Alteratives to Rare Earth

Commercial Evaluation of REpLaCeR® FCC Catalysts at Montana Refining Company

Abstract

After the sweeping reduction of Chinese export quotas, rare-earth metals experienced price hyperinflation in the range of 2700% between August 2010 and July 2011. FCC catalyst has experienced unprecedented inflation as a result. Rare earth is used to stabilize FCC catalyst zeolite in order to provide high FCC catalyst activity, liquid selectivities and superior coke selectivity. Removing rare earth from FCC catalyst will provide relief in catalyst expenses; however, it is not an economical solution in most FCC operations due to a lower activity and product value.

Alternate materials and processing must be used to stabilize the FCC zeolite to ensure a profitable yield slate without rare earth. Grace has recently developed and commercialized its new REpLaCeR® family of catalysts, a portfolio of low and zero rare-earth catalysts applicable to a broad range of FCC applications. Presently, over 50 units worldwide use REpLaCeR® FCC technology.

Montana Refining Company (MRC) partnered with Grace to commercialize a rare-earth-free REMEDY™ catalyst from Grace’s new REpLaCeR® family of catalysts. MRC has successfully applied a zero rare-earth REMEDY™ over a moderate rare earth GENESIS® FCC catalyst. Commercial results demonstrate similar unit conversion at similar catalyst additions. Coke selectivity and slurry cracking were maintained with REMEDY™ while gasoline selectivity increased.

MRC is an independent refiner located in Great Falls, MT. Sour heavy crudes are processed in their complex refinery producing low sulfur gasoline, ultra-low sulfur diesel, jet and a full slate of asphalt products. W.R. Grace & Co. is the world’s leading supplier of FCC catalysts and additives with headquarters in Columbia, MD.
Grace's zero and low rare-earth REpLaCeR® catalyst portfolio quickly gained momentum in 2011. The explosive growth of the technology was sparked by rare-earth hyperinflation stemming from Chinese export quota restrictions in 2010.¹

Grace's REpLaCeR® technologies include zero and low rare-earth catalysts for all FCC applications.² Today there are over 50 applications of REpLaCeR® technologies ranging from low to moderate metal vacuum gas oil (VGO) applications to operations with high metals residual feedstocks. Those REpLaCeR® applications are described in Table 1. In over 20 current REpLaCeR® applications, all of the rare earth has been removed from the FCC catalyst. These applications range from low metals to as high as 4700 ppm Ni plus V. For higher metals operations, 20 to 80% of the rare earth can be eliminated with REpLaCeR® catalyst. Some current resid applications are operating with Ecatal Ni plus V levels greater than 10,000 ppm and V plus Na levels higher than 9,000 ppm.

The purpose of zeolite stabilization is to preserve acid site density and control catalyst activity and product selectivities. Rare earth has been traditionally used to stabilize the zeolite by controlling de-alumination, which increases hydrogen transfer and activity.³

Unit cell size (UCS), as measured by x-ray diffraction, is a common benchmark to judge zeolite stabilization and acid site density. Until recently, rare earth was the most cost effective material to stabilize the zeolite. Now Grace is using alternative materials and processing to stabilize the zeolite to achieve desired catalyst activity, stability and selectivity without rare earth.

Grace's current catalyst portfolio is described in Figure 1. The REpLaCeR® catalysts are the grades listed in blue. Catalysts listed on the far left are high zeolite to matrix catalysts while the low zeolite to matrix catalysts are shown on the right. Catalysts listed in the middle, such as GENESIS®, incorporate a combination of technologies and provide excellent coke selectivity and slurry cracking.

### Table 1: REpLaCeR® Catalyst Commercial Successes

<table>
<thead>
<tr>
<th>Application No.</th>
<th>% RE Reduction</th>
<th>Ni + V, ppm</th>
<th>V + Na, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100</td>
<td>56</td>
<td>2,700</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>250</td>
<td>3,500</td>
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<td>22</td>
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<td>5,276</td>
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<td>23</td>
<td>100</td>
<td>4743</td>
<td>5,466</td>
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<td>24</td>
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<td>1798</td>
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<td>30</td>
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<td>7,759</td>
</tr>
<tr>
<td>52</td>
<td>20</td>
<td>11195</td>
<td>5,810</td>
</tr>
</tbody>
</table>

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**Figure 1: Grace Has the Broadest Catalyst Portfolio in the Industry – [REpLaCeR® Technologies Shown in Blue]**

Grace Catalysts Technologies Catalagram®

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REMEDI™ technology is zero or low rare-earth catalyst designed for VGO applications. REDUCER® catalysts incorporate low levels of rare earth for FCC units that process high metals residual FCC feedstocks.

