High Rare Earths Prices! Options for Reducing FCC Catalyst Costs

Ray Fletcher, Engineering Fellow

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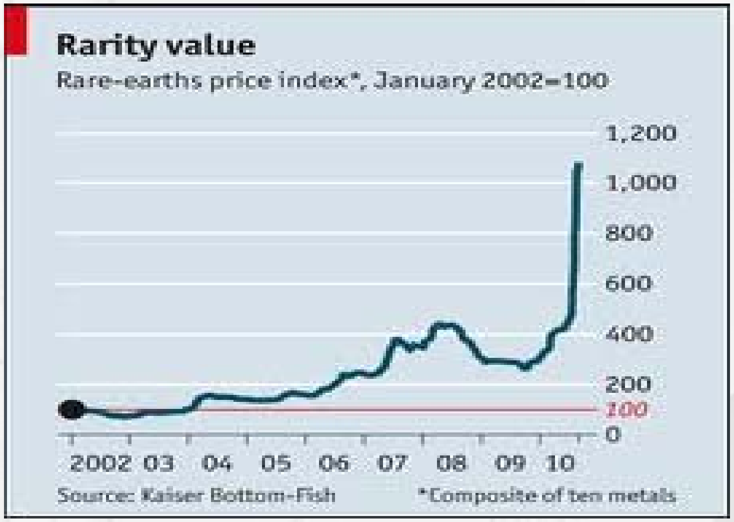
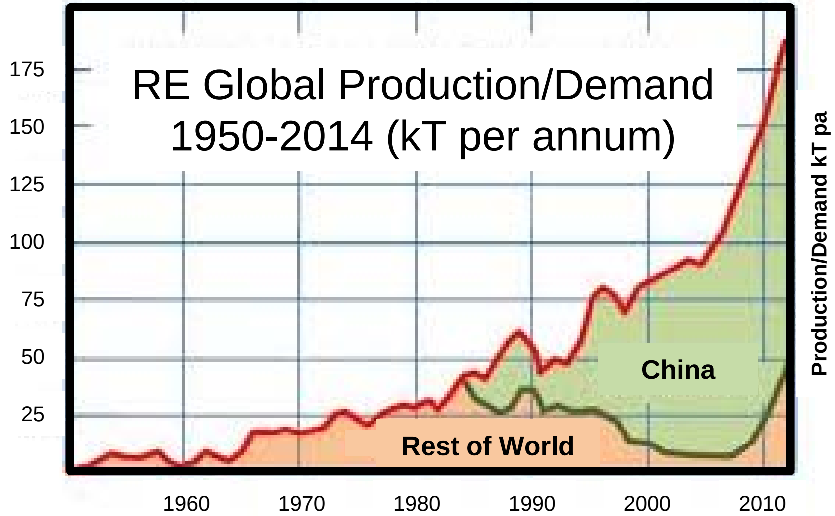
Overview

- **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**





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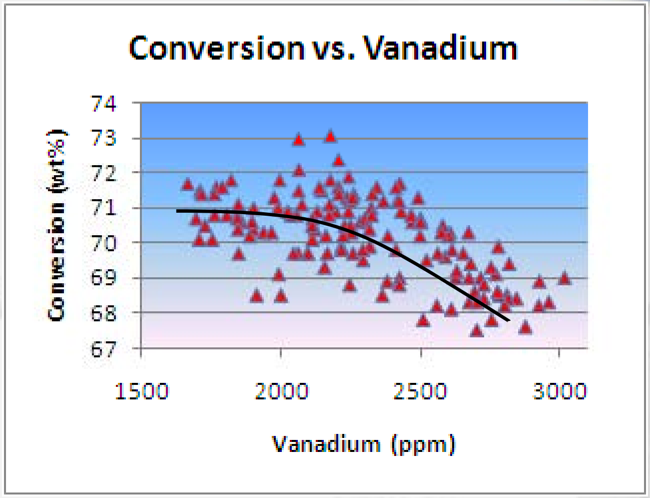
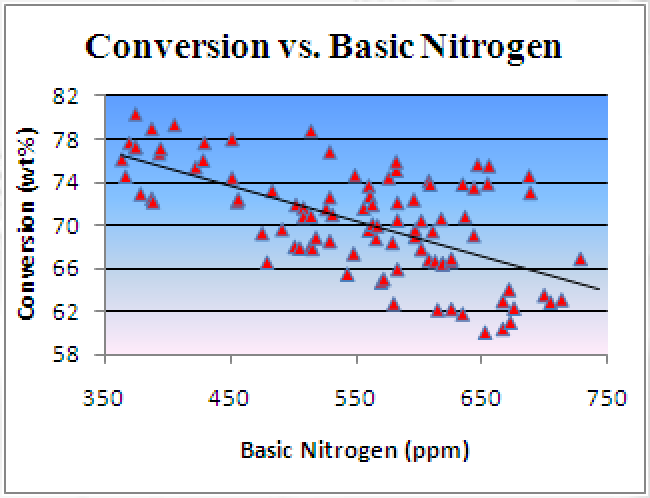
FCC Feed Contaminants

