewater. In addition, the Abreu e Lima and Petrobras Revap refinery both implemented water reuse technologies in 2009.

China’s 12th Five Year Plan includes lower effluent targets that directly affect refineries. The China National Petroleum Corporation refinery in Anning, and more recently, the Sinopec Jiujiang refinery in Jiangxi province, have implemented water reuse strategies. In Russia, an increased focus on water treatment technology at the Antipinski Oil refinery, the Moscow Oil refinery, and the Bashneft Oil refinery in Ufa illustrates how enforcement of stringent effluent limits is growing. In this regulatory light, current refinery opportunity crude processing creates a challenge nexus between crude blends, desalter and wastewater operation. Higher contaminant levels and variability...
combine to make the desalter and wastewater train operation much more difficult and unpredictable at a time when wastewater discharge requirements are tightening; in other words, opportunity crudes plus increased regulations equal greater operational risk.

Solutions for risk mitigation

The goal then is to mitigate risk in wastewater operations during opportunity crude processing. The two main approaches are to focus on minimising contributions to the problem either (a) before the wastewater plant, namely in or upstream of the desalter, or (b) after the desalter, as part of the wastewater operations. This is not an either/or scenario. The best overall solution involves improvement on both ends for an optimum overall result. Figure 1 presents an integrated view of a refinery crude unit and wastewater operations and will serve as a roadmap in our discussion of possible solutions.

Crude preparation solution components

GE’s solution leverages its knowledge of the interplay between chemistries and their application. These include practices such as split feed, whereby the primary emulsion breaker is injected into both the oil and the water. Crude stabilisers, wetting agents, reverse emulsion breakers, amine/metals removal aids, and pH modifiers comprise the balance of the suite of chemistry tools in the solution mix. The common points of application of the chemistries are shown in the key in Figure 1.

Analytics and predictive modelling of crude instability

When paraffinic tight oils are blended with asphaltenic crudes, the resulting blend may change the asphaltene to resin ratio and cause asphaltenes to destabilise and agglomerate. These asphaltene particles are in effect ‘active solids’, and in combination with already high filterable solids in the blend, may lead to stabilised emulsions in the desalter, and increased oil and toxicity in the brine effluent. This can negatively impact wastewater plant operations.

If crude instability is not addressed in the desalter, asphaltenes will likely entrain oil into the effluent brine and require aggressive treatment at the dissolved gas floatation unit (DGF) for removal with the emulsified oil. If they are not mitigated in the DGF, they will move onto the secondary (biological) part of the wastewater train, negatively impacting the biomass. This will decrease contaminant removal effectiveness and potentially contribute to chemical oxygen demand (COD) in the final effluent.

It is critical to understand whether conditions exist for incompatible crude blends, and if so, to rapidly respond with crude stabilising chemistry to ensure good desalter operation. This includes acceptable quality brine being discharged to the wastewater treatment plant.

Being able to process discounted crude oils also depends on the other crudes that are blended in. GE developed a testing methodology to predict crude oil incompatibility and created innovative chemical crude stabiliser solutions to help successfully process these incompatible crude oils.
Crude blend instability may manifest itself as viscous emulsions, oily effluent brine, or as poor salt and solids removal that compromise both downstream processing and wastewater operations. GE’s proprietary laboratory test measures crude instability by stressing the fluid with heptane. Several measurements are taken over a short time period at various heptane addition rates to determine flocculation intensity. The flocculation intensity is compared to a benchmark crude, known to have stability issues, to calculate a ‘relative instability number’ (RIN). Measurements with and without chemical additives allow for the calculation of a ‘relative chemical stabilisation’ number (RCS). From these data, a database can be populated to predict crude compatibility based on various blend order scenarios. As a result, the critical characteristics of changing opportunity inclusive crude blends can be determined and matched to the appropriate crude stabiliser chemistry.

**Crude stabilisers**

As previously mentioned, when paraffinic tight oils are blended with asphaltic crudes, the asphaltenes can destabilise and agglomerate, leading to emulsion stabilisation, increased oil in the effluent, and preheat exchanger and furnace fouling. GE’s crude stabilisers are designed to condition the crude oil and keep asphaltenes from precipitating. They are applied independent of the emulsion breaker to minimise the rag layer build up in the desalter and to control effluent water quality.

