Combating the Negative Effects of Iron in the FCCU at Philadelphia Energy Solutions Refining and Marketing, LLC

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Abstract
The growth in domestic crude production, specifically tight oils, has resulted in new challenges for refiners. Elevated levels of contaminant iron in crude are becoming the norm. Downstream, iron poisoning in the FCCU was once an isolated phenomena, limited to a handful of refiners processing opportunity crudes. Today, as domestic crude processing grows, more refiners are experiencing the effects of elevated iron in the FCCU. Even in the face of dynamic global crude prices, processing of domestic shale oils is expected to remain an important part of the refining landscape in North America and other regions throughout the world. To maintain operating flexibility and profitability, refiners need effective strategies to manage unconventional contaminant metals and minimize the unfavorable consequences those metals can have on FCC unit operation, including loss in fuels selectivity, unstable circulation, and reduced bottom of the barrel conversion, ultimately leading to lower margins across the FCCU.

Philadelphia Energy Solutions Refining and Marketing, LLC (PES) operates a refinery complex on the US East Coast and processes a high percentage of domestic crude containing elevated iron levels. As a result, PES has observed iron poisoning impacts at its resid FCCU. With a combination of operating strategies and FCC catalyst optimization, PES has learned how to maintain profitable operations within a dynamic and challenging refining environment. Together with Grace, PES will describe the methods utilized to monitor, manage and minimize the impacts of high iron levels in the resid FCCU. This paper describes in detail the multi-faceted strategy, which includes feed property monitoring, troubleshooting and optimization of the FCC operation, catalyst make-up strategies, and PES’s catalyst reformulation to Grace’s MIDAS® Gold FCC catalyst.
Executive Summary

Iron poisoning of FCC catalyst was first discovered in the 1990’s commercially and not experienced within the Philadelphia Energy Solutions Refining and Marketing, LLC (PES) refining system until 2013. In large part, iron contamination of FCC catalyst was not widely publicized due to low-iron feedstocks [1] however, as seen in crudes from newly developed domestic fields, iron in FCC feeds and subsequently on FCC Ecat has been increasing and needs to be managed. Iron can react with alkali metals to form a barrier layer on the equilibrium FCC catalyst surface that blocks access, thereby preventing oil from penetrating into the catalyst and reaching active cracking sites. This pore blockage will decrease conversion and increase low value bottoms yield. In addition, this barrier layer often presents a “nodule” morphology. Iron nodules on the surface of the catalyst can disrupt catalyst fluidization. PES operates two FCC units in their Philadelphia area refining system. One FCCU is a Kellogg Ultra-Orthoflow design and is referred to as 868 (Point Breeze) Unit, while the other is a Kellogg Model III design referred to as the 1232 (Girard Point) Unit. PES first experienced iron poisoning at 868 in 2013 and more recently at 1232. In both cases the catalyst activity and fluidization properties were restored by reducing the feed iron and flushing with catalyst additions. This paper will discuss these events as well as methods PES used for addressing contaminant iron.
Background on Iron Contamination

Metal contaminants such as sodium, vanadium, nickel, calcium, and iron enter the FCC unit via the hydrocarbon feed. Iron tends to concentrate in the heavier cuts of the crude oil, much like other metal contaminants. While particulate tramp iron from rusting refinery equipment does not have a significant detrimental effect on catalyst, finely dispersed iron particles in feed (either as organic compounds or as colloidal inorganic particles) can deposit on the catalyst surface, reducing catalyst effectiveness [2, 3]. The iron in the feed can come from corrosion products (such as iron naphthenates) or from iron containing compounds in the rock formations [4].

Deposited iron combines with silica, calcium, sodium and other contaminants to form low melting temperature phases, which occludes the pore structure of the exterior surface, preventing feed molecules from entering the catalyst particle and reducing conversion [5]. Figure 1 presents cross-section iron mapping showing the formation of iron rings on catalyst particles. Iron in combination with calcium and/or sodium can have a greater negative effect on catalyst performance than iron alone. Symptoms of iron and calcium poisoning include a loss of bottoms cracking, as feed particles are blocked from entering the catalyst particle, and a subsequent drop in conversion. In addition to a drop in conversion and a decline in bottoms cracking, poor catalyst circulation is often a symptom of iron poisoning of FCC catalyst due to nodule formation as shown in Figure 2.

