Worried about the high cost of rare earth? Grace has the solution:

REpLaCeR™

Rare earth price inflation is the most serious issue facing the global refining industry. Grace, with our long history of innovation and strong R&D, leads the industry with the first line of commercially successful zero/low rare earth FCC catalysts: the REpLaCeR™ family.

Launched in the first quarter of 2011, the REpLaCeR™ family includes five new catalysts for both hydrotreated and resid feed processing with zero and low rare earth content. The REpLaCeR™ family of catalysts utilizes proprietary zeolites and state-of-the-art stabilization methods to deliver performance similar to current rare earth-based FCC technologies.

We’re also investing in our plants to bring these products to the refining industry quickly and globally.

So if you’re concerned about rare earth pricing and availability, but need optimal FCC performance, call the technical experts at Grace. We’ll customize a solution using one of our new zero/low rare earth catalysts that delivers the yields you expect.

Grace Refining Technologies
7500 Grace Drive
Columbia, MD USA 21044
+1.410.531.4000

www.grace.com
www.e-catalysts.com
Global Reach, Local Presence

It's almost become a cliche in current business jargon: Only Company X can bring your business its global expertise and local touch. Certainly, those of you who work for global majors hear this type of talk all the time.

But what do the words actually mean? At Grace, it means our people are our greatest resource and their expertise and experience allow us to develop new catalysts for our broad portfolio, to manufacture those catalysts efficiently in our plants around the world and the flexibility to optimize the formulation for your operation no matter where you are located.

This issue of the Catalagram® highlights our global reach with stories from all geographic regions. Our lead article “Optimizing FCC Operations in a High Rare-Earth Cost World” is an update of the success of our RepLaCer™ family of low and rare-earth free catalysts in North America and EMEA. Next, we highlight the commercial performance of ResidUltra™ at S-Oil’s refinery in Ulsan, Korea. We also include an article on joint catalyst developments between Ecopetrol, in Colombia, and Grace. We are honored to have co-authors from both S-Oil and Ecopetrol contributing to these testimonials.

We at Grace are committed to the success of you, the global refiner, and we are dedicated to living our motto, “Enriching Lives. Everywhere.”

Sincerely,

Rosann K. Schiller
Senior Marketing Manager
Grace Davison Refining Technologies
In 1992 Chinese leader Deng Xiaoping declared, “The Middle East has its oil, China has rare earth; China’s rare earth deposits account for 80 percent of identified global reserves, you can compare the status of these reserves to that of oil in the Middle East: it is of extremely important strategic significance; we must be sure to handle the rare earth issue properly and make the fullest use of our country’s advantage in rare earth resources.”  

In actuality, rare earth controversies between China and the West are not new. In the second half of 2010, however, the gravity of China’s market dominance over rare earth resources peaked. The price of lanthanum began a zealous climb to levels never before seen. Catalysts are generally a refinery’s second-highest raw material cost after crude oil. It is therefore not surprising that refiners are increasingly asking catalyst suppliers to relieve their cost pressures while maintaining or even improving product performance.

A year later, the escalation has abated, but lanthanum prices remain 12x’s higher than the base level in early 2010.

Grace has been diligently working to achieve solutions that would either lower or fully eliminate rare earth content of FCC catalyst without sacrificing performance. In 2011, Grace Davison Refining Technologies launched the REpLaCeR™ family of zero- and low-rare-earth FCC catalysts. This new series includes five new catalysts for both hydrotreated and resid feed processing with zero and low rare earth content, and their successful commercialization will be discussed.

**The Role of Rare Earth in FCC Catalysts**

Lanthanum and cerium are the two main rare earths (RE) used in FCC catalysts. These metals limit the extent to which zeolite dealumination occurs (thus stabilizing the structure) under the conditions of the FCC unit. The aluminium atoms within the zeolite structure are the primary catalytic sites in FCC catalysts and therefore play an important role in providing activity and selectivity. For example, a higher amount of aluminium atoms will increase the amount of hydrogen-transfer reactions that occur. Such reactions compete
with cracking reactions and are important for preserving molecules in the gasoline range. Therefore, by restricting the loss of aluminium atoms in the zeolite, rare earth increases the activity and gasoline yield of FCC catalysts. Rare earth also plays an important role to prevent metals deactivation, as it is a very effective vanadium trap. Therefore, for resid processing in particular, RE metals play an important role in maintaining stability and activity.

Grace Davison has a long history of providing innovation in the development of FCC catalysts, including the addition of rare earth metals to stabilize the zeolite Y component of the FCC catalyst. Grace also introduced RE free zeolites, that were extremely popular in the 80-90’s, which delivered high gasoline octane as well as stable activity. Grace Davison has now developed the REpLaCer™ family of zero- and low-rare-earth FCC catalysts, which are based on two rare-earth free Z-21 and Z-22 zeolites, utilizing proprietary stabilizing compounds and unique manufacturing processes to deliver similar or even improved performance compared to rare-earth containing catalysts.

Reducing Rare Earth via Traditional Means
While the Grace Davison’s zero rare-earth RepLaCer™ catalyst family is gaining commercial momentum, many refiners have pursued more traditional avenues of reformulation to achieve a lower rare-earth solution without sacrificing unit performance. One such customer, Refiner A, worked with Grace Technical Services to reduce the RE level by nearly 20% via a reformulation of GENESIS® to GENESIS® LX. This was accomplished without detriment to unit operating objectives of maintaining conversion and bottoms upgrading.

The GENESIS® catalyst system provides the ultimate flexibility to optimize Z/M in each unique application. The fundamental component is MIDAS® which maximizes conversion of bottoms with excellent coke selectivity by converting coke precursors into liquid products. The other component, as was the case here, is often IMPACT®. The inclusion of IMPACT® provides critical zeolite surface area and activity. Most prominently known for its superior coke selectivity, gas selectivity, and metals tolerance in a broad range of feeds, IMPACT® also gained recent recognition for another characteristic – high rare earth content.

In the new GENESIS® LX catalyst formulation, a lower RE high zeolite Aurora® alumina sol catalyst replaced IMPACT®. The Ecat Re₂O₃ trend is shown in Figure 1. Although the reduction in rare-earth content seems modest, this did in fact, equate to substantial savings. Using third quarter 2011 AMI averages, the re-

![Figure 1: RE₂O₃, wt.% Versus Date](image-url)
finery recognized a savings of over $1,000 per ton.

After reformulation, Refiner A not only realized some relief from rising rare-earth costs but also benefited to unit operation. The fresh activity GENESIS® LX is two numbers higher than the previous GENESIS® grade. The activity boost is maintained within the unit as shown in Figure 2.

Some variability in the Ecat activity data is present and can be attributed to the volatility in feed quality and metals levels. As verified via Figure 3, the catalyst weathered the fluctuations without difficulty and realizes a two to three number activity increase in the unit.

The reformulation to GENESIS® LX also bestowed additional conversion to the unit as expressed in Table 1. Refiner A benefited from a small decrease in catalyst additions.

The higher Ecat pore volume inherent to the new reformulation in tandem with the increased activity yielded improved bottoms conversion, as well.

**Reducing Rare Earth with ALCYON™ and ENCORE™**

Akin to Refiner A, Refiner B employed a catalyst that also contained the innovative resid catalyst, IMPACT®. As a unit that operates on the higher end of the Ecat metals spectrum, Refiner B needs to maintain activity

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### FIGURE 2: MAT Activity is Maintained at Lower Rare Earth

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### FIGURE 3: Activity is Higher with Lower Rare Earth at Equivalent Metals

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### TABLE 1: Refiner A FCC Unit Data

<table>
<thead>
<tr>
<th></th>
<th>GENESIS®</th>
<th>GENESIS® LX</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrected Conversion, Δ from Base</td>
<td>BASE</td>
<td>11%</td>
</tr>
<tr>
<td>Catalyst Additions, % Reduction</td>
<td>BASE</td>
<td>15%</td>
</tr>
<tr>
<td>Conversion / Feed API, Δ from Base</td>
<td>BASE</td>
<td>0.02</td>
</tr>
<tr>
<td>Slurry / Slurry API, Δ from Base</td>
<td>BASE</td>
<td>-1.0</td>
</tr>
<tr>
<td>Slurry / Pore Volume, Δ from Base</td>
<td>BASE</td>
<td>-3.2</td>
</tr>
</tbody>
</table>
and bottoms upgrading without an increase in dry gas production. Until mid 2010, 100% IMPACT® easily and economically achieved these objectives. The exacerbating predicament, of course, was the increasing cost associated with rare earth catalyst content.

Utilizing ENCORE™, a high quality spent catalyst, Grace formulated a solution with the ultra-active ALCYON™ catalyst. With ENCORE™ in the mix, Refiner B was subject only to the surcharges associated with the ALCYON™ catalyst. This relieved them of a significant portion of the cost imposed by rare-earth hyperinflation.

The eventual result will be a significant reduction in overall rare-earth catalyst content. ENCORE™ contributes roughly half of the rare earth added to the unit. Note that Refiner B uses a SOx reduction additive that also contains rare earth. Accordingly, the rare earth observed on Ecat is a shared contribution from both the catalyst and the additive and the downward trend is variable. The slight upward trend illustrated in Figure 4 is a result of increased SOx additive injection.

Inherent to the testing protocol, feed type and reactor temperature were held to produce the constant conversion yields shown in Table 2. Results establish that the reformulation successfully provides Refiner B with

![FIGURE 4: RE₂O₃, wt.% Versus Time](image)

<table>
<thead>
<tr>
<th></th>
<th>IMPACT®</th>
<th>ALCYON™/ENCORE™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>63</td>
<td>63</td>
</tr>
<tr>
<td>Catalyst to Oil Ratio</td>
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<td>6.6</td>
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<tr>
<td>Dry Gas, wt.%</td>
<td>2.0</td>
<td>1.9</td>
</tr>
<tr>
<td>Propylene, wt.%</td>
<td>3.9</td>
<td>3.9</td>
</tr>
<tr>
<td>Propane, wt.%</td>
<td>0.8</td>
<td>0.8</td>
</tr>
<tr>
<td>Total C₄+s, wt.%</td>
<td>4.8</td>
<td>4.9</td>
</tr>
<tr>
<td>IsoButane, wt.%</td>
<td>2.0</td>
<td>2.8</td>
</tr>
<tr>
<td>n-C₄, wt.%</td>
<td>0.7</td>
<td>0.6</td>
</tr>
<tr>
<td>LPG, wt.%</td>
<td>13.3</td>
<td>13.1</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>42.9</td>
<td>43.6</td>
</tr>
<tr>
<td>LCO, wt.%</td>
<td>25.5</td>
<td>25.8</td>
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<tr>
<td>Bottoms, wt.%</td>
<td>11.5</td>
<td>11.1</td>
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<tr>
<td>Coke, wt.%</td>
<td>4.7</td>
<td>4.6</td>
</tr>
<tr>
<td>RON</td>
<td>92.7</td>
<td>92.7</td>
</tr>
<tr>
<td>MON</td>
<td>80.9</td>
<td>80.7</td>
</tr>
</tbody>
</table>

**TABLE 2: Refiner B ACE Test Constant Conversion Yields**
considerably more activity. In fact, the catalyst is approximately 4.5 wt.% more active as shown in Figure 5. Figures 6 and 7 illustrate increases in gasoline and 1 wt.% lower bottoms per unit of coke. ALCYON™/ENCORE™ catalyst was able to achieve these improved yields without an increase in dry gas. Nearing 50% turnover, the unit continues to show the responses exhibited in the ACE study.