Two principal zero rare-earth catalysts that can be used in Grace’s REMEDI™ technology are REACTOR® and REBEL™ catalysts.

REACTOR® is a zero rare-earth catalyst which incorporates Grace’s Z-22 zeolite. Relative to rare earth ultra stable Y zeolite (RE USY), Z-22 provides equivalent activity, higher LPG olefins and gasoline octane as a moderately exchanged rare earth zeolite. A proprietary stabilization process is used to provide zeolite acidity and preserve activity similar to what has traditionally been accomplished by rare earth.²

REACTOR® catalyst is high zeolite to matrix catalyst from Grace’s Alumina-Sol catalyst platform. As a Grace Alumina-Sol catalyst, REACTOR® will provide excellent yield selectivities, low attrition index and flue gas stack particulates similar to other Grace Alumina-Sol catalysts such as AURORA® and IMPACT®.⁴

REBEL™ is a zero rare-earth, low zeolite to matrix catalyst formulated with Z-21 zeolite. REBEL™ is an extension of Grace’s industry leading bottoms cracking MIDAS® catalysts. Z-21 also uses a distinctive proprietary zeolite stabilization process to provide necessary activity and yield selectivities without rare earth.²

Isobutylene, iC₄⁺, selectivity is a common benchmark to judge hydrogen transfer activity. Figure 2 shows the relative iC₄⁺ selectivity of two catalysts with RE USY zeolites together with rare-earth free catalysts, one using Z-21 and the other Z-22 zeolite. This data was generated in an Advanced Cracking Evaluation Unit (ACE) using metals free deactivated catalysts.⁵

The catalyst with an 8% rare earth on zeolite RE USY (8% RE/Z corresponding to a UCS of ~24.31Å) produces the lowest iC₄⁺ selectivity and hence the highest hydrogen transfer activity. Isobutylene selectivity was the highest from the 3% rare earth on zeolite catalyst (3% RE/Z corresponding to a ~UCS of ~24.27Å).

The catalyst using Z-21 provided similar iC₄⁺ selectivity as the catalyst with 8% RE/Z. The high hydrogen transfer activity exhibited by the Z-21 zeolite suggests similar acid site density and zeolite stabilization as the 8% RE/Z base catalyst. Z-22 zeolite, which is used in the REACTOR® catalyst, provided slightly less iC₄⁺ selectivity than the 3% rare earth on zeolite catalyst, confirming slightly higher acid site density for the Z-22 system.

Figure 3 shows total acidity for catalysts with a 3% RE/Z USY zeolite, Z-21 and Z-22 zeolites. Total acidity was measured by a NH₃-STPD technique. STPD method (Stepwise Temperature Programmed Desorption) can be used to differentiate acid site density in aluminas, clay, zeolites, fresh catalysts, and deactivated catalysts. Zeolites, especially, possess heterogeneous acid sites of discrete strengths which can be identified by measuring ammonia desorption.

Z-21 provides higher total acidity than the RE USY zeolite catalyst. Z-22 zeolite has less total acidity than Z-21, but similar acidity as the RE USY with 3% RE/Z. The relative acidity of the catalyst shown in Figure 3 is consistent with the iC₄⁺ selectivity ranking shown in Figure 2.

Figures 2 and 3 suggest that the proprietary materials and processing used for Z-21 and Z-22 zeolite provide similar hydrogen transfer activity as a traditional rare-earth system.

Rare earth has also been used to control zeolite surface area stability especially in high metals applications. Zeolite stability is commonly judged by zeolite surface area retention, the ratio of de-
activated zeolite surface area to fresh zeolite surface area, as a function of deactivation temperature and contaminant metals. Figure 4 shows zeolite surface area retention for REBEL™ with Z-21 compared with a MIDAS® catalyst with 8% RE/Z as a function of contaminant metals. Rare-earth free REBEL™ with Z-21 zeolite provides similar zeolite surface area retention as MIDAS® with a RE USY zeolite.

In Figure 5, a similar comparison of zeolite surface area retention is made between rare-earth free REACTOR® with Z-22 zeolite vs. an AURORA® catalyst with approximately 4% RE/Z. In this Figure, Z-22 provides a slight improvement in zeolite stability compared to a RE USY AURORA® catalyst.