- **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*





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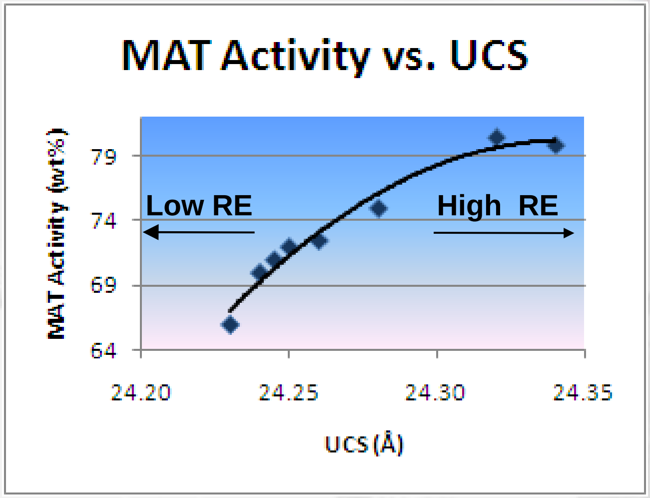
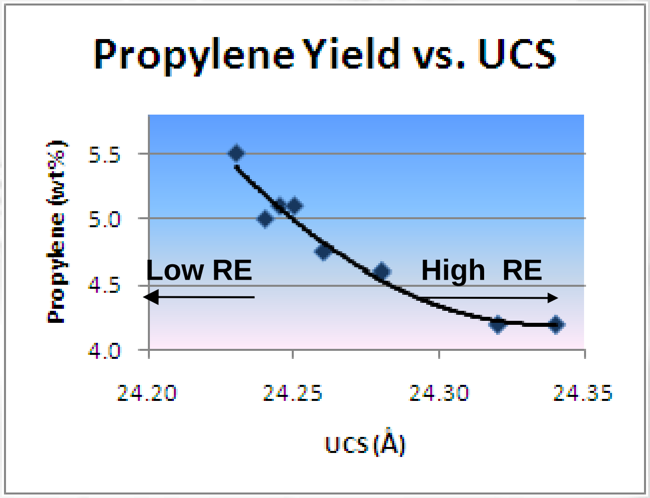
Rare Earth Impact on FCC Catalyst

