Understanding Iron Contamination on FCC Catalysts

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REFCOMM
GALVESTON
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Overview

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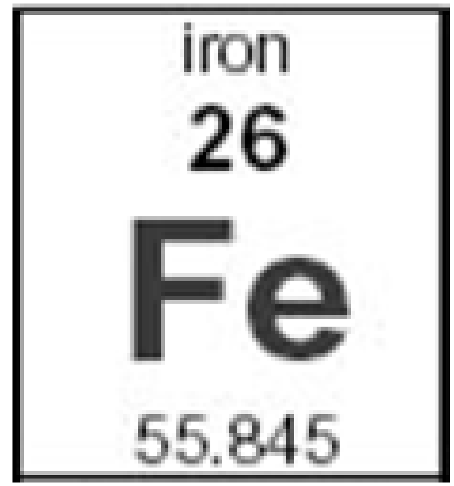
- Why iron? Iron contamination background and history
- Chemical and physical effects of added iron
- What happens to iron once it hits the catalyst?
  - Deposition
  - Mobility
- BASF examples of high iron unit examples
- Steps to mitigate iron contamination

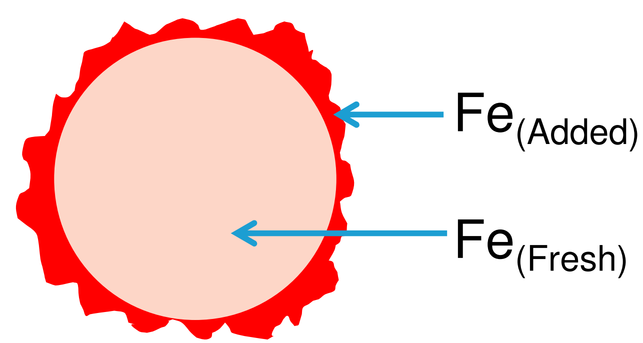
FCC Iron Contamination

- First recognized in the ’90s, has since been a concern for FCC Ecat
- All regions of the world have reported concerns of iron contamination
- The introduction of tight oil in North America has brought the issue of iron to attention again
- BASF launched a new R&D project to further understand the iron effects



Sources of Iron

- Fresh catalyst Fe comes from the clay source
  - Varies 0.25 to 0.75 wt%
  - Incorporated within the silica/alumina framework
    - Does not impact surface accessibility
    - Does not participate in side chemical reactions
- "Added Fe" deposits on the surface of the catalyst
  - $Fe_{(Added)} = Fe_{(Ecat)} - Fe_{(Fresh)}$
- Added Fe sources:
  - Organic Fe from feed
  - Inorganic Fe from equipment corrosion



Equilibrium Catalyst

Ecat Benchmarking: Iron

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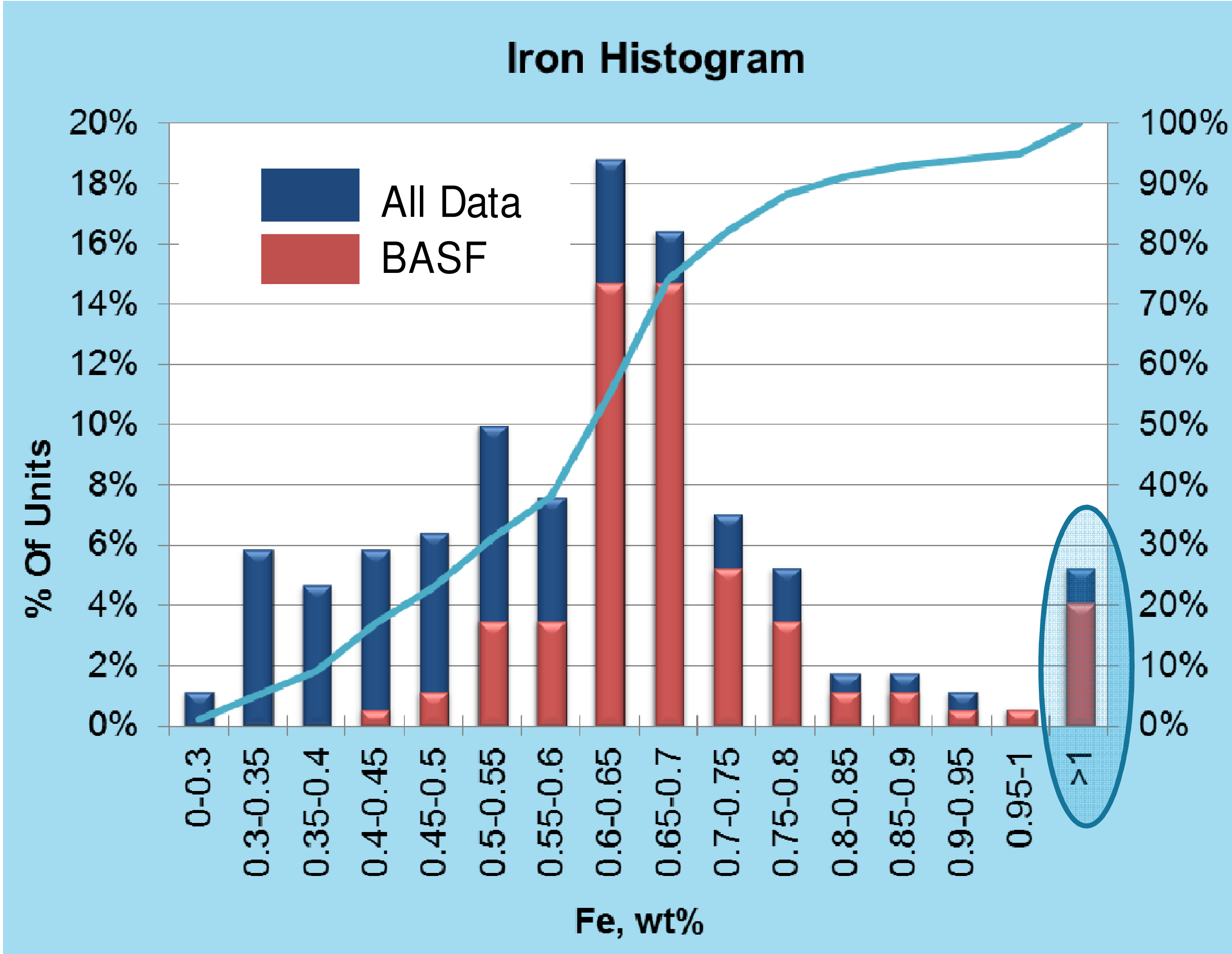
- BASF supplies the majority of high iron accounts above 1 wt%
- BASF's high porosity catalysts have high tolerance to iron pore-mouth plugging



Impacts of Added Fe on Performance

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Chemical Effects

- **Dehydrogenation**: equivalent Ni = Ni + V/4 + Cu + Fe/10
- Mild CO **promoter**
- Transfers S from reactor to regenerator as FeS for increased **SOx**

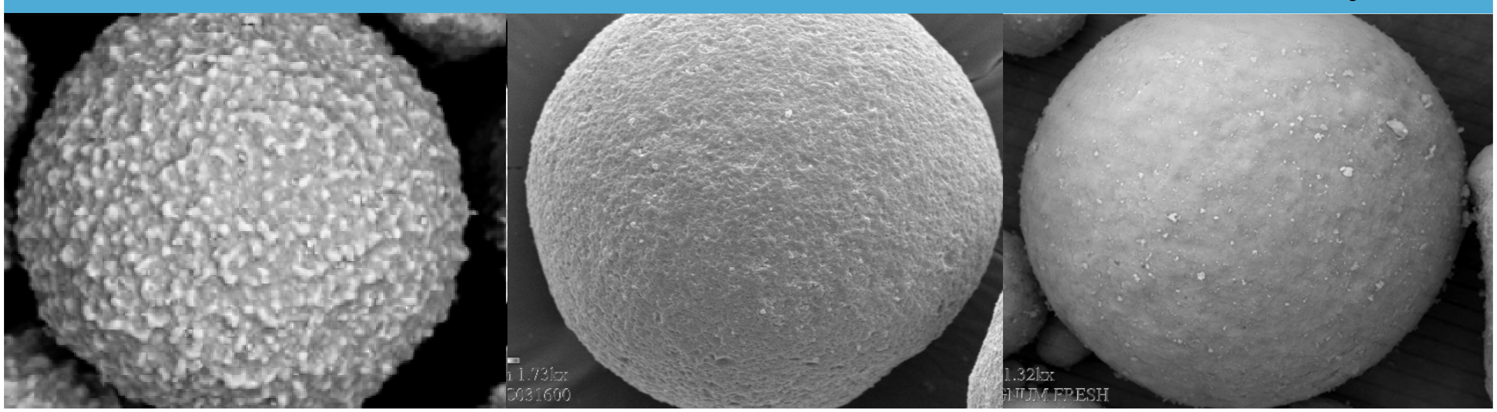
Physical Effects

- Surface **nodule** formation, which can impact catalyst **circulation** via ABD changes
- **Vitrification** on catalyst surface, loss in surface area
- Severe poisoning leads to surface blockage and reduced **conversion** and high slurry yield

