The Analytical Services Center (ASC) Tech Service group at Grace Davison receives equilibrium fluid cracking catalyst (Ecat) samples from refineries spanning the globe. On average, Grace receives over 200 Ecat samples each week from the world’s FCCU’s. The resulting information is of critical importance for the FCC unit engineer, who is responsible for continuous optimization and troubleshooting of his/her operation.

The subsequent discussion highlights the trends observed in Ecat properties over the last ten years. The data reflected is not exclusive to Grace Davison products. Samples containing competitive catalyst, additives, and products are also included.

As the refining industry as a whole is challenged by the supply constraints of rare earth, it is interesting to see the trends in properties over the last ten years. Ecat contaminant levels maintain their upward trend as the world
moves to more and more resid processing. Rare-earth remains the most effective means to maintain activity and selectivity in severe operations. However, we are working diligently to reduce the rare-earth content of the catalyst, and maintain performance. At the same time, refiners need to consider the economic tradeoffs associated with rare-earth reductions and assess what process changes can be made in the unit operation to offset any resultant performance differences.

**Vanadium**

Figure 1 illustrates the trend in vanadium over the first decade of the 21st century. With the exception of 2000 to 2001, the Asia Pacific market unfailingly maintains the highest levels of contaminant vanadium. Interestingly, while all other markets have experienced an increase in average vanadium levels in the latter part of the decade, the Asia Pacific market average has experienced a sudden drop of almost 20% from 2009 to 2010. In its entirety, the averaged FCC world contaminant level has been consistent in a band centered around 2,000 wppm. The North American market continues to demonstrate the lowest levels of vanadium in the world (1,626 ppm).

**Nickel**

Falling for the first time below 3500 wppm, the Asia Pacific market reliably maintains the top ranking spot for average nickel level in Ecats. As shown in Figure 2, there is a
tremendous differential between Asia Pacific and the rest of the world. The gap never closes to less than 1,600 wppm. The growth in resid processing in Asia will continue this trend in years to come. As with vanadium, the Asia Pacific market has demonstrated a decrease over the past few years while all other markets have shown a small increase. Similar to vanadium, the North American market maintains the lowest average nickel levels (1,363 ppm).

Iron

The movement in average iron level on industry Ecat, shown in Figure 3, can best be explained as diverse. The North American market has consistently maintained the highest average levels of iron overall increasing from 0.52 wt.% to 0.6 wt.% Beginning in 2002, the European average iron level began a steady descent from 0.52 wt.% to 0.46 wt.% and has remained at this level since 2007. The worldwide average indicates a downward trend overall for the last three years.

Calcium

In 2004, most of the industry Ecat averages faced a steady 4 to 5 year climb in calcium. Asia Pacific led the pack when average levels rose from 0.09 wt.% to 0.2 wt.% Figure 4 shows that during the past year, the worldwide trends have tilted downward and will likely continue in that direction.
Sodium

With few exceptions, sodium (Figure 5) has been steadily trending down for over ten years. Latin America continues to maintain the highest values with a median value over the past three years of 0.35 wt.%. North America dropped to a decade average low of 0.26 wt.%. The average vanadium and nickel levels that characterize the Asia Pacific market indicate that this region continues to process feeds that are vastly different from the rest of the world. As alluded to earlier, the average Ecat results from this territory continue to report the highest average levels for 80% of the primary FCC catalyst contaminants. Up until 2008, most worldwide contaminant trends were directionally consistent. The coming years will be exciting as the industry is challenged to process higher amounts of discounted feedstocks to maintain profitability.

Activity

Until 2004, most of the industry saw a steady climb in Ecat activity. As indicated by Figure 6, over the next four years, activity trends flattened with slight periodic increases. In 2009, activity numbers regained momentum to reach decade highs in all but the European market. With the highest numbers amongst all four regions, North America experienced an average 3.4 number increase from 69.9 to 73.3 over the last decade. The world-wide average
gained 2.9 activity numbers from 68.7 to 71.6 over the same time period.

The continued upward trend in catalyst activity occurred despite a parallel upward trend in contaminants such as vanadium and nickel to decade high levels. Grace’s advanced metals trapping technologies have enabled many refiners to retain activity despite increasing contaminant levels.