- **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?**





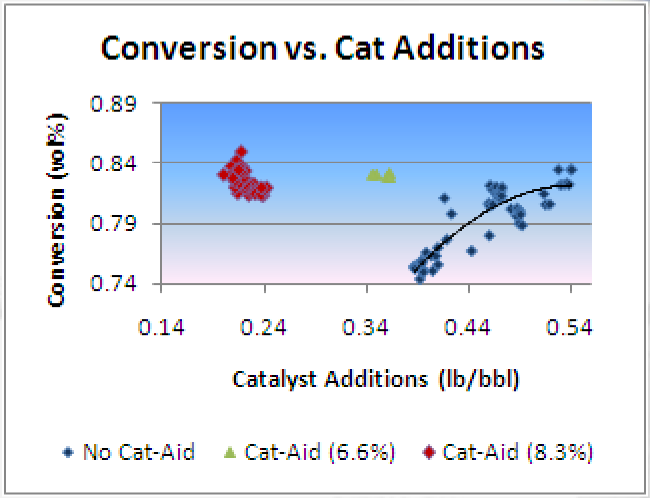
Pine, Maher, et.al., O&GJ, Aug 1984

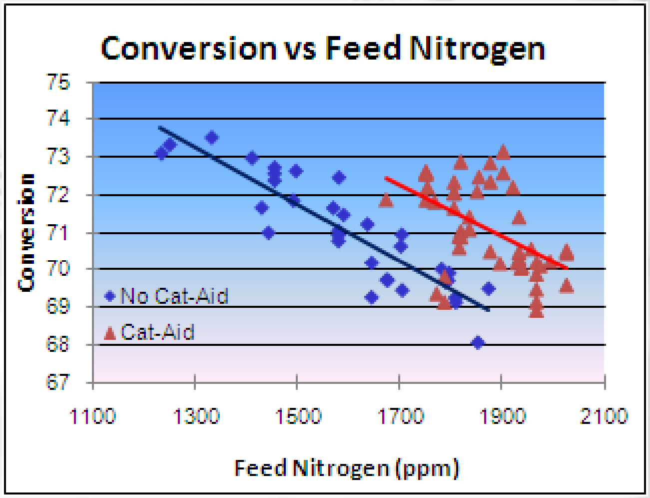
Cat-Aid: Helping The FCC Catalyst

- **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





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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 (621ºC) to achieve targeted metals level*
    - *Steam deactivation (788ºC, 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: 788ºC, 20 hours*

Feed Properties	
Density, SG	0.950
CCR, wt%	7.7
Sulfur, wt%	1.98
Total N, ppm	1530
Nickel, ppm	13.3
Vanadium, ppm	12.5

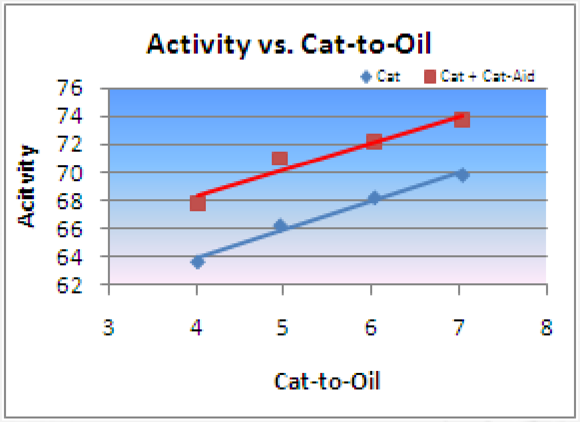
Fresh Catalyst	
Total SA, m^2/g	243
Alumina, wt%	52.5
Rare earth, wt%	3.75
Na20, wt%	0.28
ABD, c/cc	0.76

