

HP

Special Focus

Refining Technology Developments

A. SHACKLEFORD and M. CLOUGH; BASF, Houston, Texas

## Iron poisoning investigations enable opportunities for success

The function of fluid catalytic cracking units (FCCUs) is to maximize profits from a given barrel of oil. In the US, tight oils and residue-containing (i.e., resid) feeds represent opportunity crudes with high potential profits for refineries. With the right tools, refineries can take advantage of these low-cost feed options. However, these opportunity crudes often contain higher amounts of contaminant metals. Typically, tight oils contain higher amounts of iron (Fe), calcium (Ca) and sodium (Na), while resid feeds contain higher amounts of Fe, nickel (Ni) and vanadium (V). The effects of Fe contamination on catalyst performance in the FCCU are explored here.

Fe contamination of FCC catalysts has come to the forefront of FCC issues in the past few years due to the increased processing of tight oils in the US and greater use of resid feedstocks around the world. In the past year, Fe excursions were seen in all regions. Problems associated with Fe include reduced conversion, increased bottoms and circulation issues. Due to these issues, BASF conducted extensive research on the effects and mobility of Fe. Deeper understanding of Fe poisoning phenomena allows the industry to better prepare for a potential spike in Fe, and to better troubleshoot existing or ongoing Fe excursions.

The mobility of Fe, both inter-particle and intra-particle, has been examined via numerous laboratory techniques. This work was enabled by cooperation with three refineries in the US that experienced high Fe on equilibrium catalyst (Ecat). Industry data were also analyzed, including fines data and refinery case studies. Furthermore, various catalyst technologies were examined for their potential to withstand Fe poisoning. These investigations have culminated in

a greater understanding of the impacts of Fe on FCC catalyst. This information enables refiners to choose and implement technologies and troubleshooting strategies to ensure success.

**Background.** In 2010, an FCCU processing residue-containing feed was experiencing high Fe. The Fe on Ecat was rising and approaching the unit limit of 1 wt% total Fe (approximately 0.4 wt% added Fe). The unit would historically increase catalyst addition rates or change the feed diet to keep the Fe below 1 wt%, thereby limiting operation and profitability. A hard limit was set based on a perceived notion that above 1 wt% total Fe, additional Fe would cause extreme operation issues and significant loss of catalyst activity. The authoring company worked with the refiner to lift the limit, allowing the refiner to operate successfully at Fe levels above 1 wt% with no adverse effects and allowed increased profitability. This example demonstrates that many misconceptions exist in the industry about Fe and its impact on the FCCU.

The FCC catalyst encounters various feed contaminants, depending on the source of the crude oil. Common elements of concern include Ni and V, both of which contribute negatively to catalyst performance. However, Fe contamination is becoming increasingly common. Fe contamination was first recognized in the 1990s in Asia, and today refiners in all regions have experienced high Fe. Opportunity crudes, including tight oils, that contain higher amounts of Fe than previously seen have been introduced. These new feeds have again brought the issue of Fe to the forefront of FCC. The effects of Fe and the mobility of Fe under FCCU conditions are covered here. Understanding how Fe behaves allows

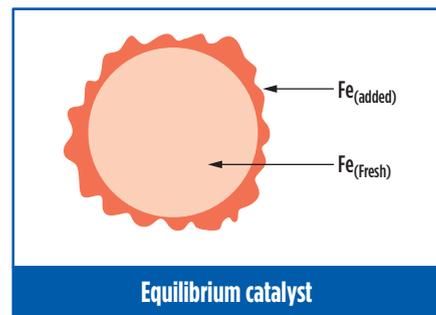
a better catalyst solution to be designed and encourages the correct choice of mitigation strategy.

**Iron contamination.** Extensive research continues to be conducted on the effect of Fe poisoning on FCC catalysts.<sup>1</sup> The source of Fe on the FCC catalyst must first be identified. Fresh catalyst contains Fe levels between 0.25 wt% and 0.75 wt%, depending on the catalyst supplier and the catalyst technology. Fresh Fe comes in with the kaolin clay bound in the silica/alumina matrix during the manufacturing process. As a result, it does not participate in side reactions or cause catalyst surface blockage. Of concern is the Fe that comes in with the crude oil. Fe can also come from equipment corrosion (tramp Fe), which is less of a concern than organic Fe; the latter is more detrimental to performance.