**Rare Earth**

As shown in Figure 7, worldwide rare earth averages are characterized by a steady upward slope from 1.9 wt.% to 2.9 wt.% Re₂O₅ over the 2000 to 2010 time period. Reaching a high of 3.0 wt.% Re₂O₅ in 2008, the North American average upheld the highest values for the last six years. Consequently, as shown in Figure 6, activity levels also increased with rare earth.

After the price of rare earth increased nearly twenty times in eight months, the topic of rare-earth has quickly become the focal point of many reformulation and new technology efforts. Although market trends have yet to show a significant response, the debut of low and zero rare earth catalysts from Grace will produce a significant shift in Ecatalyst rare-earth levels from here on out.

**Unit Cell Size**

Figure 8 illustrates the trend in unit cell size. Between the years of 2000 and 2005, there was significant variability and
disparity amongst regions. In 2005, the difference between the Latin American and European regions averaged 0.04 Å. The European region also registered an average unit cell size decade high for all regions at 24.32 Å. During the latter part of the decade, market unit cell size began to converge to an average 24.31 Å. The exception, the Latin American region, remains slightly lower at 24.30 Å but the overall regional divergence is significantly reduced in comparison to years prior to 2005.

Particle Distribution (0 to 40 microns)

In November 2009, Grace’s routine Ecat particle size test was changed to new instrumentation. The new particle size properties no longer have the micro-mesh factors applied and the results are directly from the equivalent spherical analysis model of the measurement data. As a result, a significant shift in the 2010 data can be seen in Figure 9.

Nonetheless, previous years’ data tells that while there is little variance over time within each region, there is substantial offset amid regions. The worldwide average for 0-40 particle size is 6%. High average catalyst age or low catalyst additions per volume of inventory will decrease the 0-40 fraction and increase average particle size.

Grace remains committed to providing Ecat analyses as a key component of our technical service package for customers. The historical results for any unit can provide an invaluable reference point for troubleshooting activities or assessment of performance deltas after major turn-arounds. Ecat results are available 24/7 on our customer website, www.e-catalysts.com. Contact your sales representative to gain access to your unit’s sample results as well as a host of other technical literature and information.
GDNOX™ 1 Additive - Grace Davison’s Next Generation NOx Reduction Additive

Eric Griesinger
Marketing Manager, Grace Davison Refining Technologies, Columbia, MD

GDNOX™ 1 additive is the next generation NOx reduction additive for the FCC regenerator unit. Unlike traditional NOx reduction additives, GDNOX™ 1 additive utilizes a new technology platform that builds on the success of DENOX®, while allowing refiners the ability to achieve greater NOx reduction. And, unlike earlier generation NOx reduction additives, GDNOX™ 1 additive greatly mitigates H₂ and/or dry gas penalties. GDNOX™ 1 additive is formulated to reduce exposure from inflation in rare earth pricing.

As extensive pilot plant testing shows in Figure 1, refiners have the ability to incrementally improve NOx reduction, by upwards to 80%, with increased GDNOX™ 1 additive dosing rates. To achieve targeted NOx reduction, the recommended dosing rate for GDNOX™ 1 additive typically ranges between 2.5 wt.% and 7.5 wt.% of catalyst inventory.

GDNOX™ 1 additive allows refiners to:

- Meet local/federal NOx regulations,
- Meet EPA constraints without the cost of capital,
- Process feeds high in nitrogen with greater economic flexibility,
- Balance refinery wide NOx emissions, and
- Maintain FCC throughput

Ask your Grace sales representative for more information.

<table>
<thead>
<tr>
<th>GDNOX™ 1 Additive Addition Rate% of Inventory</th>
<th>Base Line NOx (ppm)</th>
<th>NOx After GDNOX™ 1 Additive Addition (ppm)</th>
<th>Percentage NOx Reduction/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.5% GDNOX 1</td>
<td>292</td>
<td>139</td>
<td>50</td>
</tr>
<tr>
<td>5.0% GDNOX 1</td>
<td>287</td>
<td>110</td>
<td>60</td>
</tr>
<tr>
<td>10.0% GDNOX 1</td>
<td>287</td>
<td>62</td>
<td>80</td>
</tr>
</tbody>
</table>