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 C3+ 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 C3+ 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.¹ Feed injection nozzles that atomize the feed will also a 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?

Eric Griesinger, Grace Davison Refining Technologies

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.

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

<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 15: Performance and Economic Comparison of Low Rare Earth and REMEDY™ Technologies

<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>
</tr>
<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>1.03* Base</td>
<td>1.03 Base</td>
</tr>
<tr>
<td>Wet Gas Compressor</td>
<td>Base</td>
<td>214</td>
<td>220</td>
</tr>
<tr>
<td>Dry Gas, scfh</td>
<td>6.3</td>
<td>7.1</td>
<td>7.0</td>
</tr>
<tr>
<td>iC₄, vol.%</td>
<td>3.1</td>
<td>2.7</td>
<td>3.0</td>
</tr>
<tr>
<td>C₄+, vol.%</td>
<td>7.3</td>
<td>7.8</td>
<td>7.9</td>
</tr>
<tr>
<td>Gasoline, vol.%</td>
<td>54.9</td>
<td>53.2</td>
<td>53.7</td>
</tr>
<tr>
<td>RON/MON</td>
<td>92.5/80.5</td>
<td>93.4/80.9</td>
<td>93.4/80.9</td>
</tr>
<tr>
<td>Slurry, vol.%</td>
<td>4.5</td>
<td>4.8</td>
<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 (Mg$_2$SiO$_4$), 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.
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 Ecats 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 6000 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?

Ann Benoit, Grace Davison Refining Technologies

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.  

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

### FIGURE 43: Effect of Metals on ZSM-5 Additive Deactivation

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. 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 nodules 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. The color of Ecat could potentially indicate high levels of Fe. Ecat samples can have a reddish brown tint when poisoned by iron. 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.

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.