



Title: Antimony passivation of E-cat nickel

Issue:

When should we consider the use of Antimony for Nickel passivation?

Background:

Please see comment below from latest service report.

The antimony chemical remains off. The E-cat nickel level has stabilized and even come down some (955 ppm on 8/19/09 vs. 858 ppm on 8/28/09). The E-cat vanadium level has also come down a little (1534 ppm on 8/19/09 vs. 1488 ppm on 8/28/09).

Question:

Do you have a guideline on a H₂/CH₄ ratio or ECAT metals level in which you think we should absolutely put the antimony back in?

Response

Background information:

1) Freshly deposited Ni is the most active. Ni will deactivate on its own over time as it becomes "encapsulated" within the catalyst as the catalyst ages, and as additional Ni deposits on top of the original Ni, reducing the surface area available for generating H₂. In addition, we would use some judgment as to how fast the metals are being deposited. The faster it deposits, the more active it will be.

2) Catalyst type would be important. Specifically, how much Matrix Surface Area (MSA) is available (>50m²/gm)? The Ni will mostly deposit onto the Matrix. Therefore, if there is a lot of MSA the Ni will spread more effectively/efficiently and be more active/efficient at generating H₂ than if an equivalent amount of Ni were deposited onto a catalyst with a low amount of MSA (<45m²/gm).

3) There are other H₂ generating elements besides Ni; (V, Fe, Cu, Co all contribute to H₂ generation) but at different rates generally referred to as Ni equivalent: (Ni) + (0.25*V) + (0.1*Fe) + (Cu) + (2*Co). Sb appears to work only on passivating Ni. There are other methods or mechanisms that will work on passivating V. Nothing works on passivating Fe, Cu or Co.

4) There is a specific target Sb/Ni ratio for employing Sb technology; 0.35 for catalysts that do not utilize Ni trapping technology, and 0.25 for catalysts that do utilize Ni trapping technology.

5) There are situations where the "deactivated" Ni can become "reactivated". This generally is following the introduction(s) of a Halogen(s). Specifically, these would be Cl, F. Cl can be found in the Crude unit "rag-layer" which finds its way into the gas oil feed or as salt water found in purchased gas oils. F can be found when processing ASO (Acid Soluble Oil) from an HF Alky.

6) High levels of Sb usage has been observed to increase fouling/coking tendencies within the Main Fractionator Bottoms (MFB) circuit. Therefore, it is extremely important not to overfeed Sb additives and to monitor Sb concentrations in MFB liquid stream.

7) At multiple FCCU sites, Sb usage has been observed to dramatically increase NO_x emissions. The increase in emissions will return to base levels within days of removing Sb additive.

Now to your questions:

1) H₂/CH₄ ratio and Sb Usage: The typical "rule-of-thumb" value is 0.8 H₂/CH₄. However, that value tends to be fairly conservative. Most historical users (please read as old-timers) of Sb technology choose 0.85 as a trigger point. Again, we would target a ratio of 0.25 Sb/Ni ratio for catalysts *employing* Ni trapping technology; or a 0.35 Sb/Ni ratio for catalysts *not employing* a Ni trapping technology.

2) Given the impact Sb has on MFB fouling/coking, the refiner should try to minimize the use of Sb technology unless the H₂/CH₄ ratio is consistently over 0.85 and the Wet-Gas Compressor (WGC) is limiting the unit throughput or conversion. Just having the H₂/CH₄ ratio over 0.85 is not enough to trigger the use of Sb. The elevated H₂ production has to be impacting the unit's ability to generate a profit.

3) Generally, I would not even consider employing Sb under 1500 ppm Ni. At levels under 2500 ppm, I would strongly recommend that a refiner employ Ni trapping technology incorporated within their catalyst (directly from their catalyst manufacturer).

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