In today’s refining environment, you need to be ready for anything.

The new ACHIEVE® series of FCC catalysts from Grace hands you the versatility and functionality you need for today’s dynamic refining environment. Select the ACHIEVE® advantage that’s right for your feeds, your process, and your business requirements.

<table>
<thead>
<tr>
<th>ACHIEVE® 100</th>
<th>High activity for light feedstocks</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACHIEVE® 200</td>
<td>Coke-selective bottoms conversion</td>
</tr>
<tr>
<td>ACHIEVE® 300</td>
<td>Propylene selectivity</td>
</tr>
<tr>
<td>ACHIEVE® 400</td>
<td>Octane and butylene selectivity</td>
</tr>
<tr>
<td>ACHIEVE® 800</td>
<td>Maximum metals tolerance and resid conversion</td>
</tr>
</tbody>
</table>

Get all the tools you need.

Visit grace.com/achieve to learn more about how we can tailor a formulation to meet your most challenging requirements.
It has been several months since we became “new Grace” following the spinoff of Grace Construction Products (GCP), and I have been enjoying my new role as President of Refining Technologies, which includes our FCC catalyst business and our ART Joint Venture with Chevron Products Company. Al Beninati continues to serve as President of our Specialty Catalysts business, and we will continue to collaborate on the publication of the Catalagram® to serve our customers across the businesses.

After serving as President of our former construction products business, being back in Refining Technologies feels like a homecoming—I joined the FCC business back in 1994 as a research engineer—and I have really enjoyed getting reacquainted with the business and meeting a number of our customers around the world.

Following the split with GCP, Grace has entered a new era focused on our core strengths. To some, those strengths are product technologies in catalysts and materials. To me, our core revolves around the items in our company tagline: talent, technology, and trust. Those three areas all support one common goal of our company—they guide Grace to provide the best possible products and service to our customers.

Throughout this issue of the Catalagram®, you will read a number of articles that focus on customer collaboration—a very important element in all of our catalyst businesses. We recognize that your business needs and objectives change over time. It is therefore increasingly important for us to work with you to ensure that we are providing the best possible solutions, featuring the right products and technologies to optimize your operations.

We have taken great strides in increasing our collaborative efforts to ensure that our customers realize the most financial value from our products. To that end, we have created a new global organization focused on providing the best possible technical service. I am happy to report that Dennis Kowalczyk, who has led the FCC business for the Americas, has been named Vice President of Global Customer Technology for FCC. Dennis will lead a specialized team that will provide high-level service around the world, and develop best practices and tools to help our customers get the highest financial value from our catalysts. Additionally, this team will represent our customers’ view in our R&D product development activities to accelerate new product commercialization and ensure we are working on the most important problems to our customers.

I am also pleased to welcome Jeff Balko back to Grace as Vice President of Sales for FCC Americas. You will find Jeff to be a strong partner, leveraging his prior FCC experience from Grace and Mobil Oil.

I look forward to working together with you to meet the challenges of today’s refining industry head-on, and continue to develop products to meet the challenges of the future.

Tom Petti
President
Refining Technologies
W. R. Grace & Co.
IN THIS ISSUE of the Catalagram® publication you will find several key examples of the close collaboration that is paramount between Grace and its customers. Each of these success stories demonstrates the inherent value that partnership with Grace brings, from choosing the correct catalyst to allowing our technical experts to make recommendations regarding the streamlining of operations, to provide maximum refinery profitability.

What’s Inside

EDITORIAL
1. GRACE—FOCUSING ON OUR CUSTOMERS

GRACE IN THE NEWS
4. FCC EVENTS PROVIDE INFLUENTIAL INSIGHTS TO CUSTOMERS
5. GRACE AND ADVANCED REFINING TECHNOLOGIES ATTEND AFPM ANNUAL MEETING IN SAN FRANCISCO
6. FCC TECHNOLOGY WORKSHOP HOSTED IN HEIDELBERG, GERMANY
6. GRACE PRESENTS AT ABU DHABI INTERNATIONAL DOWNSTREAM SUMMIT
7. GRACE CREATES NEW CUSTOMER-FOCUSED FCC ORGANIZATION

SUCCESS STORIES
10. COMBATING THE NEGATIVE EFFECTS OF IRON IN AN FCC UNIT
23. IMPROVED CATALYST TECHNOLOGIES MANAGE REFINER’S NEED FOR INCREASED MIDDLE DISTILLATE YIELDS
29. COMMERCIAL SUCCESS OF ACHIEVE® 400 FCC CATALYST AT A U.S. REFINER
34. GSR® CATALYSTS AND ADDITIVES—THE ONLY PROVEN SOLUTIONS FOR FCC GASOLINE SULFUR REDUCTION
GRACE IN THE NEWS
FCC Events Provide Influential Insights to Customers

In April and May, Grace held two beneficial, customer-focused FCC events—a Gulf Coast FCC Technical Seminar at the Lake Charles, LA Manufacturing Complex and an FCC Technology Workshop at the Grace global headquarters in Columbia, MD. The events were attended by technical representatives from customer companies, as well as a host of Grace staff members from the sales, marketing, tech service, and R&D fields.

Over the course of the events, attendees participated in interactive presentations regarding various technical aspects of FCC operation, including FCC troubleshooting, FCC catalyst reformulation, and case studies. Additionally, at the Lake Charles event, speakers from Equilibrium Catalyst, Inc. and Wood Mackenzie provided perspectives on emerging trends within the industry.

The events each concluded with tours of Grace’s manufacturing complexes in Lake Charles and Curtis Bay, (Baltimore) MD, where attendees were able to witness firsthand several aspects of the catalyst manufacturing process. Additionally, the plant tours provided some unique insight into the people, processes, and technology that differentiate Grace from other FCC catalyst suppliers.