![Cross section iron mapping of 1232's Ecat dated 6/19/14 with 0.79 wt% Fe.](image.png)
While iron can be present in many crude sources, it has been found to be especially common in tight oil derived feeds. As a result of the increasing amount of tight oil in the refinery feed slate, PES protocol has been set up to sample all incoming crudes. In the limited time that PES has been testing crude sources, it has become apparent that iron can be variable within a specific crude source. Shale oils in particular have tended to have more variability. There tends to be additional sediment in the shale oils that contain high levels of iron and calcium [4]. In particular, PES has seen some variability in iron levels in the shale crude as shown in Figure 3 below.

![Figure 2: Example of Ecat Nodules due to Iron Poisoning.](image1)

![Figure 3: Delivered Shale Oil A iron analysis to PES.](image2)
A spike up to 55 ppm as shown above is substantial equating to over 4,000 lbs of iron more than the base crude, leading to significant impacts to the operation of the FCCU. Due to the variability and limited iron information, PES has implemented iron and calcium testing on all incoming crudes. The testing of the feed sample allows the refinery to anticipate and make adjustments in fresh catalyst additions.

While feed testing helps monitor the level of iron entering the FCCU, it is also important to do analysis of Ecat to track iron poisoning. The levels of iron and calcium can be measured via chemical analysis of the Ecat. Since both iron and calcium primarily deposit on the surface of the catalyst, most of the catalyst particle is unaffected by these metals. In monitoring the iron level of the Ecat, it is important to note that in addition to entering with the feed, iron is present in FCC catalyst as an element in the clay used in manufacture. Hence, the iron content of the fresh catalyst is dependent on the clay source and the clay content of the catalyst and will vary from supplier to supplier and catalyst to catalyst. It is important to look at incremental iron rather than total iron since the iron from clay does not impact catalyst performance. If the iron level of the fresh catalyst is known, incremental iron can be tracked. Since iron poisoning mostly affects the surface of the catalyst particle, surface area and pore volume may not necessarily change. Bottoms conversion in Ecat ACE testing will drop and in cases of severe iron poisoning, nodules will be apparent on the surface and the ABD will drop. A drop in ABD is due to the nodule formation on the catalyst which prevents the Ecat from packing as densely [5].

The surface plugging of pores can be monitored by utilizing inverse gas chromatography to determine the effective diffusion of a bulky probe molecule into the catalyst pore system in the gas phase [6]. This test provides an effective diffusivity ($D_{eff}$) coefficient for the Ecat, with higher values indicating a structure with better diffusion. As witnessed during 1232’s event, the Grace diffusivity test gave reliable and consistent data which indicated an iron poisoning event. (Figure 4) The gas based inverse gas chromatography test proved more responsive than a competitive liquid phase diffusion test used to measure diffusion resistance.
Factors such as catalyst type, unit conditions, and the presence of other catalyst poisons will influence the iron tolerance of the catalyst. Unit 1232 has a low riser residence time, therefore the contact time between oil and catalyst is low. Iron has been observed to be a greater problem for units with low contact times due to catalyst diffusion impacts [7]. Since 1232 and 868 units process feeds with high levels of calcium, both catalyst are susceptible to iron poisoning at lower levels of iron than other units with lower levels of calcium in the feed. As seen below in Figure 5, Girard Point and Point Breeze’s catalyst have the highest levels of contaminant calcium in North America.

Iron may also cause dehydrogenation reactions, however nickel has ~10 times the dehydrogenation activity of iron [8]. Due to relatively high levels of nickel on both 868 and 1232 catalyst, the dehydrogenation reactions attributed to iron were not apparent.