Reducing Rare Earth with ResidUltra™

Debuting in the first quarter of 2011, ResidUltra™ catalyst technology utilizes a re-optimized version of the ground-breaking IMPACT® matrix functionality for metals trapping and bottoms cracking technology.

Relative to IMPACT®, the ResidUltra™ catalyst reduces rare earth content by 40% without sacrificing activity or selectivity. Commercial experience proves that unit performance between IMPACT® and ResidUltra™ is nearly interchangeable (see article on page 13). Refiner C employed a GENESIS® catalyst system made up primarily of IMPACT®. Refiner C replaced the IMPACT® component with ResidUltra™ and similar to the prior examples, desired equivalent performance at lower rare earth. Although still in the midst of turnover, the goal is an eventual reduction in overall fresh rare earth requirement of 35%.

Thus far, the unit is nearing a turnover of 85% from GENESIS® to GENESIS® LX as illustrated in Figure 8.

Despite the reduction in rare earth content, the Ecatalyst unit cell size has remained constant. This is vital to maintaining catalytic activity in the unit.

An ACE study was performed against the original GENESIS® grade at 50% turnover to the GENESIS® LX containing ResidUltra™. The difference in rare earth between the base case and the reformulation was 15%. Other key catalyst properties were essentially constant. Specifically, both samples had similar Ni, V and Na levels, and Ecatalyst surface area. This unit does add ZSM-5, and the GENESIS® LX sample, did contain a higher amount of additive (approximately 2%).

As is the standard, feed type and reactor temperature were held unchanged to produce the constant conversion yields shown in Table 3. ACE results indicate that relative to the base catalyst, GENESIS® LX delivers benefit beyond simply a reduction in rare-earth costs. At just 50% turnover, GENESIS® LX is more active by over 1 wt.% and contributes nearly 1.5 wt.% to 2.0 wt.% additional conversion at constant coke. As a result of the higher activity and improved coke selectivity, GENESIS® LX catalyst produces lower bottoms yield.

In an effort to abate any uncertainty related to the equivalency of the two catalysts, it is worth acknowledging that there is a shift in the LPG and gasoline yield. Notice from Table 3 that GENESIS® LX is
offering more LPG and gasoline octane. Conversely, there is a decrease in gasoline make. These shifts are produced by increased levels of ZSM-5. Both grades would demonstrate similar wet gas and gasoline yields at equal additive levels.

Confirming the ACE results, the unit demonstrates that hydrogen make on both catalysts is very similar. The gas factor is effectively indistinguishable between the two grades containing ZSM-5. Commercial data showing this is contained in Figure 9.

TABLE 3: Refiner C ACE Test Constant Conversion Yields

<table>
<thead>
<tr>
<th></th>
<th>Genesis® / ZSM-5</th>
<th>Genesis® LX / ZSM-5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>69</td>
<td>69</td>
</tr>
<tr>
<td>Catalyst to Oil Ratio</td>
<td>7.7</td>
<td>7.1</td>
</tr>
<tr>
<td>Dry Gas, wt.% FF</td>
<td>2.1</td>
<td>2.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Propylene, wt.% FF</td>
<td>4.5</td>
<td>5.7</td>
</tr>
<tr>
<td>Propane, wt.% FF</td>
<td>1.2</td>
<td>1.3</td>
</tr>
<tr>
<td>Total C₅⁺s, wt.% FF</td>
<td>4.8</td>
<td>5.0</td>
</tr>
<tr>
<td>IsoButane, wt.% FF</td>
<td>4.0</td>
<td>4.4</td>
</tr>
<tr>
<td>n-C₄, wt.% FF</td>
<td>0.9</td>
<td>0.0</td>
</tr>
<tr>
<td>LPG, wt.% FF</td>
<td>15.5</td>
<td>18.2</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>46.9</td>
<td>44.4</td>
</tr>
<tr>
<td>LCO, wt.%</td>
<td>22.3</td>
<td>21.0</td>
</tr>
<tr>
<td>Bottoms, wt.%</td>
<td>8.7</td>
<td>9.1</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>4.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

FIGURE 9: Ecat Gas Selectivities are Maintained
Moving Towards Elimination of Rare Earth with REMEDY™

Refiner D operated with a grade of GENESIS® LX that contained 1.3 wt.% rare earth. Taking the ultimate step in minimizing the impact on catalyst cost, the AURO-RA™ component of the GENESIS® LX catalyst system was replaced with the zero rare earth REACTOR™ technology. REACTOR™ is formulated with Z-22, which uses a proprietary non-rare-earth compound to stabilize the zeolite. The rare earth content of the new catalyst system, REMEDY™, is half that of the previous GENESIS® LX.

Figure 10 illustrates the steady reduction in rare-earth content as the unit turns over to REMEDY™.

At approximately 65% turnover to REMEDY™, the performance of the unit is analogous to what was observed while operating on GENESIS® LX. Figure 11 demonstrates that Ecat MAT has been preserved as the unit continues to increase the level of REMEDY™ in the circulating inventory. Evident from Figure 12, the response to metals is equivalent if not better when compared to the rare earth analog, GENESIS® LX.

FIGURE 10: RE₂O₃ Versus Time

FIGURE 11: Ecat MAT is Maintained Despite the Reduction in Rare Earth

FIGURE 12: Metals Tolerance of REMEDY™ Is Equivalent or Better than GENESIS® LX
Even with higher metals levels, REMEDY™ shows equivalent or lower Ecat hydrogen scfb, gas factor, and coke factor. This is illustrated in Figure 13.

ACE testing of Ecat samples was performed against the original GENESIS® LX grade at 40% turnover to REMEDY™. The two samples tested were equivalent in Ni, V and Na levels as well as Ecat surface area. ACE testing confirms the trends that have been observed in the routine Ecat analyses as shown in Table 4. In addition to the advantages of ZSM-5, further benefits from the new catalyst system are already surfacing.

Consistent with refiner feedback, Ecat analysis, and ACE testing, activity has been maintained and hydrogen make reduced with REMEDY™.

Figure 14 exhibits additional ACE test findings, where the coke selectivity of REMEDY™ delivers greater gasoline selectivity and superior bottoms upgrading over the base GENESIS® LX.

The breadth of the Grace portfolio presents refineries with a myriad of RE reduction options. As demonstrated, scrutiny of market driven operating conditions.

### Table 4: Refiner D ACE Test Constant Conversion Yields

<table>
<thead>
<tr>
<th></th>
<th>GENESIS® LX</th>
<th>REMEDY™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>Cat-to-Oil Ratio</td>
<td>6.9</td>
<td>6.8</td>
</tr>
<tr>
<td>Hydrogen, wt.%</td>
<td>0.19</td>
<td>0.14</td>
</tr>
<tr>
<td>Dry Gas, wt.%</td>
<td>1.8</td>
<td>1.6</td>
</tr>
<tr>
<td>Propylene, wt.%</td>
<td>7.4</td>
<td>6.4</td>
</tr>
<tr>
<td>Propane, wt.%</td>
<td>1.2</td>
<td>1.1</td>
</tr>
<tr>
<td>Total C4s, wt.%</td>
<td>8.3</td>
<td>7.5</td>
</tr>
<tr>
<td>IsoButane, wt.%</td>
<td>4.8</td>
<td>4.3</td>
</tr>
<tr>
<td>nC4, wt.%</td>
<td>1.0</td>
<td>0.9</td>
</tr>
<tr>
<td>LPG, wt.%</td>
<td>22.7</td>
<td>20.2</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>43.3</td>
<td>46.0</td>
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<td>LCO, wt.%</td>
<td>20.1</td>
<td>20.9</td>
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<tr>
<td>Bottoms, wt.%</td>
<td>7.9</td>
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<tr>
<td>Coke, wt.%</td>
<td>4.1</td>
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<tr>
<td>RON</td>
<td>92.1</td>
<td>92.3</td>
</tr>
<tr>
<td>MON</td>
<td>80.8</td>
<td>80.6</td>
</tr>
</tbody>
</table>

**FIGURE 13:** REMEDY™ Maintains Ecat Selectivities
goals in tandem with unit tailored reformulation efforts allows refiners to realize enhanced operations and unit profitability.

Continuous development in the area of rare earth free catalysis by Grace adds even further opportunity for overall cost savings and optimization.

**Commercial Experience of Zero Rare Earth Catalysts**

Rare-earth free RESolution™ catalysts are based on the Z-21 zeolite and are sourced from our manufacturing site in Worms, Germany. RESolution™ catalysts are designed for hydrotreated and VGO applications. Within the first six months of commercialization, the RESolution™ catalyst has been successfully used in over seven refineries in the EMEA region. One such application is at the MiRO refinery in Germany. In February 2011 they switched from a catalyst with 3.1 wt.% rare earth to the rare-earth free RESolution™ catalyst. ACE pilot plant Ecat testing was used to evaluate the performance of the RESolution™ catalyst at 30% change-out. As can be seen in Table 5, conversion, dry gas yield and bottoms upgrading were similar for the RESolution™ catalyst, while delta coke was improved.

Table 5 shows a comparison of the product selectivities in more detail, where the increased LPG yields (at the expense of gasoline) can be attributed to the fact that more ZSM-5 additive was used with the RESolution™ catalyst. The catalyst change-out has since reached over 75%, and the RE₂O₃ content of the Ecat has been reduced from 3.1 to 0.7 wt.%. The refinery reports that the performance has not only been maintained using the rare-earth free RESolution™ catalyst, but it has actually improved. To summarize, MiRO has observed similar bottoms upgrading and dry gas yield, as well as lower delta coke.
We are currently commercializing a high matrix catalyst based on the Z-21 technology called REBEL. Two refineries have just begun application of REBEL catalyst in North America. Look for an update on commercial experience in our next Catalagram® No. 111.

**Commercial Experience of Low Rare-Earth Catalysts for Resid Feed Applications**

REDuceR™ catalyst based on Z-22 zeolite technology is an effective means to reduce the overall rare-earth requirement in resid applications. Figure 15 shows the activity retention of different REDuceR™ catalyst blends with NEKTOR-ULCC™ resid catalyst as measured in ACE pilot plant testing with 2000/3000 ppm Ni/V at constant cat-to-oil. Activity can be maintained at blends of up to 60% REDuceR™ catalyst. It is possible to utilize more than 60% RE free catalyst in the blend, depending upon your unit’s severity and flexibility to optimize the unit conditions.