Surface Effects
Nodule Formation and Circulation Effects

- Under FCCU conditions, very high iron forms very distinct nodules on the outer surface of the catalyst
- Nodules result in lower ABD and can impact circulation
  - Anecdotal reports of a “cliff”
  - Upset threshold varies from unit to unit
  - Typically manifests as regen slide valve delta P instability

Nodulated Ecat	Normal Ecat	Fresh Catalyst



Surface Effects
Formation of an Outer Iron Shell

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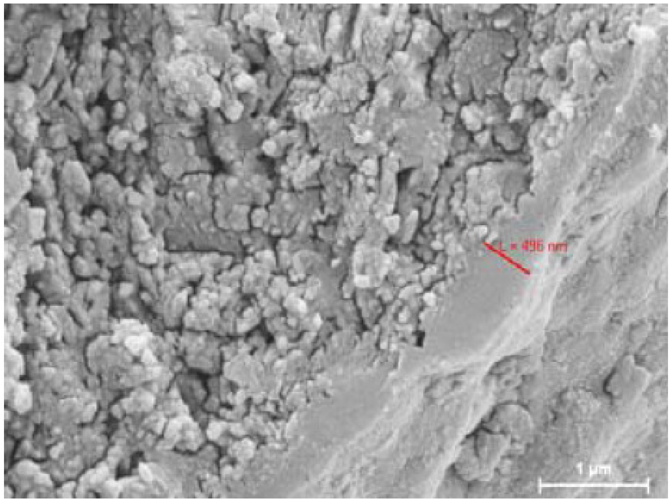
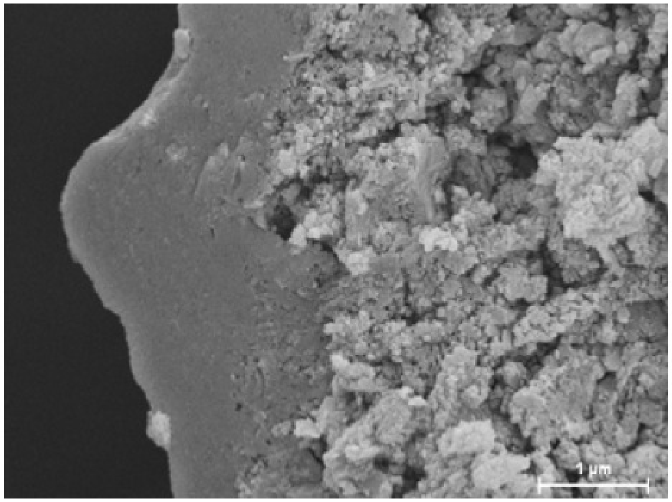
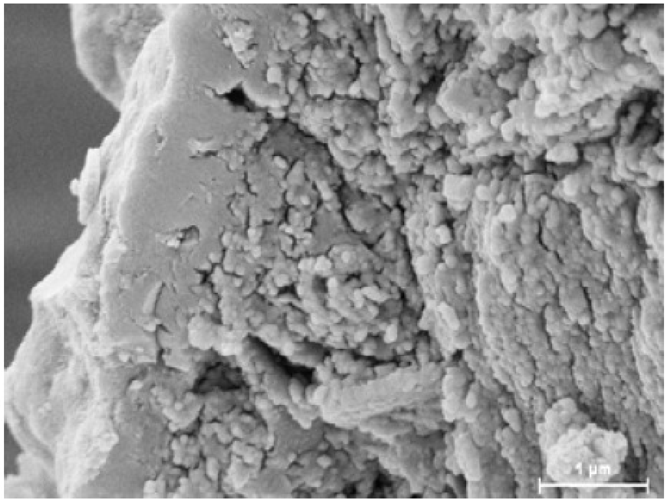
Refinery A



Refinery B



Refinery C



Shells as thick as 1 micron can form

Surface Effects
Vitrification and Glassy Surfaces

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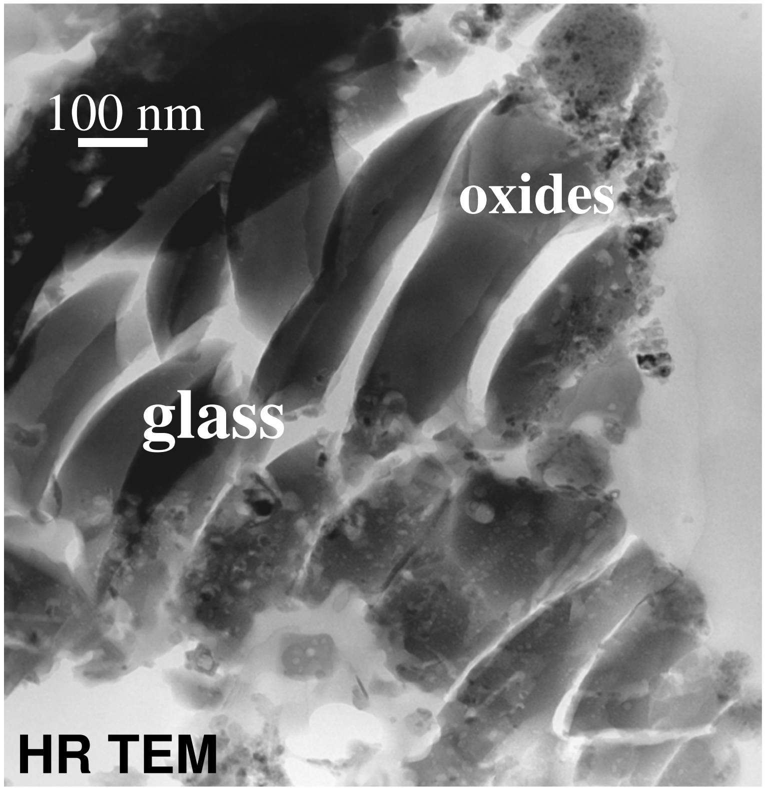
- Added Fe can react with some catalyst components to form a glassy surface (low temperature melting point eutectics)
- Alkali/alkaline elements/oxides and hot spots in regenerator accelerate their formation
- Reduces catalyst performance via loss of SA due to surface blockage
- Survey of high iron FCCUs showed that nodule formation and surface vitrification are not a function of binder technology, porosity, or overall chemical composition of the fresh catalyst
- What about the role Si plays?
  - BASF does not use binders
  - Catalysts that do not use Si binders still have >30% Si in the catalyst



Wieland W. S., Simulation of Fe Contamination, Hydrocarbon Engineering, March 2002

