Question 9: How do you track chloride in liquid/gas/LPG? What are your criteria for replacing adsorbent in chloride treaters?

DAVINDER MITTAL (HPCL Mittal Energy)
Chlorides have been a long standing issue in catalytic reformer operation. Until a few years ago, the focus on preventing operational problems from the chloride compounds in the catalytic reformer product stream was to remove HCl. More recently, a growing concern for many refinery operators has become the removal of organic chloride species besides HCl. These compound are less easy to detect and measure and also less readily adsorbed or absorbed. The effectiveness of the available chloride guard products is limited although significant improvements have been made and are being made to the formulations.

Total chloride tracking and removal presents a different challenge which requires amended chloride guard formulations that can either co-remove HCl and organic chloride compounds or alternatively a combination of two materials, one specific for each problem.

Adsorption of organic chlorides is competitive with other components in the process stream. HCl is more polar than RCl and is likely to preferentially adsorb on many surfaces. Thus the adsorbent may be effective when relatively new while both HCl and RCl are removed. The more efficient HCl removal may occur in the bed inlet zone while RCl removal further down but RCl breakthrough will occur as HCl front moves down the bed and starts to displace RCl as the active surface.

Many Refiners struggle to accurately measure chlorides in CCR liquid streams/LPG. The best practice is to use detector tubes (say Drager 0.2/A) of correct range for detection of inorganic chloride/ HCl in gas (applicable for H2 and LPG in gas phase). Correct range means, if expected range is 1 ppm for example, detector tube should be of range 0.2 to 5 (preferable) or 10 at Max. Using larger range tube possess the risk of losing accuracy of measurement due to higher measurement interval/least count.

For both liquid and gas samples, care should be taken to choose appropriate sample container. Suitable metallic bomb with PTFE coating is suggested to avoid chloride interaction with metal and wrong measurement. Sample collection point should be short and copper tubing to be avoided. Ensure that sample point is hot while collection. Perform detection tube analysis as quickly as possible.

UOP 910 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%.

UOP 930 method is for determining sum of organic chlorides 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(liquefied petroleum gas) samples or 0.02 to 1000 ng/ml for gas samples. Other halogens present are determined as chloride.

For detection of total chlorides in liquid (applicable for Reformate/Isomerate), ASTM D 7536 is another – uses MWDXRF analyzer to detect chloride content of sample.

Alternatively, HCl content of liquid sample can be tested by OXY-HYDROGEN COMBUSTION of sample and combustion product are absorbed in a dilute solution of sodium carbonate. The chloride ion in aqueous absorber solution is titrated by potentiometry with standard silver nitrate solution (IFP-9316).

If liquid phase chloride testing capabilities are not available, the alternative option is to analyze LPG sample in vapor phase. It is important to ensure that sample is fully vaporized so that an accurate measurement can be made. Once the sample is in 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. It is recommended to convert the concentration back to ppmw as is customary for liquid applications.

Analysis, and particularly speciation of organic compounds at low ppm level is not trivial. A number of specialized techniques can be used which include oxidative coulometry and gas chromatography with an electrolytic conductivity detector. Methodology has been developed by specialist companies to use gas analysis tubes for detection of total chlorides and HCl.

In order to determine when a chloride treater 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 outlet of the chloride 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 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 expected capacity. The baseline chloride concentration and flow rate across the bed over time can be used to calculate expected or residual life of the bed.

A corroboration for chloride at inlet of guard bed can be made through reformer chloride balance once a while. Chloride intake at LPG treater inlet is estimated based on balance and can be used in conjunction with the review of past spent absorbent analysis. A determination can be made as to the appropriate time to make the change out on the absorbent without experiencing any breakthrough. Change out can then be scheduled to occur during a downtime that is close to the time breakthrough is expected to occur.

Concerning adsorbent replacement of chloride treater, when arranged in LEAD-LAG position, the best time is to plan for replacement is when chloride content of effluent at the outlet of LEAD treater vessel reached a value @ 10% of inlet chloride concentration. Keeping more time in service the LEAD bed, though Refiners can maximize the left over adsorbent life but it possess threat of over- chloriding of alumina due to excessive HCl loading, thereby increasing risk of polymerization/green oil formation if olefins are present in streams (for example CCR hydrogen rich gas).

For a standalone chloride adsorber, it is better to replace as soon as it crosses guaranteed cycle length under normal operation or as soon as chloride break through appears if this guard bed is exposed to

some upset operation. For standalone chloride guard bed, additionally use sample point a few places within the absorber bed. From a practical view point, since chloride analysis at inlet and outlet of chloride guard bed is not followed regularly, it is difficult to estimate end of life and refiner may keep an emergency spare to avoid operating a guard bed without any remaining adsorbent life and contaminating downstream equipment and tanks with chloride.