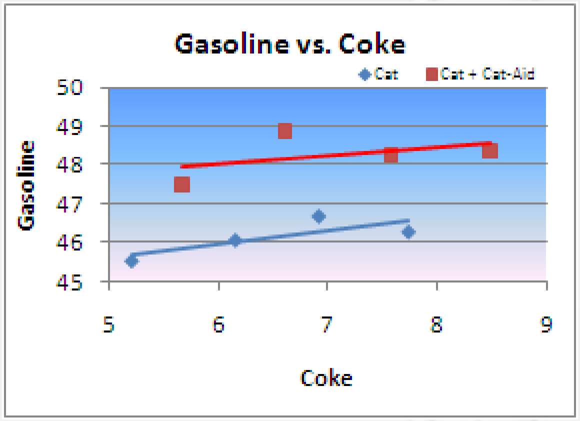
Cat-Aid: Laboratory Results

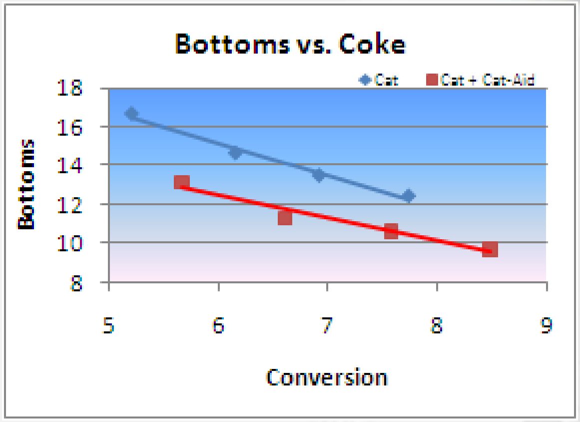
- **Laboratory study shows clear benefits for Cat-Aid**
- **Fresh Catalyst vs. Fresh Catalyst + 10% Cat-Aid Constant Coke comparison:**
  - Conversion: +3.1 wt%
  - Gasoline: +2.1 wt%
  - Slurry: -2.5 wt%

Constant Coke	Fresh Cat Metallated	Fresh Cat Metallated+ Cat Aid
Temperature, °F	989	989
Temperature, °C	532	532
Conversion, wt%	65.90	69.01
Catalyst-to-Oil, wt/wt	4.85	4.35
Delta Coke, wt%	1.24	1.38
YIELDS, WT%:		
Coke	**6.0**	**6.0**
Dry Gas	2.0	2.0
Propane	0.6	0.7
Propylene	3.4	3.8
n-Butane	0.5	0.6
Isobutane	2.3	2.7
C4 Olefins	5.0	5.2
1-Butene	1.1	1.1
Isobutylene	1.4	1.4
c-2-butene	1.1	1.2
t-2-butene	1.4	1.5
Butadiene	0.0	0.0
Gasoline	46.1	48.0
LCO	19.2	18.6
Bottoms	14.9	12.4
TOTAL	100.0	100.0

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

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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!*

Feed Quality	Base	Cat-Aid
Density (SG)	0.927	0.928
Sulfur	1.3	1.6
Total nitrogen	1658	1837
CCR	2.7	3.4
Unit Operations		
Feed Rate	58,206	57,452
Feed Preheat	403	393
Riser Outlet	996	999
Regen Dense T	1,374	1,384
Fluegas CO2	16.5	17.6
Fluegas CO	0.0	0.0
Fluegas excess O2	1.0	1.2
Fluegas SOx	643	277
Cat/Oil	7.2	7.3
Fractionator btms temp	662	650
Cat cooler duty	122	122

FCC Catalyst	Base	Cat-Aid
Fresh Cat Adds	17.0	14.7
Ecat ReO	3.5	2.3
Flushing ECat Adds	8.5	8.5
Cat-Aid %	0%	8.1%

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*

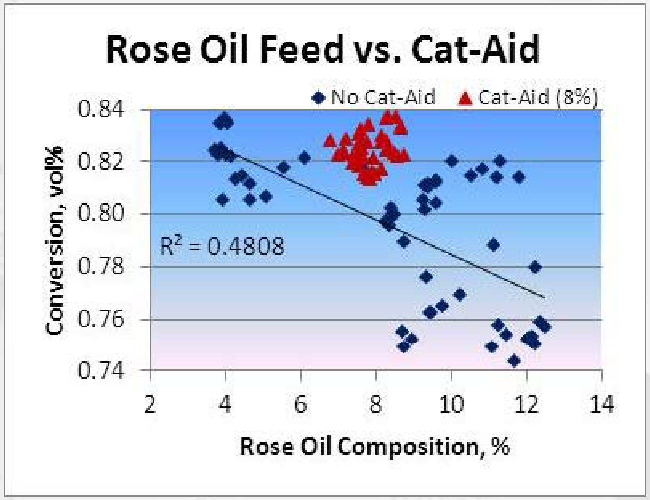
- **Unit conversion increased, despite lower MAT activity**
  - *Unit conversion: +1.7 vol%*
  - *MAT Activity: -1.8 wt%*
  - *RE Content: -1.2 wt%*

- **Cat-Aid enabled the FCC to operate at equivalent conversion with a lower Rare Earth catalyst**