The REDuceR™ catalyst has been successfully commercialized, and is currently applied in more than 10 resid applications in Europe. One such example is at the Bayernoil, Vohburg refinery in Germany, which processes a resid feedstock with typical Ecat Ni+V levels of > 7,000 ppm. This refinery was previously using a NEKTOR™ catalyst that contained 3.1 wt.% RE₂O₃, and performed extremely well. In April 2011, Bayernoil, Vohburg began to blend 30% of the rare-earth free REDuceR™ catalyst with the NEKTOR™ catalyst and the FCCU data is shown in Figure 16. The REDuceR™ catalyst blend provides similar/better bottoms upgrading, a lower delta coke, lower regenerator bed temperature and increased conversion at constant feed atmospheric residue content.

The refinery considered the performance of the REDuceR™ catalyst to be such a success that they increased the blending ratio from 30% to 50%, thus reducing the overall rare earth content of the catalyst to 1.5 wt.%. Table 6 shows the FCCU product yields obtained with the 50% REDuceR™ catalyst blend compared with the NEKTOR™ catalyst. For the purpose of evaluating the actual catalyst performance the yields shown are calculated on the basis of constant feed properties and independent operating conditions. The key objective of the refinery was to maintain conversion and bottoms upgrading while reducing rare-earth content. As can be seen these key objectives were met, and in addition conversion and bottoms upgrading were even improved. The REDuceR™ catalyst provided a similar coke yield but an improved delta coke, and allowed regenerator bed temperature to decrease by 60°F.

**Conclusion**

In response to the increasing cost and decreasing availability of rare-earth metals, Grace Davison Refining Technologies has successfully commercialized the REpLaCeR™ family of low and zero

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**TABLE 6: FCCU Data of the REDuceR™ Catalyst Blend at 50%**

<table>
<thead>
<tr>
<th></th>
<th>NEKTOR™</th>
<th>50% REDuceR™</th>
<th>50% REDuceR™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-to-Oil</td>
<td>Base</td>
<td>Base -0.4</td>
<td></td>
</tr>
<tr>
<td>Conversion, wt.%</td>
<td>Base</td>
<td>Base +0.5</td>
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<tr>
<td>Hydrogen, wt.%</td>
<td>Base</td>
<td>Base +0.02</td>
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</tr>
<tr>
<td>C₅+C₆’s, wt.%</td>
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<td>Base +0.2</td>
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<tr>
<td>Propylene, wt.%</td>
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<tr>
<td>C₄ Olefins, wt.%</td>
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<td>Base +0.6</td>
<td></td>
</tr>
<tr>
<td>LPG, wt.%</td>
<td>Base</td>
<td>Base +2.0</td>
<td></td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
<td>Base</td>
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<td></td>
</tr>
<tr>
<td>LCO, wt.%</td>
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<tr>
<td>Slurry, wt.%</td>
<td>Base</td>
<td>Base -0.2</td>
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</tr>
<tr>
<td>Coke, wt.%</td>
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<td>Base -0.1</td>
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<td>Delta Coke, wt.%</td>
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<td>Ecat Ni, ppm</td>
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<td>Base</td>
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<td>Ecat V, ppm</td>
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<tr>
<td>Regen Bed Temp, °C</td>
<td>Base</td>
<td>Base -15°C</td>
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</table>

FIGURE 15: Activity Retention of REDuceR™ Catalyst Blends for Resid Applications
rare-earth catalysts. RESolution™ and REBEL™ catalysts are based on the Z-21 zeolite, while REACTOR™ and REDuceR™ incorporate the newly developed Z-22 zeolite. Grace’s experienced Technical Services team has successfully applied each of these technologies in hydrotreated/VGO applications as well as resid operations. Alone or blended with a rare-earth containing conventional catalyst, these new FCC technologies have demonstrated excellent stability, selectivity and activity retention, which minimizes potential exposure to rare-earth inflation. As shown in Figure 17, the REPLaCeR™ family of catalysts have received rapid global market acceptance.

Through the development of proprietary non rare-earth stabilized Z-21 and Z-22 zeolites Grace Davison is the only catalyst supplier that provides zero rare-earth FCC catalysts. Grace Davison’s Technical Service team is well experienced in the application of our broad portfolio of FCC catalysts. Let Grace’s RT team help you find the optimal catalyst solution for your operation.

References

Commerical Demonstration of ResidUltra™ Catalyst in a Resid Processing Application at S-Oil Corporation

Introduction

The recent spike in rare earth prices due to China’s restricted export quota system and pending environmental regulations caused a significant rise in catalyst prices. In response to these high rare earth prices, Grace introduced a number of RE-free and low RE catalysts for various feedstocks. Refiners processing resid feedstocks need FCC catalysts that crack larger molecules while delivering optimal coke selectivity. These catalysts typically have higher amounts of rare earth in order to trap contaminant metals in the feed, protecting activity and selectivity. Grace introduced a breakthrough resid catalyst called, IMPACT® in 2003. IMPACT® contained a proprietary Integral Vanadium Trap (IVT) technology and has demonstrated step-out improvements in coke selectivity and bottoms cracking in over 70 units worldwide.

Despite the tightening of supply, rare earth metals remain key components in FCC catalysts for resid cracking and there are no easy substitutes. Grace launched a new resid catalyst called, ResidUltra™ early in 2011. ResidUltra contains the next generation IVT metals trap and matches the performance of IMPACT® catalyst with 40% lower RE content. ResidUltra™ catalyst formulation is optimized for bottoms cracking, coke selectivity and metals trapping and retains the same activity and selectivity with all the benefits of Al-sol technology.

In Figure 18, an electron microprobe image of ResidUltra™ shows a strong correlation of vanadium with rare earth. The resultant rare earth vanadates are very stable and inert under FCC conditions, greatly reducing zeolite deactivation and coke and gas production.

S-Oil Corporation located in Ulsan, Korea has a 40,000 BPD IFP RFCC unit processing hydrotreated VGO and vacuum residue feedstock. Over the years of revamping and debottlenecking, the RFCC unit can now process 73,000 BPD.

S-Oil has used IMPACT® catalyst successfully over the past couple of years, benefitting from its excellent coke selectivity and activity retention. With the increase in rare earth prices in 2010, Grace knew that S-Oil
would face increased catalyst costs in the coming months and approached the refinery for mutual discussion. The refinery understood that the RE content of 5.5 wt.% in IMPACT® will make it less attractive from an economic standpoint. Immediately, both Grace and S-Oil started to work together for a resid catalyst that can match the performance of IMPACT® but at reduced RE levels. ResidUltra™ catalyst is the result of Grace’s R&D effort.

Catalyst samples were evaluated in pilot plant testing prior to the commercial production and application. The lab-made catalysts were deactivated with standard CPS method at 1450°F with 2000 ppm Ni and 3000 ppm V. ResidUltra™ catalyst had the same unit cell size after deactivation as IMPACT®, and produced similar hydrogen, dry gas and bottoms yields at lower coke than the IMPACT® sample. These lab test results, shown in Table 7, confirming similar performance between IMPACT® and ResidUltra™, were presented to S-Oil Corporation prior to the commercial trial. S-Oil also performed the same lab test and the results showed the similar performance between IMPACT® and ResidUltra™.

S-Oil Corporation began the commercial testing of ResidUltra™ in February 2011 with the expectation of equal performance to IMPACT® but with about 35% reduction in rare earth content. The properties of both catalysts are summarized in Table 8.

### Equilibrium Catalyst Evaluation

The RE content dropped to 3.5 wt.% confirming a complete catalyst turnover. The zeolite surface area, MAT and Ni+V content are plotted in Figure 19 against the time period. In recent months, the unit shifted to higher metals content. As expected, the SA gradually dropped with the increase in both Ni and V contents. The rate of decrease is approximately 10 m²/g per 1000 ppm increase in V+Na content. The MAT activity dropped slightly but remained within the historical range.

<table>
<thead>
<tr>
<th>IMPACT®</th>
<th>ResidUltra™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen, wt.%</td>
<td>0.26</td>
</tr>
<tr>
<td>Dry Gas, wt.%</td>
<td>2.3</td>
</tr>
<tr>
<td>Propylene, wt.%</td>
<td>4.5</td>
</tr>
<tr>
<td>Total C₃'s</td>
<td>5.5</td>
</tr>
<tr>
<td>Total C₄'s, wt.%</td>
<td>5.5</td>
</tr>
<tr>
<td>Gasoline, wt.%</td>
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<tr>
<td>LCO, wt.%</td>
<td>18.0</td>
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<tr>
<td>Bottoms, wt.%</td>
<td>6.0</td>
</tr>
<tr>
<td>Coke, wt.%</td>
<td>7.7</td>
</tr>
<tr>
<td>RON</td>
<td>90.9</td>
</tr>
</tbody>
</table>

**TABLE 7: The ACE Lab Test Results Confirm ResidUltra™ Can Match Impact® Performance**

<table>
<thead>
<tr>
<th>IMPACT®</th>
<th>ResidUltra™</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina, wt.%</td>
<td>48</td>
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<tr>
<td>Rare Earth Oxides, wt.%</td>
<td>5.5</td>
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<tr>
<td>APS</td>
<td>75</td>
</tr>
<tr>
<td>MicroActivity</td>
<td>83</td>
</tr>
<tr>
<td>DI</td>
<td>5</td>
</tr>
</tbody>
</table>

**TABLE 8: Catalyst Properties of IMPACT® and ResidUltra™**
The plots of coke factor, H₂ yield along with levels of nickel equivalent (Ni + V/4 – [1.21 x Sb]) over the period of time are plotted in Figure 20. The coke factor decreased with Ecat activity. The hydrogen yield remained the same despite increased levels of equivalent nickel content.

Based on the Ecat data the following conclusions can be made:

- The SA trends very closely with V+Na content
- MAT activity decreased with higher V+Na content
- Coke selectivity is similar despite higher Ni Eq
- Gas factor is higher with increasing Ni Eq, but H₂ selectivity was maintained
- No significant changes were observed in Ecat physicals, hence fluidization is largely unchanged

**Commercial Operating Data**

The changes in the operating conditions and yield differences for ResidUltra™ are summarized in Table 9 and Figure 21. The 90% BP of feed is significantly higher due to an increase in vacuum residue (VR) in the feed. The unit is currently processing almost 100% VR as opposed to 90% in the past. Hence, the feed quality is considered significantly more aromatic even though micro carbon residue (MCR) and API gravity appear to be similar.

The reactor temperature remained the same. The regeneration temperature dropped along with the conversion. The C/O ratio remained the same and delta coke increased slightly due to a small increase in the coke yield.

An economic review indicated that operation at higher Ecat metals is more profitable due to the reduced catalyst cost. As a result, targeting higher Ecat metals led to a decrease of fresh catalyst addition rate by about 17% equivalent to 4.0 MT/d.

The yield differences, summarized in Table 9, after the unit changed the catalyst to ResidUltra™, are at constant Ecat metals level (7,000 ppm), feed rate and cat-to-oil ratio. During this period, there was a substantial absolute increase of 8% of vacuum residue to the RFCC feed and the feed 90% BP increased from 657˚C to 722˚C. As a result, there is a significant impact on the conversion and product yields with the increase in feed aromaticity.

