Questions and Answers from the Halliburton Webinar

UPSTREAM QUESTIONS

1. **You briefly touched on polymer floods. Is this becoming more common? What chemistries are typically used in polymer floods?**
    a. As fields mature, they'll move to a water flood to continue production, then generally into polymer floods. Polymer floods are becoming more common as fields mature and producers want to extract as much oil as possible with existing assets.
    b. Polyacrylamides are typical polymers used in polymer flooding. Alkali-surfactant-polymer (ASP) or surfactant-polymer (SP) floods contain an added surfactant to the injection fluid to help increase oil recovery. Both surfactants and PAM/HPAM polymers could impact downstream operations.

2. **Silicon defoamers are also reported as "poison" for refinery catalysts. In this case, would fluor silicones be more effective due to their lower dosages?**
    a. Yes, the refinery impact is generally dependent on the Si concentration. While the fluoro-silicones still contain Si, the lower usage rates (where they work) could help reduce the severity of downstream issues.

3. **How can asphaltene and paraffin be controlled?**
    a. In the production environment, the goal is to prevent paraffin and asphaltene from agglomerating in assets and blocking the fluid flow. For paraffin, most common methods of control are either through mechanical means (periodic hot oil/hot water jobs, increase fluid temp), or chemical. Paraffin inhibitors prevent wax precipitation, paraffin dispersants allow precipitation but keep wax dispersed throughout oil phase so it does not deposit.
    b. Chemical asphaltene control is similar to paraffin, with both inhibitors and dispersants. Dispersant chemistries are similar to paraffin, inhibitor chemistries vary. Oil blending, such as with diluent, also plays an important role in asphaltene control. Many heavy crudes that need to be diluted are high in asphaltene content. Producers generally run a study to understand how much diluent can be added to their export crude without de-stabilizing asphaltenes.

4. **Do you know what types of crude typically contain the highest amount of silicon?**
    a. Gulf of Mexico platforms have limited space, so separation vessels tend to be smaller. That, coupled with large pressure changes, can lead to foaming issues that need to be controlled with defoamers. Many offshore platforms use silicone-based defoamers.
    b. Some new wells in shale plays will begin their lives with high production and small separators. They may need defoamer for the first few weeks or months, then no longer need it as production declines. New wells were steadily coming on-line pre-COVID, so while a specific well may cease defoamer use, there's usually a new well coming on somewhere else in the field that needs it.
    c. Some gas fields may use foaming agents to increase their gas production, but then may need to add defoamer on the surface to kill the foam in separators.

5. **What are the typical crudes that contain higher amounts of phosphates which cause fouling in crude column?**
    a. It's not necessarily location specific, more specific to the upstream chemical treatment program in use. In general, locations with higher scaling tendencies (higher TDS produced water) would be more prone to containing phosphates/phosphonates.

6. **What are typical crudes with high H_2S scavengers?**
    a. This is generally location specific. Light tight oil (LTO) in the continental US like the Eagleford, Permian shale plays, etc may contain high amounts of scavenger, as well as some Canadian heavy crudes.

DOWNSTREAM QUESTIONS

1. **Can you share "best practices" around blending and processing crudes that are significantly different in gravity or asphaltene content?**
    a. Segregation of incompatible crudes is the primary method of preventing asphaltene or paraffin precipitation, although some crudes are "self-incompatible". Designate "Heavy, Medium and Light Crude tanks and only mix them as they are being fed to the unit, or to a daily charge tank. In that case, good mixing is critical.
    b. If asphaltene or paraffin dispersant are used, they need to be injected prior to the two incompatible crudes are mixed. There are no dispersants that will resolubilize the asphaltenes or paraffins after they have precipitated.

2. **Is there any other jet fuel additive other than Dow methyl carbitol which is cost effective?**
    a. Dow's methyl carbitol is the brand name for Diethylene Glycol Monomethyl Ether (DEGME). It is used in jet fuel as an anti-icing agent. Great care must be used when substituting any products used in jet fuel. Some products approved for commercial jet fuel may not be allowed in military jet fuel. Speak with a competent fuels additive company and consult ASTM and customer specifications before making any changes in Jet Fuel additive programs. ASTM D-1655-20C is a good starting point to determine specifications and treatment of aviation turbine fuels.

3. **Will lowering the pH of water injected into the desalter drastically reduce the MEA triazine?**
    a. Modeling and real-world treatment suggests that lowering the pH of the desalter wash water will reduce MEA in the oil phase. There are issues with desalter acidification, and just lowering the MEA content of the crude may not reduce the corrosion in the distillation and condensing system of a crude tower.

4. **Regarding jet fuel, can any oilfield chemicals cause problems with smoke or cetane?**
    a. We are not aware of smoke point being impacted by production chemicals, this is more function of the composition of the actual crude oil and how it relates to the paraffin, naphthene and aromatic content of the jet fuel. Cetane is only an issue for compression ignition engines (i.e. diesel) and does not apply to turbine combustion in jet engines.

5. **Is there a maximum amount of asphaltenes that guarantee stability not dependent on the amount of resins, i.e. 0.5%?**

   a. Typically, crudes with low levels of asphaltenes, (<1.0%) are not problematic with regards to asphaltene precipitation, but there are no guarantees. The lower the content, the less opportunity for agglomeration occurs. We have seen even small amounts of these types of crudes can significantly increase asphaltene precipitation when blended with high asphaltene stable crudes.

