Refining Tight Oils and Dealing with a High Iron Environment in Fluid Catalytic Cracking

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ABSTRACT

Argentina has seen a change in crude oil production in recent years, in particular as a result of light tight oils (LTOs) from shale plays. Compared to crude oil from conventional oil wells, LTOs offer unique challenges to refiners. LTOs are often paraffinic and easy to crack, have low sulfur, have low amounts of contaminants such as nickel and vanadium, but introduce the complexity of increased iron content. This presentation will give an overview of operating and catalyst technology strategies to overcome the challenges of processing LTOs in the fluid catalytic cracking (FCC) unit.

The paraffinic nature of LTOs can lead to several operational changes in the FCC unit; the FCC might not produce enough coke which can affect heat balance, and LTOs typically produce higher amounts of liquefied petroleum gas (LPG), which may constrain the wet gas compressor. These feeds often contain higher iron than conventional crudes, which impacts the catalyst. FCC catalysts are based on Y-zeolite structures and chemistry, and the structure-function relationships between zeolites and crude oils are important. The impact of added iron from feeds continues to be researched by BASF to expand on the understanding of iron contamination of FCC catalysts. The research presented here will detail both the physical and chemical impacts of iron contamination, both of which impact FCC unit operations. Examples of the impacts include surface nodule formation, dehydrogenation activity, CO promotion activity, SOx emissions, slurry yields, and bottoms cracking impacts. Also to be discussed are catalyst technologies capable of withstanding iron poisoning and case studies from refineries processing tight oils who are faced with increased iron in the crude oil slate. This type of research and understanding allows the refining industry to continue taking advantage of this competitive natural resource.

INTRODUCTION

The fluid catalytic cracking (FCC) unit is an integral part of any refinery. An FCC uses a fluidized solid catalyst that is mainly composed of silica and alumina. During the FCC process, crude oils come into contact with the catalyst and metals contained in the crude oil deposit onto the catalyst as contaminants. The main contaminants of concern include heavy metals such as nickel (Ni) and vanadium (V). Nickel deposits on the outside of the catalyst and promotes dehydrogenation reactions, an unwanted reaction in an FCC unit, resulting in higher hydrogen production and higher coke. Vanadium deposits on the catalyst also, but unlike nickel, vanadium is highly mobile both from catalyst particle to catalyst particle, as well as within the catalyst particle. As such, vanadium is found throughout the bulk catalyst. Vanadium results in a loss in catalyst activity and is also a mild dehydrogenation catalyst (about $1/4^{th}$ that of nickel). The loss in catalyst activity by vanadium is even more pronounced in the presence of sodium. Other contaminants that enter an FCC with the crude oil include alkali and alkaline earth metals such as calcium (Ca), sodium (Na), and magnesium (Mg), all

of which act as bases and deactivate the acid sites on the FCC catalyst. The focus of this paper is on a different heavy metal contaminant: iron (Fe). Iron is found in most residual feeds, which are heavier than vacuum gas oil feeds and contain a higher level of contaminant metals. Iron is also found in crude oils that are produced from shale formations, i.e. light tight oils (LTOs). Argentina has seen an increasing amount of oils produced from shale formations, and in the first half of 2015, Argentina, along with China, has been in the lead for shale development outside of North America.[1] The story of tight oil and its contaminant iron is a long term development.

IRON RESEARCH

BASF has conducted extensive research on the effect of iron poisoning on FCC catalysts.[2] This paper describes BASF's recent findings.

