Question 58: What issues have you seen in your wastewater treatment plant caused by crudes containing biocides? If so, what parameters have you established to control these effects?

BRADEN (NALCO Champion)

Biocides: Typically, the upstream group wants to kill bugs and the downstream wastewater treatment plant wants to keep them alive. So, you have bacteria in light tight oils, as well as in the oil sands, during crude oil production. The upstream group uses a biocide to prevent the sulfide-reducing bacteria to produce H2S, and the dosage is usually between 25 to 500 parts per million. The injection can either be slug feed or a continuous feed. Most common oilfield biocides are glutaraldehyde, tetrakis hydroxymethyl phosphonium sulfate (otherwise known as THPS), quat (quaternary) amines, and 2,2-dibromo-3-nitrilopropionamide, which is DBNPA, as well as a variety of other eracids. The biocides fed in the oilfield typically do not reach the refinery. They are oxidized out and reduced down, so they do not play a role in refining.

At the refinery, we are seeing biocides being added to the crude tanks to inhibit bacteria growth. Sulfate-reducing bacteria will produce H2S leading to downstream corrosion issues. Typically, a water-soluble biocide is used. It may be a peracid or THPS that is used there. The type of biocide used is based on consultation with the refinery's chemical vendor. Sometimes groups within a refinery do not like to communicate with one another. But when you put this program in place, the tank farm has to be in contact with the wastewater treatment plant. And when you are drawing down the water from the tank, you must let the wastewater treatment plant know when the drawdown is scheduled.

In the wastewater treatment plant, you have a primary system to separate the oil from the water. The secondary system is where the bacteria will work to remove the water-soluble hydrocarbons, ammonia, and phenols out of the wastewater, thereby allowing the wastewater plant effluent that is discharged to meet the stringent and strict requirements by the state and federal government. The wastewater plant will have to know what types of contaminants are in the washwater plant influent, particularly if a biocide is being used at the tank farm. It is best to use a stepwise approach, such as drawing down the tank using three or four steps, to avoid overwhelming the biological system and killing the bacteria needed to reduce the soluble organics. The wastewater treatment plant will need to develop a monitoring and respiratory program to determine if the dissolved oxygen in the secondary system is being maintained at a minimum level.

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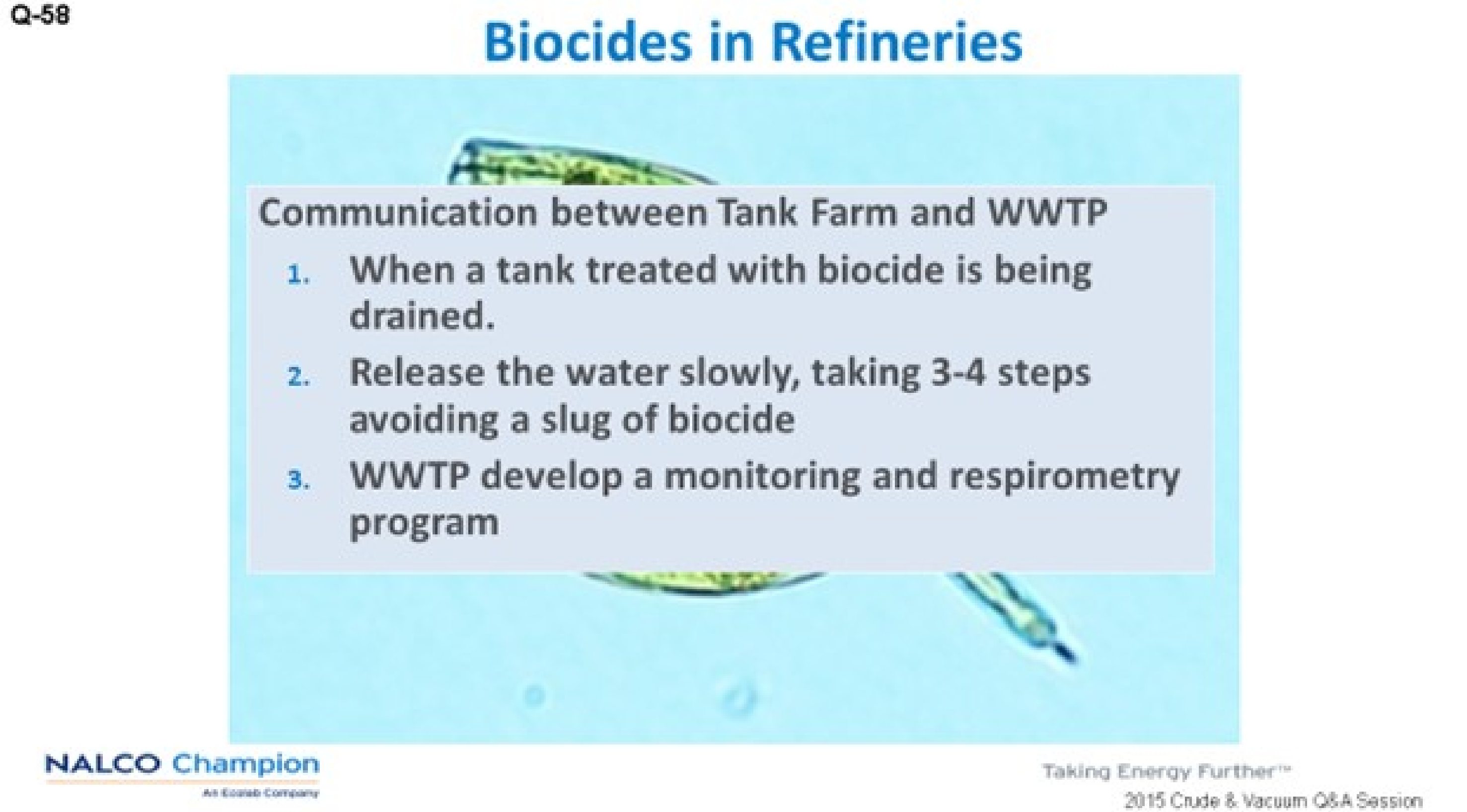

