Combating iron poisoning in FCC catalysts: effective mitigation with metals trap additive

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Introduction

The increasing availability of lower value feedstocks is creating opportunities for oil refiners to boost profitability. In the past 15 years, oil production from unconventional sources like oil sands and shale has surged[1,2]. However, these feedstocks often contain a higher metals content, especially iron, posing processing challenges. As a result, iron contamination is becoming an increasing problem for refiners globally. Feed iron is particularly an issue in the FCC (Fluid Catalytic Cracking) unit as it deposits on the base catalyst, reducing the catalytic activity. This leads to increased usage of base catalyst, lower process efficiency and increased costs.

With the correct strategy, refineries can take advantage of opportunity, high-iron crudes turning them into valuable products and boost their profitability. This paper will detail iron poisoning mitigation strategies that can be adopted using a unique metals trap additive. Leveraging on cutting-edge R&D capabilities, the newly understood mechanisms by which this additive mitigates iron poisoning will be described. Finally, a refinery case study demonstrating how this mitigation strategy can be deployed at commercial scale will be shared.

Impacts of iron poisoning on FCC catalyst and operations and usual mitigation strategies

The two main sources of iron can usually be identified in FCC units as organic iron from the feed (such as those found in porphyrins and naphthenates) and inorganic iron from equipment corrosion. Rust particles from corrosion are known to have minimal impact on FCC catalyst performance, whereas feed iron can be very detrimental[2]. Feed iron can be deposited on the catalyst external surface leading to deactivation of the cracking sites, increase of coke and hydrogen production and reduction in fluidization.

Due to their larger molecular size and steric hindrance, iron-containing compounds are unable to diffuse into the internal structure of FCC catalyst particles. Instead, they preferentially deposit and accumulate on the catalyst surface, forming low-melting point eutectics nodules. This alters the surface of the catalyst particles from being smooth with open pores to being covered with a thick, rough coating, called iron nodules. These nodules lead to a drop in catalyst apparent bulk density which can cause catalyst circulation rates to become erratic. These iron-rich deposits, which can be up to several microns thick, further accelerate catalyst deactivation[3]. They form a barrier that inhibits the movement of both feed into the catalyst and products out of the catalyst particle. The inability of feed compounds to enter the catalyst particle prevents cracking which reduces the activity resulting in lower conversion. The restricted ability of cracked products leaving the catalyst particle can lead to secondary reactions occurring within the particle. A negative impact of this is reduced LPG olefinicity. Moreover, iron itself catalyzes dehydrogenation reactions, leading to increased coke and hydrogen. Finally, iron poisoned catalysts often behave as inverse SOx reduction additives, capturing H_2S in the riser as FeS and releasing it as SOx in the regenerator as SO_2. This can be effectively countered by using SOx reduction additives.

Iron poisoning is known to start having significant negative impacts at levels over ~0.2 wt% added iron[4, 5]. Usual mitigation strategies include increasing catalyst make-up rate or adding substantial quantities of purchased equilibrium catalyst (Ecat) to dilute the iron by flushing it out of the unit. Both strategies lead to increased OPEX. Additionally, added Ecat can present different properties than the base catalyst chosen for the unit and lead to different product selectivity that may not be optimal.

An alternative strategy can be to reformulate the base catalyst to a more metals-tolerant one (e.g. high matrix content) or including iron-trapping functionality. This solution can soften the impact of iron poisoning. However, this will not completely prevent it and most often higher catalyst addition rate or Ecat additions will still be required[2,6].

Another solution is the use of a metals trap additive[7,8], a solution that will be detailed in the next section.