In July 2014, GE introduced new Embreak oil based crude stabiliser technology to facilitate the processing of incompatible crude oil blends. It can be used in desalters, as well as other oil and water separation equipment. Traditional asphaltene dispersants can contain contaminants, such as phosphorous or calcium, which can poison catalyst and foul downstream equipment. The new Embreak technology is ashless and does not contain metal. The combination of Embreak and the aforementioned crude stability analytics, allows for the successful processing of incompatible crude oils.

**Case study**

A US refinery adopted an aggressive blending strategy of Western Canadian Select (WCS) and other heavy Canadian crudes to improve its profit margin and supply flexibility. This blend contained significantly higher levels of solids and asphaltenes than had historically been processed at the unit.

Unfortunately, this blend strategy resulted in periodic oil undercarry in the desalter brine, strained wastewater treatment plant operations, and increased slop reprocessing. The refinery struggled to maintain performance, particularly in the area of oily undercarry, which exceeded 2500 ppm of oil and grease at one point.

Technology experts at GE’s Hydrocarbon Process Laboratory measured the stability of various blends using GE’s proprietary testing methodology and determined that the blends were unstable, but would respond positively when treated with Embreak crude oil stabiliser.

GE’s crude oil stabiliser technology virtually eliminated oily undercarry, high amp excitations, level swings and significantly compressed the rag layer. Figure 3 shows the desalter brine before and after the addition of Embreak.

**Wetting agents for solids removal**

Both oilsands derived crude and tight oils contain much higher levels of solids than standard crudes, and the solids themselves are of smaller particle size. Decades ago, solids loading in raw crude may have ranged from 20 - 100 lbs/thousand bbls. Currently it is not uncommon to have as high as 300 lbs/thousand bbls when processing certain tight oils; at least a two fold increase. For instance, a 200 000 bpd refinery processing crude containing 100 lbs/thousand bbls of solids with 50% solids removal across the desalter will send 5 tpd of solids to the wastewater plant, that is more than 1800 tpy. The increased solids loading can easily overwhelm the desalter’s ability to remove them.

High levels of oil coated solids with smaller particle size may challenge the primary waste treatment equipment and lead to recycling of the solids back to the desalter via the slop oil system with increased levels of COD to downstream sections of the wastewater plant. Breaking this cycle through the proper use of solids wetting agents and possibly other adjunct chemistries in the desalter is necessary to avoid stabilised emulsions that lead to water carry over in the oil, and oily brine effluent. The wetting agents help strip the oil layer from the particles and make it easier for them to be removed in the desalter with subsequent solids harvesting points in the wastewater treatment plant.

These new crude issues now require a comprehensive approach to adjunct desalter chemistry with a site specific suite of solutions that incorporate one of more of demulsifiers, reverse breakers and wetting agents in the desalter, as well as crude stabilisers upstream.

**Amines removal**

Tramp amines are defined as amines not intentionally introduced to the crude unit for halide neutralisation. Tramp amines found in tight oil crudes are predominantly the result of triazine based H2S scavengers required for safe handling. These amines will contribute to increased salt potential in the crude tower and overhead system, and if not properly managed, severe corrosion can result when these amine salts form in the crude column.

There is tremendous benefit associated with chemically removing amines at the desalter to extract amines into the desalter brine. GE offers a patented blend of products to extract both metal naphthenates and amines into the desalter brine effluent. However, the additional amines loading into the waste treatment plant must be managed carefully to avoid nitrogen overload to the secondary biological treatment system.

**Wastewater system solution components**

Even with foregoing improved desalter treatment, there will be times when upsets occur that ripple through the wastewater train. Refinery biological wastewater treatment processes (i.e. secondary treatments) are notoriously unstable due to frequent shocks of toxic or inhibitory contaminants being released into wastewater from multiple influent streams. The role of the DGF unit in the wastewater plant is to help level the upsets by removing solids and excess emulsified oils before entering the activated sludge process. Specialised blends of proprietary coagulants and flocculants can improve the performance of the DGF and remove coarser contaminants from the waste stream. That said, it is likely that some level of problematic organics will pass to the activated sludge system.