“Everyone left with a better understanding and appreciation for the role Grace plays within the FCC refining industry.”

Bob Riley
Marketing Team Leader
Americas

The events were organized by Bob Riley, Marketing Team Leader, Americas; Ann Benoit, Technical Service Leader, Americas; and Portia Sharp, Americas RT Sales Event Coordinator.

Riley was pleased with the attendance at the seminar from several perspectives. “We were able to engage with customers who, either directly or indirectly, are responsible for numerous metric tons of FCC catalyst per day,” said Riley. “Everyone left with a better understanding and appreciation for the role Grace plays within the FCC refining industry.”

Customer representatives and Grace staff gathered at Grace global headquarters in Columbia, MD for a biannual FCC Technology Workshop in May. The event featured technical presentations, networking opportunities, and sharing of best practices.
Grace and Advanced Refining Technologies Attend AFPM Annual Meeting in San Francisco

Grace and Advanced Refining Technologies LLC (ART)—Grace’s joint venture with Chevron—sent 25 attendees to the American Fuel & Petrochemical Manufacturers (AFPM) Annual Meeting in San Francisco March 14-16. The AFPM Annual Meeting is the world’s premier refining meeting, assembling key executives and technical experts from refining and marketing organizations worldwide, as well as representatives from associated industries.

Over the three days of the meeting, Grace and ART participated in several events that allowed for face-to-face interaction with customers, business partners, and industry colleagues. Sunday featured the Grace/ART annual brunch event, where nearly 100 attendees enjoyed an early afternoon gathering of food and networking while overlooking the San Francisco Bay. Monday’s technical presentations featured two sessions from Grace and ART. Doc Kirchgessner joined Patrick Salemo of Philadelphia Energy Solutions Refining and Marketing, LLC (PES) to present “Combating the Negative Effects of Iron in the FCCU at Philadelphia Energy Solutions Refining and Marketing, LLC.” Also, ART’s Alex Yoon presented “New Technologies for Hydrocracking and Diesel Hydrotreating.” Both sessions were well attended and well received.

FCC Technology Workshop Hosted in Heidelberg, Germany

Grace held the spring edition of its FCC Technology Workshop in Heidelberg, Germany, April 18–22. This event, which occurs twice a year, is very well recognized by Grace customers for key training and updating on different aspects of FCC. The workshop included presentations on unit operation and optimization, process troubleshooting, and FCC catalyst/additive design fundamentals. In total, 25 participants from 14 countries were present at the workshop, including representatives from 14 refineries and one research institute. The participants enjoyed technical presentation sessions spread over five days combined with social activities and the opportunity to network. The workshop was considered very informative and beneficial for the professionals that attended, and the good mix of different topics presented was highly appreciated.
Grace Presents at Abu Dhabi International Downstream Summit

The 17th Annual Abu Dhabi International Downstream (ADID) Summit took place May 8–10, 2016 in Abu Dhabi, UAE. Grace was an exhibitor and hosted a networking reception as part of the event activities. Key themes of the conference included catalyst selection, testing, and recycling. Grace’s Matthias Scherer and Nathan Ergonoul presented an update on the FCC catalyst portfolio, in particular focusing on EnhanceR 4G, MIDAS®, and ACHIEVE® Technologies. In addition, since it is of particular interest in the Middle East, Grace demonstrated its ongoing commitment to the people and the economy of the region by investing in a local manufacturing site in Kizad, as well as forming a partnership with Sohar University to create a catalyst evaluation laboratory. The ADID event provided the ideal platform to discuss the latest market developments, partnership opportunities, strategies, and innovative technologies that are shaping the refining and petrochemical complexes of the future.

Grace Creates New Customer-Focused FCC Organization

Grace has created a new Global Customer Technology organization for its FCC catalysts business. As designed, this team will cover critical high-level service needs for customers around the world, develop best practices and tools for use by regional technical support teams, develop models to quantify financial value of Grace’s catalyst and service offerings, and provide insight into product needs.

The new Global Customer Technology Team will be led by Dennis Kowalczyk, Vice President, Global Customer Technology, FCC. Dennis previously led the FCC business for the Americas. He will lead a team that will provide a full range of advanced FCC technical services to our customer base including site visits for troubleshooting of complex problems and unit-specific FCC consultation. In addition, the new team will provide field application and commercial insight into product development activities required to both meet customer needs and accelerate new product commercialization.

“Dennis and his team will provide a strong understanding of the customers’ view to our R&D product development activities in order to accelerate new product commercialization and ensure we are working on the most important problems to our customers,” said Tom Petti, President of Refining Technologies.

The first two appointments to the Global Customer Technology Team are Michael Federspiel and Stéphane Montmasson, who will focus on enhancing the value provided by Grace to our global customer base.

“Dennis and his team will provide a strong understanding of the customers’ view to our R&D product development activities in order to accelerate new product commercialization and ensure we are working on the most important problems to our customers.”

Tom Petti
President, Refining Technologies

Nathan Ergonoul presenting at the Abu Dhabi Conference.
Grace Exhibits at the IICHE 2016

Grace exhibited at the Israel Institute of Chemical Engineers Conference & Exhibition (IICHE) in Tel Aviv, Israel, on June 21, 2016.

Grace’s participation in the conference was personally requested by Malachi Alper, the President of the Institute of Chemical Engineers, who is also PAZ Ashdod Refinery CEO. PAZ Oil Company Ltd. is the largest Israeli fuels company, and the Ashdod refinery is the second largest oil refinery in Israel.

The conference served as an excellent platform to show Grace’s commitment to provide innovative and valuable solutions to our customers. It was well attended by students and professionals from the refining industry in Israel.

The PAZ Ashdod FCC unit utilizes Grace’s state-of-the-art NEKTOR™ 4G catalyst for resid processing, and OLEFINSULTRA® additives for increasing propylene yields. In addition, the refinery is also using Super DESOX® additives to control SOx emissions.

