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-
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 benefits 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.

![FIGURE 2: MAT Activity is Maintained at Lower Rare Earth](image)

![FIGURE 3: Activity is Higher with Lower Rare Earth at Equivalent Metals](image)

<table>
<thead>
<tr>
<th>Corrected Conversion, Δ from Base</th>
<th>BASE</th>
<th>GENESIS® LX</th>
</tr>
</thead>
<tbody>
<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>

**TABLE 1: Refiner A FCC Unit Data**
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 Ecata 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-url)

### TABLE 2: Refiner B ACE Test Constant Conversion Yields

<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>
<td>7.7</td>
<td>6.6</td>
</tr>
<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 C₅+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>
</tr>
<tr>
<td>Bottoms, wt.%</td>
<td>11.5</td>
<td>11.1</td>
</tr>
<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>
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>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 C₄’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 8: RE₂O₃ Was Decreased Yet Unit Cell Size Remained Constant

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 AUORRA™ 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 rareearth 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, scrutinization of market driven operating...
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 Ecattering 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 applica-
tions. 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 opti-
mize 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 regener-
ator bed temperature and increased conversion at constant feed at-
mospheric 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 cata-
lyst 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 cata-
lyst 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 up-
grading were even improved. The REduceR™ catalyst provided a
similar coke yield but an improved delta coke, and allowed regenera-
tor 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 suc-
cessfully commercialized the REpLaCeR™ family of low and zero
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


