High Rare Earths Prices! Options for Reducing FCC Catalyst Costs

Ray Fletcher, Engineering Fellow
Overview

- Introduction

- How to reduce Rare Earths (RE) in FCC catalyst
  - Metal & nitrogen trapping
  - Laboratory analysis
  - Commercial Results
  - Application recommendations

- How to reduce Rare Earths (RE) in SOx additives
  - Effect of rare earth
  - Low rare earth SOx technology
  - Application recommendations

- Conclusions
FCC Feed Contaminants

- **Conradson Carbon:**
  - Higher delta coke / Higher Regen. Temp.

- **Vanadium:**
  - Mobile Vanadic acid species deactivate zeolite in the FCC catalyst
  - Typical responses:
    - *Increase catalyst RE (catalyst stability)*
    - *Increase fresh catalyst additions*
    - *Inject equilibrium catalyst as flushing media*
  - Higher catalyst deactivation rates

- **Nitrogen:**
  - Higher delta coke / Lower conversion
    - +100 ppm → -1 wt% conversion
  - Typical responses:
    - *Increase catalyst activity and/or additions*
Rare Earth Impact on FCC Catalyst

• The Rare Earth trade-off:
  – Increasing Rare Earth:
    • Lower catalyst make-up rate:
      – higher activity and hydrothermal stability
      – Improved vanadium resistance
    • Higher hydrogen transfer activity:
      – Higher gasoline selectivity
  – Decreasing Rare Earth:
    • Lower hydrogen transfer activity:
      – higher light olefins (C3=, C4=) selectivity
      – higher gasoline octane

• Most common situation today:
  – High RE used to minimize catalyst additions
  – ZSM5 is added as needed to compensate for LPG/octane loss

• How can we lower Rare Earths without significantly increasing fresh cat adds?

Pine, Maher, et.al., O&GJ, Aug 1984
Cat-Aid: Helping The FCC Catalyst

- Cat-Aid traps FCC feed contaminants

**Benefits when using Cat-Aid:**
- Improved catalyst stability
  - *Fresh adds decreased by up to 50%*
- Improved coke selectivity
  - *Ability to process heavier, more contaminated feed-stocks*
- Increased FCC unit conversion
  - *Cat-Aid reduces nitrogen poisoning effect*
- Reduced SOx emissions

- Cat-Aid permits a refiner to decrease Rare Earth on fresh catalyst
  - Without loss in conversion
  - Without increase in fresh catalyst additions
Cat-Aid: Laboratory Evaluation

- **Cat-Aid improves catalyst activity & selectivity when co-deactivated with base fresh catalyst**
  - Procedure:
    - Metal deposition on fresh catalyst / Cat-Aid mixture via cracking of a metals doped feed
    - Multiple cycles (5-10) of cracking/regeneration (621°C) to achieve targeted metals level
    - Steam deactivation (788°C, 20 hours, 95% steam/air)
    - XRF metals analysis

- **Performance testing**
  - Catalyst systems:
    - Fresh catalyst
    - Fresh catalyst + 10% Cat-Aid
  - Deactivation conditions:
    - 5000 Ni, 5000 V
    - Steaming: 788°C, 20 hours
Cat-Aid: Laboratory Results

- Laboratory study shows clear benefits for Cat-Aid
- Fresh Catalyst vs. Fresh Catalyst + 10% Cat-Aid
  - Constant Coke comparison:
    - Conversion: +3.1 wt%
    - Gasoline: +2.1 wt%
    - Slurry: -2.5 wt%

<table>
<thead>
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<th>Constant Coke</th>
<th>Fresh Cat Metallated</th>
<th>Fresh Cat Metallated+ Cat Aid</th>
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<td>Temperature, °F</td>
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<td>Temperature, °C</td>
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<td>TOTAL</td>
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</table>
Cat-Aid Effect on Residue Catalysts

- **Cat-Aid increases activity at constant cat-to-oil**
  - Zeolite protection through metals absorption
  - Activity enhancement through nitrogen tolerance

- **Cat-Aid increases gasoline at constant coke**
  - Activity enhancement leading to increased conversion
  - Bottoms upgrading to gasoline

- **Cat-Aid increases bottoms conversion at constant coke**
  - Much deeper slurry destruction
  - Enhanced profitability
Cat-Aid: Commercial Experience

- Cat-Aid recently used at a US Gulf Coast Refinery
- Residue content of feed increased
  - 11% increase in Nitrogen
  - 26% increase in Concarbon
- Similar operating conditions
  - Similar fresh feed rate
  - No change in riser outlet
  - SOx reduced by Cat-Aid (- 57%)
- Catalyst RE content was reduced at the same time
  - Lower costs, but lower stability
  - Addition rate actually decreased!
Cat-Aid: Commercial Yield Effects

- Cat-Aid allowed heavier feed processing with lower RE catalyst

- Yield effect was positive, despite increased reside content of feed
  - Yield selectivities:
    - Conversion: +1.7 vol%
    - Slurry: -0.5

- Unit conversion increased, despite lower MAT activity
  - Unit conversion: +1.7 vol%
  - MAT Activity: -1.8 wt%
  - RE Content: -1.2 wt%

- Cat-Aid enabled the FCC to operate at equivalent conversion with a lower Rare Earth catalyst
Residue Processing: Unit #1

- Cat-Aid enabled this refiner to run a higher percentage of deasphalted oil at higher conversion.

