Question 19: What are the common locations and adsorbent types for chloride treating beds in gasoline process units? What practices are you using to best manage this asset?

Soni O. Oyekan (Prafis Energy Solutions)

The question posed is specific for hydrogen chloride management and it is necessary to broaden it to encompass the numerous challenges associated with chloride induced fouling, corrosion and reliability issues in catalytic reformers, fired heaters and downstream hydroprocessing units. Most of the chloride guard beds and adsorbents are used around the catalytic reformer as it is in that process unit that we need to intentionally add significant amounts of organic chloride for catalyst reactivation and reforming performance.

Foremost, the oil refiner should be operating as ideally as possible limiting nitrogen and sulfur to specific levels in the catalytic reformer feed. That is the naphtha hydrotreater should be operating as required and meeting reformer feed contaminants specifications. Secondly, chloride addition to the reactor section is as per the catalyst/technology licensor specifications and excess organic chloride is not being added. Thirdly, that the catalyst state is adequate, and the catalyst is neither contaminated with metals nor close to the end of life as either of those conditions would necessitate greater catalyst chloride addition rates and lead to increased hydrogen chloride in the net gas and in the debutanizer or stabilizer feed.

Fourthly, water management for the catalytic reformer is practiced satisfactorily so as not to lead to greater use of organic chlorides than necessary in the catalytic reformer in order to maintain catalyst performance. The basis for ensuring that the naphtha hydrotreater is operating satisfactorily and optimal water/chloride management and catalysts state are being maintained in the catalytic reformer is use and maintenance of sound catalyst and process unit monitoring programs. A number of the key performance indicators to be monitored have been discussed separately over the past years at AFPM Q&A Forums. The key performance indicators are, however, still important items as we discuss chloride guard bed locations and practices for effective management of chloride guard beds and adsorbents.

The locations for chloride guard beds are based on a variety of chloride management objectives and they are listed below:

•Upstream of booster compressors in continuous catalytic reformers product separation section

•For the gas and liquid products downstream of Re-contacting drums in continuous catalytic reformers

•Feed to the stabilizer

•Recycle gas and net hydrogen gas

•The off gas or refinery fuel gas

•The LPG product stream of the debutanizer

•The reformate

•The regenerator effluent gas of fixed bed cyclic regenerative reformers to meet RMACt 2 HCl regulation

•The reactor section of some cyclic regeneration reformers for excess chloride control

•The effluent gas from the catalyst (platinum/metals)) reduction section of a CCR

•In the reformer Debutanizer overhead section

As can be determined some of the chloride guard adsorbent locations are for managing specific chloride containing streams such as the off gas or refinery fuel gas to protect fired heater burner tips and regenerator effluent gas to meet RMACT 2 HCl regulation. Typically, the primary stream treated extensively in the refinery is the H2 make up or net hydrogen gas. As per past AFPM discussions, this stream must be treated adequately to enhance reliability of downstream Hydrotreating units, PSA units and equipment in refineries.

The majority of the adsorbents used are promoted alumina type despite formation of byproducts such as green oil and organic chloride that can eventually render them and other adsorbents ineffective. Various chloride guard bed operating strategies are in use including single guard beds with aggressive adsorbent replacement frequencies, lead/lag guard beds and effective monitoring to limit green oil, organic chlorides formation and HCl breakthrough or adsorbent saturation in order to effect timely adsorbents replacements.

Other adsorbents such as mixed oxides, zeolitic materials, “mixed” beds of zeolitic materials and mixed beds of promoted alumina and zeolitic materials in varying proportions and loading configurations are also in use.

Current practices for maximizing the use of chloride guard bed adsorbents include the following:

•Operate the naphtha hydrotreaters and catalytic reformers adequately.

oEffectively operate the NHT to minimize nitrogen, sulfur and water entering the catalytic reformers as resultant ammonia, hydrogen sulfide and water in the catalytic reformers would displace catalyst chloride leading to greater organic chloride usage and higher than necessary recycle gas, net gas, Debutanizer feed, off gas, LPG and reformate HCl.

oAmmonia would also lead to ammonium salts deposition in the product separation section and cause fouling and corrosion.

•Use appropriate, active catalysts in the catalytic reformers to ensure minimizing chloride use as discussed previously. Replace catalyst as often based on catalytic performance and the physical and chemical characterizations of the catalyst.

•Use lead/lag chloride guard beds strategy and replace the adsorbents frequently as required as

breakthrough HCl in the treated net gas is likely to be too late due to green oil and organic chloride formation.

•Minimize water and Hydrogen sulfide concentrations in the net gas as that would interfere with effective HCl removal by the adsorbent due to competitive adsorption via the first practice item above.

•Use high performance adsorbents that are either capable of retarding the rates of formation of byproducts such as green oil and organic chlorides or capable of adsorbing organic chlorides.

Steve Philoon and **Ka Lok** (UOP)

In recently designed CCR Platforming units, chloride treaters may be used on a number of streams with the treaters placed in a variety of locations.

In the case of net gas treating the chloride treaters may be placed upstream of the net gas compressor or downstream of any recontact section and chiller-based product recovery system but upstream of a PSA hydrogen purification system (preferred). If chloride is a potential source of problems in the fuel gas system, then a treater can be placed on the Reformate Stabilizer Off gas line to fuel gas. Similarly, overhead liquid stream can be treated to remove chlorides from the LPG stream. For the principle liquid product, chloride treaters can be placed feed to the stabilizer column or on the reformate product line itself. The location selected may influence the sizing of the treater vessels and\or the stabilizer feed\bottoms exchanger and will influence on the adsorbent selection.

Use of molecular sieve has the advantage of reducing the risk of green oil formation over the activated alumina-based absorbent.

For treaters in gas service simply monitoring the outlet of the treater for HCL is not always effective. As the adsorbent (usually alumina) increases in chloride concentration, it can become acidic and catalyze the reaction of HCL with the light olefins present in the net gas. The products of these reactions are light organic chloride compounds that will not be detected by HCL detector tubes or laboratory tests for HCL. For this reason, UOP recommends that the refiner determine the change-out frequency of the alumina based on the calculated chloride loading on the alumina.

Gasoline Processing

Catalysts

Catalytic Reforming

Chlorides

Corrosion

Fouling

Heat Exchangers

Hydrogen

Naphtha Hydrotreating

Process

Reactor Vessel

Reforming

Reliability

Year

2014