Chemical Effects:
Iron Increases Promotion Activity

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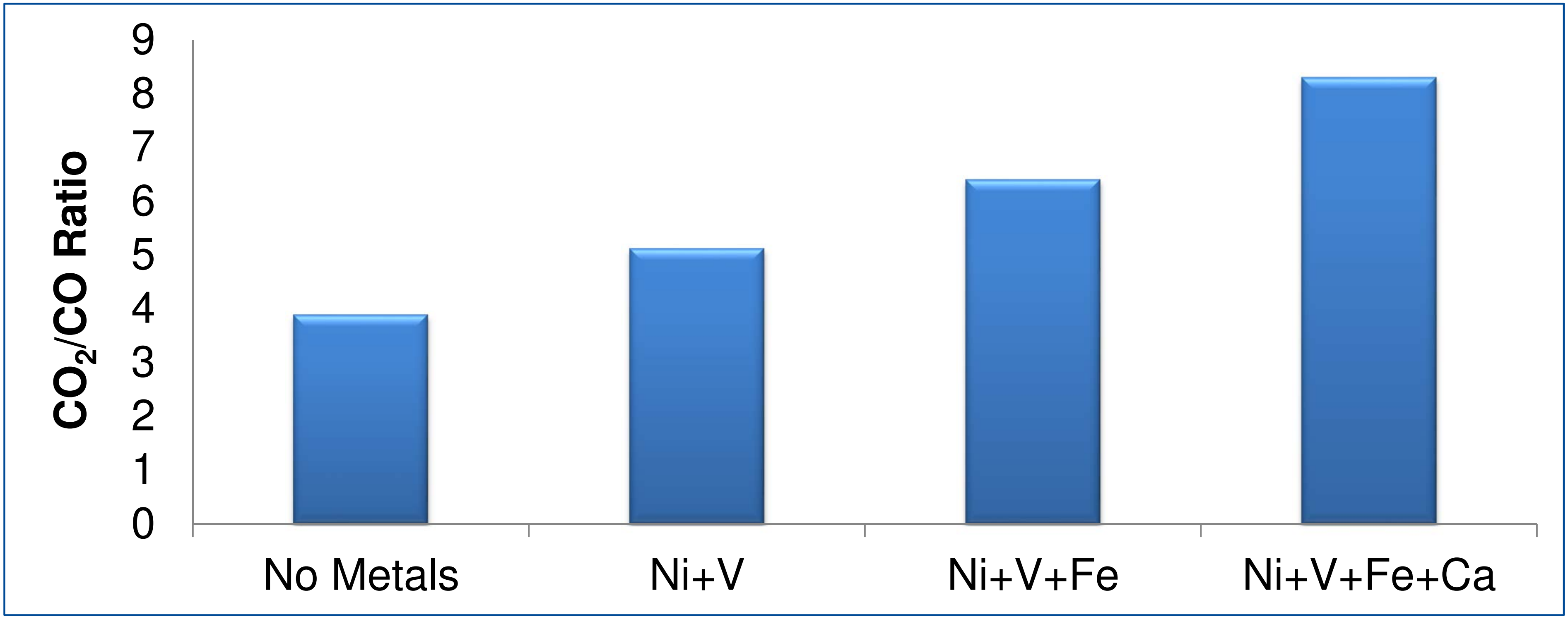
- CPS Metals Deactivation
- Test ability of catalyst to convert CO to CO_2
- Iron shows increased promotion, along with all metals



Fines vs. Ecat Analysis

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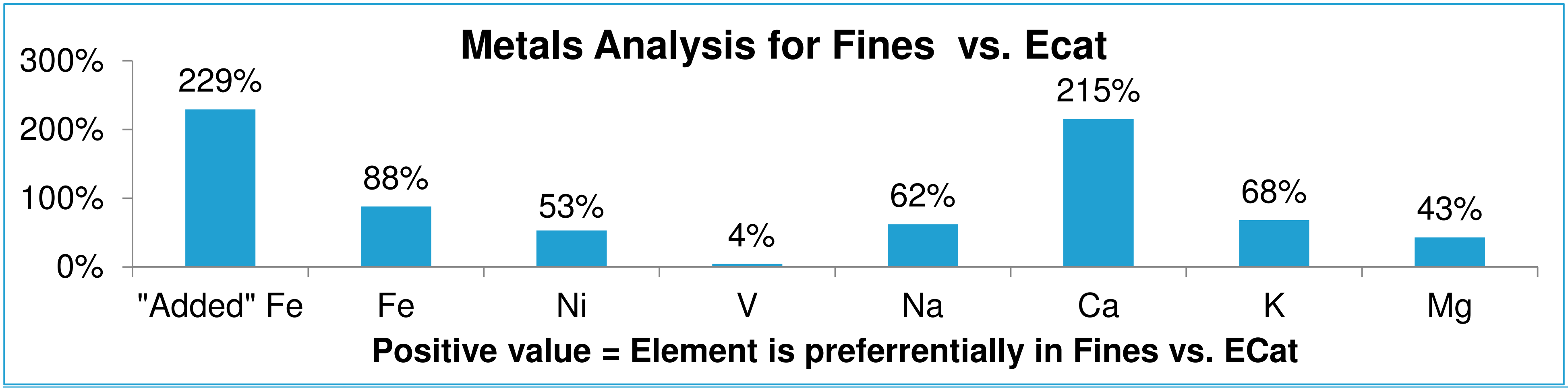
- Fe nodules are fragile and are attrited easily
- Higher Fe values expected in the fines

- Identified 19 high iron FCCUs, with Fe_{Added} > 0.2, for which BASF analyzes both Ecat and Fines (ESP, TSS, scrubber water, or slurry) samples

What does the data say?

- 14 out of the 19 units show enrichment of Fe in the fines
- Of the 5 that don't, other elements (Ni and V) were also less in the fines suggesting the fines are being diluted with either high losses from SOx additive or high FCat losses
- Average added Fe is 2.3x higher in the fines; excluding the 5 units, added Fe is *3.1x higher in the fines*

