Question 62: When increasing the vacuum tower cutpoint, what measures have you employed to mitigate the impact of chlorides in the overhead diesel or light vacuum gas oil sections of the vacuum tower?

WEBER [Marathon Petroleum Corporation (MPC)]

Just take all of the salt out from within your desalters, and you will not have chloride problems. [Laughter] That is probably the simplest and least helpful answer. But obviously, the better job you do desalting your crude, the fewer chloride problems you will have in both towers. Short of that, the chloride issues in the vacuum tower are going to be driven by the difference in transfer temperature on your crude tower and your vacuum tower. Magnesium chloride will hydrolyze very easily and occurs primarily in the crude tower.

Calcium chloride is likely the bigger culprit in vacuum towers. If there is a 100°F difference in crude and vacuum transfer temperatures, some hydrolysis in the vacuum tower will occur. If the desired vacuum tower cutpoint can be achieved in a different way other than maximizing vacuum heater temperature, such as lowering column pressure, hydrolysis and subsequent salt formation will be reduced. Most refiners are maximizing vacuum heater transfer temperatures; so again, managing the chlorides coming out of you desalters is the key. I will note that we have seen an increase in fouling in the LVGO (light vacuum gas oil) pumps and exchangers, which is a more recent phenomenon. One item to note is that although we have not done enough work to be conclusive, we have observed more bromine or bromides when those salts were analyzed.

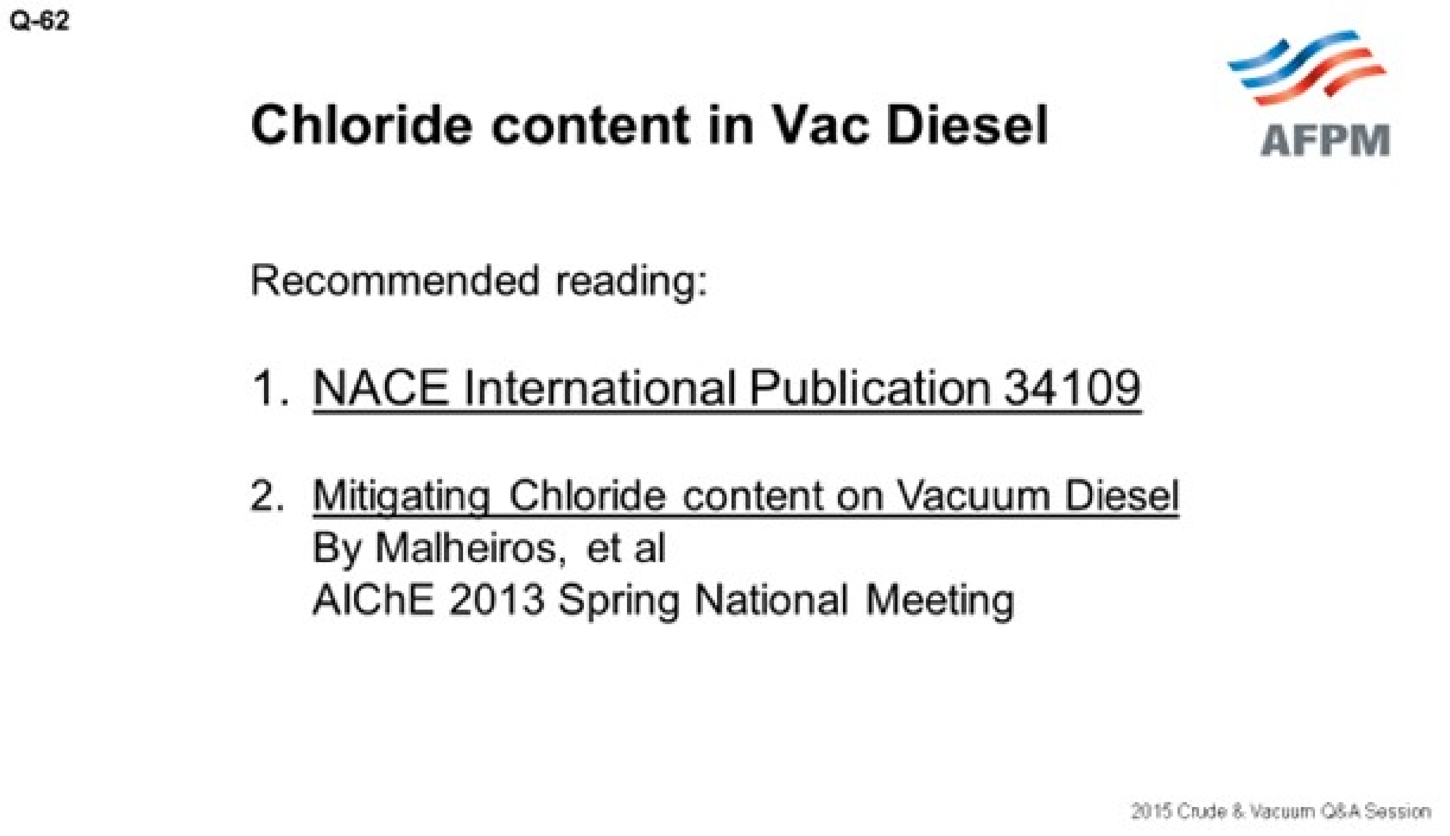
BRADEN (NALCO Champion)