Iron poisoning of FCC catalyst has been an area of major discussion and research in the FCC industry, and many of the challenges observed in the field have been challenging to translate to the laboratory environment for more rigorous study. Iron feed typing plays a critical role, as does the rate of total Fe deposition, the interaction with alkali earth metals, the hydrothermal environment in the FCC, and the total incremental Fe present on the FCC Ecat. Based on all of these factors, detecting Fe poisoning in the FCC often requires close monitoring and extended analytical testing to be carefully detected.
The next sections will discuss in detail two specific iron excursions that occurred at PES and the impact they had on the FCC units.

**PES Iron Excursions**

**FCCU 868 Event**

The first event occurred in March of 2013, the Point Breeze Fluid Catalytic Cracking Unit, 868, experienced severe fluidization problems. The 868 unit is a full burn unit with the disengager located above the regenerator. The catalyst travels from the disengager stripper down a large internal spent catalyst standpipe to a plug valve before entering the regenerator. The fluidization instances in March 2013 were manifested in the form of an increase in the disengager stripper level. The operations team was able to temporarily resolve the issue by reducing riser outlet temperature and overall unit charge rate to reduce the required catalyst circulation rate.

![Figure 6: 868 Disengager Level during a Defluidization Event.](image)

During this time frame, it was noted that the Ecat and ESP fines had turned a brownish hue as seen in Figure 7 below. Ecat analysis of the circulating inventory showed an iron concentration increase of 0.27 wt% within a month and 0.14 wt% in a week. ABD of the catalyst decreased over 0.05 g/cc during this time frame. Minor fluidization issues persisted until the catalyst addition rates were increased to flush the metals and restore fluidization properties.
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Figure 7: 868 Ecat (left) and Catalyst Fines from March 22, 2013 exhibit a brownish hue, attributable to the iron poisoning event.

Figure 8: Ecat iron trends at unit 868.
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Figure 9: SEM of 868’s Ecat dated 3/27/13 with 0.77 wt% Fe.

![SEM Image]

Figure 10: ABD decreased with iron at unit 868.

868 ECAT (Feb - April 2013)

- ABD, g/cc
- Fe, wt %

0.77 0.78 0.79 0.8 0.81 0.82 0.83 0.84 0.85 0.86 0.87 0.88
0.50 0.55 0.60 0.65 0.70 0.75 0.80
FCCU 1232 Event
The second event occurred in late June of 2014. The Girard Point Fluid Catalytic Cracking Unit, 1232, witnessed higher than expected slurry yields, lower than expected residual processing, and catalyst circulation limits. The slurry yields were relatively high from mid-May to mid-June while processing opportunity crude. This crude produces a poor FCC feedstock that is low in aniline point and UOP K factor, highly viscous, as well as high in basic nitrogen, nickel, and vanadium. The lower resid processing was mostly blamed on the feed quality, however, when the feed quality improved in late June, resid processing continued to suffer.

The catalyst circulation limitations were noted in the form of low slide valve differential pressures as seen by the drop in Figure 11. 1232 has a large slanted regenerated catalyst standpipe with 10 aeration nozzles. The aeration nozzles rates were adjusted several times in attempts to improve circulation, however, only small benefits were noted.

![Slide Valve DP, in. H₂O](image)

Figure 11: 1232 Total Slide Valve Differential Pressure.

This launched a root cause failure analysis (RCFA) that included checking: feed/slurry leaks, feed atomization, catalyst circulation problems, feed quality, fractionator tower performance, fresh catalyst quality, purchased equilibrium catalyst quality, and catalyst loader reliability. During the RCFA, it was noted that the actual slurry yield was approximately 3 vol% higher than predicted as demonstrated in Figure 12.
Since the 2007 major revamp of 1232 unit until 2014, the iron on the catalyst remained in the range of 0.45 to 0.65 wt % (Figure 13). In early 2014, the iron on Ecat started to climb. The level peaked just above 0.8 wt % iron or just more than 0.5 wt % incremental iron in early June of 2014.