First it is important to understand iron sources and how to quantify iron on FCC catalyst. Iron comes in with fresh catalyst and can vary between 0.25 and 0.75 wt% depending on the catalyst supplier and the catalyst technology. This iron is inherent in the kaolin clay that is used to manufacture catalyst, and is thus bound in the silica/alumina matrix. For this reason, it does not participate in any side reactions or cause any kind of catalyst surface blockage. The iron that is of concern is that which comes in with the crude oil, in the form of iron napthenates, for example. Iron can also come from equipment corrosion (tramp iron), which is less of a concern. The calculation to derive the amount of troublesome iron, therefore, is below. Added iron is calculated by subtracting iron on fresh catalyst from iron on Equilibrium Catalyst (Ecat). Also below is a graphical representation of this calculation in which added iron is in red.

$$Fe(Added) = Fe(Ecat) - Fe(Fresh)$$

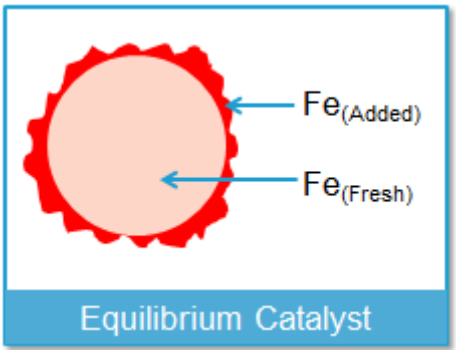

Figure 1: Graphical Representation of Added Iron and the Accompanying Calculation

EFFECTS OF ADDED IRON ON FCC ECAT

Added iron can have an impact on FCC catalyst in two very different ways: a) chemically and 2) physically. First discussed are the chemical effects of added iron on FCC catalyst. Iron is a mild dehydrogenation catalyst, and does participate in these reactions, much like nickel and vanadium do (as described above). The dehydrogenation activity of iron, however, is very low, at one tenth that of nickel. This is described in the below calculation in

which “equivalent nickel” demonstrates the relative dehydrogenation activities of the various contaminant metals.

$$\text{Equivalent Ni} = \text{Ni} + \text{V}/4 + \text{Cu} + \text{Fe}/10$$

Added iron can also act as a mild CO promoter. This can be a concern for FCC units running in partial burn mode. The relative capacity of iron to participate in CO promotion, that is promoting CO to CO_2 in the regenerator, is on par with other contaminant metals such as nickel and vanadium. Lastly, from a chemical point of view, iron can act as an inverse SOx additive by reacting with sulfur from the feed in the reactor and releasing it in the regenerator as SOx.

More important to most refiners are the physical effects of added iron. Added iron on Ecat creates very distinct iron nodules which are visible under scanning electron microscopy (SEM). Below is an SEM image of a nodulated BASF catalyst. This catalyst represents 1.28 wt% iron on Ecat. At the time, this refinery did not experience circulation or yield impacts. It is important to note that surface nodulation is not a diagnostic for iron problems in a refinery. Nodulation is identified via routine monitoring of Ecat. If an increase in iron is seen corresponding with a drop in ABD (apparent bulk density), this indicates iron nodules. The drop in ABD is due to the particle not able to pack as tightly.

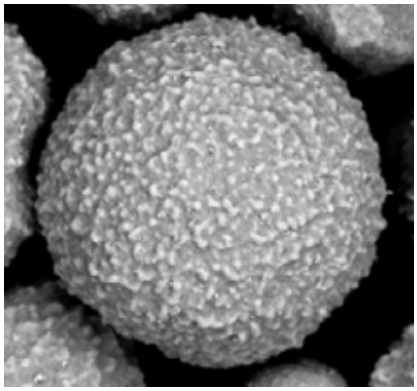

Figure 2: Scanning Electron Microscopy Image of an Iron-Nodulated Ecat

BASF has studied where iron on Ecat eventually ends up. By looking at a database which includes many refineries around the world, we compared units that had an added iron amount of 0.2 wt% or greater, and for which we analyzed both the Ecat and fines. The results indicate that the fines are typically enriched with iron, with around 2-3 times more iron in the fines than in the Ecat. Other metals are also enriched such as nickel and calcium. Vanadium is not enriched which is intuitive given the mobility and homogeneity of vanadium as a contaminant.