When examining Fe contamination, added Fe is the focus. Added Fe comes from the feed and is calculated from fresh catalyst Fe and Fe on the Ecat, as shown in Eq. 1 and graphically represented in **FIG. 1**.

$$\text{Fe(Added)} = \text{Fe(Ecat)} - \text{Fe(Fresh)} \quad (1)$$

**Effects of added iron.** The effects of Fe



**FIG. 1.** Added Fe on the catalyst, which comes from the feed.

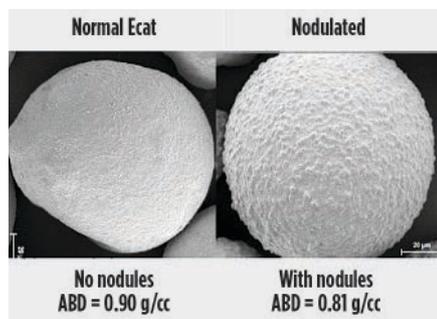
on FCC catalyst are divided into two broad categories: chemical and physical effects. Chemically, Fe can act as a mild carbon monoxide (CO) promoter, which can be a concern for FCCUs running in partial-burn mode. The relative capacity of Fe to participate in CO promotion is on par with other contaminant metals, such as Ni and V.

Fe can act as an inverse sulfur oxides (SO<sub>x</sub>) additive by reacting with sulfur from the feed in the reactor and releasing it in the regenerator as SO<sub>x</sub>. Lastly, Fe is a very mild dehydrogenation catalyst similar to Ni and V, which contribute to increasing coke and hydrogen (H<sub>2</sub>) yields.

However, the ability of Fe to catalyze dehydrogenation reactions is much lower than that of Ni or V, and is often represented as one-tenth that of Ni. When looking at the dehydrogenation activity of metals on FCC catalyst, “equivalent Ni” is often calculated as shown in Eq. 2, and takes into account the relative dehydrogenation activities of the various contaminant metals.

$$\text{Equivalent Ni} = \text{Ni} + \text{V} \div 4 + \text{Cu} + \text{Fe} \div 10 \quad (2)$$

The physical effects of Fe tend to be the



**FIG. 2.** SEM image of an Fe-nodulated Ecat compared to normal Ecat.

most detrimental to refiners. Physically, added Fe creates distinct Fe nodules, which are visible under scanning electron microscopy (SEM), an example of which is shown in **FIG. 2**. **Note:** Surface nodulation is not a diagnostic for Fe problems in a refinery. Nodulation is identified via routine monitoring of Ecat. If an increase in Fe is seen corresponding with a drop in apparent bulk density (ABD), then this indicates Fe nodules. The drop in ABD is due to the particles' inability to pack as tightly. In the Ecat particle shown in **FIG. 2**, this refinery operated well (i.e., no conversion losses) with Fe nodules; Fe nodulation does not necessarily mean Fe poisoning. Anecdotal evidence of nodules causing unstable

circulation has been reported.

Depending on the catalyst type and technology, added Fe on the surface can lead to surface blockage, wherein the pores are inaccessible to the feed molecules. In effect, feed is not able to enter the catalyst and crack, which leads to reduced conversion and higher slurry yields. The slurry gravity would also become unusually light due to uncracked feed, with an increase of 10°API reported in severe cases.

Another phenomenon previously reported was vitrification on the catalyst surface. In rare cases of vitrification, or the formation of a glassy surface, Fe complexes with other elements to create a low melting point eutectic phase that melts at FCC temperatures, causing the characteristic glassy surface. Like the nodules causing pore blockages, this low melting point also creates a loss in porosity at the surface of the catalyst. However, in recent research examining a number of units with Fe nodules, no evidence of vitrification has been found.

**Conversion loss due to iron.** When a refinery reports Fe resulting in a decrease of conversion, other elements are usually also increasing. In most cases, Fe does not increase independently. Other contaminants result in the loss of conversion. Different experiments were designed to try to separate the effects and focus on only Fe impacts.