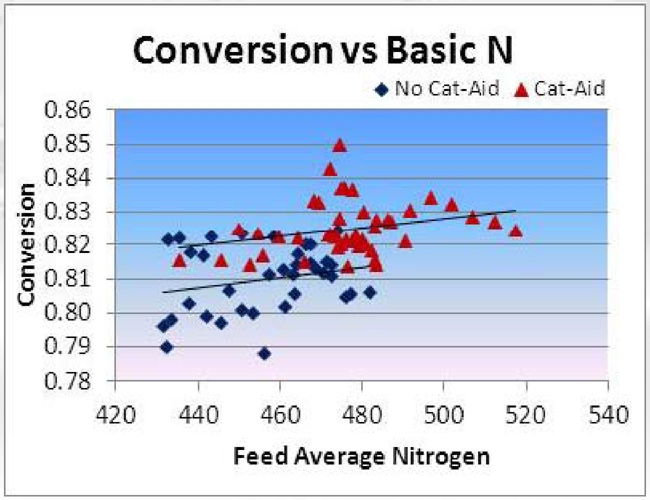
Yield Selectivities	Base	Cat-Aid
Conversion	69.5	71.2
Drygas	5.0	5.5
Propane	1.7	1.7
Propylene	4.9	5.2
Isobutane	2.3	2.4
Normal butane	0.7	0.7
Butylene	6.3	6.4
LPG	16.0	16.2
Gasoline Total	39.0	39.2
LCO	25.5	24.3
Slurry	6.9	6.4
Coke	6.9	7.3
Slurry density	1.08	1.11
Equilibrium Catalyst		
Activity	67.8	66.0
Total surface area	120	125
Zeolite surface area	79	79
Meso surface area	40	46
Nickel	3073	2415
Vanadium	2759	2517
Al2O3	40.2	38.2
ReO	3.5	2.3
Carbon	0.02	0.04

Residue Processing: Unit #1

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



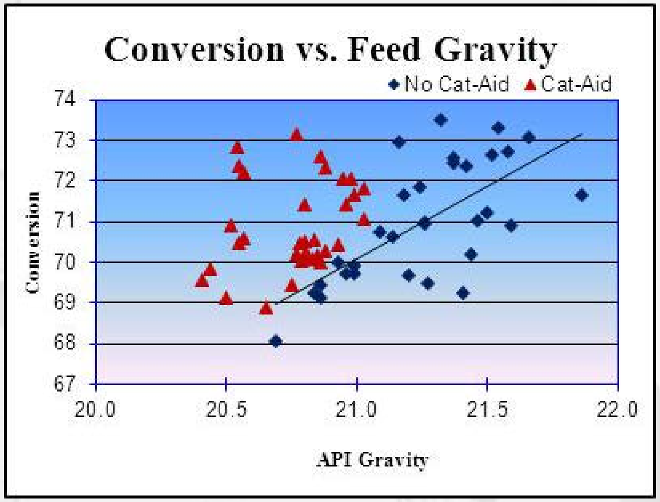
- **Cat-Aid increased fractional conversion at constant basic nitrogen**