Figures 4 and 5 confirm the proprietary stabilization compounds used for Z-21 and Z-22 can maintain zeolite surface area like a traditional RE USY catalyst.

Montana Refining Company

MRC is an independent energy company engaged in crude oil refining and the wholesale marketing of refined petroleum products. They operate one of the last small, independent full production refineries in the USA, producing approximately 10,000 barrels per day of various petroleum products.

The refinery is a complex refinery (Nelson Complexity Factor of 9.3) able to process heavy sour crude oil that is received via pipeline and railcar. A basic process flow for the MRC facility is shown in Figure 6. MRC produces a wide range of high quality products ranging from multiple grades of low sulfur gasoline (including ethanol blended gasoline) to ultra-low sulfur diesel, jet fuels, LPG’s and asphalt products. The finished gasoline and distillate products are distributed through MRC’s terminal in Great Falls and the asphalt products are marketed over racks at the refinery.6

MRC, with nearly ninety years in the Great Falls community as a petroleum refiner with stringent quality control standards, has earned a reputation as a dependable supplier of high-quality fuel and road paving products. MRC is a wholly owned subsidiary of Connacher Oil and Gas Limited, a Calgary-based Canadian crude oil and natural gas company.6

The FCC at MRC processes a hydrotreated VGO at a nominal rate of ~3,000 barrels per day. During the summer months the unit is constrained by the air blower and main column overhead condensers hydraulics. Reactor temperature is controlled to a relatively low value of ~940°F as the unit generally operates in a maximum Light Cycle Oil mode.

FIGURE 4: Z-21 Provides Similar Zeolite Retention as RE USY

FIGURE 5: Z-22 Delivers Greater Zeolite Stability than a RE USY Formulation
Grace’s Super DESOX® OCI is used to control SOx to less than 25 ppm. NOx is controlled by minimizing excess O₂ levels and the use of Grace’s low NOx CP® P combustion promoter.

FCC gasoline is not hydro-treated at the facility. As a result gasoline sulfur specifications are met by controlling the end point and FCC feedstock sulfur. Grace’s SuRCA® gasoline sulfur reduction technology is used to extend the VGO hydrotreater run length by providing ~30% gasoline sulfur reduction, allowing lower FCC feed hydrotreater temperature for a target FCC gasoline sulfur.

MRC meets its FCC flue gas particulate limits without any external particulate recovery device such as tertiary separator or electrostatic precipitator (ESP). As a result, FCC catalyst attrition and retention qualities are critical.

Grace is a long-term supplier of FCC catalysts and additives to MRC. During that time several Grace products have been commercialized at MRC including:

1. D-PrisM® and SATURN® Gasoline Sulfur Reduction technologies
2. XP® and LIBRA® FCC catalysts
3. Super DESOX® OCI – reduced rare-earth SOx reduction additive
4. CP® P – Non Platinum Low NOx Combustion Promoter

**Reformulations Ahead of the Surcharge**

In 2011, Grace offered MRC FCC catalyst technology from its new REpLaCeR® portfolio to avoid pending rare-earth surcharges.

MRC reformulated their fresh FCC catalyst in two steps. REMEDY™ 1 GSR® reduced rare earth by a third, while REMEDY™ 2 GSR® completely removed rare earth from the catalyst. Fresh catalyst properties are shown in Table 2. The objective of each reformulation was to maintain the current yields, gasoline sulfur and gasoline octane as the base rare-earth containing GENESIS® grade.

REMEDY™ 1 GSR® incorporates Grace’s REACTOR® technology together with MIDAS®. MIDAS® is low zeolite to matrix, industry-leading bottom cracking catalyst. REMEDY™ 2 GSR® uses both REACTOR® and REBEL™ technologies and is a rare-earth free catalyst. The original GENESIS® GSR® incorporated Aurora® and MIDAS® technology. All FCC catalyst technologies incorporate Grace’s gasoline sulfur reduction SuRCA® technology which provides ~30% gasoline sulfur reduction.