Depending on the catalyst type and technology, the iron on the surface of the catalyst particle could lead to surface blockage in which the pores are not accessible by the crude oil feed. In effect, the feed is not able to enter the catalyst and crack, which would lead to reduced conversion and higher slurry yields.

The mobility of iron within a catalyst particle was explored. To undertake this study, we used an SEM technique that looked at the cross section of many catalyst particles. On each particle, two measurements were taken: one on the outside of the catalyst and one on the

inside of the catalyst. By taking the ratio of the two, the Peripheral Deposition Index (PDI) can be calculated.[3] The PDI value of a very mobile element would be 1, since the concentration on the inside of the catalyst would be equal to the concentration on the surface of the catalyst. The PDI measurement process is indicated in Figure 3 below.

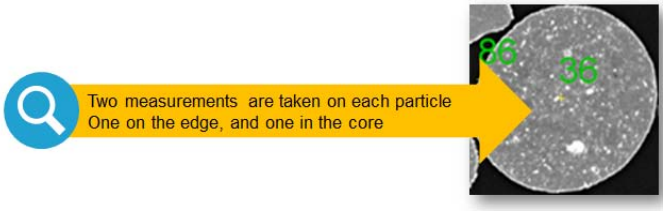

Figure 3: Peripheral Deposition Index Measurements in SEM

In previous studies, PDI values of the contaminant metal nickel on various Ecat samples were found to range from 2 to 5. In the current study, three refineries with high iron on Ecat, ranging from 1.2 to 1.6 wt%, were examined (Refineries A-C) and the data is described below.

Table 1: PDI values of various elements on 3 Ecat samples

PDI	Refinery A	Refinery B	Refinery C
V	**1.5**	**0.7**	**1.3**
Ni	**2.0**	**6.5**	**7.5**
Fe	**4.5**	**5.4**	**7.1**
Ca	**9.5**	**7.0**	**8.0**

The PDI values of near one for vanadium indicate very high mobility, which is expected. Nickel ranges from 2 to 8 indicating very low intraparticle mobility. Iron and calcium also show low intraparticle mobility, as they range from 4 to 7 and 7 to 10, respectively.

In terms of iron tolerance, our learnings have indicated that the key to strong performance in relation to iron poisoning is enhanced surface porosity. In-situ FCC catalyst manufacturing allows for not only enhanced bulk porosity for molecular diffusion, but also optimal surface porosity that allows the catalyst to withstand the common phenomenon of iron poisoning, i.e. surface blockage, as discussed above.

A visualization of the surface porosity is offered in the image below, in which the high surface porosity (right) is examined via SEM, whereas an alternative manufacturing process can produce catalyst with hindered surface porosity (right).[4]

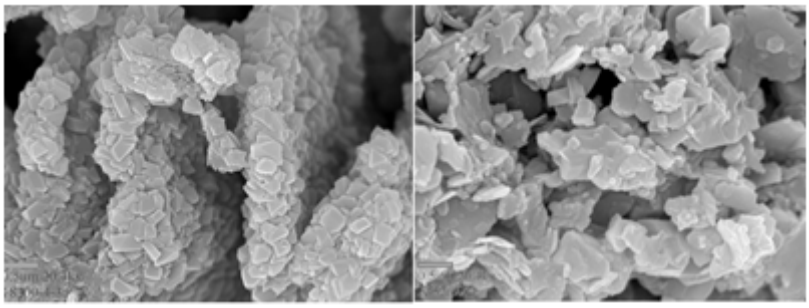

Figure 4: Enhanced surface porosity (left) via in-situ manufacturing and hindered surface porosity (right).

In terms of operating with high added iron, Table 2 is a snapshot from the most current benchmarking system, which tracks Ecat from around 200 refineries around the world. It shows the top 8th percentile of units around the world using BASF catalyst in terms of iron content in Q2 2015. Also included are other contaminants, Ni, V, and Ca, which all span a wide range. Added iron currently is as high as 0.6 wt% and successful operation is achievable at these levels. As indicated previously, Ecat iron in the past has even been above 2 wt% with no operational issues.

