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## **Question 9: What has been your experience with antimony and phosphorous poisoning on hydrotreating catalyst performance? What is the maximum level?**

### **Kaspar Vogt (Albemarle) Antimony (Sb)**

The effects of antimony in oil on hydrotreating catalyst have not been directly studied, but we can infer the likely impacts of antimony from a variety of information sources and past experiences.

As background, contaminant metals such as nickel can deposit on the FCC catalyst. This will result in increased dry gas (H<sub>2</sub> in particular) and delta coke. Depending on the unit constraints this can lead to lower FCC conversion and lower feed rate. Many refiners use antimony in the FCC riser to passivate the detrimental effects of nickel. Antimony will cover the nickel enriched catalyst surface. Side effects are that the Sb will also cover the CO and NO<sub>x</sub> promoter metals and make these additives less effective.

Excess antimony mainly accumulates in the FCC slurry. However, antimony can be present in the heavier FCC products which are hydrotreated downstream. If the antimony enriched FCC catalyst fines are entrained into the hydrotreater, they can deposit in the catalyst interstices. This will impact bed pressure drop but not catalyst activity. The bed pressure drop build up can be managed by a guard bed catalyst system of sized and shaped catalysts to increase the void fraction and create more particulates capacity.

By analogy with the FCC experience, we would expect antimony in oil to preferentially coat nickel and cobalt promoter metals on the NiMo and CoMo catalysts. Ultimately, this would completely poison the catalyst. During the buildup of coating/poisoning, the activity will likely see a shift towards direct desulfurization (DDS) vs. indirect/aromatic saturation, thus the hydrogenation-to-hydrogenolysis ratio will change. A given concentration of Sb on catalyst would be expected to have a more severe effect on the catalyst performance in high severity HDS/HDN operations like ULSD and hydrocracker pretreat (HC-PT) service than in lower severity hydroprocessing applications such as NHT and LSD.

We seldom, if ever, detect antimony in the interior of spent hydrotreating catalysts where it would be expected to impact activity.

Furthermore, given its position in the periodic table, we would expect that Sb attacks the catalyst's active (NiMo and CoMo) sites, and that it would be a relatively severe poison, similar to arsenic (As), sodium (Na) and lead (Pb). Therefore, we would expect ~1.0 wt% Sb would reduce HDN/HDS relative volumetric activity (RVA) by approximately 50% in non-severe applications, and that even lower Sb concentrations could severely reduce catalyst activity for high severity operations like ULSD and HC-PT.

### **Phosphorous (P)**

Phosphorous (P) can come into the hydrotreater feed from:

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- crudes
  - drilling fluids
  - phosphated ZSM
  - phosphorous-based corrosion inhibitors and flow improvers
  - phosphorous from solid phosphoric acid catalyst
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In catalyst manufacturing, phosphorous added on hydrotreating catalyst acts as a promoter and provides additional acidity to enhance HDN, hydrogenation and cracking reactions. Phosphorous also improves metals dispersion on the catalyst surface.

In one instance, we saw that 3 wt% of phosphorus on the catalyst terminated all the exotherm in bed, although other poisons were also present. Organic phosphorous can penetrate into catalyst pores. In general, our understanding is that the poisoning was similar to sodium where ~1.0 wt% concentration halves the catalyst activity.

In a separate instance, we found SiP coming from a solid phosphoric acid catalyst, used in certain FCC gasoline desulfurization processes with some iron deposited at the external surface of the catalyst extrudate. Some phosphorous and silicon also penetrated the catalyst pores. However after the first 0.1 mm, no contaminant phosphorous and silicon were found on a main bed CoMo catalyst. In this case, a layer of P-Si-Fe had deposited at the pore mouth and restricted the diffusion into the catalyst.

Photos of the outer surface including chemical composition are shown below. They show that Alumina, Molybdenum and Cobalt are homogeneously distributed within the catalyst particle, while phosphorous, silica and iron are located at the outer surface of the particle.