MRC reformulated to REMEDY™ 1 GSR® in January 2011 minimizing the first quarter 2011 rare-earth surcharge by one third. When REBEL technology was available in August 2011, MRC reformulated to REMEDY™ 2 GSR® and avoided the large third and fourth quarter rare-earth surcharges entirely, as shown in Figure 8.
### Results

The following REMEDY™ 2 GSR® data reflects operating data after over 50% of the La₂O₃ had been purged from the inventory. GENESIS® GSR® data represents weekly test run data from March 2010 to July 2010, while REMEDY™ 2 GSR® data is from November through December 2011 operations. During the GENESIS® GSR® operation ~7.5% OlefinsMax® (ZSM-5) was used, while the REMEDY™ 2 GSR® operation employed just 2.5% OlefinsMax®.

### TABLE 2: Montana Refining Company Fresh Catalyst Properties

<table>
<thead>
<tr>
<th></th>
<th>GENESIS® GSR®</th>
<th>REMEDY™ 1 GSR®</th>
<th>REMEDY™ 2 GSR®</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activity, wt.%</td>
<td>80</td>
<td>80</td>
<td>80</td>
</tr>
<tr>
<td>RE₂O₃ wt.%</td>
<td>1.5</td>
<td>1.0</td>
<td>Trace</td>
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<tr>
<td>Al₂O₃ wt.%</td>
<td>51</td>
<td>51</td>
<td>47</td>
</tr>
<tr>
<td>Zeolite Surface Area, m²/gm</td>
<td>200</td>
<td>200</td>
<td>220</td>
</tr>
<tr>
<td>Matrix Surface Area, m²/gm</td>
<td>90</td>
<td>90</td>
<td>75</td>
</tr>
<tr>
<td>0 to 40μ, %</td>
<td>13</td>
<td>13</td>
<td>13</td>
</tr>
</tbody>
</table>

**FIGURE 7: REMEDY™ 2 GSR® and GENESIS® GSR® Technology**

**FIGURE 8: Each Reformulation Occurred Prior to an Increase in Rare-Earth Price**

Grace Catalysts Technologies Catalagram®
Much of the MRC operating data is represented in box plots. An example of a box plot is shown in Figure 9. A box plot is a graphical summary of the distribution of a data set that shows its shape, central tendency, and variability.

Figure 9 shows the key parts of the box plot. Box plots can be used to quickly understand a data distribution and are particularly useful for comparing different data sets. The following box plots compare the data distribution between GENESIS® GSR® and REMEDY™ 2 GSR® at MRC.

Figure 10 shows that mean catalyst additions on a pound of catalyst per barrel of feed basis were maintained at ~0.14 lb/b for both GENESIS® GSR® and REMEDY™ 2 GSR® operations. Conversion corrected for 430°F for the REMEDY™ 2 GSR® operation was within the conversion range with GENESIS® GSR®. The median value conversion was 77.5 vol.% during the REMEDY™ 2 GSR® operation compared to 76 vol.% for the GENESIS® GSR® period.

General operating conditions and feed properties are shown in Figure 11. Feedstock API was lower with REMEDY™ 2 GSR® with a median value of ~26.5°API compared to 27.3°API with GENESIS®. Reactor temperature increased to 940°F while using REMEDY™ 2 GSR® and feed rates were ~150 bpd lower. Differences in key independent operating conditions:

**FIGURE 9: Example Box Plot MRC Ec Cat Activity**

**FIGURE 10: EMRC Conversion was Maintained at Similar Catalyst Additions**
variables including reactor temperature, feedstock properties and feedstock temperature were modeled and the conversion differences between both periods were <0.25 vol.%. As a result, the conversion shifts shown in Figure 10 are not influenced by differences in operating temperatures and feedstock properties.

Coke selectivity was maintained with REMEDY™ 2 GSR® as Figure 12 shows similar coke yield versus corrected conversion between the two catalysts. Slurry cracking is a critical attribute for all catalyst systems and Figure 12 confirms that the operation with REMEDY™ 2 GSR® provided similar or lower slurry as a function of conversion.

Gasoline selectivities increased during the operation with REMEDY™ 2 GSR® as shown in Figure 12. Gasoline and LPG yields are corrected for ZSM-5 in Figure 12. Higher gasoline selectivity from rare-earth free REMEDY™ 2 GSR® confirms that the zeolite is stabilized similarly to a traditional rare-earth catalyst. Gasoline octane was maintained with REMEDY™ 2 GSR®.

Zero rare-earth catalyst often produces higher dry gas rates. However, similar dry gas rates as a function of reactor temperature were observed between REMEDY™ 2 GSR® and GENESIS® GSR® as noted in Figure 13. Dry Gas rates are very low at MRC, consistent with the low reactor temper-
Corrected conversion values for a given catalyst-to-oil ratio are similar for both operations, suggesting similar in-unit activity from both catalysts.