These experiments include Ecat from three units listed in **TABLE 1** that use in-situ catalyst technology and no flushing catalyst. **Note:** In many cases, the experiments used more than the three units listed. One

**TABLE 1.** FCC Ecat analysis for three refineries with high added Fe

	Refinery		
	A	B	C
Ni, ppm	3,596	2,197	476
V, ppm	2,269	849	2,531
Added Fe, wt%	0.93	0.68	0.57
Ca, ppm	1,822	1,311	3,268

**TABLE 2.** PDI values of various elements on three Ecat samples

PDI	Refinery A	Refinery B	Refinery C
V	1.3	0.7	1.5
Ni	7.5	6.5	2
Fe	7.1	5.4	4.5
Ca	8	7	9.5

experiment abraded the Fe on the outside of the catalyst and tested the samples before and after. The Fe nodules are fragile, breaking off and reforming easily. (Evaluating the fines content of 19 FCCUs with high Fe and added Fe > 0.2 wt% showed that added Fe is 2–3 times higher in the fines supporting the fragile nature of the nodules.)

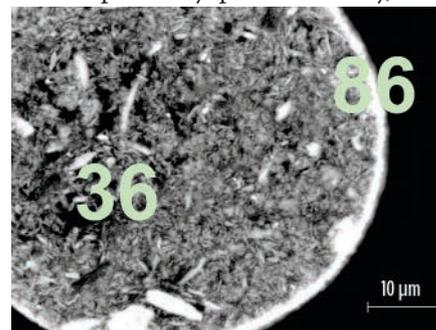
Catalytic cracking evaluations showed no statistically significant loss of conversion or bottoms upgrading. Other methods were used to see if Fe caused a loss in conversion with in-situ catalyst, with all experiments showing that Fe had no impact.

**Mobility of Fe.** Investigations into the fate of Fe were pursued. V is mobile under FCC conditions and distributes evenly in the catalyst, while Ni is documented to be immobile, staying where it initially deposits or cracks onto the catalyst particle.

Two types of Fe mobility were investigated. Intraparticle mobility is the tendency of the element to diffuse through the catalyst particle. Interparticle mobility is the tendency to transfer between catalyst particles.

The first type, intraparticle mobility, was explored via multiple methods, the first of which uses SEM. Two measurements were taken on each catalyst particle, one on the inside (the core) and one on the outside (the edge). The ratio of these two numbers is indicative of the amount of interparticle mobility and is termed the peripheral deposition index (PDI).<sup>2</sup> If highly mobile and able to diffuse through the catalyst particle, the PDI is expected to be near 1, indicating a homogeneous distribution. On the other hand, with low mobility, a PDI value of greater than 1 is expected. The PDI measurement process is shown in **FIG. 3**.

In a previously published study,<sup>2</sup> the



**FIG. 3.** Peripheral deposition index measurements in SEM, in which two measurements (indicated in this example as measurement 36 and measurement 86) are taken.

PDI values of Ni were found to be between 2 and 5. (**Note:** For lower Ni containing Ecats, like Refinery C with 476 ppm Ni, the PDI for Ni tends to be on the low end of the range.) The three refineries with high Fe on Ecat (**TABLE 2**) were consulted for this study.

As expected for V, the PDI values hover around 1, indicating relatively homogeneous distribution. However, the values for Ni, Fe and Ca are starkly different. All give PDI values greater than 1, indicating very low intraparticle mobility. In fact, Ca gives a PDI value of 9.5 in one case. The average value for Fe of 5.7 suggests low intraparticle mobility of Fe.

Next, interparticle mobility was assessed. Ecat inventory has a wide age range distribution due to the continuous catalyst addition. If an element has high mobility, then it is expected to be distributed equally, regardless of the age of the catalyst particle. For example, when looking at the deposition of V, its high mobility results in catalyst particles with a similar V content, regardless of how long they have been in the unit. When looking at EDS mapping and SEM morphology for Fe (**FIG. 4**), the images show varying amounts of Fe on catalyst particles, suggesting that Fe has low interparticle mobility. While this is a subjective assessment, the next two experiments allow an objective look into interparticle mobility.