Grace has developed a strong partnership with PAZ Ashdod based on industry-leading technology and service, which has resulted in nearly 20 years of continuous catalyst supply.
Global leader in hydroprocessing catalysts offering the complete range of catalysts and services
SUCCESS STORIES
Combating the Negative Effects of Iron in an FCC Unit

Pat Salemo
Optimization Analyst,
Philadelphia Energy Solutions
Refining and Marketing, LLC

Doc Kirchgessner
Senior Technical Specialist,
Catalysts Technologies

John Aikman
Technical Sales Manager,
Catalysts Technologies

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 U.S. 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 monitored, managed, and minimized the impacts of high iron levels in the resid FCCU with a multi-faceted strategy, which included 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.

Iron Poisoning on the Rise

Iron poisoning of FCC catalyst was first discovered in the 1990s but not experienced in the 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, 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 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.

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 occlude 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.

**Monitoring and Analysis Identifies Threats**

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.

A spike up to 55 ppm as shown in Figure 3 is substantial equating to over 4,000 lbs/day 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 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 Ecatforming 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 Ecatforming 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 (Deff) coefficient for the Ecatforming, 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, so 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 the 1232 and 868 units process feeds with high levels of calcium, both catalysts 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 catalysts, 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 Ecatforming. Based on all of these factors, detecting Fe poisoning in the FCC often requires close monitoring and extended analytical testing to be carefully detected.
PES Iron Excursions

FCCU 868 Event

The first event occurred in March of 2013, when the Point Breeze FCCU, 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 were manifested in the form of an increase in the disengager stripper level. The operations team temporarily resolved the issue by reducing riser outlet temperature and overall unit charge rate to reduce the required catalyst circulation rate.

During this time frame, it was noted that the Ecat and ESP fines had turned a brownish hue as seen in Figure 7. 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. Minor fluidization issues persisted until the catalyst addition rates were increased to flush the metals and restore fluidization properties.

Figure 6: 868 disengager level during a defluidization event.

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.

Figure 9: Ecat iron trends at unit 868.

Figure 10: ABD decreased with iron at unit 868.
FCCU 1232 Event
The second event occurred in late June of 2014. The Girard Point FCCU, 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. Unit 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.

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.

Until 2014, after the 2007 major revamp of 1232, 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.
A catalyst change at 1232 added to the complexity of the high iron and low resid processing. On April 24, 2014, Girard Point started changing out catalyst from a 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 and catalyst effects did not occur at the onset of 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 Ecatalyst 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 14-16 as evidenced by the smoother appearance of the FCC catalyst particles themselves.

Values less than 20 on the Grace effective diffusivity test can begin to show diffusion limitations. As seen in Figure 17, 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.

**Figure 14:** SEM of 1232’s Ecatalyst dated 03/27/14 with 0.69 wt% Fe and 1.15 wt% CaO.

**Figure 15:** SEM of 1232’s Ecatalyst dated 5/15/14 with 0.74 wt% Fe and 1.22 wt% CaO.

**Figure 16:** SEM of 1232’s Ecatalyst with the use of Grace’s MIDAS® Gold catalyst dated 5/22/14 with 0.79 wt% Fe and 1.14 wt% CaO.

**Figure 17:** Grace’s diffusivity data and Ecatalyst Iron vs. Time.
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 showed 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.

**Combating Fe Contamination**

The methods that PES used to overcome the effects of iron poisoning at both units are a combination of preventative, routine monitoring, and actions to help lessen the detrimental effects.

**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 ways give two possible methods for preparation (9, 10). D5708 is utilized at PES. 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 Ecats stopped closing in April of 2014 when PES began processing a significant amount of shale oil crude. 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 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%.

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 allows the refinery 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), and
- 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 focal point.

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 Ecat and feed sampling. These routine methods were used to calculate the FCC unit iron balance. Iron on Ecat, purchased Ecat (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 in Figure 21.

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 quickly distinguished 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.

<table>
<thead>
<tr>
<th>Symptoms</th>
<th>Monitoring</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Low slide valve dP's</td>
<td>- Slide valves dP's</td>
</tr>
<tr>
<td>- Reduced feed rate and/or riser temp due to alarms</td>
<td>- Slide valves % opening</td>
</tr>
<tr>
<td>- Fluidization points</td>
<td>- Pressure survey</td>
</tr>
<tr>
<td>- Grace Ecat UMB/UMF, PSD</td>
<td>- Fluidization points</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Action Level</th>
<th>Corrective Actions</th>
</tr>
</thead>
<tbody>
<tr>
<td>- Unable to achieve target feed rate</td>
<td>- Adjust PSD of fresh catalyst</td>
</tr>
<tr>
<td>- Unstable catalysts circulation</td>
<td>- Add fines to fresh catalyst</td>
</tr>
<tr>
<td></td>
<td>- Review PCAT options</td>
</tr>
</tbody>
</table>

Figure 20: Equilibrium catalyst fluidization monitoring.

Figure 21: PES 1232 Ecat ABD versus Fe wt%.

Continued on Page 18
Another non-standard method employed was scanning electron microscopy (SEM) as shown in Figures 14-16. 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. Numerous routine and non-routine analytical methods monitored the Ecat for iron contamination.

Feed Treatment
Reducing iron to the FCC by all means possible can prove very cost effective. Managing corrosion in the refinery is a good safety practice, and can limit the iron to the FCC. Desalting alone helps remove some iron, however desalting will not remove organic iron. Desalter acidification has 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 (11). Desalter acidification was applied to the PES Girard Point (GP) crude unit mainly to remove calcium from a high calcium opportunity crude oil to protect the catalyst activity at the FCC units; however a secondary benefit was the removal of iron from the crude oil as seen in Figure 23.