Yes, I have to agree with John. Optimizing the desalter using mechanical, chemical, and operational analysis is critical for removing as much of the chlorides as you can and dehydrating the crude. You have a variety of options such as mixed valve studies, crude and water level controls, mud wash analysis, and washwater analysis including the pH. The refinery can also look at the overhead water and measure it for pH, chlorides, iron, organic acids, amines, cationic metals, and ionic species. Every piece of information you can gather about optimizing chloride removal is key. Then of course, the refinery should have the right neutralizer program for the chlorides in the overhead to protect from corrosion. Lastly, have a continuous monitoring program – either Pathfinder probes or some type of monitoring system of your choice – to see what is going on.

PRICE (Fluor Corporation)

I recommend you read two articles. One is NACE (National Association for Corrosion Engineers) Publication 34109, and the other is another paper from the 2013 AIChE meeting that was published by

Petrobras. This paper is interesting as they have noted that although this problem has not been solved, Petrobras has seen some results with an increased fractionation reflux rate in the vacuum pumparounds to help mitigate the chloride content in the vacuum diesel. The increased reflux in the vacuum pumparounds also helps the endpoint of the distillation.



Q-62

Chloride content in Vac Diesel

AFPM

Recommended reading:

1. NACE International Publication 34109
2. Mitigating Chloride content on Vacuum Diesel
   By Malheiros, et al
   AIChE 2013 Spring National Meeting

2015 Crude & Vacuum Q&A Session

BILLS CATES (Hunt Refining Company)

Is this problem more prevalent in vacuum towers that are run wet using stripping steam versus running at a dry tower without stripping steam?

WEBER [Marathon Petroleum Corporation (MPC)]

I will say that we have seen it in a variety of towers, whether they are deep-cut or not. I think most of our towers do have stripping steam, so I cannot comment on the dry tower.

WATTS (LyondellBasell Industries)

We have not seen this issue at our refinery. A part of it, of course, starts with analyzing the crudes to know what you have and, as the other panelists said, managing your desalters and your overhead systems.

PRICE (Fluor Corporation)

The ones we know of all used stripping steam.

NAGASHYAM APPALLA (Reliance Industries Ltd.)

Sodium chloride is normally considered a stable salt. Is there a theory that, in presence of naphthenic acid, hydrolysis of sodium chloride does take place in the transfer line and leads to more chloride in vacuum tower overhead?

WEBER [Marathon Petroleum Corporation (MPC)]

I am not familiar with that theory, but it sounds possible.

PRICE (Fluor Corporation)

The following two articles may have information that will be of interest to you:

1. Gray, M. R., Eaton, P. E. and Le, T, “Inhibition and Promotion of Hydrolysis of Chloride Salts in Model Crude Oil and Heavy Oil” (Petroleum Science and Technology, 26:16, 1934-1944), 2008.

2. Gray, M. R., Eaton, P. E. and Le, T, “Kinetics of Hydrolysis of Chloride Salts in Model Crude Oil” (Petroleum Science and Technology, 26:16,1924-1933), 2008.

NAGASHYAM APPALLA (Reliance Industries Ltd.)

So, has anyone seen any correlation between the increased naphthenic acid versus the increased chloride in the vacuum tower?

RUSSELL (RUSTY) STRONG (Athlon Solutions)

Naphthenic acids will participate in accelerating hydrolysis. Literature primarily talks about it in the raw crude at the crude unit. You will likely see more chlorides in the crude unit tower and overhead, but that may also apply in the vacuum column. To respond to Mr. Appalla's question, there is an understanding that sodium chloride is much more thermally stable than the calcium and magnesium chloride. What is not clearly understood amongst many in the industry is that magnesium chloride, when it decomposes, does not decompose from magnesium chloride ($MgCl2$) directly to magnesium hydroxide and hydrochloric acid. There is not a complete hydrolysis. Instead, you find an intermediate step where the magnesium becomes a hydroxylchloride. One of the chlorides is lost first, and the resultant magnesium hydroxylchloride ($MgOHCl$) is actually fairly thermally stable compared to the first chloride becoming HCl.

The magnesium hydroxychloride will then enter the vacuum column where it is often subjected to more severe thermal stress, still less thermally stable than sodium chloride, and will come apart. The organic/naphthenic acids will play a role in accelerating the thermal decomposition, and more HCl may be observed in both towers as a consequence.

