Question 23: What are the sources of silicon that can impact a hydrotreater? How does silicon affect hydrotreater operations? What are your best practices for managing / mitigating silicon poisoning?

DENNIS HAYNES (Nalco Champion)

One source of silicon is antifoam chemistries. These may be introduced into HDS feeds via use in the Coker process within the refinery or via use in production upstream of the refinery. The ability to minimize the content of silicon introduced due to antifoam within the refinery is dependent on antifoam application practices and controls along with antifoam product selection.

BRANDON MILLER (Criterion Catalysts & Technologies)

What are the sources of silicon that can impact a hydrotreater?

There are many potential sources for the silicon that ends up in a hydrotreater feed stream. Historically, the principal source of silicon to hydrotreaters was the antifoam addition to delayed cokers at the refinery, which results in polysiloxanes being cracked into the naphtha and light coker distillate boiling range. Over the years, higher viscosity antifoams have been introduced, resulting in increased levels of silicon in the heavier coker product streams.

Silicon can also come into the refinery directly with the crude. Coker-derived synthetic crudes, like those from Canada and Venezuela, contain silicon due to the antifoam used during production. Silicon is also added to many crudes through the use of flow improvers/drag reducers for increased production capability. Silicon can also be present in some crudes derived from their source in sand and/or aluminum silicate clay. Many of these silicon compounds tend to end up in the distillate and VGO fractions.

How does silicon affect hydrotreater operations?

Silicon deposits on the surface of alumina-based catalysts; not on the active metals’ sites, but through adsorption of the silicon-containing molecule onto the surface hydroxyl groups of the alumina support. This results in a thickening layer of silicon being formed on the alumina surface. Over time, the pathways into the catalyst pellet become blocked, resulting in effective deactivation of the catalyst.

What are best practices for managing / mitigating silicon poisoning?

Once the silicon contamination has been minimized at the source, the next step is to mitigate in the hydroprocessing unit. Regardless of the source, effective mitigation can be accomplished with proper operational management and the appropriate catalyst solution.

However, we need to make sure that we design the right catalyst system to pull the silica out of whatever type of feed we are processing. For example, a catalyst with a high surface area and a small pore diameter can be very effective with lighter feeds, such as coker naphtha, but will not be effective in heavy feeds due to the diffusion limitations resulting in rapid pore mouth plugging or “egg shelling”.

Generally, the catalyst design to handle silicon employs three types of catalyst:

Silicon trap catalysts, which are no/low activity but high surface area, designed to be the main silicon depository for most of the silicon in the feed.

Transition/dual function catalysts, which are active but still very silicon tolerant catalysts designed to uptake a significant amount of silicon over the run while still contributing to the activity of the system.

Main bed active catalysts, which are the least silicon tolerant but the highest activity. These catalysts finish off the more difficult treating reactions and are protected by the other layers to ensure good activity throughout the cycle as the upper layers become deactivated.

Catalyst particle size is also an important consideration for silicon uptake. In many units, particularly naphtha units, silicon uptake is diffusion limited, so smaller size catalyst will directionally pick up more silicon in each reactor volume. This benefit is often balanced against reactor pressure drop limitations.

These catalyst types and relative amounts need to be properly balanced in the unit to achieve the desired performance and cycle life. To find the right balance, the silicon uptake and catalyst activity should be monitored throughout the cycle. Silicon uptake can be measured by taking routine feed composite samples and then validated through spent catalyst analysis.

In addition to the proper catalyst system and monitoring plan, reactor temperature is a key factor. Higher temperature generally leads to more Silicon uptake but may also lead to poor silicon diffusion and lay down on the catalyst surface and prematurely block sites that otherwise could be used, effectively reducing the total uptake potential of a given catalyst. However, operating at too low of a temperature may also limit the total silicon capacity of a catalyst. This is often the case for naphtha hydrotreaters where the typical temperature regimes may limit the uptake capacity of the lead catalyst beds. However, in distillate and heavier service the typical operating temperatures regime is high enough to achieve maximum Si uptake.

In some cases, space velocity may be another lever you have to manage silicon uptake. In general, higher space velocity drives less efficient silicon deposition and results in a lower overall silicon uptake capacity of a given catalyst. Space velocity is often something we can’t control; however, it comes in to play in select situations where there are multiple units of varying space velocity that could process a silicon containing feed.

Gas oil hydrotreaters must often contend with additional catalyst poisons, like nickel and vanadium. These metals do require active metals site functionality on the catalyst. Since silicon deposits on the catalyst surface, these metals are not necessarily in direct competition for a deposition site. However, the deposition of these metals can indirectly affect total uptake capacity through diffusion limitations and steric hinderance of the potential sites. These interactions should be understood and considered when designing, comparing, and optimizing a catalyst system; typically, with specific unit performance history, if possible.

RAUL ROMERO (NALCO)

Typical source of silicon on streams coming from DCU are antifoams applied on its drum during filling operation. A more general balance should be considered, including silicon-based antifoam applied upstream of DCU, like preflash or main fractionators in Crude and Vacuum units and crude feed itself. DCU feed silicon content should be considered along with best practices antifoam application on drums. By carefully assessing antifoam injection practices has demonstrated a reduction chemical consumption, hence reduction in silicon content on DKN and DKLD. Operating conditions (drum inlet temperature and drum pressure also play a key role on optimizing antifoam consumption.

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