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. This additive can improve desalter operation by reducing solids and emulsions build up inside the desalter leading to increased desalter residence times. A solids removal agent

---

**Figure 22:** PES Ecat and PCAT properties versus Time.

---
was introduced into the crude unit in September of 2014 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.

In addition, the solids removal agent 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 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%), 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.

In the case of the 1232 iron excursion, 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 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.

**Figure 23:** Iron removal vs. acetic acid rate (CRA) from March – September 2014 at the GP Crude Unit.

**Figure 24:** Iron in the FCC feed at PES before and after solids removal agent.

Continued on Page 20
Catalyst Selection

Multiple unit objectives and constraints were considered when Grace chose the optimum catalyst for the 1232 unit. Chief among these was metals tolerance. As noted, 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 with a high level of mesoporosity in the 100–600 Å range as measured by mercury (Hg) porosimetry can 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 occurring 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. 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 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

**Table 1:** Theoretical Fe removal via catalyst flushing (*assumes a charge rate of 50 MBPD and 24° API).
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 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.

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 (Umb/Umf) is a well known measure of a catalyst’s ability to meet these goals. With the switch to MIDAS® Gold, the Ecat Umb/Umf improved despite higher iron on Ecat. Adjustments were also made to fluidization media to help optimize catalyst circulation.

Conclusions
Contaminant iron in FCC feed is one of many causes that 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 crude, cat cracker feed, and Ecat for 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, refiniers 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.

Acknowledgments
We would like to thank the management of Philadelphia Energy Solutions and the Grace colleagues who contributed to this paper.
References


Join Grace and Advanced Refining Technologies for These Upcoming Events

SEPTEMBER 2016
AFPM Q&A and Technology Forum in Baltimore, Maryland

OCTOBER 2016
Grace FCC Technology Workshop in Heidelberg, Germany
The 5th Opportunity Crudes Conference in Houston, Texas
LARTC 5th Annual Meeting in Mexico City, Mexico
Middle East & Africa 2016 Bottom of the Barrel Technology Conference in Bahrain

NOVEMBER 2016
ERTC (European Refining Technology Conference) 21st Annual Meeting in Lisbon, Portugal

MAY 2017
Grace U.S. FCC Technology Workshop at the Grace Global Headquarters in Columbia, Maryland
Improved Catalyst Technologies Manage Refiner’s Need for Increased Middle Distillate Yields

H. Alex Yoon  
Hydrocracking and  
Distillate Segment Manager,  
Advanced Refining  
Technologies LLC (ART)

Brian Watkins  
Manager, Hydproprocessing Pilot Plants  
and Sr. Technical Service,  
Advanced Refining  
Technologies LLC (ART)

Meredith Lansdown  
Technical Service Engineer,  
Advanced Refining  
Technologies LLC (ART)

With the continued interest in processing domestic crude sources, as well as utilizing opportunity feed sources, refiners are exploring ways to maximize middle distillate production. Several domestic feed sources have reduced the demand on the ULSD hydrotreater making it significantly easier to treat to ULSD; however, other feed sources, with the low cost of crude, have become an issue.

A critical element in all of the approaches to increasing diesel yield is the proper design and selection of a catalyst system for the hydproprocessing unit. Improvements in catalytic solutions have made significant advances in allowing the hydrotreater or hydrocracker to increase middle distillate yield. This approach to increasing diesel yields requires a detailed understanding of feed and operating conditions to allow the hydrotreater or hydrocracker to be operated at optimum conditions for the unit cycle, and all of these have limits depending on the various feed properties.

Addressing Hydproprocessing Challenges at Chevron/ART/CLG

The optimization of new hydproprocessing catalysts plays a critical role in achieving optimum performance in refinery hydproprocessing units, especially after the unit has been in operation. As a refinery operator, Chevron pays close attention to hydproprocessing catalyst developments both as a catalyst designer and a catalyst manufacturer. With the launch of the Advanced Refining Technologies LLC. (ART) joint venture with W. R. Grace & Co.-Conn. in 2000, this focus has increased with close attention paid by the company’s senior management.

The catalyst focus has roots in the 1960s when Standard Oil of California (as Chevron was called then) developed modern hydrocracking and installed a demonstration unit. Standard Oil of California went on to build many hydrocrackers at its refineries and for other Standard Oil companies, some of which became parts of Exxon, Mobil, and BP. At that time, Chevron designed and manufactured hydrocracking catalysts, or more widely considered hydproprocessing catalysts since these were designed to perform both hydrotreating and hydrocracking. The catalyst manufacturing technology was unique in that a liquid solution of components were gelled in order to make the catalysts, hence the name cogel (1). Dual function catalysts have been the cornerstone of Chevron technology and continue to be used in Chevron refinery hydrocrackers as well as around the world in licensed hydrocrackers from the Chevron joint venture with CBI Lummus, called Chevron Lummus Global (CLG) and supplied with catalysts from ART.

Various technology providers have designed hydrocrackers with separate hydrotreating and hydrocracking reactors. However, CLG-designed hydrocrackers and Chevron refinery hydrocrackers do not have such distinctions and require that both hydrotreating and hydrocracking take place inside a single reactor. Even ART’s highly zeolitic catalysts are employed in this manner. This is especially the case with Chevron refinery units that have been revamped over the years. The conventional alumina-based hydrotreating catalyst alone is not robust enough to meet the dual objectives. In fact, both hydrotreating and hydrocracking objectives need to be met within a limited catalyst volume where other typical hydrocrackers employ conventional alumina-based hydrotreating catalysts.

To meet such severe performance requirements, Chevron led a joint research and development effort to produce its most recent developmental series, ICR 1000 catalysts, which builds on cogellation technology. Typical alumina-based hydproprocessing catalysts have faced limits on the amount of metals that can be deposited on the base which then limited their performance. The cogellation technology enabled the development of the ICR 1000 series of catalysts to overcome this limitation and improve catalytic hydproprocessing capabilities by doubling and sometimes tripling catalyst activity compared to conventional alumina-based catalysts, while meeting the dual function objectives.