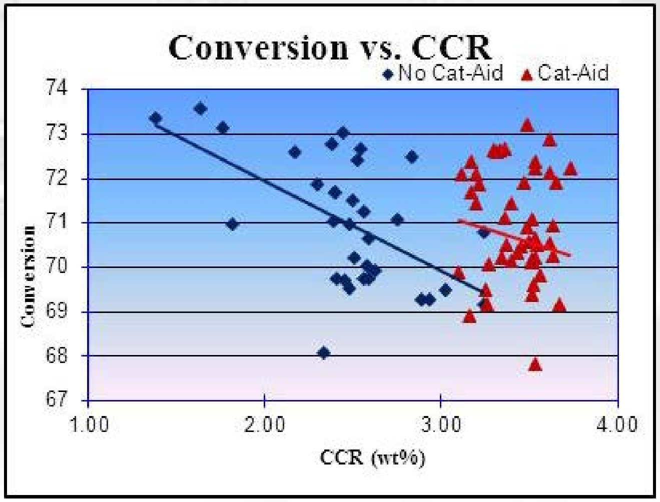


Residue Processing: Unit #2

- **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**





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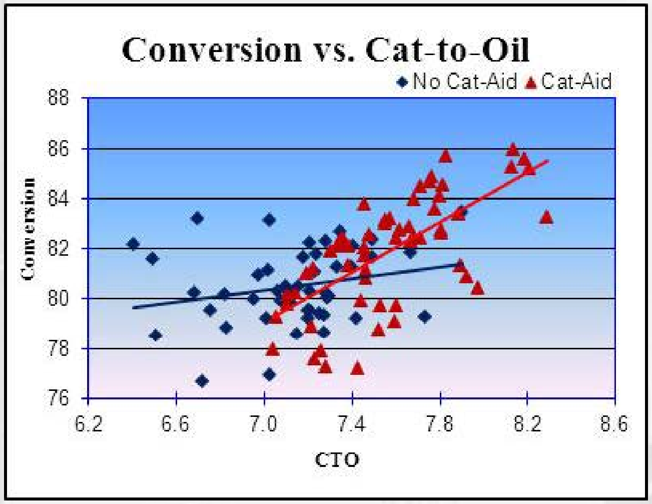
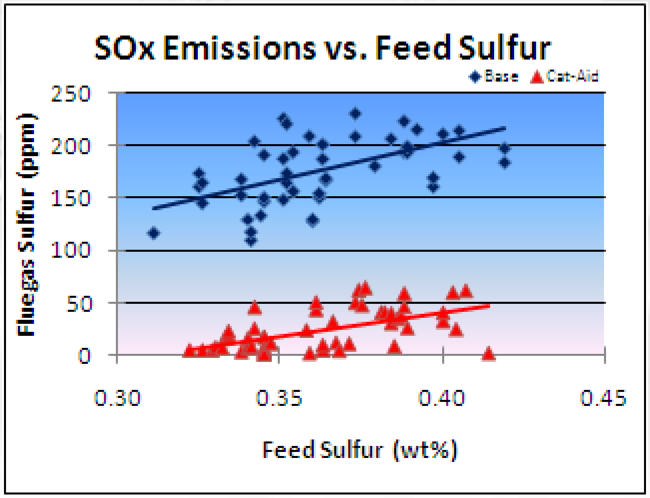
Residue Processing: Unit #3

- **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**





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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

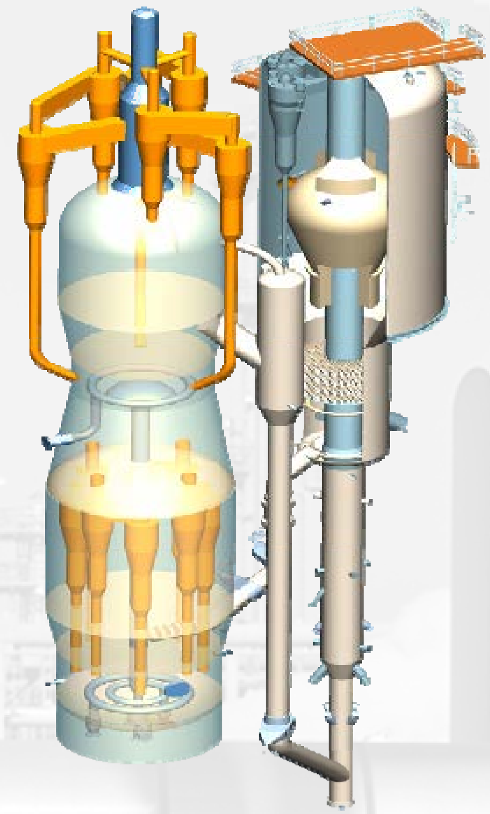

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Photo: Chinese Namching open pit mine

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Function of Rare Earth in SOx Additives