However, ResidUltra™ has proven its metal tolerance capability despite lower RE level. With a proper formulation tailored to S-Oil’s needs, activity was maintained with less fresh catalyst make up. Although the conversion decreased slightly with the more aromatic feed, the benefit of processing 8% more residue in the feed outweighed the decrease in conversion. In general, S-Oil is able to maintain satisfactory performance with an average of 4 mTPD less fresh catalyst addition and 2 wt.% lower RE on catalyst. The reformulation to a lower rare earth catalyst was a joint effort achieved through close collaboration between S-Oil and Grace Davison. It has
Properties | Delta
---|---
Feed Rate, BPD | 0.0
Feed Ratio, %VR | 8.0
Feed API | -0.2
Feed BP 90%, °C | 34.7
Cat Adds, MTD | -4.0
Fresh Cat/Feed, kg/bbl | -0.06
Feed T (°C) | -18.2
ROT T (°C) | 0.0
Regen T (°F) | 10.0

Yields, wt.% | Delta
---|---
Coke, wt.% | 0.1
Delta Coke, wt.% | 0.6
Dry Gas, vol.% | -2.1
Gasoline, vol.% | 1.1
LCO, vol.% | 0.0
Slurry, vol.% | -1.5
Conversion, vol.% | -0.5
C₄, vol.% | -0.1
C₅, vol.% | -0.1

TABLE 9: The Changes in Operating Conditions and Resulting Yields of Using ResidUltra™ vs. IMPACT®

Summary

The Ecat and commercial data demonstrate that the performance of ResidUltra™ is similar to IMPACT® catalyst. ResidUltra™ is a successful replacement for IMPACT® and has met the performance expectations in terms of coke selectivity and activity. S-Oil Corporation is very satisfied with the performance and resultant cost savings due to lower RE content and lower fresh catalyst make up rate. The reformulation would not have been as successful without the close collaboration of S-Oil and a good understanding of the unit’s performance needs by Grace. Grace Davison is committed to working with customers to re-optimize their catalyst formulation with the goal of reducing overall rare earth content of the catalyst while maintaining acceptable performance. Grace is currently exploring additional reduction in RE content via REpLaCeR™ catalyst technologies to further improve the cost savings.
Two Great Organizations
United by a Catalyst

Colombia’s largest company, ECOPETROL, and the world leader in the catalyst market, Grace, have joined their talents and resources in an innovative research project. The result is a catalyst with international projections to increase diesel production; this is evidence of the success of strategic alliances in research, development and innovation and confirmation that ECOPETROL has world-class talent.

By developing a new catalyst in a joint project with Grace, ECOPETROL has scored very high.

The implications of this new technological product are related to:

i. The quantity and quality of the fuels produced in Colombia
ii. The national and international energy market
iii. ECOPETROL’s corporate strategy and international projections
iv. Current and future models for the undertakings in Research, Development and Innovation of the Colombian Petroleum Institute (ICP)

Within the national and global scale, the trend is that diesel consumption is growing at a faster pace than gasoline consumption. This phenomenon is evident in Latin America, Europe and the Asia-Pacific region. The price of diesel is now higher than gasoline in many markets.

The refining strategy in ECOPETROL is currently focused on gasoline, and crude processing is based on Fluid Catalytic Cracking (FCC). As is customary, these types of units (four in Barrancabermeja and one in Cartagena) are designed with gasoline as the main product. The FCC also produces a stream called Light Cycle Oil (LCO) with yields usually in the 15-18% range. The LCO has a distillation range similar to diesel, and a small portion of this stream (between 4-5%) is eventually used for diesel production.
The Colombian market for diesel is growing rapidly, and it is necessary to find options to increase the availability of this product. Since the FCC technology is the main technology for processing crudes in ECOPETROL, it was logical to find alternatives for increasing diesel yields from this process.

There are many alternatives for obtaining more LCO from an FCC, which include unit severity optimization, changes in the equipment’s internal design, changes in the catalyst or a combination of these options. The engineers at the ICP concluded that it was necessary to develop a suitable solution within the existing refinery infrastructure, while the Master Plans for the Reconversion of the ECOPETROL Refineries take place. After analyzing these options, they concluded that the appropriate solution was an innovation in the FCC catalyst.

The catalyst that is used in the FCC is silica and alumina-based, which accelerates the process reactions and increases the yields of the more valuable products.

**The Best Option**

At this point the question was: What would be the most appropriate mechanism to seek this innovation? There were three routes: (1) ECOPETROL would absorb all of the expenses and would perform all of the Research and Development work; (2) Wait for an outside company to manufacture the catalyst that was required; or (3) Form an alliance with a specialized company.

Each option had its advantages and disadvantages. After evaluating aspects like time available, internal capacity, extrapolation of the laboratory results to commercial production (scalability), development costs and success probability, it was concluded that the best decision was to create an alliance for this research.

After considering various proposals, the partner chosen was W. R. Grace, a company that was founded in 1854 in Peru by an American businessman, and is presently a world leader in products based on silica and alumina oxides.

ECOPETROL found Grace to be the appropriate partner, since its researchers were thinking along the same path. The company supplies 35-40% of the FCC catalyst to the worldwide market, and has vast experience in specialty chemicals since its Research and Development team is one of the best in the world. Yet similar reasons were recognized by the American company, as Rubén Cruz, Grace RT General Manager, Latin America, explains: “In ICP we found incredible human capacity, knowledge, laboratory facilities and the desire to cooperate and to improve. It was exactly what we were looking for. It was very easy for us to make the decision. ICP is the partner with which we will associate to develop new technologies and new catalysts”. Cruz considers Colombia as a “leader” in the operation of catalytic units in Latin America and “probably the world”.

**At Work**

The challenge that the team from both organizations faced was to develop a catalyst that improved the LCO yield without affecting conversion, while minimizing the loss in gasoline. It was a major challenge, since there were no reports in the literature that revealed similar results, nor catalysts with this performance. It was necessary to complete an exploratory phase in the laboratory. During this stage, over 50 different formulations were evaluated in reactors using catalyst samples whose size varied between 5 and 8 grams. This work took almost a year and a half.

There were months of constant contact, data revisions, laboratory testing, verification of the requirements of ECOPETROL’s units and travelling of employees from both organizations to each other’s Research Facilities (Piedecuesta, Colombia and Baltimore, MD, USA) to assure good advancement on the project. The team was formed of five people from ICP, including the group leader and laboratory technicians, with the constant follow up from personnel at the management level, and a similar team from Grace.

After the initial process, the best two options were selected. Simultaneously, ICP developed process changes in the pilot plant that, which, in compliance with terms of the agreement, ECOPETROL patented as its own products. It deals with actions or mechanisms that lead to controlling many variables, including temperature, flow and feed treatment that allow optimizing the final result.

Afterward, the best formulations were tested in the pilot plant. The facilities and the procedures that were developed at ICP were used for catalyst evaluation and selection.

At this point it was necessary to perform two experimental cycles in the pilot plant, since the first formulations revealed high coke yields. The adjustments were agreed by both teams and a new group of samples was prepared.

From these, one catalyst with a very high potential was chosen. The new catalyst increased LCO yield by 4% without lowering conversion with only a slight loss in gasoline. The LCO obtained with this catalyst is of better quality than that generated from a conventional catalyst. This means that greater quantities of LCO can be added to the diesel pool (between 5 and 7%).

The results allow increasing the profitability of the refining process. At the same time, it generates an alternative to address, at least partially, the increasing demand for diesel without having to wait for the construction of new facilities.

**The Future**

The results obtained so far are very positive and both companies are working to convert this development into a commercial reality. “It is the first technology that has substantially improved the product yield
and quality. We are very proud to arrive at something that has tried to be achieved for the past 15 or 20 years, and now we have finally arrived at this point”, said Cruz.

Once the final tests have been completed, the catalyst would be commercialized worldwide. This not only meets the specific needs of ECOPETROL, its potential includes Latin America, Europe and the Asia-Pacific Region.

The product is a concrete result. It is also a success story for strategic alliances in the development of innovative technologies. In ECOPETROL’s vision for 2020, the company will be characterized as one of the 30 leading companies in the petroleum industry, known for, among other reasons, its international positioning and its innovation.

In the future, ICP is considering an expansion strategy in three areas: fundamental research leveraged from specialized centers and universities, cooperation with organizations that are leaders for specific solutions, and the drive to create technology-based companies in order to license technologies created by ECOPETROL.

The joint work with Grace demonstrates the advantages of cooperative work. “For example, Grace, which has a strength in catalyst, teamed up with us to develop a new catalyst to improve diesel production. Through agreements, where we both win, we look for solutions for ECOPETROL, with a moderate risk in research” explains Néstor Fernando Saavedra, ICP Director. To innovate is not only to invent something: it is to apply creative schemes to put technology at the service of society. That is what it means to be world-class.

Grace Introduces TITAN™

The unique catalyst designed to offer a reliable, affordable solution for removing contaminant metals from refining operations.

Rings of Titan, Saturn’s largest moon

No more concerns for the elevated NOx, hydrogen, dry gas or coke created by use of traditional equilibrium catalysts, because TITAN™ contains no nickel, no vanadium and no additives. With the benefit of Grace Davison’s unique, environmentally friendly manufacturing process, TITAN™ can be offered with no rare earth surcharge. Only Grace Davison has the logistics capability to provide blends of TITAN™ with any combination of fresh catalysts, equilibrium catalysts and additives and TITAN™s performance is backed by the support of our Grace Davison world-class Technical Service team. So if you’re looking for quality, consistency and reliability, try the unique catalyst only offered by Grace Davison: TITAN™.

For more information on TITAN™, contact Stuart Kipnis at (410) 531-8892, stuart.kipnis@grace.com.

www.grace.com
FCC catalyst is added daily to the FCC regenerator to maintain a desired catalyst activity and product selectivity. Fresh catalyst addition rates commonly range between 0.1 lb. of catalyst per barrel of hydrotreated vacuum gas oil (VGO) feedstock to over 1 lb. of catalyst per barrel of high metals resid feedstock.

During normal operations, the catalyst level in the regenerator increases as catalyst is added. Equilibrium catalyst (Ecat) is withdrawn from the FCC regenerator to maintain the regenerator catalyst inventory between maximum and minimum levels.

Due to continuous catalyst addition, the catalyst inventory has a wide age distribution. A portion of the catalyst inventory is relatively young, with lower density, high activity and low metals, while some of the catalyst circulating is older, with a higher density, relatively low activity and higher metals and may have been in the unit for weeks, months or even longer.

At Grace’s research and development laboratories in Columbia, MD, a technique called Sink/Float is used to understand the FCC catalyst age distribution. The technique can be described simply as a catalyst distillation method which separates FCC Ecat into several fractions, based on density differences, ranging from the youngest to the oldest catalyst in the unit. Understanding how Ecat age distribution impacts the overall catalyst performance can lead to unit optimization opportunities. Grace has found that the Sink/Float technique is a valuable tool that helps our customers improve their unit operations.