The ICR 1000 series catalysts have now been successfully deployed in multiple hydrocrackers within and outside of
Chevron, demonstrating higher conversion and distillate yield improvement.

Also, ICR 1000 series catalysts were tested in the ULSD hydrotreating application to determine if its hydroprocessing capabilities could be utilized in this operation. ICR 1000 series catalysts demonstrated marked improvements in hyrodesulfurization coupled with significant aromatics saturation leading to product volume enhancement without any detrimental effect on liquid yield. ICR 1000 series catalysts are in a second cycle of operation in a commercial ULSD unit at Chevron. Application of ICR 1000 series catalysts in other types of hydroprocessing units is being actively explored inside and outside of Chevron.

ICR 1000 Catalysts Application in a Chevron Commercial Hydrocracker

The refinery and the hydrocracker are both Chevron’s own. The hydrocracker is a relatively complex unit in that there are two stages, which is the preferred configuration for maximum conversion, highest liquid yield, and lowest catalyst volume. A two-stage configuration has two reaction zones with separation of light and heavy molecules in the reactor effluent stream between the zones. The separation can utilize high or low pressure equipment, including the option of a vacuum tower. Intermediate separation recovers products and prevents recracking of the lighter oil, as conversion is increased. Second stage reactors crack only the unconverted oil and, with the absence of inhibitors, are capable of utilizing a smaller quantity of catalysts compared to a single stage configuration. A single stage configuration has one contiguos reaction zone without any intermediate product separation.

In addition to two stages, this hydrocracker has multiple trains in each stage that enables on-stream catalyst change-outs and restart, which allows maximum unit utilization rate and improves the refinery utilization rate. The key unit performance metrics improved by the deployment of ICR 1000 catalysts are conversion and yield. Since there is not any individual train fractionation, the conversion is measured/estimated using effluent sampling and temperature profile. The yield effect is measured from the incremental change in the combined fractionation data.

Figure 2 shows an effluent sample distillation monitoring graph for one train with approximately 365 days of operation. The start of operation for this train B or zero days on stream is actually the Y axis intersect and not the first black mark on the X-axis. The bottom (smaller light blue X marks) represent the 50% boiling points of train B effluent stream sample and the top (larger darker blue marks) represent the 70% boiling points. As expected of typical refinery data, there is some fluctuation in the

Figure 1: Multi-train multi-stage ISOCRACKING® unit.

Figure 2: Reactor effluent distillation.
absolute numbers. This is not critical for performance comparison, as the trends indicate product changes as well as other process data that are available to validate the conclusions.

Figure 3 shows the reactor temperature profile graph for the same train B with about 365 days of data. Bed #X temperature rise, which represents per bed reaction amount, is plotted with red X marks. The temperature rise of downstream bed #X+1 below is plotted with blue diamond marks. Again, the absolute numbers are not critical to determine the performance. The performance of train B containing ICR 1000 series catalysts will be compared on the same basis with another train. At the top of Figure 3 in brown circles are the total temperature rise for train B with ICR 1000 series catalyst, representing total reaction amount for the train. The scale for total temperature rise data is different and is on the secondary Y-axis. The raw plant data are shared to showcase difficulties faced by refinery unit engineers when extracting comparative performance.

The catalyst loading schematic for two comparison trains are shown in Figure 4. The loading on the right is for train B whose effluent stream and temperature data were shown in Figures 3 and 4. Train B was loaded with ICR 1000 series catalyst along with layers of conventional hydrotreating (HDT) catalysts and hydrotreating (HCR) catalysts. This includes reverse layering where HDT catalysts are loaded below HCR catalysts in a bed to provide the correct catalyst type in the optimum location and condition. This allows the specific catalyst capabilities to match up with reaction requirements in different zones of the hydrotreating reactor. ICR 1000 series catalyst were loaded in bed #X+1 in train B and amounted to less than 10% of the total reactor load. All other trains were loaded with catalysts as shown in the schematic here without ICR 1000 series catalyst.

Since the unit changes out each reactor sequentially and often several months apart, performance comparison between trains without normalization can be made easily unlike with other hydrocrackers. In single train units, many changes can happen to the feed as well as to operational targets between catalyst cycles over many years. This makes comparison from one cycle to another very difficult with a single train unit. The unique design of this multiple train unit and its operation allow easier comparison and step-by-step introduction of new technologies.

After the unit lined out, the first sign of performance difference showed up in the effluent sampling data. Figure 5 is on the same basis as Figure 2 with non-ICR 1000 catalyst train A effluent.
stream 50% and 70% boiling point data added. The red diamond marks above the blue X marks for train B are the data plots for train A. Comparing the two trains’ effluent sampling data shows quantitative change in the distillation, indicating shifting conversion in the reactor with ICR 1000 catalyst loaded. As measured by 50% boiling point, the ICR 1000 catalyst-loaded reactor effluent stream exhibited 10-30°F lower temperatures. The 70% boiling points for two trains show smaller differences.

This performance is validated by temperature profile monitoring also. Figure 6 is on the same basis as Figure 3 with non-ICR 1000 catalyst train A, bed #X and bed #X+1 temperature rises plotted to the right of the ICR 1000 catalyst containing train B data.

Comparing the temperature profiles, bed #X+1 on train B where ICR 1000 catalyst is loaded and shown as blue diamond marks on left hand chart shows much higher temperature rise or more reaction amount than same location bed #X+1 on non-ICR 1000 catalyst train A. Train A bed #X+1 exhibits 10-15°F lower temperature rise throughout the similar calendar days of operation.