6. **We've seen high filterable solids greater than 450 ppm in crude to desalters. That is causing stable rag layer formation at desalter interphase leading to oil undercarry with brine. Is there any chemistry available to resolve this issue?**
   a. Consult with your desalter chemical suppliers. They all have chemistries, often referred to as “solids wetting” adjuncts or reverse breakers, usually fed to the wash water. They function is to help remove oil from the oil coated solids, which allows them to drop out with the water. Oil coated solids are buoyant and collect at the interface. It is to heavy to go with the oil phase, and too light to drop out with the water.

7. **For asphaltenes that do not drop out in the desalters, is there a temperature range in which you can expect them to have a greater impact on the crude preheat train fouling.**
   a. There are too many variables that impact asphaltene precipitation to come up with a rule of thumb on a temperature range. Asphaltene stability of crude blends is usually the criteria that most refiners look at. Typical temperatures on preheat exchangers that foul is in the 400-500 Deg F range. It is not unusual to see fouling in the second or third to last exchangers before the furnace, with little to no fouling in the hottest exchanger just prior to the heater. Operating issues that can move the point of precipitation can be:
      i. Velocity: laminar flow (<3.0 ft/sec) are obviously more susceptible to fouling
      ii. Desalter performance: poor desalting will increase all three of the criteria shown below. Resent research and field trial numbers suggest that elevated levels of these can increase asphaltene precipitation
         1. High salt content
         2. High solids content
         3. High water content
      iii. Low pressure: deposition of asphaltenes increase at the point of lower pressure This can occur in the preheat train as it gets closer to the furnace, across furnace control valves, and inlets to fractionation towers.

8. **What are the impacts of MEA TRIAZAMINES on downstream refineries?**
   a. The impact on the crude unit was discussed in some detail. What was not covered, but was in one of the presentation slides, was the impact on downstream processing units.
      i. Wastewater plant: a significant portion of the MEA is removed in the desalter via the wash water. These amines can be toxic to the “bugs” in the biological treaters creating high ammonia in the outfall, increased “bug” kill and high solids disposal cost.
      ii. Iron sulfide in various overhead and side cuts. One of the biggest issues with MEA is the formation of MEA-hydrochloride salts in the crude fractionator and overhead condensing system. These highly corrosive salts can generate a significant amount of free irons sulfide which can plug downcomers and trays. This could impact cut points on feed going to various downstream units. In addition, this corrosion byproduct can migrate to naphtha and diesel

hydrotreaters and create fouling and pressure drop issues on the feed side of the feed effluent exchanger as well as the reactor catalyst bed.

iii. The MEA salts can be corrosive in run down lines but when hydrotreated, break down to form ammonia and HCl in the reactor. These will form ammonium chloride salts on the effluent side of the feed effluent exchangers and the coolers upstream of the high-pressure separator. An increase in the salt formation can force the salt point upstream and out of the zone that is typically water washed.

iv. The amine is also a basic nitrogen that can be a temporary catalyst poison to the FCC which will increase hydrogen make if they leave with crude unit in the gas oil draw. It will also increase ammonia or cyanide to the main fractionator with the associated increase in fouling and corrosion.

9. **In our refinery we are facing oil carryover with brine which is a very thick emulsion. What are good practices to separate this oil from the brine?**
    a. Oil under-carry is an indication of poor oil water resolution in the desalters that can be caused by several operational, mechanical, and chemical inefficiencies. Some of these inefficiencies are undersized desalter, operating desalter water level too low, over-mixing via mix valve dP, too little wash water, poor quality wash water, poor mud-washing program, ineffective demulsifier and adjunct chemistries, high solids loading in crude oil, asphaltene instability and low desalter temperature. Some best practices to minimize oil under-carry are below:
        i. Ensure you are maintaining optimum desalter water levels to allow for good separation. Depending on where the try-lines are located in the desalter, 2-3 levels of water is desirable. It is also recommended to calculate the water residence time in the desalter bottom, and this will help decide what water level to maintain in the desalter for good separation
        ii. Wash water rate of 5-7 percent of crude charge is recommended depending on the crude slate gravity. Heavier crude slate may require higher wash water ratio, while 5 percent wash water may be optimum for lighter crude slate.
        iii. Wash water quality is equally as important as the wash water quantity. Poor quality wash water can contain surfactants which can stabilize emulsion.
        iv. An effective mud-wash program (frequency, duration and flow rate) will ensure help maintain non-oily brine and minimize solids build-up in desalter bottoms. Temperature profile around the desalter bottom will tell you if there are solids building up in the desalter and a more rigorous mud-washing program is needed.
        v. Desalter temperature should be between 240-300 F°, heavier crude requires higher desalter temperature to aid oil/water separation and reduce the oil viscosity.
        vi. Good emulsion breaker chemical program will minimize emulsion in desalter and maintain consistent non-oily brine quality. A good chemical program should also give good dose response when you are faced with challenging crude slates. If your emulsion breaker program dose not resolve oil/water separation issue when increased, the program may not be robust enough.
        vii. Evaluate and benchmark your desalter design and capability against industry standards to identify gaps in desalter operational and mechanical performance.