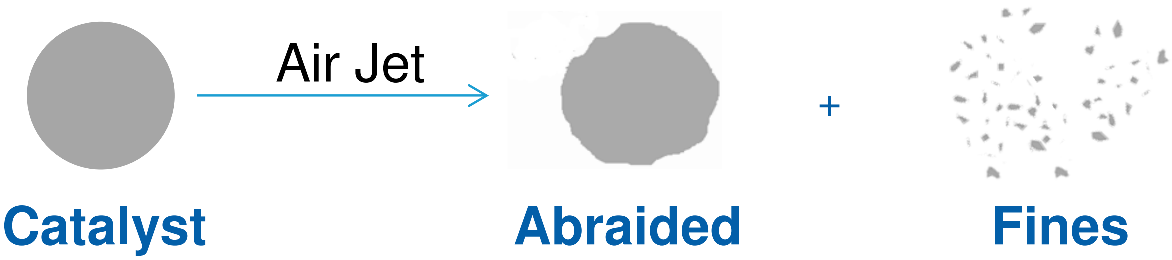
Metals Analysis for Fines vs. ECat

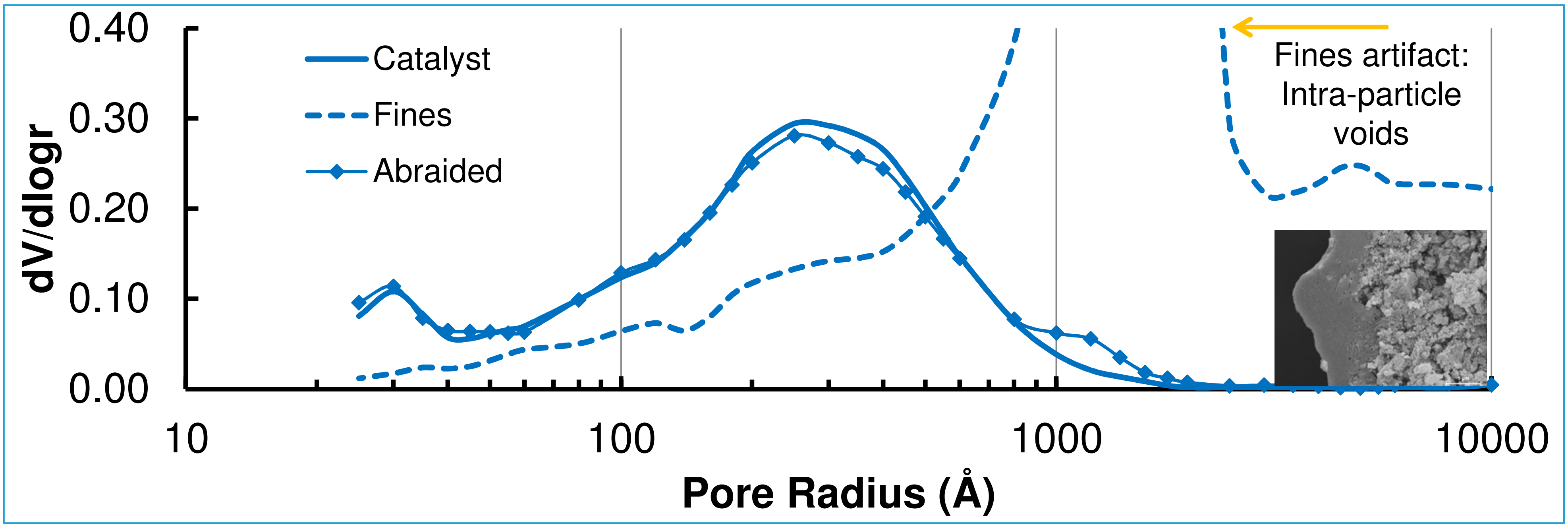


	Concentrated in fines	Comments
Fe	+	As expected
V	-	V is distributed throughout the catalyst
Ni	+	Supports BASF research saying that the dominant attrition mechanism is abrasion and that Ni concentrates on the outside of the catalyst particle
Ca	+	Very elevated, more so than can be explained from SOx additive loss (Mg marker); likely complexing with Fe

The elevated Na and K are unexpected

Porosity of Surface Nodules vs Bulk Catalyst





Surface nodules have significantly lower porosity than bulk catalyst
Catalyst and abraided show similar/same pore volume

Investigation of Iron on Performance: Deep Dive into Three Units

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- All three units use BASF catalyst with very high iron contamination
- None of the units use Flush ECat
  - Refinery A: Resid Feed using Stamina (Prox-SMZ)
  - Refinery B: Gasoil Feed using NaphthaMax (DMS), process tight oil
  - Refinery C: Resid Feed using Stamina (Prox-SMZ)

Refinery A	Refinery B	Refinery C
Ni 3596 ppm	Ni 476 ppm	Ni 2197 ppm
V 2269 ppm	V 2531 ppm	V 849 ppm
Fe 1.53 wt%	**Fe 1.17 wt%**	**Fe 1.28 wt%**
Ca 1822 ppm	Ca 3268 ppm	Ca 1311 ppm
Mg 0.75 wt%	Mg 0.16 wt%	Mg 0.84 wt%

Investigation of Iron on Performance: Deep Dive into Three Units

150 years

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- **Goal**: elucidate the effect of **iron**, keeping other variables similar
  - In this study, variables included Ni, V, REO, FACT, Ca, K, Mg, and Na
- **Question**: when **iron** is blamed, is it really due to **iron**? or is it the other contaminants that typically follow iron (Ni, V, etc.)?
- **Methodology**: Three **high iron** Ecats were identified and large samples were collected. Similar **low-iron** Ecats were matched from BASF's 200+ Ecat samples from around the globe.
- **Samples**:
  - Three sets of "sister" samples from two technology platforms
  - High iron content 1.17-1.53 wt %
  - Low iron content 0.69-0.84 wt%

Technology	Ecat Fe (wt%)	
Prox-SMZ	**1.53**	←Refinery A
Prox-SMZ	0.75	
DMS	**1.17**	←Refinery B
DMS	0.69	
Prox-SMZ	**1.28**	←Refinery C
Prox-SMZ	0.84	

Investigation of Iron on Performance: Deep Dive into Three Units

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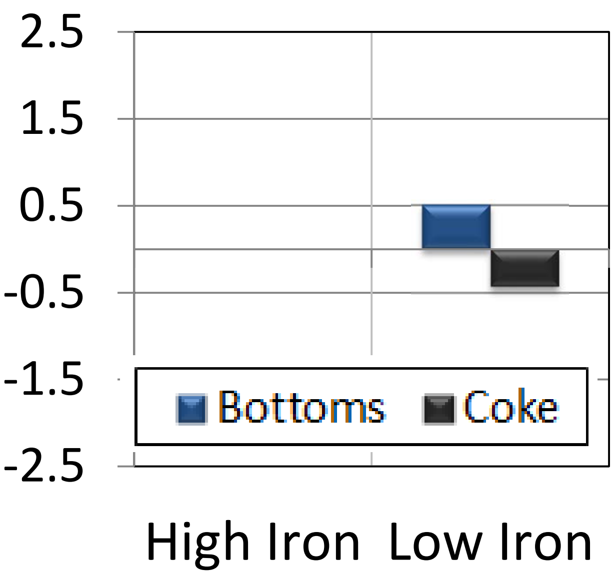
- No consistent trend showing iron increases bottoms or coke

Lower Iron Unit	BOTTOMS	COKE
Comparison to A	↑	↓
Comparison to B	↓	↓
Comparison to C	↑	↑

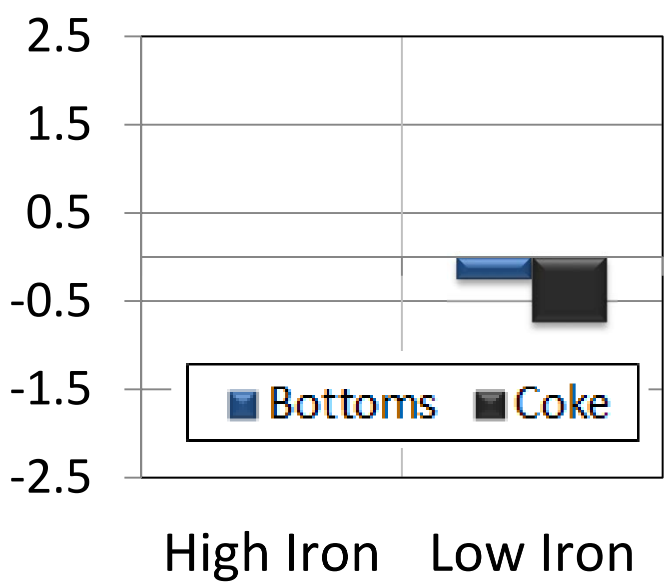
If is a factor, then yield should improve ↓