**Sink/Float Technique**

Grace’s Sink/Float technique was originally developed to determine the relative vanadium mobility in FCC Ecat.1

The technique separates a catalyst into two or more fractions by taking advantage of slight differences in catalyst skeletal density. Catalyst is mixed with tetrabromoethane (TBE) with a density of 2.96 g/ml. Since Ecat density is about 2.4 to 2.8 g/ml, it always floats in TBE. Tetrachloroethane (TCE) with a density of 1.58
g/ml is stirred into the mixture to lower the density and cause some of the heavier catalyst particles to sink to the bottom. The amount of TCE added is adjusted to obtain the desired amounts of density fractions of catalyst. Visual inspection shows whether separation has occurred and whether the separation is approximately at the desired ratio. To meet the desired ratio, TBE is added to increase the float fraction, or TCE to increase the sink fraction. All volumes and weights of liquids added are recorded in order to calculate the density at the split. The process of remixing is continued until the desired sink/float ratio is achieved.

Separation of a 100 to 200 gram catalyst sample into three or more fractions can be achieved by repeating the procedure on one or both of the original fractions, with appropriate changes in the final density of the liquids used for each fraction. Four to eight fractions may be made. Detailed chemical and physical property measurements are made on each fraction once the separations are made.

Figure 22 is a simplified block flow of the technique and Figure 23 is a photograph of the separated mixture.

The Sink/Float technique can be used to study metal distribution in FCC Ecat, and we also use it to separate additives and/or inert particles present in some FCC Ecat.
Bench scale pilot testing in an Advanced Cracking Evaluation unit (ACE) or Micro Activity unit (MAT) can be conducted on each fraction allowing comparisons to be made with the composite Ecats and between fractions.

Due to the hazardous properties of TBE and TCE, appropriate handling and storage procedures are required.

**Internal Age Distribution**

By making a few simplifying assumptions, the Internal Age Distribution (IAD), I(t), can be expressed as:

\[ I(t) = \frac{1}{\tau} \exp\left(-\frac{t}{\tau}\right) \]

Where:

- \( t \) = time (days)
- \( V \) = unit inventory (tons)
- \( m \) = catalyst addition rate (tons/day)
- \( \tau = \frac{V}{m} \) (days)

For illustration, consider a unit charging 50,000 bbls/day, adding 3.75 tons/day of fresh catalyst additions and has a circulating inventory of 300 tons. From above we see \( \tau = 80 \) days and we can generate the IAD displayed in Figure 24.

One assumption that goes into the construction of this distribution is that catalyst additions and withdrawals are made continuously. Figure 24 illustrates that even with these "ideal" conditions, 25% of the inventory has been in the unit for greater than 111 days.

**Sink/Float Example**

Consider a unit processing a heavily hydrotreated feed with catalyst additions of 0.12 lbs/bbl, \( \tau = 200 \) days (low turnover) and making frequent Ecats withdrawals. This unit’s Ecats was split into four fractions using the Sink/Float technique described above. The fractions were analyzed and the chemical assays and surface areas determined. The results are summarized in Table 10.

As one would expect, Ni and V increase with the age of the fraction. Sodium is highest on the lightest portion of the fraction consistent with higher zeolite surface area (ZSA). Also expected is the observed decrease in surface area and unit cell size (UCS). Because of the decreasing surface area and UCS, we might expect the activity of the fractions to decrease as well.

The four fractions were tested via ACE at three different cat-to-oil ratios on feed specific to this unit. The observed activity and delta coke of the fractions is displayed by Figure 25 and summarized in Table 11.

---

**FIGURE 24: Internal Age Distribution**

**FIGURE 25: Conversion and Coke by Fraction versus Cat-to-Oil**
### Implications for Severely Hydrotreated Feeds

For units using severely hydrotreated feeds, undesirably low regenerator temperatures may be observed. Low regenerator temperatures may result in exceeding limits on catalyst circulation, slide valve dp or possibly flue gas emissions. How can the refiner respond to such a situation? Ideally the activity of the catalyst would be increased. This could be accomplished by increasing the intrinsic activity of the catalyst or by increasing the catalyst addition rate. In some cases increasing the intrinsic activity may not be an option as the catalyst may already be as active as possible due to objectives or constraints.

Using the information presented above an IAD for \( \tau = 200 \) days can be constructed and conversion and delta coke estimates can be made if fresh catalyst additions are increased so that \( \tau \) is decreased from 200 days to 150 days.

Figure 26 displays the IAD for \( \tau = 200 \) days. If we assume the Float/Float fraction is the youngest fraction then, referring to Figure 26 and Table 2, we see that the 24.7% of inventory represented by the Float/Float fraction is in the unit less than 57 days in the unit and has an activity of 84.4%. Likewise the 24.4% of Float/Sink fraction of inventory is in the unit between 57 and 135 days and has an activity of 79.9%. And so on. A plot can now be made of fraction activity verses that fraction’s ‘Mid-Range Day’. Mid-Range Day is defined

<table>
<thead>
<tr>
<th>% in Fraction, wt.%</th>
<th>Ecat (XRF)</th>
<th>Float/Float</th>
<th>Float/Sink</th>
<th>Sink/Float</th>
<th>Sink/Sink</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃, wt.%</td>
<td>42.90</td>
<td>40.30</td>
<td>41.00</td>
<td>41.87</td>
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</tr>
<tr>
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<td>3.38</td>
<td>3.46</td>
<td>3.51</td>
<td>3.74</td>
</tr>
<tr>
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<td>0.60</td>
<td>0.51</td>
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<td>0.44</td>
</tr>
<tr>
<td>Ni, ppm</td>
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<td>51</td>
<td>62</td>
<td>82</td>
</tr>
<tr>
<td>V, ppm</td>
<td>1143</td>
<td>670</td>
<td>1040</td>
<td>1310</td>
<td>1550</td>
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<tr>
<td>Zeolite Surface Area, m²/g</td>
<td>152</td>
<td>193</td>
<td>163</td>
<td>143</td>
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<td>Matrix Surface Area, m²/g</td>
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<td>34</td>
<td>35</td>
<td>30</td>
<td>26</td>
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<td>Unit Cell Size, Å</td>
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<td>24.36</td>
<td>24.33</td>
<td>24.31</td>
<td>24.31</td>
</tr>
</tbody>
</table>

### TABLE 10: Chemical and Surface Area Analysis of Sink/Float Fractions

*Estimated based on Internal Age Distribution and Deactivation Curve

<table>
<thead>
<tr>
<th>% in Fraction, wt.%</th>
<th>Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conversion, wt.%</td>
<td>84.4</td>
</tr>
<tr>
<td>Delta Coke, wt.%</td>
<td>0.91</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>% in Fraction, wt.%</th>
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<tr>
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</tr>
<tr>
<td>Delta Coke, wt.%</td>
<td>0.91</td>
</tr>
</tbody>
</table>

### Table 11: Chemical and Surface Area Analysis of Sink/Float Fractions
as the day where 50% of that fraction is in the unit for a time less than that day and 50% is in the unit for a time greater than that day. Such a plot is also presented by Figure 26. Using the IAD and Deactivation Curve, the activity of an incremental fraction of the inventory can be calculated and an estimate of the unit Ecatalyst can be made by summing the increments. Using this technique, Ecatalyst activity is estimated to be 78.1% and delta coke is estimated to be 0.53 wt.%

Using the method described above, by increasing catalysts additions so that \( \tau = 150 \) days, the estimated Ecatalyst activity increases to 80.1% and delta coke is estimated to increase to 0.58 wt.%. The change in activity is graphically explained by Figure 27. As can be seen, the IAD has shifted to the left such that the fraction less than 57 days is estimated to increase from 24.7% to 31.5% while the fraction greater than 260 days is estimated to decrease from 26.5% to 17.6%

Higher delta coke will produce a higher regenerator temperature resulting in higher catalyst slide valve pressure drop and perhaps lower CO emissions. Resulting higher Ecatalyst activity will provide for additional unit conversion.

**Activity Responses at High Catalyst Additions During Increased Catalyst Losses**

Periodically, FCC’s must operate with damaged cyclones elevating catalyst losses. When this occurs, catalyst additions are increased in order maintain catalyst inventory.

Consider a unit with normal catalyst additions of ~0.275 lbs per barrel of feedstock and frequent catalyst withdrawals were made from the unit. The unit’s regenerator cyclones developed a problem and catalyst losses increased to ~0.475 lbs per barrel of feedstock. Economics did not support shutting the unit down to make repairs, so the unit continued to operate by increasing fresh catalyst additions to equal the catalyst losses, i.e. no Ecatalyst withdrawals were made.

Grace conducted a Sink/Float evaluation of this unit’s Ecatalyst to understand the Ecatalyst age distribution and the activity response of the two addition rate periods. Table 12 shows the properties of the composite Ecatalyst and four density fractions from each period.

As expected, in both cases the youngest fraction has the lowest metals, while the oldest fraction shows the highest metals. Table 12 also shows higher levels of sodium on the younger fractions; consistent with Table 10.

Figure 28 graphically displays zeolite surface areas (ZSA) from Table 12 for each Ecatalyst fraction for both periods. Ecatalyst produced during the high loss period (shown in red) shows the highest ZSA. As might be expected, ZSA of the youngest fractions is the highest, while the ZSA is lowest in the oldest fraction. Also, as might be
expected, the youngest fraction for the high loss/high addition period had higher ZSA than that of the normal operation period. However, the rate of decline in ZSA was greater during the high loss period with the oldest fraction from the high loss period having a significantly lower ZSA than the same fraction from the normal operations period, despite higher catalyst additions.

Sink/Float fractions from each period were evaluated further in an ACE test using refinery FCC feedstock. Figure 29 and Table 13 display the results of that testing.

Figure 29 shows the relationship between conversion and catalyst/oil ratio for the lightest and heaviest density fractions from both catalyst addition periods and is consistent with surface area values shown in Figure 28. As expected, the highest activity is from the lightest density fraction from the high catalyst addition period.

<table>
<thead>
<tr>
<th>TABLE 13: ACE Results Summary</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cat-to-Oil = 6.5; τ = 137 Days</td>
</tr>
<tr>
<td>% in Fraction, wt.%</td>
</tr>
<tr>
<td>Conversion, wt.%</td>
</tr>
<tr>
<td>Cat-to-Oil = 6.5; τ = 79 Days</td>
</tr>
<tr>
<td>% in Fraction, wt.%</td>
</tr>
<tr>
<td>Conversion, wt.%</td>
</tr>
</tbody>
</table>
However, the lowest activity is the heaviest density fraction, also from the high catalyst addition period. Table 13 displays the activity of each fraction at constant cat-to-oil ratio.

As in the previous example, IAD for $\tau = 137$ and 79 days were constructed using the data from Table 13 and displayed as Figure 30 and Deactivation Curves were constructed and displayed as Figure 31. As in the previous example, Ecat activity was estimated using the information from Figures 30 and 31. As might be expected, the estimated activity of the Ecat taken during the period of high adds/high losses is greater than the estimated activity of the Ecat taken during normal operations; 60.6% versus 59.2. If we use the IAD and Deactivation Curve for normal operations, i.e. $\tau = 137$ days, and decrease $\tau$ to 79 days, the estimated Ecat activity is 62.1%, 1.5% greater than the “observed” value. What could account for the discrepancy between the observed and expected activity?