How a metals trap additive can help – Fundamental understanding of mitigating iron poisoning using cutting-edge characterization techniques

Johnson Matthey's prior study found that iron is deposited on the surface of FCC base catalyst particles as highly dispersed organic iron or iron salts[6]. This is consistent with the literature that the distribution of added iron is enriched at the exterior of the FCC catalysts particles and highly localized[8]. To further probe the local structure and chemistry of the iron nodules, High-Resolution Transmission Electron Microscopy (HR-TEM) coupled with Energy Dispersive Spectroscopy (EDS) was employed to analyze cross sections of Ecat particles obtained from commercial FCC units. As shown in Figure 1, a TEM-EDS study found that only the outer surface of Ecat particles is iron enriched[6]. A closer examination (Figure 2 top) by HR-TEM reveals that the iron-rich surface layer consists of a high density of randomly oriented iron oxide nanoparticles, ranging in size from 5 to 20 nm. These nanoparticles are embedded within an amorphous matrix. Figure 2 (bottom) is a HR-TEM bright-field image (highlighting heavier metal components) of cross-sections of Ecat particles capturing the interface

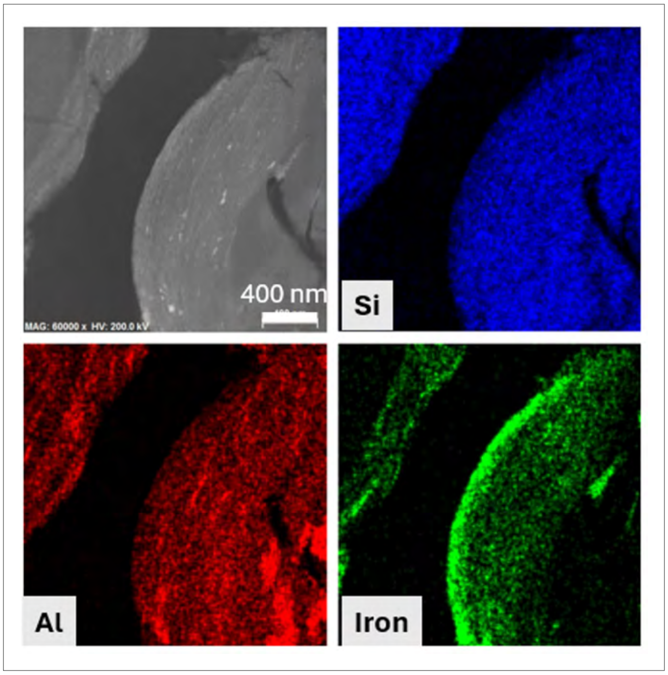

Figure 1: TEM- EDS pictures of Ecat iron nodules indicating iron enrichment on the surface

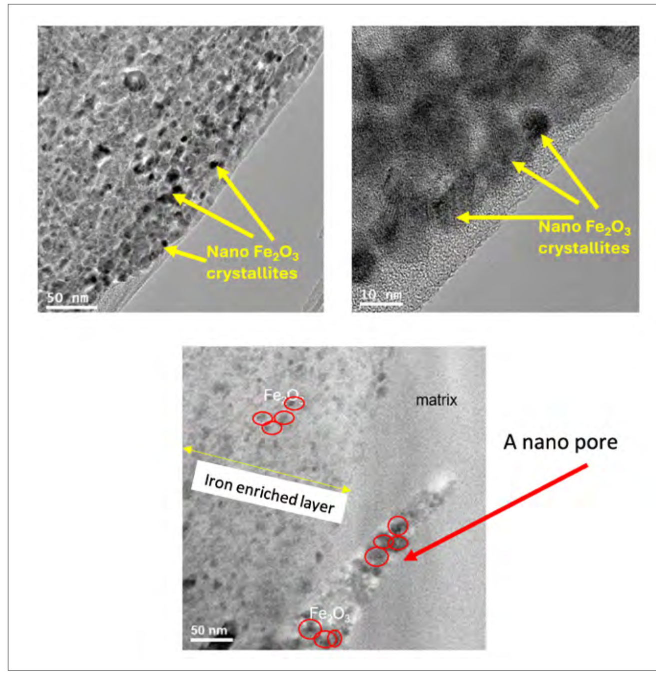

Figure 2: HR-TEM images of the iron nodules on iron-poisoned Ecat particles. (top) Nano Fe2O3 crystallites are embedded in a glassy substrate. (bottom) HR-TEM image of interface of iron-enriched nodules on the top layer of an Ecat particle indicating the blockage of nano pore by the iron oxide.

between the iron-contaminated surface and the inner catalyst matrix. This image provides a direct visualization of iron oxide nanoparticles obstructing a pore within the catalyst structure of an Ecat particle retrieved from a commercial unit, distinguishing it from iron contamination introduced via cyclic deactivation in the laboratory, as reported in the literature[3].