- **Takeaway**: other factors affect bottoms and coke yield more than iron does

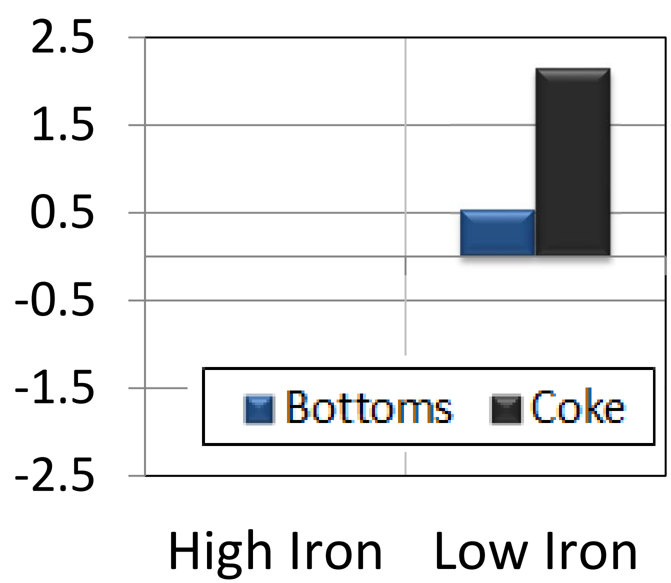
Refinery A



Refinery B



Refinery C



ACE Yields at Constant Conversion 70 wt%

Scanning Electron Microscopy: Fe and Ca Associate

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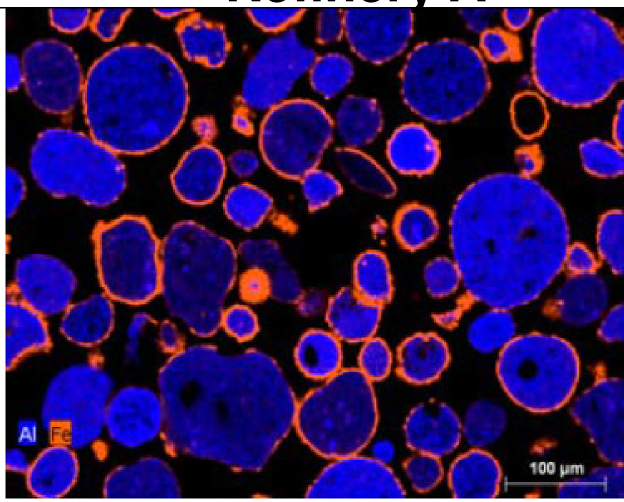
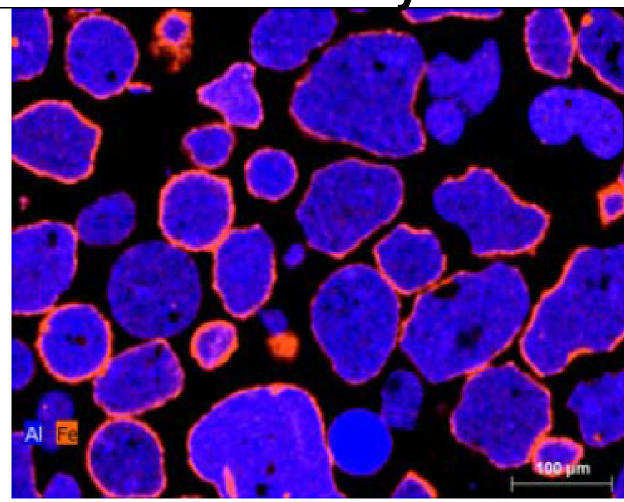
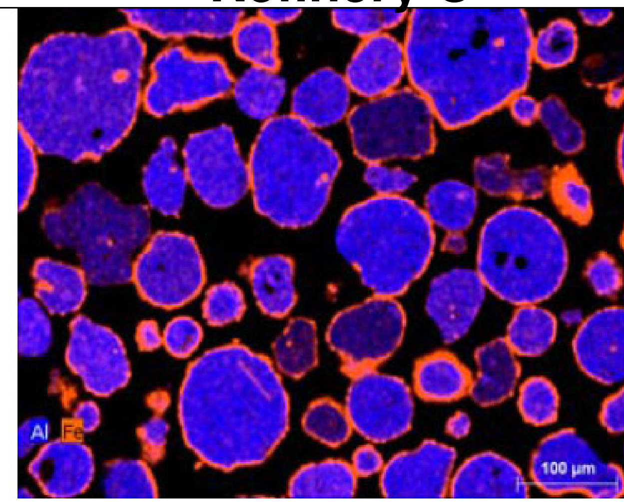
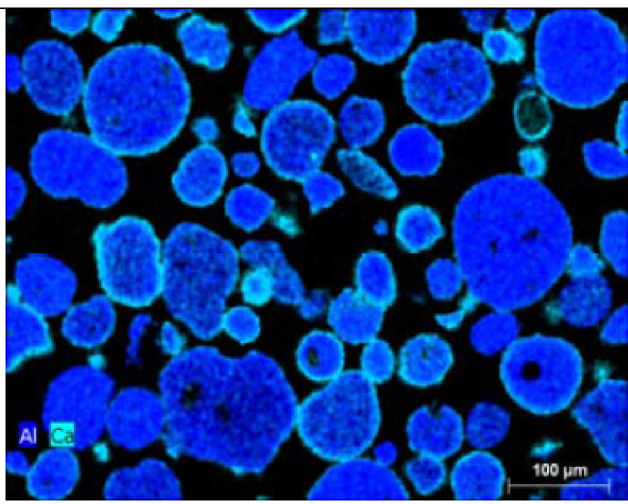
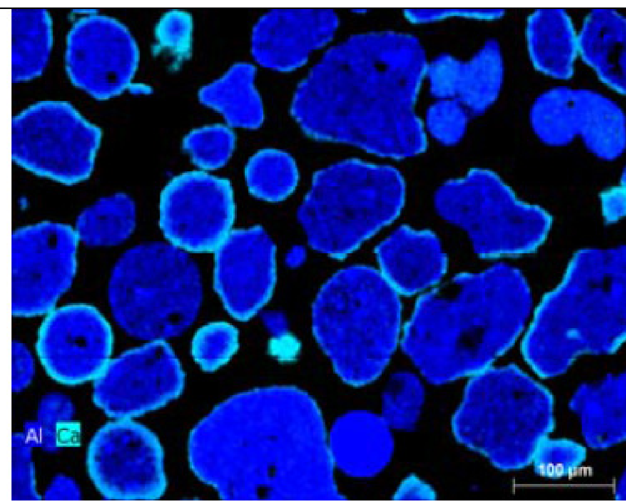
Refinery A	Refinery B	Refinery C

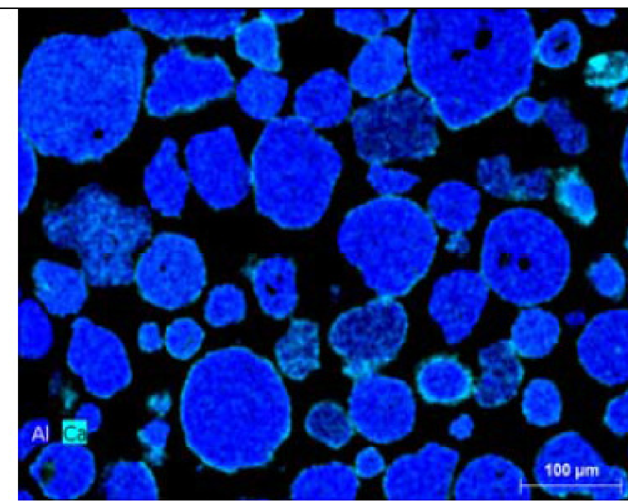








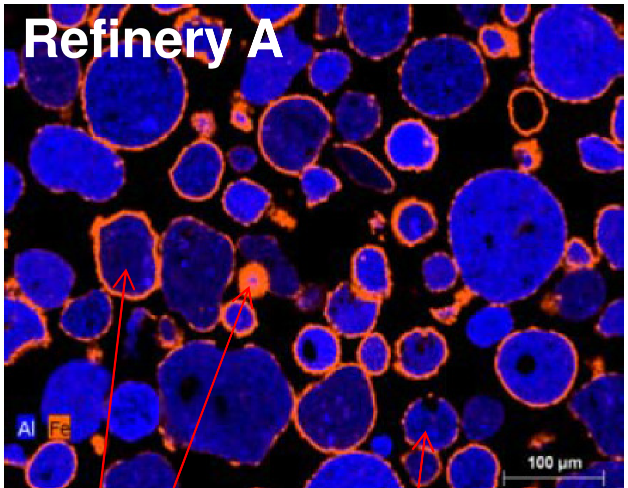




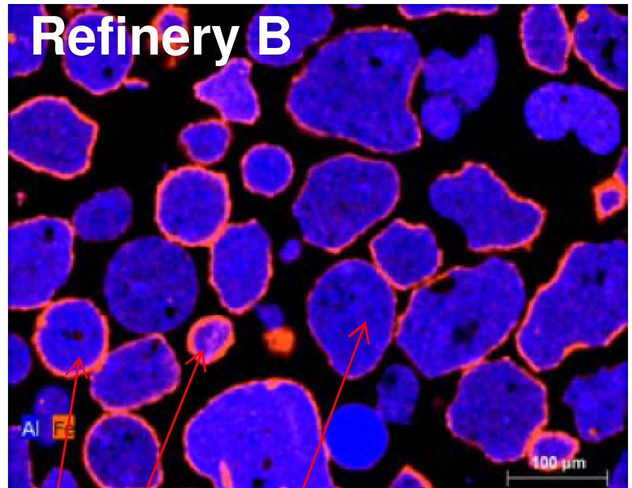
EDS Map 200X CMP

Al Fe Ca

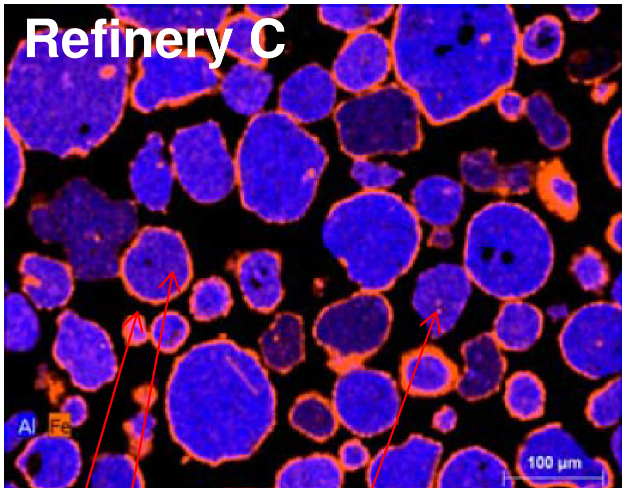
EDS Mapping and SEM Morphology: Can Discern Old and New Catalyst Particles