Equilibrium catalyst \( (E_{\text{cat}}) \) activity was maintained with REMEDY™ 2 GSR®. Figure 14 shows the median \( E_{\text{cat}} \) activity value of both REMEDY™ 2 GSR® and GENESIS® GSR® is identical at 71 wt.%. Zeolite surface area increased to a median value of 115 m\(^2\)/gm with REMEDY™ 2 GSR® consistent with higher fresh catalyst zeolite surface area. Zeolite surface retention, the ratio of \( E_{\text{cat}} \) ZSA to fresh ZSA, is 54\% for both catalyst systems, despite the lack of rare-earth stabilization in REMEDY™ 2 GSR®. Unit cell size median values dropped from 24.29Å to 24.27Å. A 24.27Å UCS confirms that the proprietary material in REMEDY™ 2 GSR® has successfully stabilized the zeolite. The traditional zero RE catalysts typically equilibriate to a zeolite UCS in the range of 24.21 to 24.24Å, depending on the severity of the unit. Constant activity and zeolite surface area retention were observed, despite a ~750 ppm increase of median values of vanadium plus sodium levels on \( E_{\text{cat}} \).

**FIGURE 13:** MRC Achieved Similar In-Unit Activity and Conversion with RE Free REMEDY™ without an Increase in Dry Gas Yield
Conclusions

Commercial data at MRC confirms that rare-earth free REMEDY™ performance is comparable to the base rare-earth GENESIS® catalyst providing a significant economic benefit. Specifically REMEDY™ showed the following at similar catalyst additions at MRC compared to GENESIS®:

- Similar unit conversion
- Similar coke and slurry selectivities
- Higher gasoline selectivity
- Similar Ecact activity

Grace offers a family of REPLaCeR® catalysts with zero to low rare-earth that has comparable hydrothermal stability and acidity as a traditional rare-earth catalyst.

The REPLaCeR® family of catalysts is currently used in 52 refineries globally processing both VGO and resid. REPLaCeR® technology is a great alternative to rare-earth containing catalysts, mitigating the risk associated with the uncertainty in price and supply of rare earth.

Acknowledgements

The authors thank MRC management for permission to publish this data and Rosann Schiller of Grace for her valuable assistance.

References


6. www.montanarefining.com

Maximize Distillate Yield to Meet Growing Market Demand

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Senior Marketing Manager
Grace
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Despite a mild winter thus far, industry analysts forecast ULSD demand growth in the second half of 2012. This is in part due to global demand growth for middle distillates and in part due to new sulfur regulations set to take effect later this year. In 2012, the State of New York will become the first state to require that all oil used for heating meet ULSD standards, which means that No. 2 heating oil sulfur levels will have to be reduced to 15 ppm. Other Northeast states have announced dates to phase-in ULSD for heating oil. The pending regulations could raise regional ULSD demand by 20%. Over the last 6 months, over 50% Northeast refining capacity has been idled as well as the HOVENSA refinery in the Virgin Islands, which was a major importer of transportation fuels into the Northeast. The loss of refining volume serving the Northeast coupled with bottlenecks in the transportation network from the Gulf Coast could potentially result in high prices and potential shortages of ULSD in New York, Pennsylvania, and New England.

FCC and ART Synergy

Refiners with additional sulfur removal capacity can increase profitability by maximizing the refinery yield of ULSD. If you have room to process additional FCC LCO in your diesel hydrotreaters, Grace® and Advanced Refining Technologies® technical service can work with you to help maximize your refinery profitability by enhancing both the yield and quality of your diesel and heating oil blending streams. We’ve published numerous articles on the topic, which illustrate that the greatest challenge in a max LCO operation is managing the incremental bottoms yield that accompanies a reduction in unit operating severity. Positive yield impact can be achieved via an optimization of key operating variables discussed below.

<table>
<thead>
<tr>
<th>Competitive Catalyst</th>
<th>GENESIS® 1 (Max Gasoline) relative to base</th>
<th>GENESIS® 2 (Max LCO) relative to base</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gasoline, lv.%</td>
<td>Base</td>
<td>+3.0</td>
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<tr>
<td>LCO, lv.%</td>
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<tr>
<td>Bottoms, lv.%</td>
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TABLE 1: GENESIS® Catalyst Delivers Flexibility to Shift Between Gasoline and LCO Operating Modes