Two facts should be considered. First, the separations by Sink/Float are performed by density differences. Second, during the high loss period, catalyst withdrawals were suspended. The combination of these two factors will contribute to the difference in expected activities. Even though the cyclones are operating with less than optimum efficiency, they will still tend to retain more dense particles. Without performing Ecat withdrawals, the denser particles will slowly accumulate in the unit as the younger, less dense particle will be preferentially lost. As is seen above, younger catalyst is more active and since it is preferentially lost due to the damaged cyclones, the unit’s inventory will be less active than might be expected.

One is tempted to infer from Figure 31 that, during the high loss/high addition period, the unit’s inventory is deactivating at a faster rate during the normal addition period. This is not the case. The IAD of Figure 30 were constructed assuming “ideal” conditions, i.e. constant catalyst additions and withdrawals. Figure 31 highlights the “non-ideality” created by not making frequent withdrawals, even during a period of high losses. The two lines shown in Figure 31 should be approximately parallel. Given the 50.1% conversion of Sink/Sink fraction of the high loss/high addition period, it is estimated the Mid-Range Day is about day 360, not the day 163 shown in Figure 31.

The particle size distribution was measured on the Ecat sample and on each density fraction from both the normal and high catalyst addition periods. During the high catalyst loss period, the average particle size increased as shown in Figure 32. Also as shown by Figure 32, as the catalyst ages in the unit and becomes more dense, the particle size also becomes more coarse. The heaviest density fraction has the largest average particle size, as smaller particles are lost over time.

Higher Ecat average particle size results in a lower Umb/Umf, which can result in catalyst circulation instability as described by Mott. As a result, units exhibiting high catalyst losses often suffer from poor catalyst circulation stability. Contributing to the poor catalyst circulation stability is the highest density and average particle size material
fraction which is not purged from the unit. With routine withdrawals, the Ecat average particle size can be lowered, resulting in higher Umb/Umf and improved catalyst circulation stability. Figure 33 shows the resulting shift in average particle size and Umb/Umf after a unit began making routine Ecat withdrawals.

A cost effective strategy to continue to run the unit with challenged cyclones would be to use a combination of fresh catalyst and purchased equilibrium catalyst such as ENCORE™. If a supply of ENCORE™ from the unit discussed in the first example were available in sufficient quantity, total catalyst additions could be raised so that \( \tau \) was lowered to 60 days. If a ratio of fresh catalyst and ENCORE™ of 40:60 were employed, catalyst withdrawals could be resumed and unit Ecat activity would be about equal to the activity before the problem started. In addition, when compared to using 100% fresh catalyst with no withdrawals, the above strategy is estimated to save catalyst costs of approximately $0.15/bbl in catalyst costs.

**Summary**

As has been demonstrated, the Sink/Float technique is a valuable tool to understand the complex age and metal distribution present in FCC Ecat and shows the advantages on catalyst performance of making routine Ecat withdrawals.

Grace can offer a customized catalyst approach using both fresh catalyst and Ecat to improve FCC performance for those units presently not making routine inventory withdrawals. If you are not currently making routine Ecat withdrawals, talk to your Grace Davison Technical Sales Manager about cost effective catalyst strategies to improve FCC performance.

**References**


79. What procedures do you use to overcome chloride fouling problems in FCC fractionators? What is the contribution of chloride from the catalyst?

Rosann Schiller, Grace Davison Refining Technologies

The question as to whether chloride from catalyst can contribute to fouling problems is occasionally raised and, in this context, the following facts are relevant. The majority of FCC suppliers utilize rare-earth chloride to exchange with sodium, stabilizing the zeolite and determining product selectivities. Chloride is also an integral feature of the Grace Davison Al-Sol binder system. The Al-Sol binder system provides the basis for formulation flexibility, as well as best-in-industry attrition resistance. Several other suppliers also utilize similar chloride based binders. Chloride binder chemistry was selected by Grace for its performance benefits; however, it has the additional advantage of being a green process to manufacture catalyst.

During the FCC catalyst manufacturing process, the Al-Sol binder is “set” using a high temperature calcination; this step also removes most (>80%) of the chloride from the catalyst. Additional processing steps can be used to further reduce the fresh catalyst chloride content. At the end of the process, residual chlorides are treated and the resulting effluent can be safely discharged into the salt water estuaries where our manufacturing facilities are located. At Grace we seek to minimize any environmental risk associated with our manufacturing processes. Alternate materials can be used, such as nitrates, however, release of nitrates into waterways can cause algal blooms that can negatively impact the local eco-system. We are dedicated to the highest standards of health and safety practices and realize our corporate responsibility to the environment.

In use, the fresh catalyst is added to the FCCU via the regenerator, where the typical temperatures are significantly higher than those used during the calcination step in the standard catalyst manufacturing process, which in turn are higher than typical reactor temperatures in the FCCU. In consequence, and accelerated by the steam which is also present, any remaining chloride on the fresh FCC catalyst is quickly removed in the regenerator before the catalyst makes its first transit to the reactor section. Typically 80-95% of the fresh catalyst chloride is therefore removed in the FCCU flue gas, depending on the regenerator design. It is therefore recommended to avoid adding the fresh catalyst to a zone where it can bypass the regenerator bed and travel directly to the riser/stripper.

Salt deposition in FCC gas concentration units can lead to various operational problems if it is not addressed. It is important for refiners to be aware of the main causes of salt deposition so that the correct procedures can be applied to manage this phenomenon. The salt that is deposited most in FCC gas concentration units is ammonium chloride (NH₄Cl), but deposits can also occur of the ammonium hydrosulphide (NH₄)SH and iron sulphide (FeS) salts, although they are less common. Grace Davison Refining Technologies’ technical service team has helped various refiners manage the issue of salt deposition and the experience gained has been previously published (PTQ, Q4 2009, Catalagram® No. 107, 2010).

There are several causes of salt deposition, but the two primary reasons are an increase in resid processing and the shift to low sulfur gasoline due to environmental regulations. Resid feedstocks typically have higher chloride content than traditional VGO streams. Some refiners also bypass the desalter when processing imported atmospheric resid, which contributes to higher feed chloride levels. To produce low sulfur gasoline, a gasoline side cut is extracted from the main fractionator (MF) and subsequently hydrotreated. This leads to MF top temperatures as low as 212°F, compared to previous temperatures in the range of 275-293°F.

To prevent ammonium chloride deposition in the overhead line, water is usually added, with typical quantities in the range of 6-7 vol.% water on a fresh feed basis. Addition of an anti-fouling additive in the reflux stream can prevent the formation of NH₄Cl deposits on the trays and packing. The salt is carried instead with the gasoline stream, in which it is insoluble. These additives have been successfully used in many refineries around the world and are said to protect against corrosion.

Another recommendation is to water wash the MF. Water is injected periodically in the reflux stream, and the MF top temperature is reduced to approximately 176°F using the reflux rate or the tip top pumparound, to allow water to condense inside the column to dissolve the salt. The water is preferably removed on a dedicated tray, where it is separated from the heavy cracked naphtha. Alternatively the MF top temperature can be increased (for instance, to above 275°F) for a given period of time to enable dissociation of the salt. This will result in full-range gasoline leaving overhead during the time period.
Hardware modifications may also be considered to mitigate salting. These can include redesign of the MF’s reflux distributor to avoid cold spots at the top of the column or the installation of a water boot in one of the trays to allow water (and the dissolved salt) to be removed without contaminating the heavy cracked naphtha. A two-stage desalter could optimize the operation at the crude unit. Lastly, a feed hydrotreater could also be considered; this will remove most of the feed chloride and significantly improve the FCC yield structure. However, this requires a large capital investment.

80. Does silica entering with the FCC feed have a negative impact on the performance of the catalyst or the product slate? Does the silica source matter? Does it matter if originated from crude oil production, antifoam injection in coker units, or from the crude itself? What proportion of the silica entering the FCC leaves with the product?

Ruizhong Hu, Grace Davison Refining Technologies

We are not aware of silica from crude oil or other source having a negative impact on the performance of an FCC catalyst. Silica is one of the main chemical components of an FCC catalyst, with a typical concentration of about 40-50%. It is known that silica in FCC catalyst is somewhat mobile under FCC regenerator conditions. Therefore, all FCC catalyst particles are subjected to a background of mobile silica already. Minor additional silica source, e.g. less than a couple of percent, from crude or other source should not have a negative impact on the performance of an FCC catalyst.

82. What are your preferred process and catalyst options to maximize LCO yield? Among the options, please discuss the ramifications of lowering the riser outlet temperature by 40-50˚F on the heat balance, including suggestions on how to best utilize any excess air blower capacity at the lower riser temperature.

David Hunt, Grace Davison Refining Technologies

In general, a maximum LCO catalyst is a low zeolite/matrix surface area catalyst with low to moderate activity and excellent slurry cracking qualities.

The primary challenge with a maximum LCO operation is high slurry yield when conversion is reduced. Grace recommends a MIDAS® or a zero rare-earth REBEL™ catalyst to ensure low slurry yields while maximizing LCO.

OlefinsUltra®, Grace Davison’s high activity ZSM-5 additive, is often required in maximum LCO operations to maintain C₅⁺ liquid yield and gasoline octane. Operating at reduced conversion to maximize LCO will reduce the total product volume. Lower product total volume can reduce the total profitability during maximum LCO operations despite additional LCO production. OlefinsUltra® is critical to ensure profitability by increasing gasoline octane and liquid yield. Lower riser outlet temperature in the order to 40 to 50˚F will greatly increase LCO but will also create other challenges including:

- Lower C₅⁺ liquid yield and gasoline octane
- Higher slurry yield
- Potentially poor feed vaporization and riser/reactor coking

OlefinsUltra® can be used to recover gasoline octane and liquid yield as discussed above. Reduced feed vaporization can be an issue when operating at reduced riser outlet temperature particularly when processing residual feedstocks. There is a practical minimum riser outlet temperature to minimize coking and ensure good catalyst stripping efficiency. Generally operations less than 920˚F are not commonly practiced and the minimum riser outlet temperature for some units could be considerably higher than 920˚F.

Injection of a recycle stream downstream of the FCC feedstock will increase the riser mix temperature at the base of the riser which will increase feed vaporization at reduced riser outlet temperature. Of course recycle and the use of a good slurry cracking catalyst like MIDAS® or REBEL™ will minimize slurry production. Optimal recycle streams to maximize LCO and total profitability were discussed by Hu.² A high porosity catalyst like MIDAS® or REBEL™ can help ensure fast feed vaporization at lower reactor temperature and minimize slurry yield or reactor coking.³ Feed injection nozzles that atomize the feed well are also critical to ensure the feed is efficiently vaporized at reduced riser outlet temperatures.