JOE PRINCE (Amec Foster Wheeler)

Since these compounds are designed to inhibit the biodegradation process, as well as other methods, prevention of negative impacts on the treatment plant can be accomplished using the following techniques:

- Maximum equalization of desalter effluent to minimize the concentration of these compounds entering the treatment plant.
- Increased Activated Sludge System Mean Cell Residence Time by either adding additional aeration capacity or by using fixed-film media (e.g., Kaldnes, hydroxyl, etc.) to promote biomass acclimation by providing longer biomass residence time. Fixed-film media has similar benefits by adding surface for anaerobic growth, as well as a level of “shock” resistance.
- Increased or modified chemical usage or chemical modifications in upstream API/DAF equipment designed to promote precipitation/flotation of the biocide(s).

MICHAEL BRADEN (NALCO Champion)

With the production of crude oils, particularly in the opportunity crudes like LTO (light tight oil) and oil sands, the same contaminants that are a challenge to the refinery also impact the wastewater treatment reliability. These contaminants are not only found in the crude oil, but also the crude will have chemical additives such as biocides, demulsifiers, hydrate inhibitors, corrosion inhibitors, and other additives. These chemical additives can cause issues in the desalter applications resulting in oil carryunder and emulsion stabilization to other downstream processes.

As this question concerns biocides in particular, the short answer is that biocides used in the upstream applications normally do not cause issues in the refinery's wastewater treatment plant (WTP). As for solubility, almost every oilfield biocide is water-soluble as that is where the microbial issues reside in oilfield applications (the water phase).

In the oilfield, dosages of biocides are all over the board, depending on the application, geography or the extent of the microbial contamination. But in general, most biocide dosages will be applied as a batch treatment somewhere in the range of 25 to 500 ppm active (although it can go up higher in some applications). Most of the biocide used will be consumed or will breakdown long before it gets to the refinery.

The most commonly used oilfield biocides are glutaraldehyde, tetrakis hydroxymethyl phosphonium sulfate (THPS), quaternary ammonium compounds, 2,2-dibromo-3-nitrilopropionamide (DBNPA), isothiazoline, chlorine dioxide, peracetic acid, and several different preservatives that are formaldehyde releasers.

However, biocide usage is being discussed and used to control bacteria growth in the refinery's crude holding tanks. The key to using the biocides is good communication between the tank farm operators and the wastewater treatment plant (WWTP) personnel including.

1. Knowing when a treated tank is going to have the water drained, so the WWTP can be notified and alerted;

2. Releasing the water from the tank slowly, as in three or four steps, so the WWTP does not get a onetime slug of the biocide; and,

3. Recommending to the WWTP that it should develop a comprehensive monitoring program and possibly respirometry to mitigate any potential issues.

Generally speaking, the issues with unconventional crudes typically fall into the categories of "high" and "variable" loading to primary treatment due to the high solids crudes, like the oil sands or shale plays; contaminants inherent in the crude, naphthenic acids which do not negatively impact biological system but result in final effluent toxicity; or, additives that are introduced during the production of the crude, H2S scavengers for the shale plays.3 Additionally, the refiner may have to introduce an additive during desalting, organic acids as an example, to remove a particular contaminant to prevent overhead or desalting issues.

Contaminants like phenols are common of all crudes, not necessarily more prevalent in the typical unconventional crudes, and readily biodegradable in the appropriate environment in an activated sludge system. Of course, we are only starting to understand the contaminants in these crudes; so again, Nalco Champion recommends a comprehensive review of the mechanical, operational, and chemical operating programs of the wastewater treatment plant to prevent any downstream consequences; or worse, to the refinery production curtailment.