old new



old new



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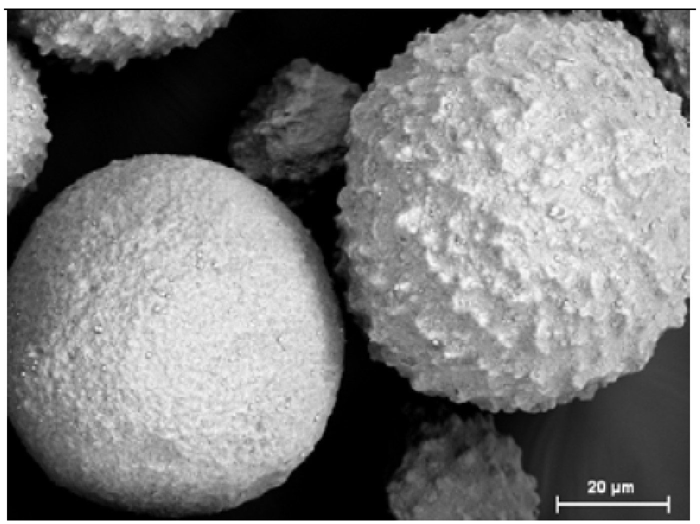
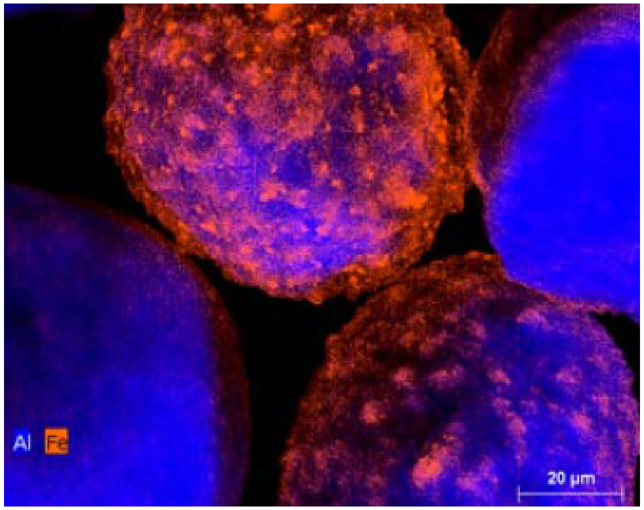
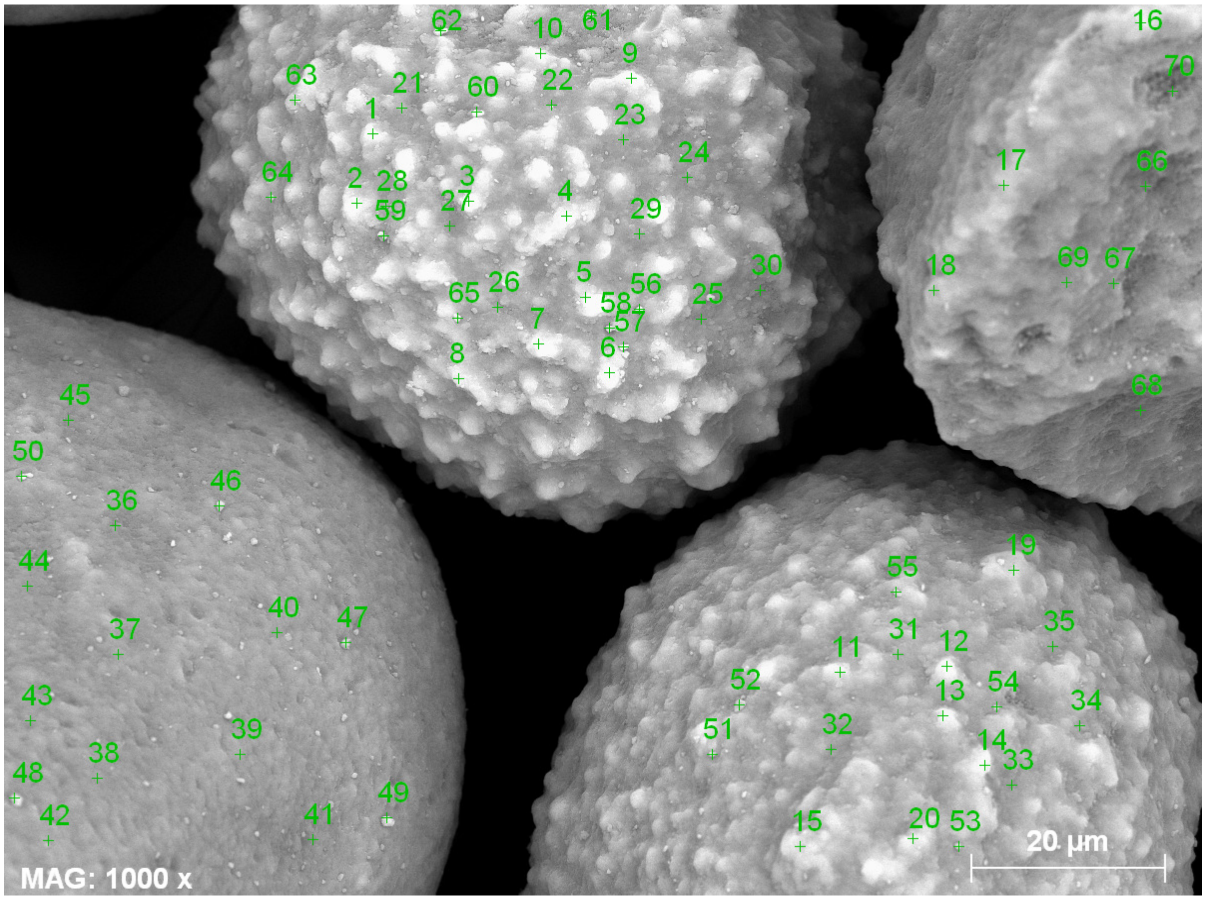