When reactor temperature is reduced and the feed temperature is increased to boost LCO yield, the air blower demand will be reduced. The wet gas compressor load will also be reduced because of less LPG and dry gas production. The refiner can take advantage of this additional capacity in many ways such as:

- Increased feed rate
- OlefinsUltra® ZSM-5 to increase LPG olefins to the wet gas compressor or alkylation unit constraint
- Heavy cycle oil or slurry recycle to minimize slurry production
To ensure full profitability, the FCC should operate fully constrained whether it’s operating in maximum LPG, gasoline or LCO modes.


95. What NOx reduction additives have been successfully used to rapidly decrease NOx during operational excursions or hardware failure? What alternatives to additives and hardware exist for NOx reduction? Is there a synergy for combining NOx reduction control methods that may reduce operating or project costs?

Eric Griesinger, Grace Davison Refining Technologies

NOx reduction additives generally fall under two categories: stand-alone NOx reduction additives, and low NOx combustion promoters.

Stand-alone NOx reduction additives are catalytic based NOx control technologies that provide NOx reduction, without providing combustion promotional activity. Generally, this NOx control technology has provided slow response to mitigating elevated NOx concentrations. Grace Davison has developed a catalytic NOx reduction additive, GDNOX™ 1, which shows the prospect of providing a quicker ability to curb NOx emissions. Additionally, GDNOX™ 1 has not been vulnerable to material surcharges. GDNOX™ 1 applications should be reviewed by local Grace Davison sales and technical service representative for additional insight specific to the application.

Current generation of low NOx combustion promoters are typically formulated with a noble metal other than platinum. Historically, the use of platinum has been demonstrated to exhibit a correlation with elevated, and prolonged, NOx concentrations in regenerator flue stack gases. Applications of Grace Davison’s current generation low NOx combustion promoter, CP® P, when dosed in higher than normal rates, whether intentionally to correct other FCCU conditions or unintentionally, has shown that a shortened duration of elevated NOx emissions is likely. This observation of shortened NOx excursion interval can provide refiner’s benefit when striving to satisfy rolling day average, or other time based NOx emission limit constraints.

Operational variables that often have an effect on NOx emission have been found to include: excess O2, regenerator hydrodynamics, platinum formulated combustion promoter, antimony based nickel passivators, and feed nitrogen. Generally, a decrease in excess O2 will directionally lead to lower NOx emissions. While regenerator hydrodynamics are complex, a change in dense bed level, and/or temperatures, may provide conditions favorable to reduced NOx emissions. Use of platinum formulated combustion promoters and/or antimony has also been widely observed to correlate with increased NOx emissions. Oddly enough, while feed nitrogen has been found to be the contributing source to NOx emissions, typically these other variables have a stronger influence over the actual NOx emissions.

96. What are your experiences using SOx reduction additives formulated with lower rare earth content?

Grace Davison’s SOx reduction additives, formulated with lower rare earth content to lessen the impact of hyperinflationary costs associated with rare earth compounds, have gained wide acceptance. Within Grace’s portfolio of SOx additive products and its accounts, customers that were able to make a change to lower rare earth formulated SOx additives have done so. FCCU locations currently operating under EPA Consent Decree trial protocol have remained with the original formulation available at the start of their trial periods. Only two additional refineries are in the midst of evaluations comparing Grace’s Super DESOX® additive and Grace’s alternative products. Otherwise, all of Grace’s globally situated customers, existing and newly acquired, are utilizing SOx additives formulated with lower rare earth content. Grace offers three new SOx reduction additives: Super DESOX® OCI, Super DESOX® MCD, and Super DESOX® CeRO. Super DESOX® OCI, optimum cerium input; mitigates costs associated with rare earth compounds, while demonstrating on par pick-up-factor efficiency to Super DESOX® additive. Super DESOX® MCD, maximum cerium dispersion, further reduces rare earth cost exposure, yielding suitable and cost effective balance between SOx transfer ability and slightly increased dosing rate. Additionally, Super DESOX® CeRO is formulated without rare earth compounds. All three of these new products build on the success of Grace’s Super DESOX® additive performance. These offerings provide refiners with a range of flexible options, enabling a balance between rare earth inflationary exposures and dosing rates, to achieve SOx emission compliance.

Figure 34 shows an example of a refiner that historically utilized Super DESOX® and then switched to Super DESOX® OCI. Observed is the ability of Super DESOX® OCI to continue controlling SOx emissions within limits, at comparable dosing rates as was the case with Super DESOX®. Utilizing Super DESOX® OCI over Super DESOX® can result in a SOx additive cost reduction of roughly 35%.

Additionally, Grace Davison’s laboratory scale research indicates that the partial burn environment performance of Super DESOX® OCI and Super DESOX® MCD is similar to that of Super DESOX®. Please contact your local Grace Davison sales and technical service representative for additional insight specific to your application.
98. What measures have you taken to minimize catalyst expenses due to rare earth price inflation? Please include an economic comparison of using a high rare earth catalyst at a lower catalyst addition rate versus using a low rare earth catalyst at a higher catalyst addition rate. Are there alternatives to replace rare earth in FCC catalyst? Are there any negative yield shifts with these new technologies?

Sudhakar Jale, Grace Davison Refining Technologies

Grace Davison Refining Technologies has responded quickly to the issues of rare earth price and availability by developing new zero or low rare earth catalysts and additives. Early in 2011, Grace commercialized a family of these catalysts, called REpLaCeR™, for both hydrotreated and resid feed processing. The family of REpLaCeR™ catalysts includes REBEL™, REACTOR™, REMEDY™ and REDUCER™. The REpLaCeR™ family of catalysts utilizes proprietary zeolites and state-of-the-art stabilization methods to deliver performance similar to current rare earth-based FCC technologies.

Simply removing the rare earth from a FCC catalyst lowers the Ecat activity significantly. Unit performance will suffer, in most operations, despite higher catalyst circulation rate which results with lower Ecat activity. Catalyst additions of a low rare-earth catalyst must be increased in order to preserve Ecat activity for those units that operate at a catalyst circulation constraints.
Table 14 summarizes a scenario comparing the base catalyst, base catalyst with low rare earth content and REMEDY™ technology where zeolite is stabilized with proprietary metals. The REMEDY™ technology provides the same activity as the rare earth containing zeolite and hence has the same catalyst additions.

The performance data and the resulting profitability for these three scenarios are summarized in Table 15. Unit constraints for the low rare earth catalyst and REMEDY™ case are air blower, catalyst circulation and wet gas compressor. The low rare earth option, where the RE content of base catalyst is lowered, is less economically attractive mainly because of higher catalyst additions and the need to reduce conversion due to a wet gas compressor constraint and a catalyst that is more LPG selective. REMEDY™ technology has good activity and selectivity retention vs. the base catalyst thus providing the economic savings of $0.50/B.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Base</th>
<th>Low Rare Earth</th>
<th>REMEDY™</th>
</tr>
</thead>
<tbody>
<tr>
<td>RE₂O₃, wt.%</td>
<td>2.6</td>
<td>0.7</td>
<td>TRACE</td>
</tr>
<tr>
<td>Zeolite SA, m²/gm</td>
<td>220</td>
<td>260</td>
<td>250</td>
</tr>
<tr>
<td>Total SA, m²/gm</td>
<td>290</td>
<td>330</td>
<td>320</td>
</tr>
<tr>
<td>Catalyst Additions, TPD</td>
<td>5</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>ECAT Activity</td>
<td>74</td>
<td>74</td>
<td>74</td>
</tr>
</tbody>
</table>

TABLE 14: Simply Lowering the RE Content Will Result in Increased Catalyst Additions to Hold ECAT Activity

The economic advantage of using REMEDY™ catalyst is plotted in Figure 35. The RE₂O₃ content in low rare earth catalyst is reduced by 75%. This results in a lower catalyst price, but the daily cost increases by about 30% due to higher catalyst additions. REMEDY™ catalyst has 90% lower rare earth compared to the base case catalyst and maintained the same activity and catalyst addition rate as the base case resulting in 30% daily operating cost. A refinery with 50,000 bpd operation increased the profitability by $9 mm/yr (using recent Gulf Coast Economics).

In summary, the REpLaCeR™ family of catalysts introduced by Grace reduces the RE content significantly while maintaining the activity and catalyst additions resulting in a decrease of daily costs by 30%.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BASE (1)</th>
<th>Low Rare Earth (2)</th>
<th>REMEDY™ (2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rector Temp, °F</td>
<td>992</td>
<td>985</td>
<td>990</td>
</tr>
<tr>
<td>Feed Temp, °F</td>
<td>600</td>
<td>590</td>
<td>598</td>
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<tr>
<td>Regenerator Temp, °F</td>
<td>1325</td>
<td>1318</td>
<td>1324</td>
</tr>
<tr>
<td>Cat/Oil</td>
<td>Base</td>
<td>Base</td>
<td>Base</td>
</tr>
<tr>
<td>Air Blower</td>
<td>Base</td>
<td>Base</td>
<td>Base</td>
</tr>
<tr>
<td>Wet Gas Compressor</td>
<td>Base</td>
<td>1.03* Base</td>
<td>1.03 Base</td>
</tr>
<tr>
<td>Dry Gas, scfb</td>
<td>214</td>
<td>220</td>
<td>211</td>
</tr>
<tr>
<td>C₃, vol.%</td>
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</tr>
<tr>
<td>iC₄, vol.%</td>
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<td>3.0</td>
</tr>
<tr>
<td>C₅+, vol.%</td>
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<td>7.8</td>
<td>7.9</td>
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<tr>
<td>Gasoline, vol.%</td>
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<td>53.2</td>
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<tr>
<td>RON/MON</td>
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<td>Slurry, vol.%</td>
<td>4.5</td>
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<td>4.5</td>
</tr>
<tr>
<td>Profitability, $/B (3)</td>
<td>Base</td>
<td>-0.14</td>
<td>+0.50</td>
</tr>
</tbody>
</table>

1. Operating at Air Blower and Catalyst Circulation Constraint
2. Operating at Air Blower, Catalyst Circulation and Wet Gas Compressor Constraint
3. Profitability includes total catalyst cost

TABLE 15: Performance and Economic Comparison of Low Rare Earth and REMEDY™ Technologies
99: Are there any uncommon FCC metal contaminants showing up on equilibrium catalyst in addition to Ni, V, Fe, Na, and Ca? Are metals traps able to protect the catalyst by selectively capturing Fe, Na, Ca, or any of these uncommon contaminants? Rosann Schiller and Sudhakar Jale, Grace Davison Refining Technologies

Appearance of an unconventional metal on your equilibrium report can be cause for alarm, but not all metals require action on the part of the refiner. Alkali metals such as sodium and potassium are naturally occurring in crude oil and their concentration is reduced by desalting processes. However, desalter upsets can cause carry-over into the FCC feedstock and result in deactivation of the FCC catalyst, particularly under the oxidizing, high temperature conditions in the regenerator. Use of alkali metal contaminated water or steam around an FCC unit can also contribute added contaminants to the catalyst. Alkali metals cause a loss in activity due to neutralization of acid sites. The result is a loss of unit conversion, but not a change in selectivity as observed with iron, nickel, vanadium, or calcium. Flushing of the metal out of the inventory with additional catalyst additions will restore catalytic activity. Typically, only low levels of potassium oxide are observed in equilibrium catalyst, as shown in Figure 36.