Table 2: Top 8th percentile of units around the world running high iron on Ecat from BASF's Q2 2015 Benchmarking System with wide ranges of contaminant metals and Rare Earth Oxide (REO) levels.

Country	**Catalyst Technology**	**Fe**	**Ni**	**V**	**Ca**	**REO***
Australia	BASF DMS Resid	1.18	3513	1104	4160	2.2
USA	BASF Prox-SMZ	1.11	1911	794	1465	2.0
Canada	BASF Prox-SMZ	1.10	529	3568	1980	1.6
USA	BASF Gasoil DMS	1.06	1126	2625	1705	2.1
France	BASF Prox-SMZ	0.94	2510	1805	1596	2.4
Canada	BASF DMS Resid	0.91	2643	5861	6949	3.5
Germany	BASF DMS Resid	0.86	3178	4536	1204	2.8
USA	BASF Gasoil DMS	0.85	420	2217	1580	1.6
USA	BASF MSRC Resid	0.84	816	1883	4735	2.7
Australia	BASF Prox-SMZ	0.84	4243	2685	3372	3.3
Italy	BASF Prox-SMZ	0.83	5649	1741	1260	2.8
Canada	BASF Max Diesel	0.82	40	171	816	0.9

BASF follows iron upsets closely in the industry. As noted above, BASF has not experienced problems with iron upsets. Below is a case study highlighting this. This historical case study describes an iron excursion at a North American refinery running BASF's Stamina catalyst. Over the course of a few months, the refinery introduced high iron feed into the FCC unit. The refinery saw iron on Ecat increase from 1.17 wt% to 1.48 wt%, representing a 45% increase in added iron (iron coming from the feed). At the same time, they also saw calcium and sodium on Ecat increase at 23% and 48%, respectively, while Ni and V were stable.

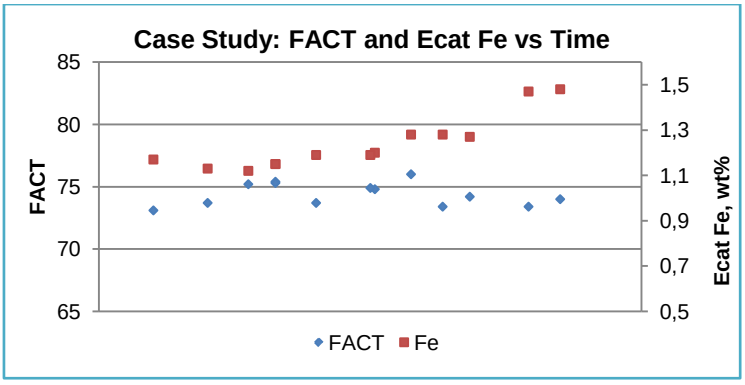

Figure 5: Case Study with Increasing Iron on Ecat with No Performance Issues

Table 3: Snapshot of Ecat contaminants and Fluidized Activity Test (FACT) before and after an iron excursion

Ecat Properties	Before iron excursion	After iron excursion
FACT	73.1	74.0
Fe, wt%	1.17	1.48
Ni, ppm	1744	1807
V, ppm	598	681
Ca, ppm	1207	1481
Na, ppm	0.21	0.31

This is one of many cases in which an FCC unit running BASF catalyst has seen a significant increase in added iron with no operational or catalyst performance problems.

CONCLUSIONS

It is important to know the catalyst limitations and operating windows when it comes to all metal contaminants, including iron. Depending on the catalyst technology and type, the operational windows for acceptable contaminant levels will vary. When dealing with iron contamination from feed, a refiner must consider different aspects of iron poisoning including chemical and physical effects. BASF has extensively investigated iron poisoning including chemical and physical effects, the ultimate fate of iron, and iron mobility.

LITERATURE CITED:

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