The total reaction amount for each train can also be compared as shown in Figure 7. The brown circles at the top of the Figure 7 are the total temperature rises for ICR 1000 catalyst system train B. The orange squares on the right chart in Figure 7 are the total temperature rises for train A without ICR 1000 catalyst. The total train temperature rise differences range from 15-20°F. The amount of extra reaction achieved with ICR 1000 catalyst in train B is estimated to be around 20-30%. Although not shown here, the differences between total reaction amounts of train B with ICR 1000 catalyst and train A are larger than the differences between reaction amounts in bed #X+1 in the two trains. This indicates that the catalyst affects not just its bed performance, but also the performance of downstream catalysts.

Often, the added activity in hydrocrackers comes at a cost of reduced liquid selectivity. That was a concern and the unit performance was carefully monitored. This was a very difficult task since the unit has multiple stages and multiple trains with catalyst change-outs at different times in each reactor and frequent product slate changes. Crude slate and feed changes were relatively minor. But as shown in Figure 8, the refinery and ART tech service team identified comparative period filtering out extraneous changes and demonstrated almost 1000 BPSD increase in jet product selectivity.

Satisfied with the safety and performance of ICR 1000 series catalysts, the refinery has loaded a second charge. The refinery is using the activity advantage in many different ways to achieve its profit objectives.
ICR 1000 Catalyst in ULSD Application

ICR 1000 catalyst can be considered a hydroprocessing catalyst, combining both treating and cracking functionality, rather than a pure hydrotreating catalyst. The old cogellation technology was used to make hydrocracking catalysts by combining a liquid solution of alumina, silica, and metals until the mixture gelled. ICR 1000 series catalysts are produced in a similar manner at the same plant and contain the active sites necessary for both carbon-to-carbon bond breaking and carbon-to-heteroatom breaking and removal. Depending on the feed and processing conditions, it can exhibit both hydrotreating and cracking capabilities. In the first example, enhanced hydrocracking capacity was prominent.

Also, ICR 1000 series catalysts were successfully tested for use in a ULSD application, where meeting the difficult aromatics target in a severe operation was critical. ICR 1000 catalyst was successfully deployed into a ULSD unit and is now in its second cycle of operation. ART studied two catalyst systems, one with the latest Type-II Ni/Mo only and the other with same Ni/Mo catalyst and a layer of ICR 1000 catalyst. The test feedstock properties are shown in Table 1.

Figure 9 shows how the product sulfur varies with temperatures applied to the catalyst systems. The catalyst system with ICR 1000 catalyst outperformed the system without ICR 1000 catalyst by more than 15°F under typical ULSD conditions and up to 40°F in higher sulfur operation.

Figure 10 shows API change between feed and product for two catalyst systems. Near the base temperature where typical ULSD units operate, the API upgrade difference approaches almost 1. As the temperature is raised, the differences disappear due to thermodynamic equilibrium effect on aromatics saturation. Comparing the hydrogen consumption of both systems show this more clearly. Figure 11 shows hydrogen consumption differences for two systems at little more than 50scf/bbl around the base temperature. The bottom set of data is included for 100% Co/Mo catalyst system results tested on the same feedstock. Again, as the temperature is raised the reverse reaction dominates resulting in lower hydrogen consumption.

Tying the information in Figures 9, 10, and 11, the system containing ICR 1000 catalyst can meet the ULSD sulfur targets and achieve higher API improvement (higher volume swell) at lower start of run temperature than...
conventional catalysts. These advantages led to the application of ICR 1000 catalyst in the Chevron ULSD unit.

Every refiner faces different constraints, process different feeds, and has many different hydroprocessing units at its disposal. ICR 1000 series catalysts and similar developments in catalyst technology can lead to improved profitable operation.

References:

Figure 9: Performance sulfur curve.

Figure 10: API upgrade performance.

Figure 11: API upgrade performance.
Commercial Success of ACHIEVE® 400 FCC Catalyst at a U.S. Refiner

Gary Cheng  
Technical Sales / Service Manager, Refining Technologies

Kevin Burton  
National Technical Sales Manager, Refining Technologies

Kent Turner  
Technical Sales / Service Manager, Refining Technologies

Chip Schaeffer  
Technical Sales Manager, Refining Technologies

Rosann Schiller  
Marketing Director, Refining Technologies

A U.S. refiner processing crude from the Permian Basin, including both sweet (WTI) and sour (WTS) crude oil, underwent a major FCC turnaround in 2014. Following this major revamp and re-baseline of the unit, the refinery sought to increase profitability via a catalyst change. Unit objectives were to:

• increase LPG olefin yield, preferably C4 olefins,
• reduce dry gas make,
• improve slurry upgrading,
• increase LCO yield,
• improve coke selectivity, and
• improve conversion, all at constant fresh catalyst addition rates.

An additional operating objective of the refinery is to keep the downstream alkylation unit full year-round, using a combination of FCC operating parameters, an optimized catalyst formulation, and traditional ZSM-5 additive as needed. The FCC feed is comprised primarily of a VGO feedstock, plus a combination of various side streams.

Technology Achieves Five Key Catalytic Functionalities

Refiners are continually challenged to respond to changing market dynamics. For example, a common challenge for refiners operating on unconventional feeds, such as shale or tight oil, is a loss of gasoline pool octane, caused by reduced volume of alkylation feedstock. Grace launched the first product in the ACHIEVE® series, ACHIEVE® 400, to address these octane debits. This breakthrough technology has delivered an economic uplift on the order of $3-7M/yr. in multiple commercial applications due to the boost in slurry conversion, FCC naphtha octane, and butylene yield.

During the ACHIEVE® R&D program, five key catalytic functionalities were developed to provide the yield flexibility desired by refiners.

1. Increased distillate yields with high diffusivity matrices.
2. Reduced dry gas with advanced metals traps.
3. Conversion driven with ultra-high activity zeolites.
4. Maximized resid processing with leading coke selectivity.
5. Boosted refinery octane with dual-zeolite technology.