- Cat-Aid increased fractional conversion at constant basic nitrogen.
Residue Processing: Unit #2

- Cat-Aid enabled increased residue to be processed with a typical conversion increase of 2.0%

- Evidence of increased residue is especially evident in the increased average CCR processed using Cat-Aid
Residue Processing: Unit #3

- Cat-Aid improved coke selectivity leading to a new conversion vs. CTO relationship
- SOx emissions were reduced by Cat-Aid
  - Many metal traps are poisoned by sulfur
  - Cat-Aid includes a “sacrificial” sulfur absorption mechanism to enable the V & N trapping functions to continue to operate
- Cat-Aid could allow a significant reduction in SOx additive usage for many refiners
Reducing Catalyst RE Costs with Cat-Aid

- Recommended methodology for reducing fresh catalyst costs:

- The following stepwise procedure is recommended for swiftly reducing FCC catalyst costs:
  1. Establish 10% Cat-Aid in inventory
  2. Reduce fresh catalyst RE by 0.3-0.5 wt%
  3. Optimize FCC operation (riser, CTO, ZSM-5 etc.)
  4. Carry out a detailed unit test run to define benefit & return on investment
  5. Repeat these steps until target RE content is reached
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Function of Rare Earth in SOx Additives

- SOx additives remove SOx from the FCC regenerator in via capture of SO₃ onto a magnesium based sorption phase
  - Most of the SOx in full burn units is in the form of SO₂ (e.g. >80%)
  - An Oxidation function is needed to drive SO₂ to SO₃ to replace the captured SO₃ as SOx pick-up proceeds

- Cerium Oxide used to catalyze the oxidation of SO₂ to SO₃
  - SO₂ + ½ O₂ -> SO₃

- Until recently, the Cerium Oxide content of most commonly used SOx additives was never really optimized
  - CeO₂ was not a high cost item, and was used in excess
  - Lab. scale performance testing of SOx is not trivial
  - Concentration of CeO₂ in Super SOXGETTER (> 12%) was a legacy of original Amoco/Arco research from over 25 years ago
Rare Earth Optimization for SSG-II

• Laboratory testing (TGA) used to evaluate the effect of changing CeO$_2$ content – several different CeO$_2$ levels evaluated
  – TGA test designed to mimic well-mixed full FCC burn units (excess O$_2$ > 1%)
  – CeO$_2$ contents ranges from 4% to 16% evaluated
  – Testing allowed CeO$_2$ content to be optimized to a new lower level
  – Successful performance has been confirmed in commercial applications

• New formulation for SSG-II developed using above provides:
  – Reduced CeO$_2$ content to 8 wt%
  – Increased hydrotalcite concentration
    • 10% more hydrotalcite means more magnesium sites for SOx pickup
  – Modified release package to improve regeneration based on work conducted with LCO-mode FCC operations (low riser temperature)
  – Same attrition and similar physical properties to Super SOXGETTER
SSG-II: Commercial Experience

- 23 Refiners are now using Super SOXGETTER-II
  - Most users were using standard Super SOXGETTER (SSG), and switched directly to using Super SOXGETTER-II (SSG-II)

- Each user achieved equiv. or improved performance vs. standard SSG

- Trial #1 demonstrated equivalent performance
  - Mid-way through trial the feed sulfur decreased
  - Additions followed feed sulfur
    - Injections: 40 to 20 lb/day
  - PUF remained constant at 15-20
SSG-II: Commercial Experience

- Trial #2 demonstrated equivalent or slightly improved performance
  - SSG-II additions matched SSG at average 300 - 400 lbs/day
  - SO$_2$ emissions remained very low at 30-60 ppm throughout change
  - SO$_2$ reduction constant at 85 - 90%
  - The PUF increased by ~6%
    - 12.1 for Super SOXGETTER
    - 12.8 for Super SOXGETTER-II
SSG-II: Conclusions

• SSG-II provides equivalent performance to standard SOx Super SOXGETTER with lower operating costs
  – Constant or slightly improved efficiency (PUF)
  – Constant or slightly reduced additive injection rate
  – Lower price due to reduced CeO₂ concentration

• Most remaining Super SOXGETTER users are currently planning to switch to SSG-II
  – Commercially proven, no risk in switching from Super SOXGETTER to Super SOXGETTER-II
  – Savings to operating budget are immediate

• INTERCAT provides full technical support and performance assessment to support the transition to SSG-II
Future Developments – SSG-III, LSXPB-II

• Improving SOx additive performance with even lower RE levels remains INTERCAT’s top priority R&D activity
  – Aim is to continue to reduce refinery operating costs with equivalent or better SOx reduction efficiency

• Integration of INTERCAT’s R&D with Johnson Matthey is yielding significant benefits
  – Johnson Matthey has significant experience and IP in usage and optimization of REO and precious metals in automotive catalysis

• First production runs of SSG-III now being produced (4% CeO₂)
  – Unique and exciting approach to SOx additive manufacture/catalysis
  – Expect commercial data within next 1-2 months
  – Will allow further cost savings for full burn units

• LoSOx-PB-II also now being commercially tested
  – Improved performance and cost position for partial burn units
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Conclusions

- Options are available to significantly reduce the negative impact of today’s high Rare Earth costs
  - Cat-Aid enables refiners to reduce rare earth on catalyst without loss of conversion
  - SSG-II decreases cerium oxide content with equivalent SOx reduction performance
- Each technology has been proven in multiple commercial applications
- INTERCAT provides the technical support and loader technology to enable refiners to take advantage of these cost saving opportunities
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