The vitrified (glasslike) outer surface of the catalyst as shown in Figures 1 and 2 ranges in thickness typically from approx. 0.50 to 3 microns. There are two forms of iron seen at the surface of Ecat particles: nano iron oxide crystals (acting as nuclei for the formation of eutectics nodules with silica) and amorphous phase iron (with silica/alumina). Iron in the amorphous phase, which is the predominant form of iron, binds with silica on the outer surface of Ecat particles. The resulting low-melting-point eutectic seals off the interior of the catalyst particles[6]. This study also suggests that the intra-particle mobility of the added iron is minimal.

However, iron can transfer from particle to particle, most likely through collisions, especially in the FCC regenerator dense bed, where sticky surfaces can facilitate matter transfer upon impact. Nevertheless, the exact mechanism of iron transfer between particles remains unclear. It has been reported that silica promotes the formation of iron nodules and may also enhance the inter-particle mobility of iron-containing species[9-11]. There are various sources of silica in the FCC unit: silica from the feed and silica from the base catalyst, mainly in the Y-zeolite. It is suggested that silica in the Y-zeolite is highly mobile under FCC regenerator hydrothermal conditions. It decomposes and migrates from particle to particle [12].

Distinguishing externally introduced silica from the silica originally present in the Ecat remains challenging. The high mobility of silica has been clearly observed on Johnson Matthey's **CAT-AID**™ metals trap additive.

When the **CAT-AID** additive initially free of silica is introduced into FCC units, it gradually accumulates silica. EDS mapping (Figure 3) reveals the formation of distinct silica-rich rings on the particle surfaces. Chemical analysis of **CAT-AID** particles isolated from Ecats via a sink-float procedure shows that over 20% silica is present on their surfaces. Since feed-derived silica is known to be minimal, mobile silica from the base catalyst appears to be the primary source of silica seen on the surface of **CAT-AID** particles. Our study provides clear evidence of the high mobility of silica under FCC regenerator hydrothermal conditions.

Iron rings are also visible on the surface of **CAT-AID** additive particles as shown in Figure 3. The inter-particle mobility of iron offers the opportunity for iron to be captured by a separate particle metals trap additive. It is proposed that when a FCC base catalyst particle with a glassy and sticky iron-silica layer comes in contact with a **CAT-AID** particle, silica in this layer reacts with magnesium present in the additive to form magnesium silicate. Silica, as magnesium silicate, is made immobile on the surface of the additive. Consequently, iron becomes trapped on the additive particle and no longer exhibits any inter-particle mobility.

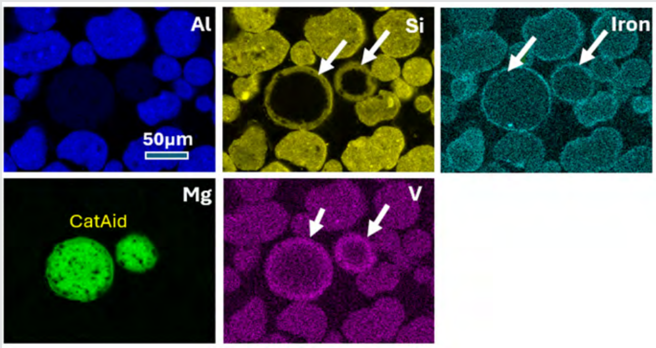

Figure 3: Scanning Electron Microscopy with Energy-Dispersive Spectroscopy (SEM-EDS) mapping of Ecat showing the elemental distribution on the cross-section of particles including Ecat and **CAT-AID** additive. **CAT-AID** particles effectively trap iron and silica as evidenced by the rings on the surface. Vanadium rings on **CAT-AID** particles are clearly evident too (arrowed).