When the iron started to decline in mid-July due to high catalyst addition rates, the slurry yield also declined allowing operations to increase resid processing. This restored Vacuum Gas Oil (VGO) and resid balances within the refinery.
Adding to the complexity of the high iron and low resid processing was a catalyst change at 1232. Starting on April 24, 2014, Girard Point started changing out the catalyst from the previous supplier to Grace. As the iron increased on the catalyst, Grace took scanning electron micrographs (SEMs) to monitor the health of the catalyst. SEMs may not show nodule formation at the start of an iron excursion. It has been suggested that iron on the catalyst can take time and temperature to vitrify and plug up the pores. In the case of 1232’s Fe poisoning event, the negative yield & catalyst effects did not occur at the onset of the high Fe measurements in the feed. This experience reinforced the value in tracking the diffusivity properties of the catalyst when metals (iron and calcium) that inhibit diffusion are high, since bulk Ecat Fe determination alone was not enough to adequately diagnose the Fe contamination.

The SEM pictures and diffusivity results showed that Grace’s MIDAS® Gold FCC catalyst had superior iron tolerance in the face of higher metals as shown in Figures 14 through 16 as evidenced by the smoother appearance of the FCC catalyst particles themselves.

Figure 14: SEM of 1232’s Ecat dated 03/27/14 with 0.69 wt% Fe and 1.15 wt% CaO.
Figure 15: SEM of 1232’s Ecat dated 5/15/14 with 0.74 wt% Fe and 1.22 wt% CaO.
Figure 16: SEM of 1232's Ecat with the use of Grace's MIDAS® Gold dated 5/22/14 with 0.79wt% Fe and 1.14 wt% CaO.

Figure 17: Grace's Diffusivity Data and Ecat Iron vs. Time.
Values less than 20 on the Grace effective diffusivity test can begin to show diffusion limitations. As seen in Figure 17 above, the diffusivity suffered once iron levels rose above 0.75 wt %. One theory is that there is a time lag for vitrification of iron on the catalyst that may explain the delay in diffusion drop off initially at high iron levels. Due to the dramatic drop off and subsequent improvement in diffusion and unit performance, this suggests that the iron threshold for the 1232 Unit is about 0.75 wt % (or 0.45 – 0.5 wt% incremental iron). The lower diffusivity values on the catalyst resulted in lower residual charge to the unit. This was not restored until the diffusivity of the catalyst increased. MIDAS® Gold catalyst has shown effective diffusivity levels up to 175 on the 1232 Ecat when contaminants returned to typical levels.

As seen in Figure 18, the resid processing was limited by nearly 10 MBPD of resid due to diffusion limits. This impacted refinery VGO and resid balances forcing crude units to cut charge to limit resid production. Refinery Linear Program (LP) predictions assumed much better bottoms cracking based on the feed quality, however, the iron poisoning explained the gap between expected and actual results. PES has since worked with the planning and economics group to ensure that the economic analyses done on different crude sources takes into account the impact of potential iron poisoning on the FCC performance.

Figure 18: 1232 Residual Processing Rate and ECAT Iron vs. Time.
Methods for Combating Fe Contamination

Now we will move on to discuss all of the methods that PES used to overcome the effects of iron poisoning at both units. These methods are a combination of preventative, routine monitoring, and actions to help lessen the detrimental effects. We will discuss routine feed and Ecat testing, optimum catalyst selection, and iron reduction methods.

Feed Testing

There are two common ASTM methods for determining iron content in hydrocarbon streams. ASTM D5708 utilizes Inductively Coupled Plasma (ICP) while ASTM D5863 utilizes Flame Atomic Absorption Spectrometry. Both methods give two possible methods for preparation [9, 10]. Since D5708 is utilized at PES, discussions below will focus on this procedure. Method A of D5708 prepares the sample by dissolving in an organic solvent while Method B uses hydrofluoric acid. It is important to perform a proper safety hazard analysis before changing from a solvent to acid digestion method, as working with acid in the lab requires different safety processes.

Grace has conducted significant research in the area of feed analysis and has found that preparing the sample with acid digestion will yield more accurate results. The acid digestion method (B) will measure the total metal content, whereas the solvent digestion method (A) will not detect metals present in insoluble particulates. This was evident with calcium in the past in FCC feed at PES, and has now been noted with iron. The balances around iron on the FCC Ecat stopped closing in April of 2014 when PES began processing a significant amount of shale oil crude. At this time, PES started testing samples via the acid digestion method to better understand the total iron and calcium levels being charged to the FCC units. As seen below in Figure 19, the iron levels measured by the acid digestion method averaged 30% higher than those measured by the solvent digestion method, with occasional differences greater than 50%.