Magnesium is not of concern at low levels (<0.5 wt.%), but at higher levels, it has a tendency to react with silica from the zeolite to form forsterite (Mg₂SiO₄), which will decrease zeolite stability and adversely affect unit conversion. Most of the MgO observed in equilibrium catalyst is due to the presence of SOx reducing additives and not feed contamination as shown in Figure 37.

Lead is well known to cause the deactivation of combustion promoter. However in large enough concentrations on Ecat, Pb can also cause a loss in catalyst activity and conversion. Historical data reports a loss of as much as 1% conversion per 0.1 wt.% Pb on Ecat. However, there are no units operating at these levels of Pb in the industry today, as shown in Figure 38.

Crude can contain significant calcium naphthenate that may not be removed by conventional desalting and will find its way to the FCC. Calcium poisoning of the FCC unit can be a serious problem, reducing bottoms cracking and catalyst activity. The severity of the impact of calcium on FCC selectivities depends mainly on the amount of incremental calcium that is deposited on the catalyst and the rate of deposition. When the incremental calcium lays down on the FCC catalyst rapidly, the apparent effects of calcium on the unit performance can be more pronounced because there is less time for the unit operator to realize what is happening, identify the route cause of the problem, and take corrective actions. Very few FCC’s operate at high levels of CaO on equilibrium catalyst, as shown in Figure 39; however, poisoning can be evident even at lower levels of contaminant if deposition occurs rapidly.
The mechanism by which calcium deactivates FCC catalyst is similar to that of iron deactivation (Yaluris et. al, NPRA 2001). The distribution of Fe levels on Ecat is shown in Figure 40. Both metals poison the catalyst by depositing on the exterior surface and over time, will build up on the surface of the catalyst forming rings typically 1-5 µm thick. As the rings form, as in Figure 41, Fe and Ca combine with silica, sodium and other contaminants to form low melting temperature phases, which collapse the pore structure of the exterior surface, blocking feed molecules from entering the catalyst particle and reducing conversion. The diffusion of the large molecules inside the particle is the first to be affected by this phenomenon, therefore, the ability of the catalyst to crack bottoms decreases first followed by a corresponding decrease in cracking activity.

As the calcium or iron builds up on the catalyst surface, and the exterior surface of the particle becomes compromised, the coke selectivity of the catalyst declines due to increased mass transfer limitations, which increase residence time of cracked products inside the catalytic particle and result in higher rates of secondary reactions such as coke. The combination of the loss of coke selectivity, combined with the loss of activity, results in further loss of in-unit conversion.

Figure 42 demonstrates the impact on conversion due to calcium poisoning from a refiner who experienced a doubling of CaO on Ecat in a short period of time due to a change in both crude source and desalter operation. Other contaminants such as sodium also increased in the same time period. In this example, laboratory ACE testing of Ecat demonstrates that the incremental calcium caused a loss of approximately 5 wt.% conversion.

The refiner first observed an increase in bottoms and LCO yields in the unit along with a loss in coke selectivity. Increased catalyst additions were used to flush out contaminated particles and catalyst formulation was optimized to better handle future metals excursions.

Since Fe and Ca are not mobile species in the FCC unit regenerator, the usual trapping technologies, especially those based on separate additive particles are not effective for preventing cracking catalyst poisoning by Fe or Ca.

Several catalytic approaches are recommended to manage calcium issues. Optimization of the pore structure eliminates diffusion limitations. Maximization of the catalyst pore volume in the 100-600 Å range is the best for conversion of bottoms without compromising coke selectivity. Improving coke selectivity of the catalyst will improve performance by offsetting the increased coke make caused by contaminant calcium. High alumina catalysts, especially catalysts with alumina based binder and matrices, are best suited for operations where high Fe or Ca feeds are commonly processed because they are more resistant to the formation of low melting temperature phases that can destroy the surface pore structure.
In summary, if the increase in contaminant level is temporary, an increase in fresh catalyst addition rate will improve the performance of the catalyst. If high metals feeds will remain a component of the FCC feed, the refiner should minimize the amount of deposition on the Ecat and utilize a catalyst system appropriately designed to handle the potential surface destruction. Such catalyst should contain the appropriate amount of pores in the optimum size of 100-600 Å to overcome diffusion limits. High alumina catalysts such as Grace Davison’s MIDAS® catalyst technology are ideally suited for such applications.

ZSM-5 based additives maintain their activity in high metals applications because they deactivate at a much lower rate than their Y-zeolite base catalyst counterparts. Grace has extensive R&D and commercial experience with ZSM-5 containing additives used in FCC units, including those that are designed for maximum propylene yield. These commercial FCC operations vary in feed metals levels, feed type, unit design and operating conditions. When analyzing commercial Ecat for ZSM-5 additive performance, it has been observed that feed metals will preferentially adhere to the base catalyst versus the ZSM-5 additive. Separation of equilibrium catalyst into its base catalyst and ZSM-5 additive components shows the ZSM-5 additive typically only contains about half the metals of the FCC base catalyst. In laboratory deactivation studies by Grace, ZSM-5 additives begin to deactivate at Ni+V loadings of 3000 ppm and greater, as seen in Figure 1. However based on our current commercial experience, a ZSM-5 additive sample containing 3000 ppm Ni+V, would likely require approximately 8000 ppm Ni+V on the circulating base catalyst.

ZSM-5 additives are very stable and maintain activity much longer than other FCC catalysts or additives. The specific half life of a ZSM-5 additive will vary from unit to unit but could easily range from two weeks to significantly longer, depending on the FCC operation. In Grace’s experience, the half life of a ZSM-5 additive strongly depends on the operating conditions of the unit and not as much on the feed type or metals levels. Variables which will impact the half life of a ZSM-5 additive include regenerator temperature, unit pressure, and circulation rate, which influences the number of cracking cycles the additive undergoes in the unit each day. We have commercially observed higher than typical ZSM-5 deactivation rates in units running clean feeds but operating at higher pressure, higher circulation rates and higher regenerator temperatures.

ZSM-5 based additives are more resistant to sodium and potassium promoted zeolite destruction than Y-zeolite. Vanadium will likely have the greatest effect on ZSM-5 deactivation, however, all contaminants in the FCC will have a much stronger effect on base catalyst deactivation, before they will adversely impact the ZSM-5 activity. Grace has not experienced any shifts in propylene selectivity due to contaminant levels or deactivation of ZSM-5, as shown in Figure 43, however, more research is needed on this subject to provide a definitive answer.

For evaluating the effectiveness of ZSM-5 additives in a commercial unit, a common approach is to monitor propylene and butylene yields as a function of corrected conversion. ZSM-5 additives will increase LPG olefins for each given level of conversion. Another recommended method to measure the effectiveness of ZSM-5 additives is to analyze the increase in gasoline octane by evaluating gasoline octane as a function of reactor outlet temperature.

Grace has also been successful in evaluating ZSM-5 based additive performance using a multivariable regression approach. By utilizing a statistical tool such as Minitab, the LPG olefin or gasoline octane...
shifts can be quantified as a function of feed properties, operating conditions and ZSM-5 concentration.

Laboratory options also exist for measuring ZSM-5 additive effectiveness in the unit. In a controlled laboratory setting, performance comparisons can be made by taking a ZSM-5 containing equilibrium catalyst sample and a non-ZSM-5 containing equilibrium catalyst sample and analyzing them in an ACE unit or riser pilot plant, using a constant feedstock. This method is beneficial for analyzing ZSM-5 performance in commercial units that have experienced large changes in feed or operating conditions, which make ZSM-5 additive performance evaluations more challenging.

In summary, ZSM-5 based additives have excellent activity and stability even in high metals applications. Grace ZSM-5 additives have been shown to perform well with all types of FCC catalysts and FCC feedstocks and under a wide range of operating conditions and unit designs. Grace manufactured ZSM-5 additives are currently in use in over 70 FCC units worldwide and in more than half of the FCC propylene maximization operations in EMEA and Asia.

101. What analytical methods can distinguish between organic and inorganic iron (Fe) compounds in the feed? What type of iron, organic or inorganic, affects catalyst performance? Considering the relatively long reaction residence time of most laboratory test units used to measure activity, will activity testing properly reflect the actual in-FCCU activity under conditions of Fe contamination? What is your best method to monitor the catalyst performance under Fe contamination? Is there a critical Fe level above which the catalyst performance is significantly impacted?

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Yaluris discussed that there are two types of iron. One type is particles of inorganic iron from hardware and is usually considered benign in FCC unit performance. The second type is organic based Fe potentially coming in with the feed and/or from hardware corrosion by naphthenic acids and other corrosive feed components. This type of iron can negatively impact unit performance.1

ACE testing is a better technique to measure the conversion impact of organic based iron contaminated catalyst, compared to traditional fixed bed MAT testing. However, ACE testing should be used together with other tests to confirm iron poisoning.

Below are several methods that can be used to monitor catalyst performance under Fe contamination:

- Ecat analysis (Fe, Na, CaO, ABD, color)
- Scanning Electron Microscope imaging (SEM)
- Optical microscope
- Ecat diffusivity

A decline in unit performance such as a reduction in bottoms conversion and/or poor catalyst circulation, coupled with an increase in equilibrium catalyst Fe levels, can indicate Fe poisoning. Yaluris discussed how pore closure and nodule formation can be potentially caused by iron contamination.1 Pore closure can negatively affect bottoms conversion in the unit. An excellent way to show the actual nodules is by Scanning Electron Microscope imaging (SEM). It is important to note that some nodules may not be a problem, but there is a problem when the nodules become obviously raised from the surface and all over the catalyst particle. A drop in ABD (apparent bulk density) on Ecat can indicate nodule formation due to iron poisoning as Ecat does not pack as densely. The ABD change, pore plugging and the potential for particles to stick together can negatively impact unit catalyst circulation.

Optical microscope is another method to indicate iron poisoning. Ecat samples with iron poisoning will show glassy reflections under an optical microscope with illumination.1 The color of Ecat could potentially indicate high levels of Fe. Ecat samples can have a reddish brown tint when poisoned by iron.1 In addition to Ecat Fe levels, Na and CaO should be monitored as well. Fe in the presence of Na and/or CaO can act as a fluxing agent which can aggravate the effects of Fe.1

Grace has recently developed a proprietary technique to measure actual Ecat diffusivity. This test, which is available by special request, quantifies catalyst pore closure due to iron contamination. Shifts in Ecat diffusivity are very consistent with shifts in bottoms conversion in commercial units due to iron contamination. Incremental iron levels above 0.2 wt.% is where one should start to get concerned about the negative impact of iron poisoning on catalyst performance. This level, of course, is unit dependent and can differ depending on factors such as fresh catalyst additions.

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