Commercial trials have shown that **CAT-AID** additive can alleviate existing iron poisoning and reduce iron deposition on the FCC base catalyst particles. Once the base catalyst is cured of iron poisoning, the **CAT-AID** additive minimizes iron nodule formation, restoring access to the inner core for cracking. Figure 4 presents Ecat particles before and after the use of the **CAT-AID** additive. Prior to its addition, the Ecat particles surface exhibits typical iron poisoning nodular features. With the **CAT-AID** additive in circulation, the Ecat particles surface becomes smoother, with significantly fewer and less prominent iron nodules.

To gather more solid evidence on the impact of **CAT-AID** additive, an advanced statistical tool was employed to analyze the elemental distribution of thousands of Ecat particles before and after **CAT-AID** additive addition. As shown in Figure 5, the surface iron distribution curve of Ecats shifts toward lower iron concentrations, with a notable reduction in the fraction of high-iron-content particles. Simultaneously, a significant increase in silica concentration on **CAT-AID** additive is observed, indicating silica accumulation on its surface. These findings suggest that **CAT-AID** additive effectively interacts with both iron and silica, reducing iron mobility within the unit and thereby mitigating iron poisoning.

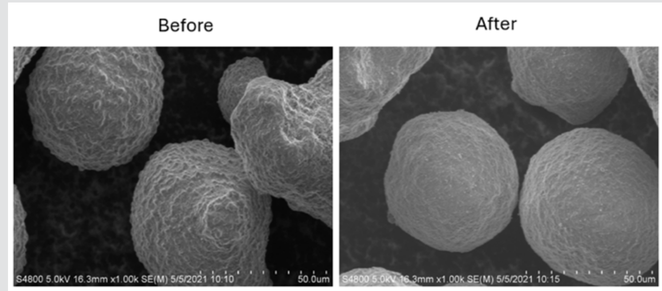

Figure 4: SEM images from Ecat samples before and after the addition of **CAT-AID** additive

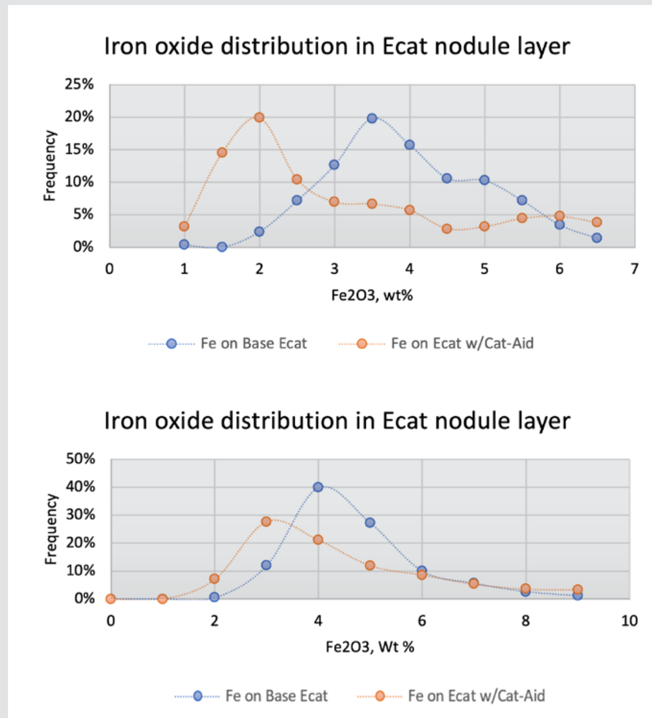

Figure 5: Iron oxide distribution in the Ecat nodule layer before and after adding **CAT-AID** additive in two commercial samples

The quantity of iron retained on the surface of **CAT-AID** particles is influenced by the extent of iron contamination in the Ecat and the iron content in the feed. When no iron nodules are present on the Ecat surface and the iron concentration in the feed is low, the iron ring observed in the EDS mapping of **CAT-AID** additive appears less distinct. Nevertheless, **CAT-AID** additive remains effective in targeting iron and other metal contaminants, particularly vanadium.