![Figure 19: 1232 Feed iron testing by ICP. Acid digestion (B) vs. solvent digestion (A).](image-url)
Not only is routine and accurate feed analyses essential for an accurate FCCU iron balance, it is also critical for maintaining healthy levels of contaminant metals, especially iron on FCC Ecat. A proactive response to unexpected spikes in feed iron can allow the Refinery to continue to operate at planned rates economically. In addition, this data can be used to work with crude purchasing groups to select the optimum crude(s) for the Refinery by minimizing difficult contaminant metals such as iron.

**Ecat Monitoring**

Grace and PES collaborated to develop an extensive monitoring matrix based around Ecat analyses and key FCC unit performance variables. This program focused on symptoms or indicators along with variables used to monitor changes with action triggers and appropriate responses.

Based upon concerns expressed by the Refinery, the key variables monitored most closely were:

- Metals levels, specifically iron and calcium
- Ecat activity range, both high and low
- Unit response to catalyst physical properties (losses and fluidization)
- Yield selectivities

Predetermined variables for each area were monitored via a gamut of catalyst and unit operational indicators. As an example the fluidization response chart is shown as Figure 20. Similar response charts were prepared for each of the above focal points.

![Figure 20: Equilibrium Catalyst Fluidization Monitoring.](image-url)
To support the unit operating health monitoring, a standard and routine sampling procedure was established to provide key information. Most of this sampling was routine to FCC audit and control, for example regular and frequent Ecaterpillar and feed sampling. These routine methods were used to calculate the FCC unit iron balance. Iron on Ecaterpillar, purchased Ecaterpillar (PCAT), and feed were all tracked. Building a database from these analyses helped to establish the added iron threshold for the PES FCCUs. Calcium balances were built using the same analyses. Shifts in catalyst apparent bulk density (ABD) were also successfully used to detect early stages of iron poisoning Figure 21.

![Figure 21: PES 1232 Ecaterpillar ABD versus Fe wt%](image)

Matching purchased equilibrium catalyst (PCAT) to the unit objectives and constraints was also important for successful FCC unit operations. Using the Grace equilibrium catalyst database, inconsistencies in properties between PCAT and the base catalyst were identified particularly in bottoms cracking and gasoline/LPG selectivity. PCAT purchases were adjusted to select materials more compatible with the catalyst and objectives as shown in Figure 22.
The non-standard Ecat testing however was very significant in terms of unit support. In particular Ecat was regularly tested for diffusivity limitations as shown in Figure 17. Using the IGC methods cited above, Grace and PES were able to quickly distinguish between true iron contamination problems and other causes of unit changes unrelated to iron in feed and on Ecat. This helped direct and more precisely focus activities and response to unit operations and yields.

Another non-standard method employed was scanning electron microscopy (SEM) as shown in Figures 14, 15, and 16. SEM’s are an excellent qualitative method for detecting iron nodules. Also, Grace used the EPMA method as shown in Figure 1 to map concentrations of contaminant metals on the surface of the catalyst.

During the initial stages of the operation with MIDAS® Gold FCC catalyst, ACE testing was conducted to differentiate between feed, operations and catalyst effects in the 1232 Unit. Calcium and iron in feed were related to different crude types and the inputs of various crude sources were continuously monitored in order to isolate and identify changes arising from these factors. As discussed, numerous routine and non routine analytical methods were put in place to monitor the Ecat for iron contamination.
Feed Treatment
Reducing iron to the FCC by all means possible can prove to be a very cost effective step. Managing corrosion in the refinery is not only a good safety practice, but it can also limit the iron to the FCC. Desalting alone can help remove some iron, however desalting will not remove organic iron. Desalter acidification has also been documented to enhance oil/water separation leading to lower salt, sediment, and water in the desalted crude as well as help with the removal of some metal contaminants in the crude [11]. Desalter acidification has been applied to PES Girard Point (GP) Crude Unit. This was done mainly to remove calcium from a high calcium opportunity crude oil in order to protect the catalyst activity at the FCC units; however a secondary benefit has been the removal of iron from the crude oil as seen in Figure 23.