- **SOx additives remove SOx from the FCC regenerator in via capture of SO_3 onto a magnesium based sorption phase**
  - Most of the SOx in *full burn* units is in the form of SO_2 (e.g. >80%)
  - An Oxidation function is needed to drive SO_2 to SO_3 to replace the captured SO_3 as SOx pick-up proceeds
- **Cerium Oxide used to catalyze the oxidation of SO_2 to SO_3**
  - $SO_2 + ½ O_2 \rightarrow SO_3$
- **Until recently, the Cerium Oxide content of most commonly used SOx additives was never really optimized**
  - CeO_2 was not a high cost item, and was used in excess
  - Lab. scale performance testing of SOx is not trivial
  - Concentration of CeO_2 in Super SOXGETTER (> 12%) was a legacy of original Amoco/Arco research from over 25 years ago

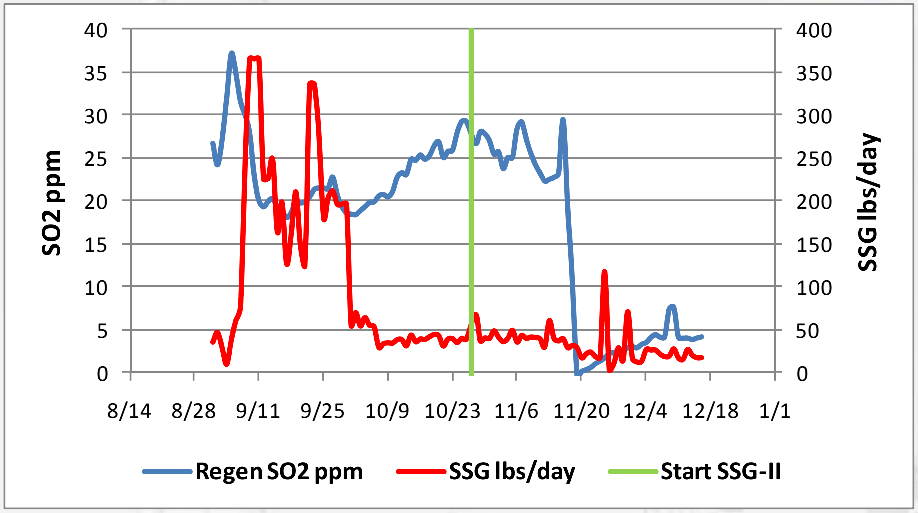
Rare Earth Optimization for SSG-II

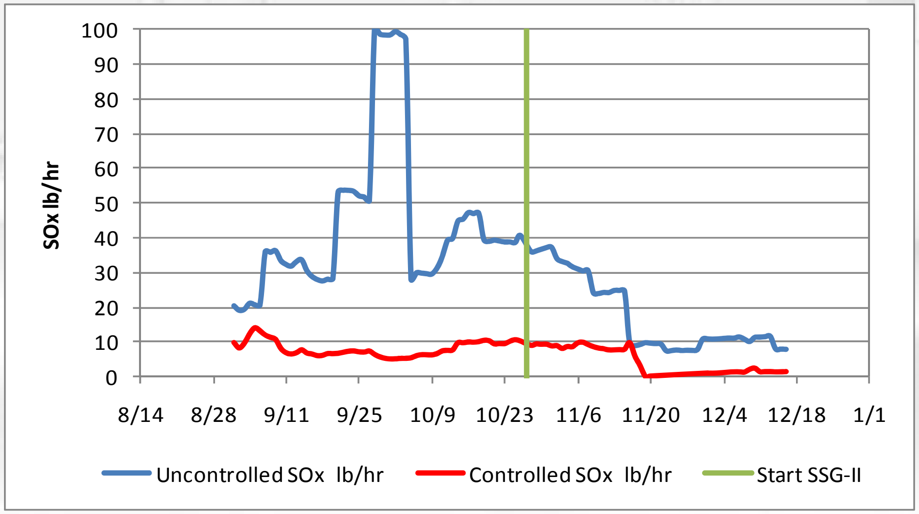
- **Laboratory testing (TGA) used to evaluate the effect of changing CeO_2 content – several different CeO_2 levels evaluated**
  - TGA test designed to mimic well-mixed full FCC burn units (excess O_2 > 1%)
  - CeO_2 contents ranges from 4% to 16% evaluated
  - Testing allowed CeO_2 content to be optimized 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