ACHIEVE® catalyst is formulated to address each of these five critical functionalities. High diffusivity matrices maximize distillate yield from the bottom of the barrel and provide resistance to poisoning from unconventional metals. ACHIEVE® catalyst can be formulated over a range of activity, rare-earth exchange, and isomerization activities. Grace’s capability to modulate hydrogen transfer activity in our self-manufactured zeolites, affords each refiner the optimal LPG to gasoline ratio for their operation. ACHIEVE® 400 catalyst also features multiple zeolites, specifically traditional Y-zeolite and pentasil-type zeolite, to selectively enhance LPG olefinicity by preferentially cracking gasoline olefins at C7 and above into butylenes.

Incorporation of isomerization activity into the catalyst particle itself results in a more desirable yield pattern than would be realized by use of a traditional octane boosting FCC additive. ACHIEVE® 400 catalyst yields higher octane, with an improved butylenes to propylene ratio when compared to ZSM-5 additives. The zeolite isomerization activity in ACHIEVE® 400 catalyst increases the yield of FCC butylene and iso-butane, keeping the alkylation unit full and maintaining refinery pool octane.

With traditional ZSM-5 technology, cracking of gasoline-range olefins continues on into the C6 range, generating a disproportionate amount of propylene relative to butylenes, as shown in Figure 1. ACHIEVE® 400 catalyst, however, works to selectively crack gasoline olefins at C7 and above into preferentially more butylene, thus generating a higher ratio of C4 to C3 olefins than separate light olefins additives.

Continued on Page 30
Grace ACHIEVE® 400 Catalyst Trial Improves Profitability for U.S. Refiner

In mid-summer of 2014, the refiner began a trial of ACHIEVE® 400 catalysts over a competitor’s traditionally formulated high activity base catalyst. The refinery previously utilized approximately 1.5–3.5 wt% ZSM-5 additive to attain the desired olefinicity and octane shift. Throughout the ACHIEVE® catalyst trial, fresh catalyst addition rates were held constant, and Ec1t activity remained at 74 wt% on average. Total LPG olefin yield increased by ~3 vol%, as shown in Figure 2. The alkylation unit remained at full capacity, despite a gradual reduction in additions of a separate particle ZSM-5 additive. The site eventually stopped adding ZSM-5 additive and was still able to keep the alkylation unit full.

Figure 1: Selectivity comparison between ACHIEVE® 400 catalyst and traditional ZSM-5 additive.

Figure 2: Total LPG, C4 olefins, and propylene yield at constant conversion.
The constrained downstream alky unit benefitted from the increased loading of C4 olefins in the alky feed. Moreover, there were minimal increases in C3 and C4 saturates commensurate with these increases in olefin yield. This can be attributed to the tailored acidity and optimal hydrogen transfer activity of the ACHIEVE® catalyst system. LPG saturate yields are shown in Figure 3.

Moving to a low Z/M, high activity matrix catalyst also helped to improve slurry upgrading and increase LCO yield. Slurry yield dropped by ~0.5 vol%, while LCO yield increased by ~0.5 vol% at constant conversion. Plots of these shifts are shown in Figure 4.

Additional benefits included reduced dry gas at comparable metals levels on Ecat, as well as improved overall conversion and volume swell.

Figure 3: LPG yield breakdown suggests minimal increase in saturate production.
Results/Conclusions

A review of the unit data shows that the refiner was able to significantly improve profitability during the trial. Stated objectives were met, and the refiner obtained an additional benefit of lowering OPEX by reducing and eventually stopping the addition of ZSM-5 additive at full FCC charge rates. Due to the success of the trial, the refiner is still using ACHIEVE® technology at this FCC today.

The favorable performance of ACHIEVE® 400 catalyst has generated an economic uplift of approximately $0.70/bbl.

As refiner needs continue to become more complex and diverse, FCC catalyst suppliers are challenged to respond with new technology to meet these evolving needs. Catalyst technologies must be flexible and adaptable, and continue to fulfill short term refinery objectives.

ACHIEVE® catalysts have been used in 30 commercial applications to date, and have delivered between $0.40-0.95/bbl of incremental value.

Figure 4: Liquid yield shifts, consistent with refinery trial objectives.
Ever wish you could remove sulfur this easily?

Grace’s gasoline sulfur reduction technologies, GSR® FCC catalysts and additives, are the leading solutions to help meet fuels regulations. Refiners achieving 25%* FCC naphtha sulfur reduction can realize as much as $2-3 million per year in incremental margin with GSR® via octane preservation and naphtha endpoint optimization.

Get that last barrel into your gasoline pool.
Contact your Grace representative to determine how much more margin you can capture now with Grace's Clean Fuels Technologies.

grace.com
catalysts@grace.com

*results may vary based on actual operating parameters
GSR® Catalysts and Additives—The Only Proven Solutions for FCC Gasoline Sulfur Reduction

Colin Baillie
Environmental Additives Portfolio Manager, Refining Technologies

Grace GSR® technologies, D-PriSM®, SuRCA®, and GSR® 5 additives, are the result of nearly two decades of innovation. GSR® technologies have been used in over 100 FCC units worldwide, with and without hydrotreating hardware, to provide 20%-45% sulfur reduction in FCCU naphtha.

In-unit reduction of FCC gasoline sulfur with Grace’s patented GSR® technologies continues to create a variety of opportunities and options for refiners to drive profitability. Grace GSR® technologies create economic advantages around:

- improved feedstock flexibility,
- reduced undercutting of FCC gasoline (increasing volume),
- gasoline octane preservation (reduced gasoline post-treatment severity),
- improved hydrotreater economics (lower operating severity),
- temporary use during hydrotreater outages, and
- avoiding capital expenditure to meet upcoming Tier 3 regulations.