Figure 23: Iron Removal vs. Acetic Acid Rate (CRA) from March – September 2014 at the GP Crude Unit.

As mentioned above, the shale oils tend to have solids that contain high amounts of calcium and iron. Therefore, it is desirable to knock these solids out if possible before the FCC. Solids wetting agents (or removal agents) can help drop solids including colloidal particles of iron and calcium into the water phase helping to remove these particulates. This additive can also improve desalter operation by reducing solids and emulsions build up inside the desalter leading to increased desalter residence times. A solids removal agent was introduced into the Girard Point Crude Unit in September of 2014 with the intent to reduce iron in the FCC feed. Results of the solids removal agent coincided with a drop in iron results as seen in Figure 24 below.
In addition, the solids removal agent also showed a slight drop in calcium to both cat cracking units. Removing calcium from the FCC feedstock as well as sodium will help reduce the degree of iron poisoning since these metals work together to limit diffusion. PES does not have a cat feed hydrotreater available to remove contaminants, therefore proper desalting is essential.

**Catalyst Flushing**

Another method for combating iron contamination is to simply flush it out of the circulating inventory at a faster rate than it is being deposited on the catalyst from the feed. It is fairly common in resid units to implement a catalyst flushing program to control contaminant metals such as Ni, V, Na, and Ca. The catalyst flushing program can be expanded to include iron. This can be accomplished with increased fresh catalyst additions, PCAT additions, or a combination of both. Studies have shown that iron present in the base clay from the catalyst manufacturing process does not contribute to surface plugging. Optimum fresh catalyst formulation is critical in higher iron services and will be discussed in detail in the next section. However, it is as important to select a good quality purchased Ecat that has low added iron content. It is recommended to sample each PCAT delivery to monitor quality of the material. This will also help with closing the “added” iron balance for the unit. Also, when using a significant amount of PCAT (>25%), you should consider other properties such as zeolite and matrix surface areas. PCAT can affect product selectivities and operating variables like fresh catalyst but to a lesser extent.

The use of incremental fresh catalyst additions is more effective because it doesn’t contain added iron as shown in Table 1. In addition, the incremental activity is often valuable during an iron excursion. However, flushing with fresh catalyst alone can lead to elevated activity which can cause other operating limitations such as high regenerator dense bed temperature. For larger resid units the optimum plan could be a mix of both fresh and PCAT. PCAT has a secondary benefit of lower OPEX.
Table 1: - Theoretical Fe Removal via Catalyst Flushing

<table>
<thead>
<tr>
<th>Catalyst Add Rate</th>
<th>Fresh Catalyst Iron</th>
<th>Unit Ecat Iron</th>
<th>Quantity of Flushed Iron</th>
<th>Equivalent Feed Iron*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ton/day</td>
<td>wt%</td>
<td>wt%</td>
<td>lb/day</td>
<td>ppmw</td>
</tr>
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<td>0.75</td>
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<td>0.75</td>
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<table>
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<th>Catalyst Add Rate</th>
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<th>Unit Ecat Iron</th>
<th>Quantity of Flushed Iron</th>
<th>Equivalent Feed Iron*</th>
</tr>
</thead>
<tbody>
<tr>
<td>ton/day</td>
<td>wt%</td>
<td>wt%</td>
<td>lb/day</td>
<td>ppmw</td>
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<td>0.75</td>
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<tr>
<td>15.0</td>
<td>0.60</td>
<td>0.75</td>
<td>45</td>
<td>2.8</td>
</tr>
</tbody>
</table>