The stripping steam: If you have velocity steam or stripping steam in a vacuum column, you most likely have a pretreated steam that has a neutralizer in it. The partial pressure of the steam in that vacuum column near the top is relatively high compared to what you see in a crude unit. As a consequence, the neutralizers involved in the stripping steam are also at higher partial pressure and can actually salt out with the chloride that is present, causing tower and top-cut corrosion and fouling.

Two of the steps that can be taken are: 1) for the vacuum column, find a way to satellite-feed your neutralizer so that the steam that gets in the vacuum column is not carrying neutralizer from the steam with it. Then, treat for pH in the overhead near the ejectors, rather than enabling steam in the tower to cause salting in the vacuum column. You will have to live with the ammonia that comes from the nitrogen-bearing crude, but you can get rid of much, if not all, of the problem by addressing the neutralizers.

JEFFREY ZURLO (GE Water & Process Technologies)

Just to add to what Rusty said, in addition to the items he talked about for changing the steam location, you can also look at what neutralizing amines you are putting into your steam system. The different amines used in the steam that can get into the crude and vacuum towers have different salt points. So that is another way to potentially control the salt fouling and corrosion in the vacuum tower.

DENNIS HAYNES (NALCO Champion)

The Best Practice is to optimize the desalter performance to achieve the best chlorides removal possible. This may include additional efforts around slop handling and better brine removal in the tank farm prior to the crude unit desalters; also, caustic use is a well-known, effective method to reduce distillation column overhead chlorides.

GLENN SCATTERGOOD (NALCO Champion)

To control vacuum tower overhead chloride concentration, the caustic injection into the desalted crude downstream of the desalter should be optimized. A quick study of caustic injection rate versus vacuum overhead chloride will provide the data necessary to determine the best caustic injection rate and help set a reasonable chloride target for the overhead. Once caustic is optimized, and during the caustic optimization step, the pH of the first dipleg condensing system should be monitored as the chloride will concentrate in the first condenser. Proper neutralization is necessary to control the corrosion in this area. Corrosion rate monitoring of the first condensing dipleg is important.

VILAS LONAKADI (Amec Foster Wheeler)

Like any other fractionator, increase the vacuum tower overhead temperature. However, this would increase the vapor load to ejector. Vacuum towers that are equipped with precondensers may be able to handle this additional load. Depending on the chlorides content and the increase in temperature, options such as operating spare ejectors, revamping ejector system, and/or adding a pre-condenser can be considered.

JOHN WEBER [Marathon Petroleum Corporation (MPC)]

Chloride salts that are not removed during the desalting process will be hydrolyzed to HCl in either the crude or vacuum tower heaters. The HCl will wind up in the tower overheads and can cause problems with corrosion or react with amines in the tower to form salts, which foul process equipment.

Obviously, minimizing salt content in the desalted crude will mitigate chloride issues in both towers and should be the primary focus for improvements. In the vacuum tower, the amount of salts hydrolyzed correlates to the difference between the crude heater temperature and the vacuum heater temperature and will be more pronounced in deep-cut vacuum towers. Mitigation of chlorides in overhead systems will be similar to control measures in the atmospheric tower.

MPC has observed salting in the LVGO circuits at several of our refineries, and it appears to be a recent phenomenon. Bromine has been observed in these salts and may be contributing to a change in salting potential in these circuits. These units run a wide variety of cutpoints and is not isolated to only the deep-cut units.

MICHAEL BRADEN (NALCO Champion)

First is to optimize the desalter via chemical program, mix valve study, crude and water level controls, mud-wash analysis, mechanical review, and a washwater analysis including pH. Second is to analyze the overhead water for pH, chlorides, and iron along with organic acids, amines, cationic metals via inductively coupled plasma (ICP) and also analyze anionic species by ion chromatography (IC). Third is to employ a neutralizer program to control the chlorides and inhibit corrosion. Fourth is to have continuous monitoring via Pathfinder®, probes, or Permasense®.

MAUREEN PRICE (FLUOR)

The hydrolysis of inorganic salts produces hydrogen chloride which will distribute between the vacuum column overhead and upper side draw(s). Improved upstream desalting and/or caustic injection can be considered to reduce the quantity of hydrolyzable salts present. See NACE International Publication 34109 for additional information. One Southern California refiner saw his chloride problem disappear after he added second-stage crude desalting.

Fluor also recommends the following paper as an excellent reference on the subject: “Mitigating Chloride Content on Vacuum Diesel” by Malheiros, et al.12 The paper notes that there is still much to learn about the subject but that a higher fractionation reflux rate has the benefit of mitigating the chloride content in the vacuum diesel, in addition to expected sulfur and end point distillation reductions.

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