Question 28: What are your Best Practices for measuring chlorides in LPG streams? What criteria do you use to determine when to change LPG chloride treater media?

KEADY (Technip)

There are three methods for measuring chlorides in LPG streams: UOP 910, UOP 930, and Dräger 2.0.2/A. I have a nice little illustration. You must have proper maintenance of your sampling stations and also of your sampling bombs. For Best Practices, use a sample point a few places within the absorber bed and sample periodically for chloride right through. This frequency will allow historical comparisons. Also, identifying any feed contaminants will help predict the remaining life of the bed.

PATEL (Valero Energy Corporation)

Chloride monitoring in the liquid LPG stream is difficult in the refinery. Typically, the next downstream gas phase stream, which is originating from the liquid stream, can be tested for the chlorides like stabilizer overhead. However, that is not an option for the LPG stream.

One of the best areas monitored is the chloride in the LPG stream. LPG chloride treater chloride content can be estimated through a reformer chloride balance. A reformer chloride balance is achieved when all of the chlorides are accounted for. The reformer releases chlorides into the hydrogen and into the reformer stream. Tracking those values for the hydrogen net gas and the liquid at the stabilizer overhead can eventually allow you to create a reformer chloride balance, as Emerson said. The reformer chloride balance can produce the amount of chlorides at the inlet of the LPG treater. Chloride intake at the LPG treater inlet is estimated based on the balance and can be used in conjunction with the review of the past spent absorbent analysis. A determination can be made as to the appropriate time to make the changeout on the absorbent without experiencing any breakthrough.

JAY RICHERT [(Marathon Petroleum Company (MPC)]

I am just wondering if the panel could suggest the traditional services within a refinery where chloride treatment is necessary. And then, are you aware of any non-traditional stream locations that have been treated in refineries in order to manage overall chloride problem at the site?

LAMBIE (KBC Advanced Technologies, Inc.)

The most common application of chloride treaters is on the net gas stream where the hydrogen is used in many downstream units. In liquid service, the common locations in the reforming unit are the inlet to a stabilizer column or the LPG from the stabilizer column. In some instances, chloride treatment of the stabilizer bottoms may be necessary, depending on where that stream is routed. Some chloride issues may result from poor desalting operation.

RATHING SABAPATHI [Kuwait National Petroleum Company (KNPC)]

The question is not related to this. Is anyone looking to produce TAME from isoamylene or isopentane? Does anyone have any outlook on this issue as to whether it is economical to produce economics or TAME for more gas? Does anyone have any units here? We have surplus isopentane. We are exploring the possibility, so we would like to see if there is an opening.

BURTON (UOP LLC, A Honeywell Company)

Our TAME unit went away when MTBE (methyl tertiary butyl ether) units went away.

LAMBIE (KBC Advanced Technologies, Inc.)

There are several TAME units processing C5 olefins in South America.

FRY (Delek Refining)

Make sure to watch the reformer off gas. We have a cryogenic recovery plant for our refinery off gases, and we make sure to put a chloride guard bed in our dryers. We do not test for chlorides frequently, but we know we get some there.

ABIGAIL SUP (Johnson Matthey Process Technologies)

Many operators do struggle when trying to accurately measure the level of chlorides in LPG streams. The Best Practice is to send LPG samples to a lab that has liquid-phase chloride testing capabilities for analysis of both HCl and organic chlorides. Some locations may have these facilities onsite, while others may require the operator to send samples to a third-party lab for independent analysis.

When sampling for chlorides, care should be taken to choose the appropriate sample container. Chlorides, similar to sulfur, have a tendency to “disappear” in the sample container. A suitable lining in the container can help ensure that the level of chlorides is accurately measured during analysis. Also, the chosen sample container should be suitable for vapor samples, commonly referred to as a “sample bomb”. The sample will likely contain a mixture of both liquid and vapor. Some have found it can be difficult to ship LPG samples offsite. Johnson Matthey can help coordinate sampling, so it may also be worthwhile to check if your catalyst supplier also offers assistance.

An alternate option to consider, if liquid phase chloride testing capabilities are not available, is to analyze the LPG sample in the vapor phase. This can be accomplished by flashing the sample into a sample bag. The flashing should be performed under a laboratory hood or other means of ventilation, while taking all proper safety precautions. It is important to ensure that the sample is fully vaporized so that an accurate measurement can be obtained. In certain cases, this may require some form of additional heating. Once the sample is in the gas phase, detector tube technology can then be used to determine the concentration of chlorides present. Keep in mind the concentration results using this method will be in ppmv (parts per million by volume). It is recommended to convert the concentration back to ppmw as is customary for liquid applications. Also, care should be taken to measure both HCl and organic chlorides as some LPG streams may only have organic chlorides present.

To determine when an LPG chloride treater/guard bed should be changed, a routine sampling protocol could be established. This sampling can include periodic measurement of the chloride concentration on both the inlet and the outlet of the chloride treater/guard bed. The inlet sample analysis would allow for calculation of the expected saturation of the chloride media. The amount of chloride that can be absorbed prior to breakthrough can be estimated based on the expected capacity of the material for a particular application. The expected capacity can be provided by the absorbent supplier. The outlet sample analysis would confirm whether or not a breakthrough has occurred.

As sampling can be cumbersome, another option would be to only take baseline chloride measurements

and then calculate the life of the bed based on the expected capacity, as discussed above. The baseline chloride concentration and projected flowrate across the bed over time can be used to calculate the expected life of the bed. Changeout can then be scheduled to occur during a downtime that is close to the time breakthrough is expected to occur.

GINGER KEADY (Technip)

Three methods [used?] to analyze the chlorides in LPGs:

1. UOP 910 method for the organic chloride: This method is for determining total chloride in gaseous hydrocarbons or liquefied petroleum gas (LPG) at concentrations ranging from approximately 1 to 1000 mg/mL (milligrams per milliliter) for gas or mass-ppm for LPG (liquefied petroleum gas). Except for fluoride, other halogens present are calculated as chloride. Chloride cannot be determined quantitatively if sulfur is present at concentrations greater than approximately 1 mass-%.

2. UOP 930 method for the total chloride (but Axens has no feedbacks regarding this method): This method is for determining the sum of organic chloride and hydrogen chloride (HCl) in LPG and refinery gas streams at concentrations ranging from approximately 0.02 to 1000 mass-ppm (mg/kg) for LPG samples or 0.02 to 1000 ng/mL for gas samples. Other halogens present are determined as chloride.

3. Dräger Tube Chlorine 0.2/A:

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Tags

Chlorides

Hydrogen

Year

2015