Could a similar iron trapping functionality be integrated in the base catalyst? **CAT-AID** additive contains basic materials to enable the trapping of iron silicate. A base catalyst with such materials incorporated would see its activity/acidity being severely penalized. Besides, since iron is not intra-particle mobile, any iron would struggle to migrate towards iron trapping sites within a base catalyst particle and escape through the glassy layer to free the catalyst particle from poisoning.

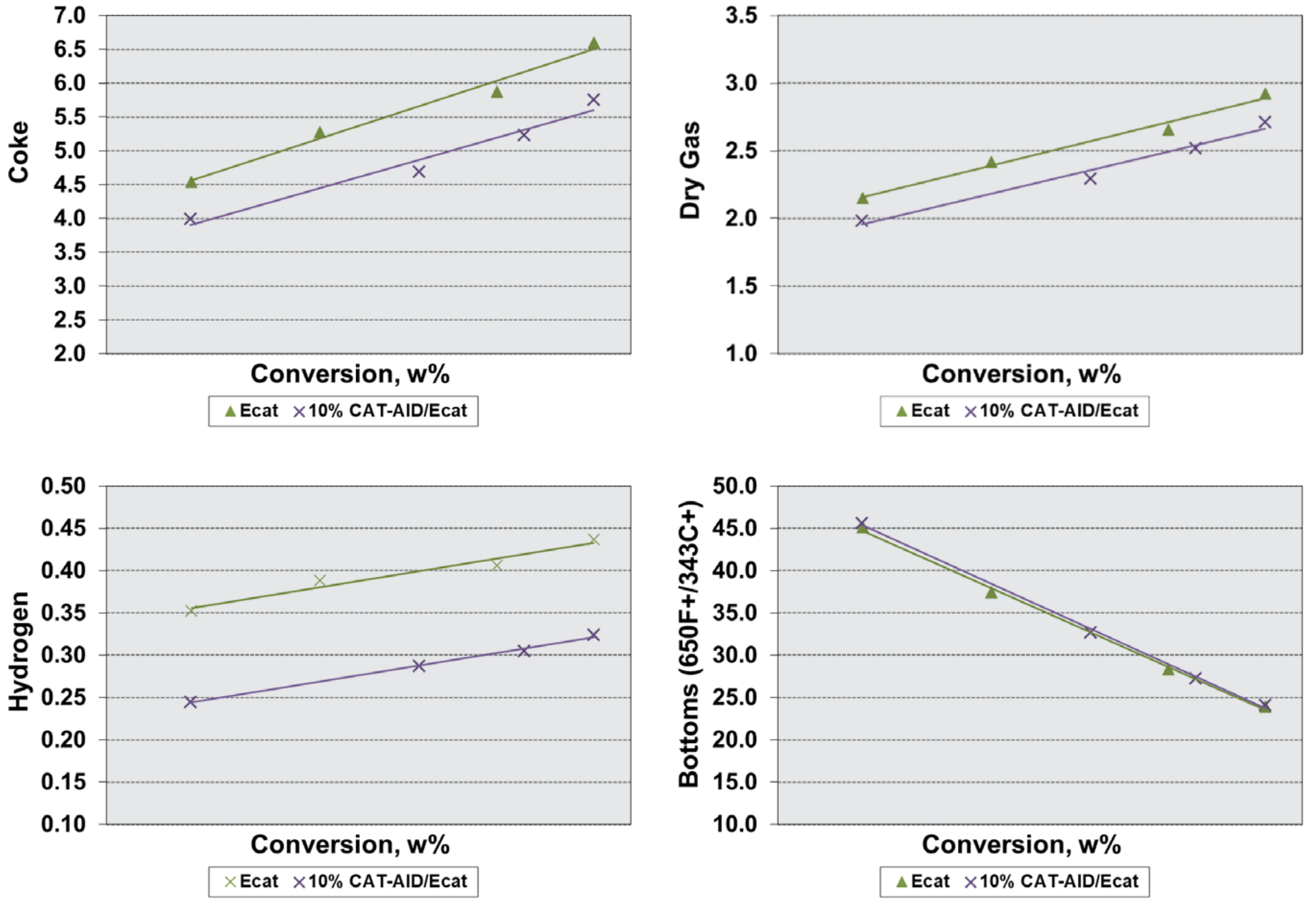

Figure 6: Selected ACE yields for a high iron Ecat steamed by itself and after co-steaming with **CAT-AID** additive

Mitigation of iron poisoning using **CAT-AID** metals trap additive – ACE study

A steamed commercial Ecat sample with iron nodules (confirmed with SEM) and nickel and vanadium levels of 2200 wppm and 2160 wppm, respectively, was evaluated using an ACE (Advanced Cracking Evaluation) unit to test the effectiveness of **CAT-AID** additive as a metals trap additive. A mixture of Ecat with 10 wt% **CAT-AID** additive underwent steaming under the same conditions prior to running on ACE for comparison purposes. The co-steamed Ecat with **CAT-AID** additive clearly showed that the Ecat particles morphology improved, having a smoother surface indicating iron poisoning control (similar to Figure 4). The ACE results depicted in Figure 6 show a 0.8 wt% reduction in coke yield from the original level of 5.6 wt%, 0.2 wt% reduction in dry gas (baseline of 2.2 wt%) and a 0.1 wt% reduction in hydrogen (baseline of 0.4 wt%) at constant conversion. Similarly, no loss in naphtha (not shown) or increase in bottoms was observed. Further delta yields at constant conversion are shown in Table 1 for a better representation of the **CAT-AID** additive impact on the ACE yields.