Given time and stability, biological processes can adapt to many types of waste. However, the periodic and large shocks increasingly seen in refinery wastewater prevent stable, acclimatised populations from evolving. Viable biomass is compromised, which results in the reduction or loss of microbial populations required for the effective removal of contaminants such as ammonia (via nitrification) or COD.
This issue is coupled with the previously described increase in frequency and severity of problematic contaminants that enter the wastewater process via desalter operations as a result of processing opportunity crudes. One example is amines that impair organisms, or, kill some of the population. Besides deliberate extraction of amines from the desalter into the wastewater plant, amines can be introduced to the system by upsets in the amine units as well as sour water strippers. While not highly toxic, some amines can cause solids separation issues in both the flotation units and secondary clarifiers. Finally, all amines contribute additional nitrogen, which can overwhelm the nitrogen removal capabilities of an already stressed secondary system. Additionally, toxic materials may be introduced into the wastewater plant such as polynuclear aromatics like asphaltenes, naphthenic acids, and periodic slugs of spent caustic. Furthermore, sporadic sources of system stress include cleaning processes taking place in process areas.

These frequent shocks of inhibitory contaminants compromise biomass and reduce system stability. Operating personnel often are caught unaware, with little warning. Existing monitoring techniques have several limitations including the inability to directly measure active biomass, the lack of sensitivity to process changes, the inability to detect multiple contaminants, and poor accuracy and/or repeatability.

Biohealth and bioaugmentation
GE’s BioHealth technology, based on the measurement of adenosine triphosphate (ATP), provides a quantified, rapid measurement of total living and viable biomass. It enables the calculation of a stress index, which can be used to measure toxicity of various streams coming into the wastewater plant. Armed with these data, we can respond with operational adjustments, treatment, and other strategies, to mitigate biological system upsets.

Immediate actions can include the temporary diversion and equalisation of problematic influent streams and/or the use of bioaugmentation technology to rebalance the biological system and offset the effects. Use of bioaugmentation via the addition of specialty bacterial products, enhances COD removal and/or nitrification in the biological treatment process. Their application can be adjusted in anticipation of, or reaction to, upset conditions to reduce the risk of losing the desired populations and the resultant impact on wastewater effluent quality.

One advantage of this monitoring approach is the almost real time nature of the activity and stress measurements. This provides a useful early warning to the frequent changes in wastewater composition being encountered in today’s refinery environment.

The new alternative to traditional sludge systems
For those refineries where conventional activated sludge and a clarification system are not enough to handle the variability and toxicity of influent streams, or where recycle and reuse of refinery wastewater is required, membrane based technology is an excellent option.

Conventional activated sludge and clarification systems (Figure 1: Scenarios 1 and 2) are constrained by the clarifiers’ ability to settle solids and meet effluent requirements. A membrane biological reactor (MBR) system using integrated ultrafiltration membranes with bioreactor can replace conventional activated sludge and clarification processes (Figure 1: Scenario 3, Figure 4). By providing a positive barrier to solids, not subject to the settling considerations of a conventional clarifier, the MBR has a much smaller wastewater plant footprint, and enables an inherently more robust design and operation.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Canadian Blend</th>
<th>Treated with Crude Stabilizer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>500 mg/ltr</td>
<td>&lt; 20 mg/ltr</td>
</tr>
<tr>
<td>Nitrite</td>
<td>2.5 mg/ltr</td>
<td>&lt; 2 mg/ltr</td>
</tr>
<tr>
<td>Nitrate</td>
<td>5 mg/ltr</td>
<td>&lt; 2 mg/ltr</td>
</tr>
<tr>
<td>COD</td>
<td>1000 mg/ltr</td>
<td>&lt; 200 mg/ltr</td>
</tr>
<tr>
<td>BOD</td>
<td>200 mg/ltr</td>
<td>&lt; 100 mg/ltr</td>
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<tr>
<td>TSS</td>
<td>100 mg/ltr</td>
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<tr>
<td>SS</td>
<td>10 mg/ltr</td>
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</table>

These fundamental design differences enable the MBR to have a biomass population with a greater concentration of nitrifying bacteria, giving the MBR an advantage in achieving complete nitrification over conventional systems, particularly in a plant subject to influent variation, as is commonly the case.

The GE refinery MBR solution also incorporates GE’s MACarrier®, a specialised carbon based biological carrier that promotes nitrification, enhances the removal of recalcitrant COD, and other toxic organic compounds. Its successful integration with GE ZeeWeed® membranes (Figure 5) prolongs biodegradation times, creates a healthier biology, and reduces effluent recalcitrant COD by more than 50%. The ability of the MACarrier to be regenerated while present in the bioreactor allows for limited additional operational costs and is a key to its success.