The first experiment uses a strong magnet to separate the high-Fe-containing catalyst. The lower-Fe-containing particles will remain in the pan. For the three units tested, the concentration of the elements from the magnet vs. the pan was taken as a ratio. A ratio of 1 would mean the metals of the magnet portion equaled 1 in the pan. V shows almost no change in concentration with a ratio of 1.08 (close to 1), supporting the claim of high V mobility. Ni is higher than 1 at 1.59, showing immobility. Fe has the highest value of 1.78, demonstrating no or low mobility (**FIG. 5**) (**TABLE 3**).

The next experiment used for assessing interparticle mobility is density separation, or sink-float separation. Older particles in a unit are more dense than fresh catalyst particles due to the forces in the FCCU (particle and wall collisions) that cause the particles to become denser over time. This density is used to separate the Ecat into age fractions.



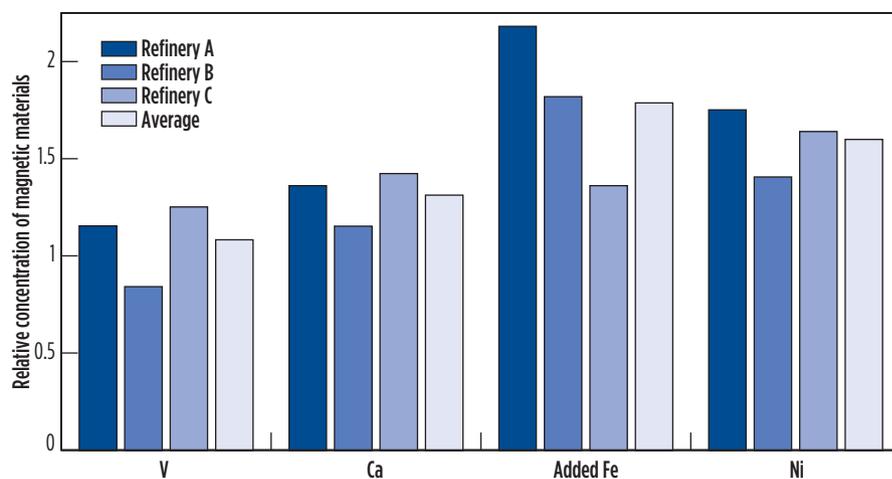
**FIG. 4.** EDS mapping and SEM morphology for Fe showing varying amounts of Fe on catalyst particles.

Here, the Ecat is separated into four approximately equal fractions (light, middle light, middle heavy and heavy fractions). The metals of each fraction were measured and normalized to 1 (heavy portion) to directly compare (**FIG. 6**) (**TABLE 4**). Vanadium shows the most uniformity of the fractions, particularly the heaviest three fractions, which are all close to 1. The standard deviation (SD) of the V fractions is 10%, implying very high mobility. (**Note:** Only a 10% difference exists among all fractions, on average.) Ni has a low-mobility SD of 26%. Fe and Ca fall between V and Ni, at 17% SD, which suggests that Fe has lower

mobility than V.

In summary, the experiments show that Fe has very low interparticle mobility and lower interparticle mobility than V. This result is important to understanding how to improve Fe tolerance. Given the low mobility, it is best to tackle the problem where the Fe deposits: at the surface of the catalyst.

The authors' learnings have indicated that the key to strong performance in relation to Fe poisoning is enhanced surface porosity. An in-situ FCC catalyst manufacturing process not only allows for enhanced bulk porosity for molecular diffusion, but also optimal surface porosity.



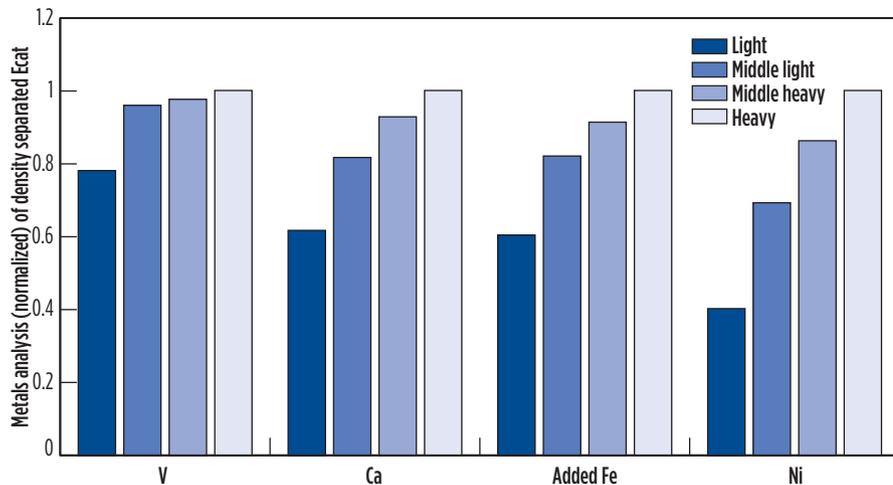
**FIG. 5.** Magnetic separation of high-Fe Ecat showing the ratio of the Ecat responsive to the magnetic separation vs. the Ecat that was not picked up for three units.