Selected yields	Ecat	Ecat w/10% CAT-AID	Confidence interval at 95% (±)
Coke	5.6	4.8	0.3
Dry gas	2.2	2.0	0.05
Hydrogen	0.4	0.3	0.02
Ethylene	0.8	0.8	0.03
Propylene	6.5	7.1	0.07
C4 Olefins	6.9	7.4	0.09
LPG	15.5	16.7	0.3
Total Gasoline	26.8	26.5	0.6
Bottoms	32.0	32.6	0.2

Table 1: Selected regressed yields at constant conversion

Refinery case study – How can **CAT-AID** additive help combat iron poisoning

In multiple refinery case studies, **CAT-AID** additive has shown the ability to reduce fresh catalyst and Ecat consumption and also to improve product selectivity, especially decreasing delta coke. The lower delta coke allowed higher levels of contaminated feed to be processed. Lower catalyst costs, improved yields, and increased residue processing led to higher refinery profitability.

The direct benefits of **CAT-AID** additive are detailed here at a North American refiner primarily seeking to lower operating expenses while maintaining similar yields in their FCC unit. This is a full-burn FCC unit which processes gas oil/resid without a feed hydrotreater. Their typical method of managing high metals was to increase fresh catalyst and purchased Ecat additions. **CAT-AID** additive was introduced into the unit targeting ~10% of the circulating inventory. An extra benefit of **CAT-AID** additive is that the additive is manufactured on a SOx adsorbing substrate which enables the additive to capture SOx and protect other metal trapping sites (i.e. for vanadium). This unit used a SOx reduction additive to control its SO_2 emissions. **CAT-AID** additive enables refiners to reduce their consumption of SOx reduction additive or caustic soda if they are equipped with a wet gas scrubber. The results of the trial are shown in the table 2.