THOMAS PORRITT (Chevron U.S.A.) (3)

Metal-catalyzed coke or MCC is formed on the metal surfaces of the reactor internals. It is also known as filamentous coke or rod coke. It is enhanced by high temperature, low hydrogen partial pressure and zones of low velocity. MCC can be prevented by passivating the metal surfaces. Most users do this by injecting an organic sulfide in the feed that converts to H2S in the process. The H2S then interacts with the Chromium in the metal surface to form a passive layer of chromium sulfide. A good rule of thumb for the sulfur injection in traditional high-pressure naphtha reformers is 0.25 – 0.5 ppmw based on the feed. For low pressure units the user should consult their technology licensor for appropriate targets.

BILL KOSTKA (AXENS NORTH AMERICA)

Although HCl is the most abundant Cl-containing species in reformer effluent streams, organic chlorides (RCls) will also be present in lesser amounts due to acid-catalyzed reaction of olefins with HCl. Removal of both HCl and RCls requires guard beds containing one or more adsorbents. Failure to trap RCls and quantify their breakthrough may lead to downstream corrosion and fouling issues since their breakthrough precedes that of the more easily trapped and quantified HCl.

Leakage rate of chlorides from the reformer increases as its catalyst incrementally loses surface area with each regeneration. Lower-surface-area catalyst requires a lower H2O/HCl ratio in order to maintain constant catalyst chloride content. Chloride addition to the catalyst must be increased in the regenerator to obtain the requisite lower H2O/HCl ratio since H2O concentration remains relatively constant. This increased chloride addition to the catalyst results in an equivalent increased loss from the catalyst once back on oil that will shorten chloride adsorbent lifetime.

Lower catalyst surface area also hinders maintenance of critically important platinum dispersion. Loss of platinum dispersion increases olefin production which along with higher HCl content can increase RCl formation as the catalyst ages. Higher RCl formation further accelerates the loss of chloride adsorbent lifetime. Catalysts with higher surface area stability extend the lifetime of downstream adsorbents, units and equipment.

Samples of liquid streams can be analyzed in a laboratory using a variety of standard methods including microcoulometry, extraction + potentiometry, MWDXRF and CIC. As listed in the following table, each technique detects specific chloride species and has different levels of quantification (LOQ).

Samples of gas streams are typically analyzed in the field with indicator tubes; however, more accurate measurements are made in the lab using a different set of standard methods. A good sampling system and technique are critical for achieving the requisite accuracy. Gas phase monitoring techniques are summarised in the following table.

Chloride Species Monitoring in Gas Phase

Standard Method	Technique	Chloride Species Determined	Limit of Quantification (LOQ)
UOP 910	Microcoulometry	Total Chloride	1 ng/ml (gas)
			1 wppm (LPG)
UOP 930	Pyrolysis +	Organic Chloride + HCl	0.02 ng/ml (gas)
	Dry Colorimetry		0.02 wppm (LPG)
Scrubbing + ASTM D512	Scrubbing + Water Analysis	HCl	
	-Mercurimetric Titration		
	-Silver Nitrate Titration		
	-Ion Selective Electrode		
ASTM D4490	Indicator Tubes	HCl	Tube Dependant
		Vinyl Chloride	
		Trichloroethylene	

Examples of indicator tubes are listed in the following table. Note that cross sensitivities and the presence of various RCl species will interfere with the accuracy of the tubes used to measure RCls, but should afford determination of chloride breakthrough.

Indicator Tubes for Gas-Phase Analysis

	Gastech	Dräger
HCl	Ref 14 L	Ref 81 03 481
	0.2-76 ppm	0.2-20 ppm

Vinyl Chloride	Ref 131 La	Ref 81 01 721
	0.25-54 ppm	0.5-30 ppm
Trichloroethylene	Ref 132 LL	Ref 67 28 541
	0.125-8.8 ppm	2-250 ppm

Ideally, chloride adsorbents should be changed once RCl breakthrough occurs to ensure chloride-free operation of downstream units and equipment.   Determination of chloride breakthrough based solely on HCl measurements may lead to months of undetected RCl leakage. Time-based replacement of chloride adsorbents is typically based on HCl breakthrough and also can lead to months of RCl leakage.

Zhen Fan (Norton Engineering Consultants, Inc.)
To prevent metal catalyzed coking, make sure that a low concentration of H2S (~1.5 ppm) is maintained in the recycle gas. Consider injection of DMDS to the reformer feed if feed sulfur from the upstream naphtha Hydrotreater is extremely low.

Print as PDF:

Tags

CAT POLY Units (CAT Poly)

Catalytic Reforming

Year

2019

Submitter

Consultant

__Licensor__

__Operator__

__Licensor__

__Operator__