**TABLE 3.** Averages for the magnetic separation of high-Fe Ecat showing the ratio of the Ecat responsive to the magnetic separation vs. the Ecat that was not picked up for three units.

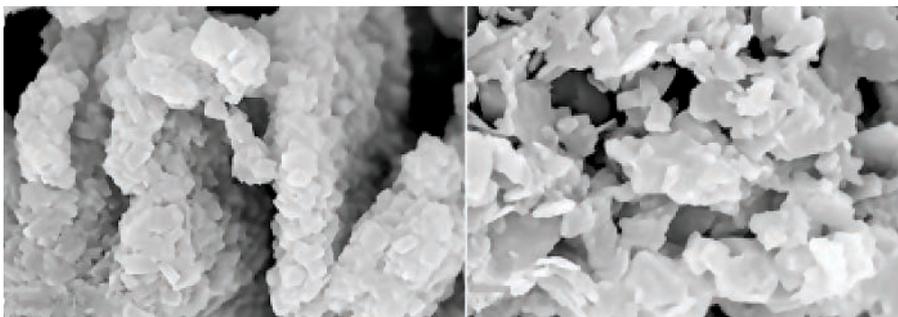
Element	Concentration on magnet vs. pan	Comment
V	1.08	Mobile
Ca	1.31	
Added Fe	1.78	
Ni	1.59	Immobile

**TABLE 4.** Standard deviation (SD) of metals levels on an Ecat density separated into four fractions (shown in **FIG. 6**). A low standard deviation implies high mobility, as with V.

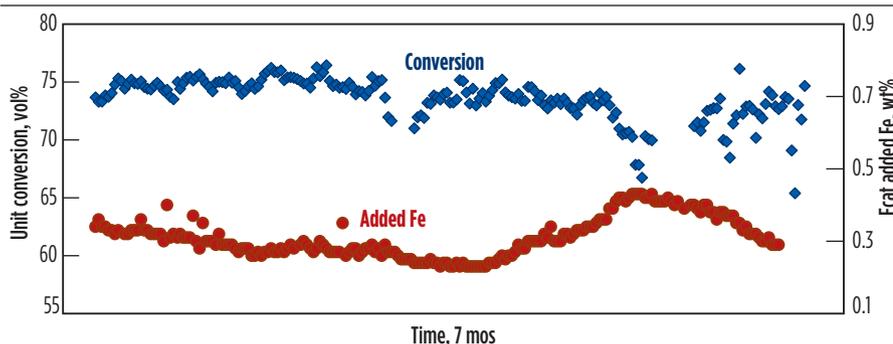
Element	SD, %
V	10
Ca	17
Added Fe	17
Ni	26



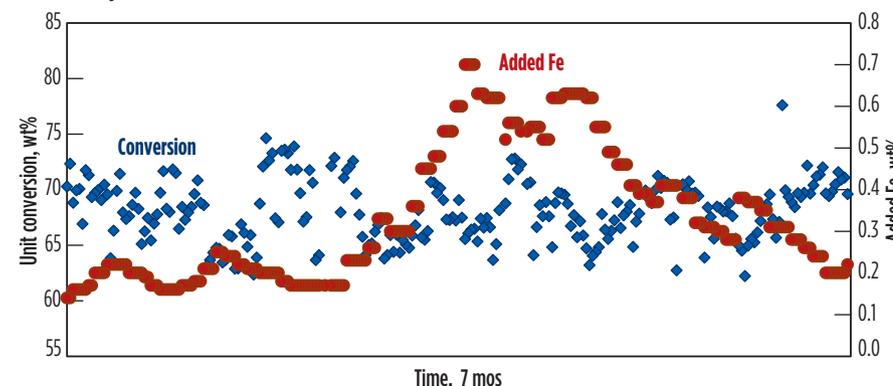
**FIG. 6.** Metals analysis on an Ecat density separated into four fractions, normalized to 1 (heavy fraction).