With **CAT-AID** additive in the unit, the refinery was able to lower the daily additions of fresh catalyst, purchased Ecat, and SOx removal additives by 7%, 75%, and 80%, respectively. The yield structure was essentially unchanged with the notable exception of additional LCO and reduced slurry. These positive benefits occurred even while the Ecat metals increased thanks to the additive ability to manage metals. **CAT-AID** metals trap enabled the refinery to reduce its operating expense by $0.10 or more per bbl of feed (does not include additional value seen in the yields improvement). The cost of **CAT-AID** additive was offset by the decrease in SOx reduction additive, fresh catalyst and flushing Ecat use.

CAT-AID metals trap also decreased delta coke and regenerator temperature (by 4°F) which offered the potential for an additional profitability improvement by processing lower-value feedstocks.

	Pre CAT-AID	With CAT-AID	Delta
Feed Quality			
Feed API	25.0	25.3	0.3
K Factor	12.11	12.06	-0.05
CCR, wt%	2.3	2.3	0.0
Operations			
Rate	Constant	Constant	-
Riser Temp, °F	991	992	1
Dense Temp, °F	1335	1331	-4
Yields			
Gasoline, vol%	54.4	54.5	0.0
LCO, vol%	20.3	22.2	1.9
Slurry, vol%	6.0	5.2	-0.8
LV yield, vol%	108.7	108.9	0.2
Ecat			
Ecat V, ppm	1,909	2,033	124
Ecat Fe, wt%	0.67	0.70	0.03
Additions (per bbl feed)			
Fresh Adds, lb/bbl	0.70	0.65	-0.05
Ecat Adds, lb/bbl	0.70	0.18	-0.52
SOx reduction additive Adds, lb/bbl	0.05	0.01	-0.04

Table 2: Results of the **CAT-AID** additive trial

The results seen here are just one example of a budget-minded refiner attempting to optimize OPEX while managing metals. Other refiners may take advantage of the benefits of **CAT-AID** additive differently. It begins with the additive's ability to trap iron and vanadium which directly leads to more desirable reactions in the unit lowering delta coke. The chart below (Figure 7) shows multiple (6) cases where the FCC's delta coke was reduced while managing metals.

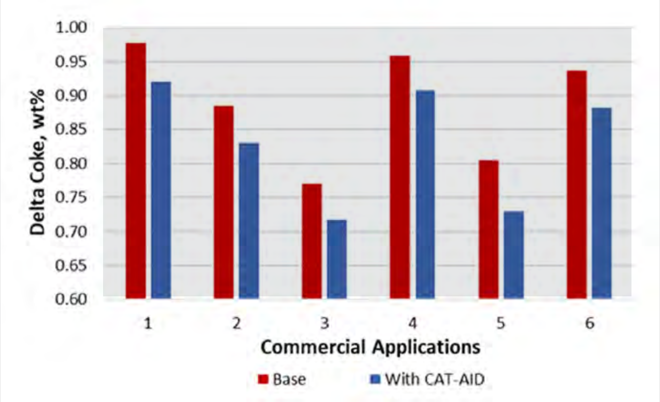

Figure 7: Reduction of delta coke in multiple commercial applications with **CAT-AID** additive

Refiners then have options to take advantage of the improved heat balance for their specific optimization goals. These benefits can be a combination of all the advantages provided by **CAT-AID** additive:

- Increased feed rate and residue processing
- Lowered delta coke and regenerator temperature
- Increased conversion, decreased H_2/dry gas
- Increased LPG olefinicity
- Lowered fresh and/or flushing Ecat addition rates
- Lowered SOx emissions, SOx reduction additive usage, and/or scrubber caustic soda consumption
- Improved Ecat circulation/fluidization properties

Conclusions

The growing abundance of lower value feedstocks, along with the availability of effective metals trapping technologies such as **CAT-AID** additive, creates opportunities for oil refiners to enhance profitability. Iron contamination, which can significantly increase OPEX if not managed properly, can be effectively mitigated through commercially proven strategies. As the mechanisms behind iron poisoning become better understood through advanced characterization techniques, more efficient metals trapping solutions are being developed, enabling refiners to fully capitalize on the expected OPEX savings from processing lower value feedstocks and managing catalyst additions.

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