Question 7: Are there any standard sampling and analytical methods that can be used in the refinery labs to accurately determine the silicon content in the feed to the coker naphtha hydrotreater?

Tim Lewer (Shell)

The issue is how to accurately determine the silicon content. Standard Inductively Coupled Plasma (ICP) techniques will give a result that is equal to or greater than the true amount of silicon present depending on if the silicon is in a volatile form (low molecular weight silicones). So, ICP can be used to screen samples and ensure silicon levels are below a desired limit. However, if silicon is detected, it could be a false high number due to nebulizer enhancement effects. Alternatively, a new ASTM method using Monochromatic Wavelength Dispersive X-ray technology may be able to accurately measure even volatile silicon species, but the instrumentation is new to the market and does not have a long track record to verify its applicability. A direct injection nebulizer ICP system will accurately measure silicon including volatile forms but is typically too customized of a system for application in a refinery setting.

Be aware of cross contamination when taking samples for silicon analysis. Some plants have seen false high silicon lab results due to silicone grease used for lubrication or certain silicates used in the manufacture of glass bottles. There has also been cross contamination from puncturing certain silicone sample bottle lids during the sample collection process.

Some plants have established a sample station that takes a small sample every 15 minutes into a compositor that is used for a weekly composite analysis. This method doesn't improve sampling speed but does reduce the frequency and improves accuracy.

Kaspar Vogt (Albemarle)

Inductively Coupled Plasma (ICP) is the technique most used. ASTM D-5708, which is intended for determination of nickel and vanadium in crudes and residual oils, has become the de-facto standard for preparing hydrocarbon samples for elemental analysis by ICP. This is probably the most appropriate method for analyzing the silicon derived from the anti-foam agents added to the feedstock, as opposed to the silicon you might find associated with FCC fines suspended in the sample. The detection limit is around 0.5 ppm. The standard deviation is +/- 0.25 ppm.

During operation, silicon addition is minimized in the coker cycle however the refinery does not want to experience a foam over. Understanding the amount of silicon fed to the hydrotreater is complicated as the anti-foaming agent dosage varies during the coker cycle. More sophisticated continuous sampling systems are available and are capable of sampling hourly or periodically and can create a one or multi coker cycle composite sample.

A spot sample value should not be used to predict the life expectancy of the hydrotreating catalyst; the composite sample will be more useful. We recommend to measure the silicon concentration present on the spent catalyst after the cycle is complete and back calculate the average concentration of silicon in the feed. A properly designed guard catalyst system can significantly lengthen the cycle by catching silicon and other poisons before they reach the main bed high activity catalyst.

Martin Gonzalez (BP)

Spot samples of coker naphtha taken for measuring silicon content can have high variability. To obtain a reliable average, you can use a sampling system that accumulates volume over several hours. X-ray fluorescence technology has developed to where a limit of detection of 0.5 ppm silicon is achievable. Gas Chromatography-Mass Spectroscopy (GC-MS) is also useful to quantify the specific siloxanes formed from decomposition of coker anti-foam.

Gerianne D’Angelo (ART)

Accurately measuring silicon in naphtha streams can be done but it takes a bit of work to get a representative sample of the naphtha. The silicon in the coker naphtha depends on the type and amount of antifoam chemical at the delayer coker unit. Delayed cokers have cycles ranging anywhere between 8 – 24 hours. The coker unit is continually producing a coker naphtha stream during these cycles which is typically being sent from the fractionator straight into the naphtha hydrotreater feed drum. The antifoam chemical is usually not added for the entire coker cycle. This means that the silicon in the naphtha stream will vary with the timing of the coker cycle. In order to get a representative amount of silicon in the coker naphtha stream a composite should be made of hourly samples mixed together for the time of the cycle. For example, for an eight hour cycle eight samples would be mixed and the composite sample analyzed for silicon. To measure the silicon an ICP-MS (Inductively Coupled Plasma Mass Spectrometry) instrument can be used. This instrument/method can measure very low metal concentrations.

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