**FIG. 7.** Enhanced surface porosity (left) via in-situ manufacturing and hindered surface porosity (right).



**FIG. 8.** A unit using other catalyst experienced a loss of conversion when added Fe was increased by 0.2 wt%.



**FIG. 9.** A unit using in-situ catalyst saw no decrease of conversion when added Fe was increased by 0.55 wt%.

This enhanced surface porosity is the key to withstanding Fe poisoning. With a greater number (and diameter) of surface pores, the tolerance to added Fe is much higher.

Surface porosity can be measured by sophisticated techniques, but a visualization of the surface porosity can be obtained via SEM. In **FIG. 7**, the high surface porosity (left) is demonstrated via SEM, whereas an alternative manufacturing process can produce catalyst with hindered surface porosity (right).<sup>3</sup> In-situ manufacturing can be used for catalyst to provide excellent Fe tolerance (**FIG. 7**).

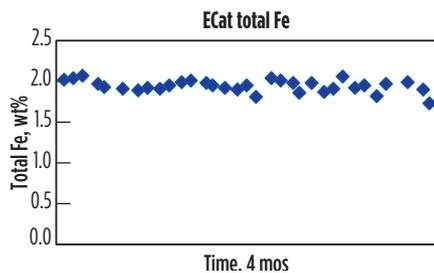
**Case studies: FCCUs with high Fe.**

Fe poisoning can lead to a loss in unit conversion and an increase in slurry API gravity with catalysts that have hindered surface porosity. This scenario is demonstrated by a case study of a Middle East refinery using non in-situ catalyst that ran a 19°API (0.94 standard gravity, or SG) feed with Ecat Ni of 5,800 ppm–6,700 ppm, Ecat V of 4,000 ppm–6,300 ppm, and Ecat added Fe of 0.2 wt%–0.43 wt%. Over the course of 7 mos, the refinery saw an added Fe increase from 0.23 wt% to 0.43 wt% ( $\Delta 0.2$  wt%).

At the same time, unit conversion dropped 4 vol%, and slurry API gravity increased significantly. When monitoring an Fe excursion, it is imperative to track other contaminants to rule out impacts from Ni or V. During this 7-mos period, the Ni and V were constant or decreasing. Therefore, the problem at the refinery was attributed to Fe coming in with the feed (**FIG. 8**).

The second example is taken from a residue FCCU at a refinery in Asia-Pacific using in-situ catalyst. The unit ran a 21°API–26°API (0.894 SG–0.929 SG) feed with Ecat Ni of 1,500 ppm–3,000 ppm, Ecat V of 1,100 ppm–2,800 ppm, and Ecat added Fe of 0.1 wt%–0.7 wt%. The Fe increased significantly, from 0.15 wt% to 0.7 wt% ( $\Delta 0.55$  wt%) over 7 mos with no observable loss in unit conversion. During the same period, other contaminants (Ni, V) decreased or stayed the same (**FIG. 9**).

The third commercial example came from a unit in North America. The resid unit processed a feed of 24°API–26°API with Ecat Ni of 2,200 ppm–4,100 ppm, Ecat V of 2,000 ppm–3,800



**FIG. 10.** A unit was successfully run, without operational issues, with 2 wt% Fe using in-situ catalyst.

ppm, and Ecat added Fe of 0.6 wt%–1.5 wt%. With in-situ catalyst, the unit was run successfully above 2 wt% total Fe (FIG. 10). The catalyst demonstrated high tolerance to Fe. During an Fe excursion where Fe increased from 0.6 wt% to 1 wt% (0.4 wt% increase), the unit maintained the same high unit conversion of 75 vol%–80 vol% (FIG. 11).