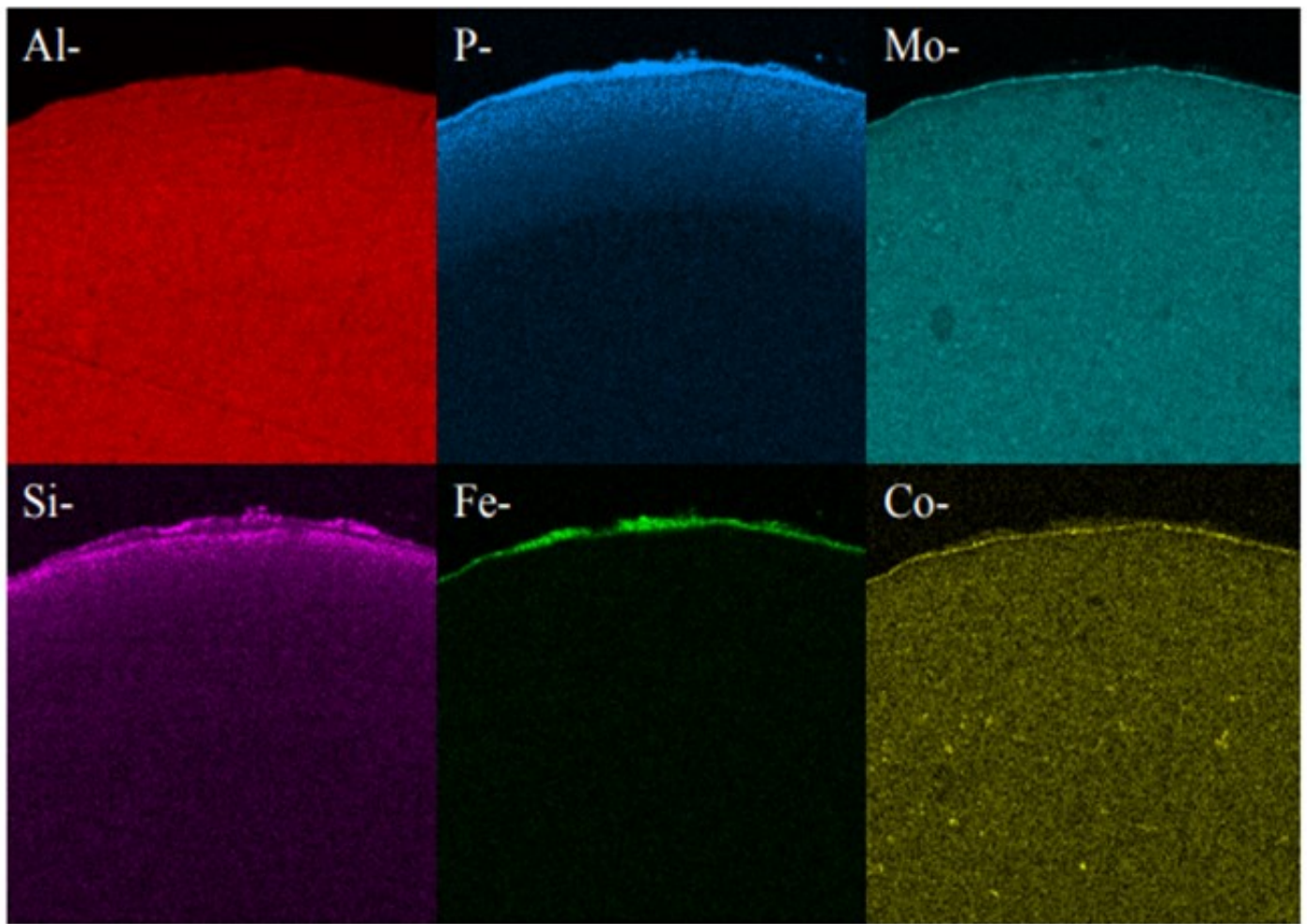


Figure 1, Spot analyses with SEM of a high activity CoMo catalyst.

We observed that the Si & P from this process behaves totally differently from Si from anti-foaming agents. There are Si-P particles which cannot penetrate the internal pores of the catalyst and are deposited on the catalyst outer surface. The accumulation of these particles cannot be prevented. Therefore, sooner or later, bridges from particle to particle are formed, thus causing pressure drop buildup.

The bottom line is that the quantitative effects of phosphorous on hydroprocessing catalyst performance and the maximum allowable levels are highly dependent on the source and form of the phosphorous compound. It is also dependent on catalyst properties and the process application.

#### **Martin Gonzalez (BP)**

Phosphorus can sometimes be found in crude as alkyl phosphates added to passivate metals or protect against naphthenic acid corrosion. Phosphorus esters in crude may originate from waste oils, or from

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additives injected into wells to improve recovery. Some of the phosphorus may be in a form that volatilizes into distillate fractions bound for hydrotreaters. We have encountered some Canadian crudes containing phosphorus originating from fracturing fluids used in production. Phosphorus content in light sweet crudes seems to be declining, but it may be becoming more prominent in heavy crudes. There have been reports in the industry of ULSD units suffering catalyst deactivation as result of phosphorus from these crudes. From our experience, at 1 wt% on catalyst, it is reasonable to expect a 15-30% activity loss.

### **Charles Olsen (ART)**

Phosphorous (P) contamination in oil has been traced to frac fluids that are often used in crudes from the Western Canadian Sedimentary Basin. The source is diphosphate esters which are soluble in the crude oil. Refineries that run large percentages of light Western Canadian crude have reported crude column and crude furnace fouling for many years. Improvements made to crude columns to minimize fouling have transitioned the depositing of phosphorous to the downstream hydrotreaters.

Other sources of phosphorous include gasoline slop tanks, imported feeds and lube oil wastes. If phosphorous does manage to make its way into the hydrotreater it will poison the active sites of the catalyst causing a loss in activity. A level of 1 wt% of phosphorous on the catalyst results in roughly 10°F loss in activity. ART recommends that a feed content of < 0.5 wppm be maintained whenever possible as well as the use of feed filters to assist in trapping of phosphorous sediment.

Historically, phosphorous contamination has not been very common, but with the increasing use of opportunity crudes it is being observed more frequently. A recent example is summarized in the table below shows the results of some spent catalyst analysis from a diesel unit. This unit experienced extremely rapid catalyst deactivation shortly after start up. It was so severe that within several months the unit required an unplanned turnaround and fresh catalyst was installed. The spent catalyst analysis indicates the catalysts were exposed to high levels of several poisons including sodium and phosphorous. The contaminants penetrated well into the catalyst bed. The level of contaminants indicates the catalyst in the top half of the bed had lost over 60°F of activity.

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	Na, wt%	P, wt%
GSK-9	1.71	4.43
GSK-6A	0.21	2.29
Top Catalyst	1.66	2.29

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Year

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