The MACarrier provides a large, bacteria friendly surface area where dense and strong biofilm is quickly formed. It adsorbs and concentrates the problematic recalcitrant organic compounds where the biomass degrades the adsorbed compounds and regenerates the MACarrier. Additionally, the MACarrier:
- Handles amine upsets much better, solving nitrite/nitrate toxicity issues with wastewater.
- Eliminates benzene outfall issues.
- Promotes nitrification for nitrogen removal.
- Maintains stable flux and transmembrane pressure (TMP) with less fouling.
- Contributes to a robust design relative to conventional activated sludge systems resulting in a more stable and reliable process under variable and upset conditions.

The effluent from the refinery MBR with MACarrier can be discharged, or further upgraded for reuse within the refinery. The

Figure 2. Example of crude stability results. At the point of greatest stress (the largest volume of heptane) the Canadian blend treated with the crude stabiliser falls below the benchmark crude and into the stable range.
amount of additional upgrading for reuse depends on the application. Cooling water make up requires less upgrading than boiler feed make up.

**Case study**

An extensive onsite refinery pilot of the GE MBR plus MACarrier technology was conducted over a two year period. The high COD laden wastewater was mainly a result of the desalting process. Average feed COD was 700mg/ltr, with shock loadings up to 2100 mg/ltr. The testing protocol included the gamut of influent quality and volume conditions.

- GE MBR plus MACarrier achieved further 50% more COD reduction compared to that without MACarrier (effluent MBR COD <30 ppm versus an average of 60 ppm).
- Tested GE MBR plus MACarrier under various upset or shock loading conditions (high COD/NH3-N/O&G) and demonstrated much quicker system recovery.

**Case study**

Bashneft, a Russian oil company, will use GE’s ZeeWeed MBR plus MACarrier technology for treatment of refinery wastewater from the Bashneft-Ufaneftekhim oil processing complex and other enterprises of the Northern Industrial Block of Ufa. The technology will be core to Bashneft’s rebuilding of its biological effluent treatment facilities to comply with strict discharge regulations and to enable the reuse of treated water. GE’s solution, which includes electrodialysis reversal (EDR), reverse osmosis (RO) and ion selective ionic exchange technologies will efficiently remove oil products, phenols and other toxic substances. In addition to avoiding discharge of the former ‘wastewater’, the upgraded final water will be a new and sustainable ‘resource’ to be reused within the plant, thereby minimising fresh water consumption. The total volume of treated wastewater will be up to 84 000 m³/d (84 million ltrs, or 22.2 million gal). This is an unprecedented amount in terms of the volume of wastewater to be treated and reused at an industrial facility. The equipment will be delivered by the end of 2014, and the startup of production facilities is scheduled for the end of 2015.

**Turn the lights on**

At several points in this complex sequence of inputs, processes and output, there is data, and lots of it. There are physical, chemical and biological measurements all along the way. The source of these data can be inline instrumentation or offline testing. It could be collected by refinery personnel, suppliers, or a combination of the two. If the site has one, its repository could be the refinery’s historian, or a log book. Unfortunately, much of this data winds up as ‘dark data’ and is largely unstructured,untagged or untapped in terms of the insights it holds and the value it can provide.

With the advent of the industrial internet, the tools to aggregate previously disconnected data sources, illuminate cause and effect relationships, and facilitate preventative or corrective actions by people is a major step forward. At GE, the manifestation of the industrial internet is the cloud based platform called InSight.* In a fast paced world, where everybody is on the go, mobile devices (smart phones and tablets) have made huge contributions to personal productivity. InSight’s mobile applications provide the user with the same abilities to see the system health, current data, trends, reports and even enter operational data and notes. Being able to visualise system status, or respond to operational issues with speed and efficiency is obviously the win.

**Conclusion**

The successful processing of opportunity crudes presents a real profit maximisation opportunity for refiners. However, their use creates significant challenges for reliable and compliant wastewater operations. These challenges and the associated risks can be successfully mitigated with a comprehensive, holistic approach.

This begins with an integrated desalter and wastewater system approach. Available solutions should focus on both minimising the contribution of the problem upstream of the wastewater plant, as well as within the wastewater treatment plant using new technologies to mitigate the effects of variability upstream. The optimal solution involves working the levers of improvement in each category for the best overall result. Making sure that all available data are captured, shared and acted upon by operators is also critical.

**Notes**

*A trademark of the General Electric Company. May be registered in one or more countries.