For units that are experiencing Fe-related problems, a number of operating strategies to help mitigate the effects are available:

1. Ensure that the fresh catalyst type is suitable for handling high Fe levels and surface blockage effects, such as in-situ technology
2. Flush excess Fe from the unit, preferably with flushing catalyst (since Fe does not destroy zeolite activity, fresh catalyst is not needed), which will also help with any circulation concerns
3. Maximize the catalyst-to-oil ratio by decreasing feed preheating or minimizing regenerator temperature by adjusting CO/CO<sub>2</sub> or catalyst cooler duty; however, avoid raising the riser outlet temperature, which can cause excess dry gas if at a dry gas limit
4. Seek ways to reduce Fe in the feed through crude desalting or feedstock selection
5. Increase fines content, either in the fresh catalyst or by using

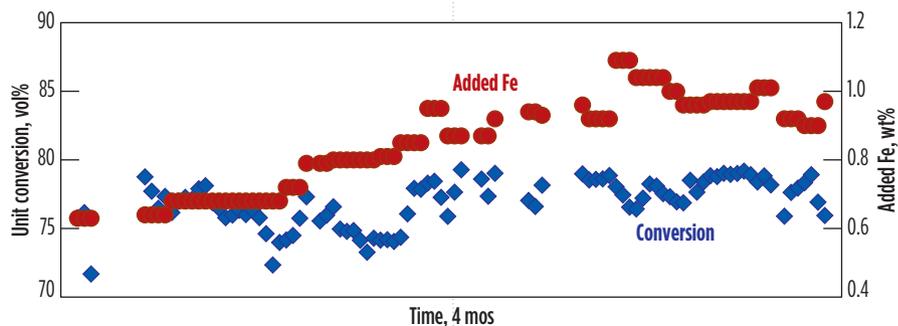
a fluidization additive if circulation instability is present.

**Recommendations.** Understanding catalyst limitations and operating windows for all metal contaminants, including Fe, allows a refinery to operate in a safe window and foresee problems that might arise with changing crude slates. Depending on the catalyst technology and type, the operational windows for acceptable contaminant levels will vary.

When dealing with Fe contamination from feed, a refiner must consider different aspects of Fe poisoning, including chemical and physical effects. The authors' company has extensively investigated Fe poisoning, including chemical and physical effects, the ultimate fate of Fe, and Fe mobility—it effectively attributes Fe tolerance to optimized surface porosity.

In general, the physical effects of Fe cause the most operating trouble. Fe deposits on the outside surface of the catalyst, which can physically block the access of feed molecules to the interior of the catalyst particle if the incorrect catalyst is used.

An investigation of Fe mobility shows that Fe has low mobility, close to that of Ni and lower than V. Due to the low mobility, the key to strong Fe tolerance appears to be surface porosity. In case studies, the use of a catalyst with high surface porosity has given high performance, even with Fe of greater than 2 wt% and no conversion debit. **HP**



**FIG. 11.** Added Fe increased by 0.4 wt%, with no impact on conversion, using in-situ catalyst.

#### NOTE

This paper was originally presented at AFPM Annual Meeting 2017.

#### LITERATURE CITED

- <sup>1</sup> Wieland, W. S. and D. Chung, "Simulation of Fe contamination," *Hydrocarbon Engineering*, March 2002.
- <sup>2</sup> Vincz, C., R. Rath, G. Smith, B. Yilmaz and R. McGuire Jr., *Appl. Catal. A*, Vol. 495, 2015.
- <sup>3</sup> McLean, J. *et al.*, "Distributed matrix structures—A technology platform for advanced FCC catalyst solutions," NPRA Annual Meeting, March 2003.



**ALEXIS SHACKLEFORD** is the Technical Service Specialist for BASF. She is involved in FCC catalyst troubleshooting, technical service, publications, presentations and new product introduction, and has provided FCC research and development testing support. She joined BASF's refining catalyst division in 2009. Prior to BASF, Ms. Shackelford worked at Shell Oil Co.'s Deer Park Refinery for 3 yr as a process engineer in various roles supporting projects and operations. She holds a BS in chemical engineering from Michigan State University.



**MELISSA CLOUGH** is an FCC technologist with BASF. She has worked with BASF since 2012 and has held multiple roles prior to FCC, including pharmaceutical research and development, and industrial gas procurement. In her present role, Dr. Clough is involved with new product development and introduction, catalyst testing and technical service requests. She holds a PhD in chemistry from Texas A&M University, a BS in chemistry from the University of Florida and an MBA from the University of North Carolina.