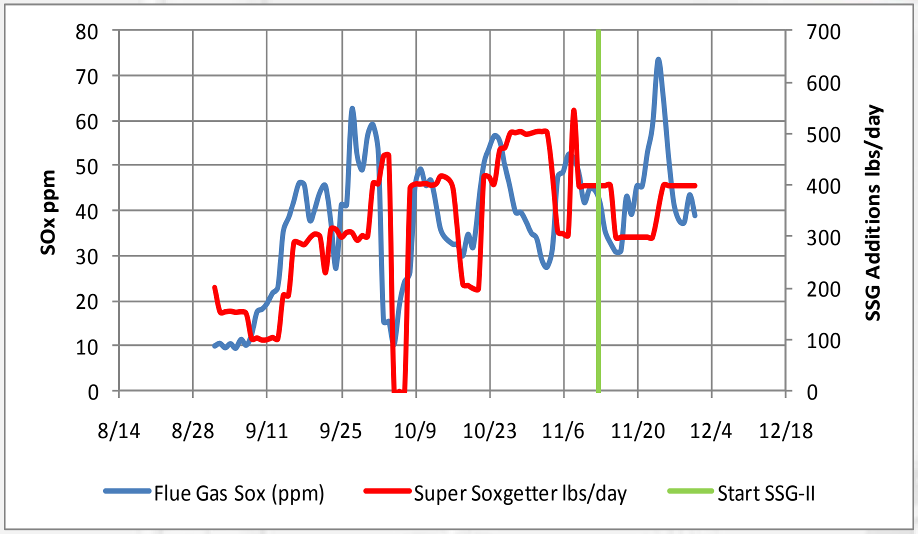
- **23 Refiners are now using Super SOXGETTER-II**
  - Most users were using standard Super SOXGETTER (SSG), and switched directly to using Super SOXGETTER-II (SSG-II)
- **Each user achieved equiv. or improved performance vs. standard SSG**
- **Trial #1 demonstrated equivalent performance**
  - Mid-way through trial the feed sulfur decreased
  - Additions followed feed sulfur
    - *Injections: 40 to 20 lb/day*
  - PUF remained constant at 15-20

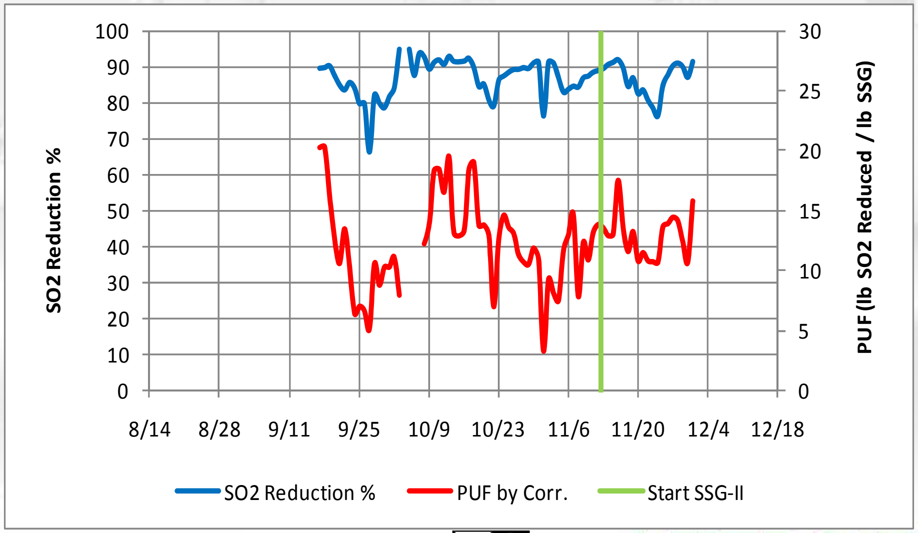




SSG-II: Commercial Experience

- **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 CeO_2 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% CeO_2)**
  - 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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Photo: Chinese Bayan-Obo open pit mine

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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**

Contact Information

Ray Fletcher
rfletcher@intercatinc.com
+1 713 927 2170