Numerous case studies and references have supported the robust performance of GSR® technologies for:

- 20-40% gasoline sulfur reduction,
- all feed types,
- all feed sulfur levels,
- all base gasoline sulfur levels, and
- usage varying from 10% to 100% of circulating inventory.

Sulfur Reduction Mechanism

Nearly all of the sulfur species in gasoline are thiophene-based molecules. The cracking catalyst component catalyzes the hydrogen-transfer (HT) reactions between thiophenes and tetrahydrothiophenes (THT). GSR® technology works by increasing the cracking of THT (which are Lewis bases) into hydrocarbons and hydrogen sulfide, as shown in the figure below.

Using a wide range of spectroscopic and other scientific techniques, it has been proposed that the mechanism involves both Lewis acid and basic oxygen site pairs. The Lewis acid site selectively adsorbs the Lewis base sulfur of the THT molecule. The basic sites promote the abstraction of protons to catalyse the cracking of THT to butadiene and hydrogen sulfide. The proposed mechanism accounts for high selectivity for THT cracking due to the balance of surface acid-base properties.
D-PriSM® Additive: Description

The D-PriSM® additive is effective for reducing light to intermediate gasoline sulfur species. The additive usually replaces between 8-15% of catalyst addition rate, with no FCCU yield deterioration observed. Sulfur reduction of between 20-35% in the light-to-intermediate gasoline cut is typically achieved commercially. The D-PriSM® additive can be used in partial or full-burn operations.

D-PriSM® Additive: Commercial Experience of Increasing Gasoline Volume

Figure 1 illustrates the performance of the D-PriSM® additive in a commercial FCC unit. Gasoline sulfur was reduced by 25%, which allowed gasoline endpoint to be increased, resulting in ca. 5 vol.% gasoline yield increase at constant gasoline sulfur level.

SuRCA® Catalyst: Description

The SuRCA® catalyst family offers a solution to full-range FCC gasoline sulfur reduction. SuRCA® catalysts are designed to completely replace conventional FCC catalysts in the circulating inventory, and are tailored to meet specific FCC unit objectives. SuRCA® catalysts contain sulfur-reduction functionality, which typically provides full-range gasoline sulfur reductions of between 25-35% commercially.

SuRCA® Catalyst: Commercial Experience of Meeting Gasoline Quality Legislation

Tier 3 regulations in the U.S. require the reduction of average gasoline pool sulfur levels to less than 10 ppm with an 80 ppm cap by January 2017, compared to the current limit of less than 30 ppm with an 80 ppm cap. Grace has substantial experience in similarly demanding environments like Japan. In the mid 2000s, Japan committed to lower gasoline sulfur levels. As early adopters of more stringent gasoline quality regulations, Japanese refiners faced similar challenges that U.S. refiners are facing today in meeting Tier 3. Since 2005, these refiners have successfully utilized Grace’s GSR® products to maintain compliance, observing 35%-40% reduction in the gasoline sulfur/feed sulfur ratios allowing them to meet the 10 ppm gasoline specifications (1). An example of a Japanese refiner meeting 10 ppm gasoline sulfur spec without increasing gasoline post-treater severity can be seen in Figure 2. In this case, as much as 35% gasoline sulfur reduction was achieved with the SuRCA® catalyst.

GSR® 5 Additive: Description

The GSR® 5 additive offers a solution to full-range FCC gasoline sulfur reduction. The additive typically

Figure 1: Increasing gasoline yield using D-PriSM® additive.

Figure 2: A Japanese refiner achieved 35% gasoline sulfur reduction using the SuRCA® catalyst.
replaces 25% of fresh catalyst additions, and contains zeolite and matrix formulations to maintain the catalytic cracking performance. The sulfur-reduction functionality used in the GSR® 5 additive is based on SuRCA® technology, and similar full-range gasoline sulfur reductions of between 25-35% are achieved commercially.

GSR® 5 Additive: Commercial Experience of Controlling Sulfur During a Feed Hydrotreater Outage

Refiners have created operating flexibility during hydrotreater outages by utilizing Grace’s clean fuels GSR® additive technology. Proper management of FCC feed hydrotreater outages becomes increasingly important as more and more refiners rely on hydrotreating to meet their per gallon gasoline sulfur limits. Running at higher severity increases the frequency of turnarounds. Conventional methods of ensuring that the gasoline pool stays below the sulfur limit during the hydrotreater turnaround are purchasing low sulfur feed or reducing FCC throughput. Either approach can significantly reduce refinery profitability. An alternative is to use one of Grace’s gasoline sulfur reducing technologies during the outage to provide operational flexibility while maintaining sulfur compliance and profitability. One such example of a refiner that used Grace GSR® 5 sulfur reduction additive during a feed hydrotreater outage is shown in Figure 4. The refiner was able to process higher than typical feed sulfur and maintain gasoline pool sulfur compliance. Use of GSR® 5 additives began two months prior to the 45-day feed hydrotreater outage. During that time, feed sulfur increased by as much as 35%. The three periods represented are typical operation (base period), GSR® 5 additive used before and during the outage where gasoline sulfur reduction ranged from 20-25%, and finally GSR® 5 additive used following the outage. The customer estimated that use of GSR® 5 additives resulted in $1.7 million of savings during the hydrotreater outage. The results were so encouraging that the customer elected to continue using GSR® technology, switching to a SuRCA® catalyst and operating with post-outage feed sulfur 10-15% higher than the typical operation. This change to their operation grew annual profits by approximately $8 million (2).

References

Figure 3: SuRCA® catalyst reduced gasoline sulfur by 40% at constant gasoline cut point.

Figure 4: GSR® 5 delivered 25% gasoline sulfur reduction during a feed HT outage.
When you can’t predict what’s in the pipeline

THINK MIDAS® FCC CATALYST
TO CAPTURE THE VALUE OF OPPORTUNITY CRUDES

grace.com