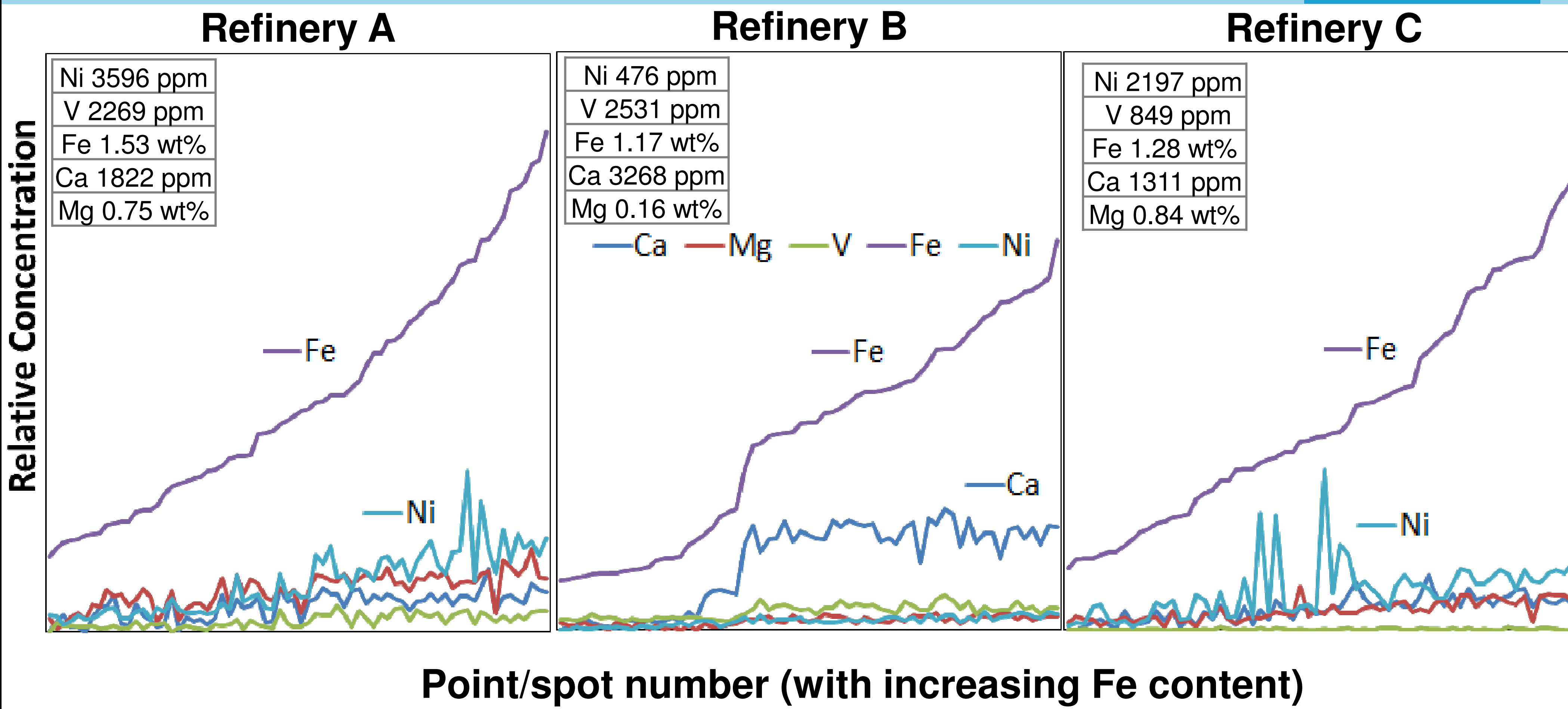
Multi-Point Analysis (via SEM)



- All three high Fe units investigated via multi point analysis
- Each point’s chemical loading is independently measured
- Good statistical tool to look at metals correlation
- Looks at nodules, canyons, and smooth surfaces

Multi-Point Analysis (via SEM)

Metals Trends



Ca trends with Fe especially when Ca is high.
Trending is less pronounced at low Ca levels

Defining Mobility:
What *is* “mobility”?

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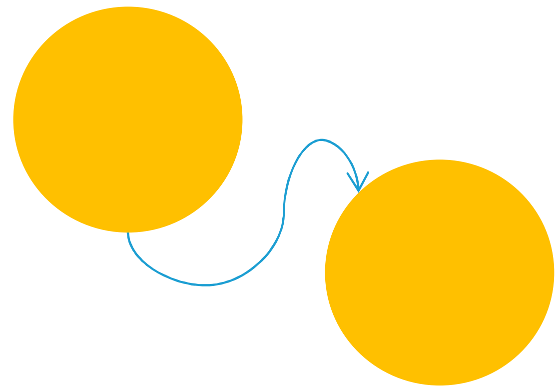
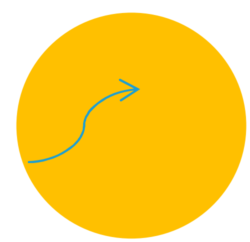
Interparticle mobility – the tendency to transfer between catalyst particles. It is well known that vanadium has high interparticle mobility, while nickel does not transfer from particle to particle.



Intraparticle mobility – the tendency to diffuse through the catalyst. It is well known that vanadium has high intraparticle mobility and is well dispersed throughout the catalyst particle, while nickel remains mostly on the outer part of the catalyst.



What about iron?

Intraparticle Mobility: Peripheral Deposition Index (PDI)

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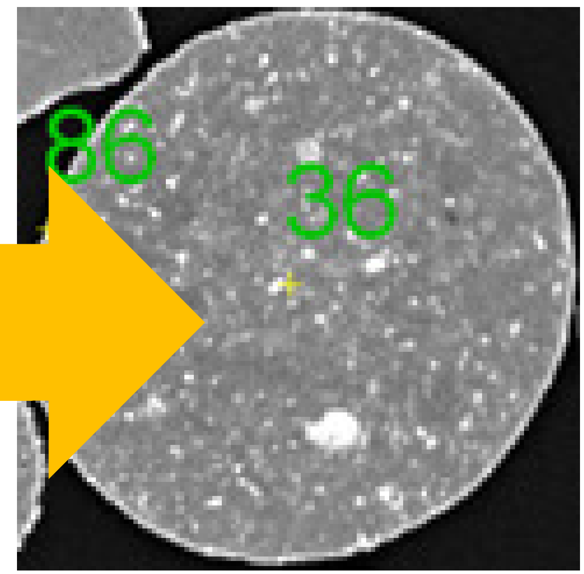
- BASF developed a method for measuring intraparticle mobility.
- PDI = concentration on edge of catalyst / concentration in core of catalyst
- Can quantify using EDS, SEM spectroscopy by looking at the cross section of many catalyst particles
- High intraparticle mobility, PDI = 1

Two measurements are taken on each particle
One on the edge, and one in the core



- BASF found nickel profiles corresponding to PDI values of 2-5 indicating high concentrations on the outer surface of the catalyst and low intraparticle mobility

Vincz et al. 2014

Intraparticle Mobility: Peripheral Deposition Index (PDI)

PDI	Refinery A	Refinery B	Refinery C
Fe	7.1	4.5	5.4
Ni	7.5	2.0	6.5
V	1.3	1.5	0.7
Ca	8.0	9.5	7.0
La	1.1	1.1	1.0

- Iron and calcium exhibit similar (low) intraparticle mobility as nickel
- As expected, vanadium shows high intraparticle mobility and is homogeneously dispersed on the catalyst particles

Iron is NOT mobile within each catalyst particle

Global Survey: Effects of Iron Contamination

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- 39 FCCUs evaluated using Ecat data over a period of 1 year and commercial information provided by the refiners.
  - $Fe_{Added} \geq 0.20$ wt%
  - Had experienced iron nodules within the past year
- Two separate phenomena
  - Iron nodules
  - Partial surface vitrification
- Units categorized as to whether or not performance problems were reported
  - Sorted by FCC supplier and catalyst technology type

BASF Global Customer Survey, 2000-2001

Survey Says:
All FCC Technologies are Susceptible to Iron Related Performance Problems

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FCC Supplier	Catalyst Technology Type	# of Units	% With Performance Problems
BASF In-Situ	A	12	25
BASF incorporated	B	7	57
Competitor 1	C	6	83
Competitor 1	D	6	67
Competitor 2	E	2	50
Competitor 2	F	5	60
Competitor 3	G	1	100
Total		39	59

BASF Global Customer Survey, 2000-2001

Comments from Customers

150 years

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- “Had problems with other suppliers but not BASF”
- Testing shows improved iron tolerance with BASF catalyst
- BASF “has shown increased total metals resistance”
- Refinery experienced loss in activity with iron peaks with other supplier
- “Record levels on Ecat above ~1%” (in past needed to flush with another supplier)
- Customer uses BASF catalyst at two locations stating, “BASF catalyst has better Fe tolerance (conversion, circulation) than another supplier’s catalyst”
- “No circulation issue in using BASF catalyst”