*Assumes a charge rate of 50 MBPD and 24° API

In the case of the Girard Point 1232 iron excursion mentioned above, a combination of increased fresh catalyst and good quality PCAT additions was used to combat the negative effects of iron poisoning. To overcome equipment limitations, PES worked with Grace to increase the capacity of its catalyst loading system. It is important to work closely with the fresh catalyst and PCAT suppliers to develop the best flushing plan for each respective unit. Several factors such as catalyst selectivities, catalyst activity, and unit limitations should be considered to ensure a successful recovery while maximizing product yields.
Catalyst Selection

Multiple unit objectives and constraints had to be considered when Grace chose the optimum catalyst for the 1232 unit. Chief among these was metals tolerance. As noted throughout, overcoming the effects of contaminant iron and calcium were key factors. As high levels of resid were commonly processed, coke-selective bottoms cracking was essential. Moreover, catalyst fluidization was critical for this older FCC unit with long standpipes.

Pore Size Distribution Considerations

The importance of pore size in FCC catalysts to selectively crack resid fractions while avoiding diffusion limitations is well known [12]. Catalysts that have a high level of mesoporosity in the 100-600 Å range as measured by mercury (Hg) porosimetry are able to selectively crack heavy hydrocarbons that might ordinarily be coke precursors.

Equally important is the minimization of sub-optimal micropores of less than 100 Å diameter. Cracking that occurs in micropores is severely diffusion limited leading to excessive yield of coke and gas. As shown in Figure 25, MIDAS® catalysts have a substantial advantage over the base catalyst in use at PES in both mesoporosity and low level of micropores.

![Hg Porosimetry for MIDAS® FCC catalyst compared to other catalysts](image-url)
Resid cracking involves the destruction of complex, metals-laden hydrocarbons. Design of the MIDAS® Gold FCC catalyst for the 1232 unit took into account the need to resist the deleterious effects of nickel (Ni) and vanadium (V), as well as iron and calcium in the feed.

In combination with the selective bottoms cracking matrix component present in MIDAS® Gold, additional components were included in the formulation to selectively react with Ni to form a nickel aluminate which is drawn away from the catalyst active surface and retards dehydrogenation reactions caused by Ni on equilibrium catalyst. These reactions are primarily related to formation of hydrogen and coke.

The zeolite chosen for use in the PES 1232 unit application has an appropriate degree of rare earth stabilization to protect the zeolite against attack by vanadium from the FCC feed. As shown in Figure 26, this goal was readily achieved and the catalyst showed better vanadium tolerance than the previous catalyst as measured by microactivity retention.

![Figure 26: MIDAS® Gold retained higher Ecat MAT activity at constant Vanadium in the PES 1232 Unit.](image-url)
Catalyst Fluidization

The ability to fluidize and circulate catalyst is critical for this Model III FCC unit. The ratio of minimum bubbling velocity to minimum fluidization velocity ($U_{mb}/U_{mf}$) is a well known measure of a catalyst’s ability to meet these goals. With the switch to MIDAS® Gold, the Ecat $U_{mb}/U_{mf}$ actually improved despite higher iron on Ecat. Adjustments were also made to fluidization media to help optimize catalyst circulation.
Conclusions
There are numerous causes that lead to poor FCC yields and profitability. Contaminant iron in FCC feed can have severe impacts on the operation of the FCC leading to significantly lower profitability. The first step to steady reliable operation is to routinely monitor crudes, cat cracker feed and Ecat for advance warning that iron is on the rise. It is important to properly analyze the feed with the appropriate ASTM method as discussed. Next, the Refinery should work closely with their catalyst supplier to monitor the unit Ecat for total incremental Fe, diffusivity, and nodule formation with SEM’s. If economical, refiners should work to minimize feed iron through selective crude purchases and/or chemical feed treatment. Units with the possibility of elevated iron should consider selecting an FCC catalyst with an optimized pore size distribution such as Grace’s MIDAS® technology. Finally, refiners should implement a catalyst flushing program that can be 100% fresh catalyst or a combination of fresh and purchased Ecat. Sometimes this requires an upgrade in catalyst storage and loader capacity, but can be justified by the prevention of a single iron poisoning event.

With appropriate planning, monitoring, and collaboration, it is possible for refiners to maintain profitable operations in the face of highly variable feed contaminants such as iron.

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Works Cited