With that said the same contaminants that challenge refinery operation also impact wastewater treatment reliability. With respect to the heavy bitumen crudes of the Canadian oil sands, tight, hard-to-resolve emulsions can result in oil undercarry if not properly treated in the desalter. Even with optimum desalter performance, the higher level of solids inherent in these crudes increases the loading to the WWTP, which can impede the plant's primary treatment facility from effectively removing oil and solids prior to discharge to a biological treatment plant. Finally, the oil sands hydrocarbons contain significant levels of naphthenic acids and other high molecular weight organic acids which can be extremely toxic to aquatic organisms.4 Tight oils of the U.S. shale plays are also high solids crudes yet have the added complexity of variability between shale plays and shipments. Various additives are required to extract these crudes from their source and can challenge the biological treatment plant's ability to meet effluent requirements.

OIL SANDS HYDROCARBONS

The majority of the world oil reserves are controlled by national governments with only 20% accessible to the private sector; the Canadian oil sands comprise 56% of that fraction.5 Located in three primary locations in Northern Alberta, the Canadian oil sands are a combination of sand, water, clay, and bitumen, a heavy viscous oil. The first separation of the oil from the deposit was performed in 1929 by Dr. Karl Clark using a hot caustic wash. The method, known as the Clark Hot Water Extraction Process, remains the most common method for recovering bitumen from the oil sand deposit.6 Once extracted, the bitumen must be mixed with a diluent to facilitate flow, and it is this practice that increases the tendency to form stable water in oil emulsions during the desalting practice. Although advances in heavy oil demulsifiers have minimized the potential for oil undercarry, other techniques used to enhance the crude unit performance (namely, changes in desalter mud-wash procedures and washwater rates) only exacerbate the negative effect to wastewater treatment.

High Solids

Heavy oil demulsifiers are effective at reducing the water, salt, and solids content from the crude but produce effluent brine that is very high in total suspended solids (TSS). If operational changes are not made in the primary treatment plant to compensate for the higher solids loading, poor oil removal efficiency in the API – and to a lesser extent, flotation equipment – can result.

Naphthenic Acids

Although ubiquitous in all petroleum, naphthenic acids (NA) are more predominant in heavy crude oil sources.7 The term “naphthenic acid” refers to a complex group of carboxylic acids that are relatively insoluble in water at neutral pH levels, yet which will partition to the water phase under alkaline conditions. Although NAs are not inhibitory to a wastewater treatment plant’s biological system, they are extremely toxic to some aquatic life at very low levels.8 They only represent a fraction of the wastewater influent chemical oxygen demand (COD) and are typically not detected with conventional activated sludge monitoring techniques. Therefore, extreme focus must be directed to the operation and control of the wastewater treatment plant’s primary and secondary treatment systems to avoid effluent toxicity.

Light Tight Oils (LTOs)

Unlike the unconventional oil sources in Northern Canada, the tight oils of the United States are light crudes that are found in reservoirs with low permeability. Although not limited to shale, the majority of the oil is located in shale and is therefore often referred to as shale oil or a shale play. The highest concentration of production and reserves are located in the Bakken play in North Dakota and Montana and the Eagle Ford play in Texas. Similar to the heavy Canadian crudes, tight oils may contain significant quantities of solids and can be even more challenging due to the wide variations in characteristics between plays. Also, surfactants are added during production and can result in tight emulsion and oil undercarry in the desalter. The effects to wastewater are the same as those highlighted for Canadian crudes, so the mitigation techniques previously discussed (chemical treatment, operational changes, automation, etc.) are successful during the production of tight oils.

Other commonly used additives in tight oil production are hydrogen sulfide (H2S) scavengers. To date, the consequences of the scavenger have not been significant enough to cause catastrophic upsets in any of the wastewater treatment plants surveyed. That is not to say, however, that a threat does not exist.

H2S Scavengers

Triazine compounds are frequently used to react with the hydrogen sulfide generated during the production of the tight oils. Work by Gardenhire in 20099 demonstrated that the water-soluble reaction products, monoethanolamine (MEA) and methylamine (MA) of the most common scavenger chemistries, are biodegradable up to levels as high as 200 ppm. The overall BOD and nitrogen loadings, however, will increase. It is, therefore, important to implement a comprehensive monitoring program to ensure system health and effluent quality.

Another situation becoming more prevalent in refineries processing shale oils is acid addition in the desalter to manage pH levels and prevent oil undercarry in the brine. The acids, low molecular weight organic acids, are readily biodegradable and often translate to settling issues in the biological clarifier. The settling issues may be related to either filamentous or viscous bulking or both. In the case of filamentous bulking, chemical treatment can alleviate some of the issues; however, chemical treatment has minimal success on viscous bulking conditions. It is, therefore, desirable to correct the issue starting with a comprehensive microscopic analysis which includes filament identification to identify the source of the settling problems. Depending upon the root cause, the mitigation approach could be as simple as additional additives or more complicated, such as infrastructure modifications; namely, alterations in recycle or influent configurations.

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