BASF Global Customer Survey, 2014

Success Stories:
BASF Catalysts Processing High Iron Feeds

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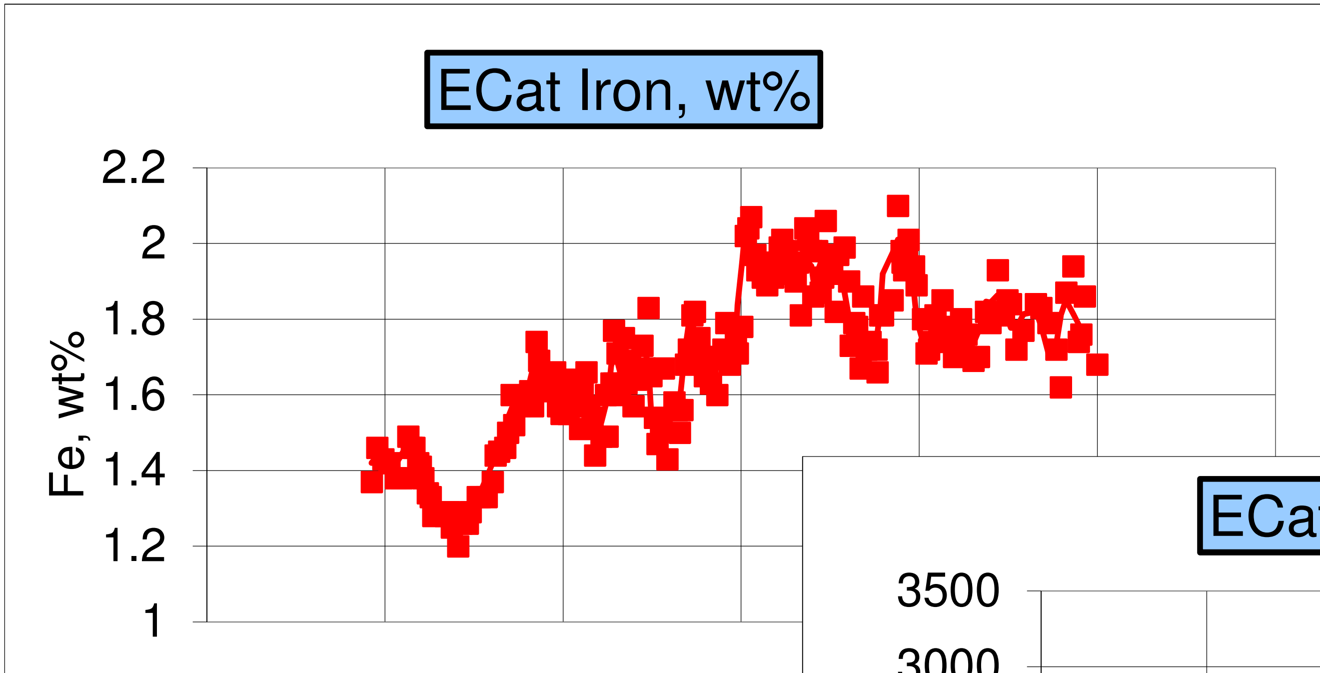
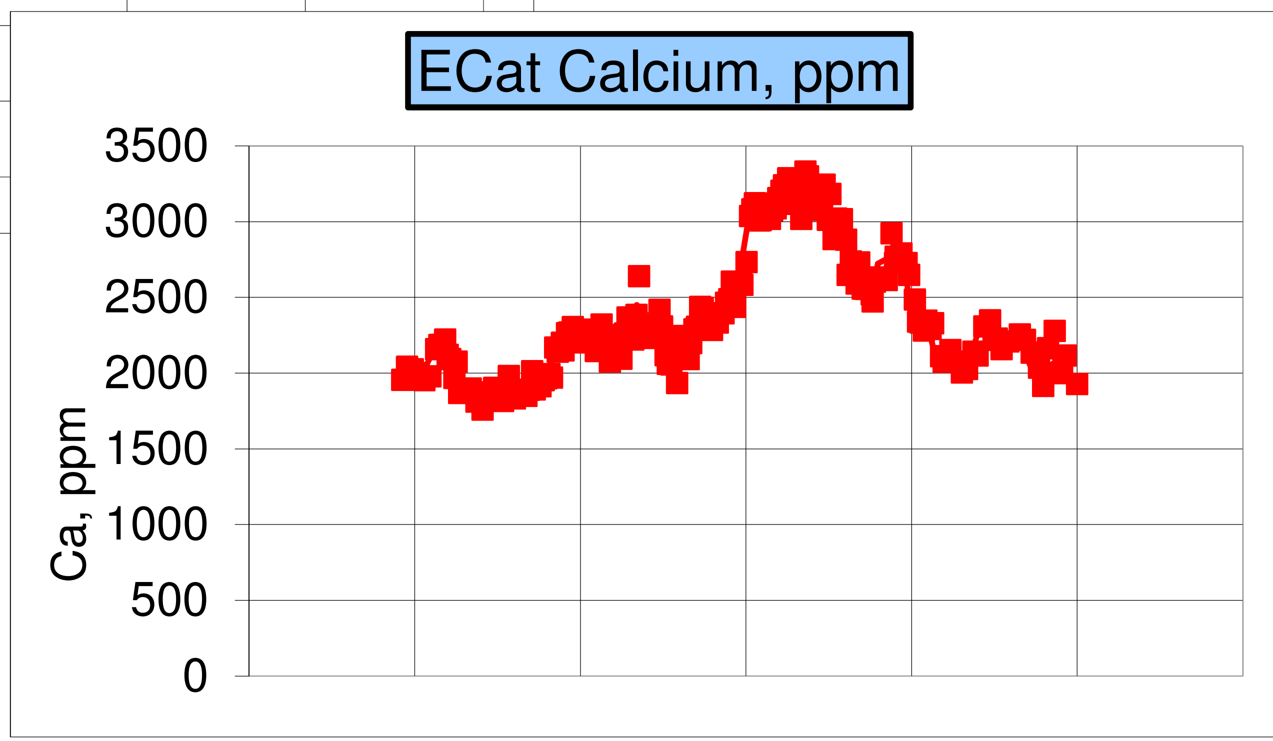
Country	Catalyst	Ni	V	Fe	Na	Ca	Activity
USA	ResidProx-SMZ	3014	2484	1.36	0.34	1713	69.6
USA	Resid Prox-SMZ	2320	867	1.32	0.24	1192	74.3
USA	Gasoil DMS	712	2869	1.29	0.66	4771	71.6
USA	Gasoil DMS	1554	3321	1.27	0.36	1459	66.5
Canada	Resid Prox-SMZ	640	2943	1.08	0.19	1228	63.4
Australia	Resid DMS	3466	967	1.00	0.27	1538	68.2
Canada	Resid DMS	2837	5039	0.96	0.34	5511	69.5
Japan	Resid DMS	1436	1458	0.94	0.25	2915	67.8
Germany	Resid DMS	2912	3904	0.91	0.36	1121	70.9
USA	Gasoil DMS	976	3349	0.88	0.29	1170	75.7
Australia	Resid Prox-SMZ	2858	2696	0.85	0.18	1559	68.9
USA	Resid DMS	1159	2803	0.85	0.9	3363	68.6
Switzerland	Resid MSRC	4252	5967	0.85	0.26	1726	68.4
Italy	Prox-SMZ	4691	1844	0.83	0.56	1087	70.7
USA	Gasoil Prox-SMZ	377	1380	0.8	0.21	770	70.9
USA	Resid DMS	664	2307	0.79	0.45	2084	69.8
Australia	Resid DMS	3957	1424	0.78	0.37	2081	72.1
USA	Gasoil DMS	3622	4087	0.78	0.37	833	69
Australia	Prox-SMZ	4990	1728	0.76	0.37	4423	74.5
USA	Resid DMS	4333	2599	0.75	0.44	1279	72.1
Canada	Gasoil Prox-SMZ	25	162	0.75	0.17	320	72

Example of High Iron Unit

150 years





Unit has been running successfully for years with high Fe and Ca using BASF's Flex-Tec, Fortress and Stamina catalyst technologies

Mitigating the Impacts of Iron

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- BASF has good history with high iron FCC operations
- **High porosity** catalysts from **in-situ manufacturing** ike BASF's DMS and Prox-SMZ will be more tolerant to the detrimental effects of surface vitrification and blockage by iron nodules
- Increase catalyst addition rate or add ECat to flush iron
- Increase fines content to combat seeing circulation issues
- Improved crude desalting
- Increase acetic acid at desalter

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