Question 26: When you test for free HF and organic fluorides in alkylation unit products (alkylate, butane, propane), what are your typical observed levels? After HF breakthrough in our butane product, why does our treater still have plenty of KOH remaining? Is there any way to regenerate KOH during the run? Do others maintain a heel of KOH in the bottom of the alkylate storage tank to neutralize traces of HF?

Erik Myers (Valero)

These series of questions overlap quite a bit. The following answers address each question in the approximate order of those questions.

Our sites vary in the type of testing with most sites testing for combined (organic) fluorides in at least the propane and butane streams. Multiple stream points are typically tested dependent on what the monitoring goals are. Typical levels upstream of any treating are:

- Propane - 200 ppm

- Butane – 600 - 1000 ppm

- Alkylate – less than 100 ppm

Combined fluorides measured upstream of treating can be used as an indication of the completeness of the alkylation reaction. There will always be some level with the typical values noted above. Higher levels indicate potential issues with the upstream operation. The above values are for typical operations. Key contributors to increases in combined fluorides are low acid strength (below 85%), low reactor temperature (less than 80 o F), decreased contact time and low I:O ratio. Any of these can lead to increases in the amounts of all levels of combined fluorides. Propyl and butyl fluoride can increase by orders of magnitude with low acid strength. Post treatment levels of combined fluorides should be well under 10 ppm, typically.

Defluorinators are typically installed on the propane and butane streams, followed by KOH treating. These systems are occasionally used on the alkylate product stream. Water and HF are the products of the defluorination reaction. HF reacts with the defluorinator alumina to make aluminum fluoride trapped as part of the defluorinator alumina. This leads to potential of trace HF in the defluorinated stream if the remaining active alumina does not convert the HF. There is typically a lead – lag arrangement on the defluorinators to allow continued treating of the product streams. The downstream KOH treater is installed to dry the defluorinated product and remove any trace HF. It is less common to have a lead – lag for the KOH treaters but two of our sites have this arrangement on at least one stream. Some of our sites have water collection pots upstream of the KOH treaters to lessen the load of those treaters. To measure the effectiveness of the defluorinators and as an aide in determining optimum change out frequency, the streams are ideally measured before, between and after the treaters (with the downstream measured after KOH treating). The sample between the lead and lag defluorinators is used for confirmation of whether an alumina changeout is required. The upstream sample, along with the product flow rates can be used a predictive tool in scheduling lead defluorinator changeouts. The spent alumina can also be sampled and analyzed by the alumina supplier and compared to these predictive results for further alumina changeout optimization as well as verification of the hydrocarbon stream fluoride testing. One site uses a typical fluoride concentration and then a throughput totalizer to determine changeout timing, then analyzing the spent alumina to confirm loading.

Aside from the trace HF noted from the defluorination reaction free HF should not exist in the alky propane if the HF Stripper has adequate reflux and never show up in the normal butane or alkylate product. The primary cause for free HF is spent alumina in the defluorinators or severe loss of tower temperature profile in the alkylation fractionation tower(s). less than 1 ppm. Only one of our sites typically checks for free HF with the values being less than 5 ppm.

The KOH treater is typically a walnut bed downstream of the defluorinators. Our sites utilize both walnut and flake KOH, with walnut being typical. Our units are split with 50% have upflow and the other half downflow. This is typically an indication of the original unit licensor design. As noted earlier, water and HF are the products of the defluorinator. If the there is an HF breakthrough to the KOH treaters, it is most likely due to a spent defluorinator, where there is no more alumina to react with the HF. Significant breakthrough is important to avoid. Large amounts of free HF can cause the KOH treater to heat up resulting in hydrocarbon vaporization and unfavorable conditions for HF removal. (In a propane KOH treater, melting of the KOH and then freezing it in the outlet piping has actually been observed). One of our sites has an emergency alarm for high butane KOH treater outlet and delta temperature with another site having an SIS diversion for high C3 KOH treater temperature. The noted upstream and downstream sampling of each defluorinator is a key to staying on top of this processing area of the alky.

If KOH is still present in the treater while HF is measured in the product it is most likely caused by poor distribution through the KOH bed, either from channeling or crusting on the top of the KOH bed, sometimes caused by low amounts of water in the feed to the KOH treater. This low water content prevents the removal of KF (formed by the reaction of the KOH and the HF) from the KOH treater. Our sites have utilized either routine steam or water injection to the KOH treaters to prevent this.

Circulating KOH (typically used in the acid relief system neutralization system) can, and typically is, regenerated in a batch mode. We are not aware of a method to regenerate the solid fixed bed units as the KOH is converted to water and drained from the system. Three of our sites have two KOH treaters (either in parallel or series), allowing monitoring and changeout to be accomplished without compromising product quality. Residual KOH / water from the KOH treater changeouts can be utilized for make up in the circulating KOH system noted above.

Only two of our sites presently utilize a caustic heal in the alkylate product tank. This has been utilized at other sites in the past. This was done either as a preventative measure or as a result of previous issues with tank bottom corrosion. It is a common recommendation from the licensor. If this method is used, the tank water draw should be monitored frequently to measure changes and prevent loss of protection. The mechanism for tank bottom corrosion is either HF breakthrough from slumping of the fractionators, an exchanger leaks that routes acid to the tank or water in the alkylate product tank that leads to hydrolysis of the combined fluorides in the alkylate to HF if the residence time in the tank is long enough. The noted monitoring of any water draws and then ensuring that there is not water is another preventative measure for this.

Brad Palmer (ConocoPhillips)

Typical organic fluoride levels in alkylation unit products, upstream of any post-treatment, have been reported as 40-60 ppm (Alkylate), 200-400 ppm (Butane), and 300-600 ppm (Propane). Inorganic fluorides are not typically measured. Defluorination and KOH treating will reduce propane and butane organic fluorides to 10 ppm or less. Inorganic fluorides will be less than 1 ppm after treatment. Thermal defluorination, occurring in the heater passes, can further reduce organic fluorides in alkylate. Maintaining the fractionator bottom temperature above 320°F will thermally defluorinate any organic fluorides in the tower bottom thereby minimizing organic fluorides in the alkylate.

Un-used KOH material at breakthrough signifies bed channeling and/or a very dry system that allows KF to coat the KOH material. Defluorinator chemistry reacts organic fluorides with alumina to form alumina fluoride and water; an intermediate reaction product is HF, which may leave the defluorinator unreacted. The KOH treater is primarily a dehydrator and secondarily an HF neutralizer. As the KOH dries the LPG stream, the water "cleans" the KOH as it makes a sludge that is drained from the vessel. Any HF breakthrough from the defluorinator will react with the KOH to form KF and H_2O. If there is very little organic fluoride to react in the defluorinator, there will not be much water formed to slough the KF off the KOH pellets. Some sites have used water injection to help "clean" and utilize the KOH material under dry conditions.

There is no effective way to regenerate solid KOH in the KOH treater with the vessel on-line. Water injection might be effective to refresh KOH that has been coated with KF as previously described.

It is a common practice to use an alkali heel in the alkylate storage tank. This is not for neutralizing HF, but is to counter-act iron fluoride scale leaving the process with alkylate which can form low pH hydrates on the tank bottom. The alkali heel should be tested routinely to ensure it remains basic.

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