Strategies for Managing Contaminant Metals in the FCC Unit

RefComm Galveston – May 2017

Rebecca Kuo, Technical Service Engineer

BASF
We create chemistry

Agenda

- Feedstock variations
- Contaminant metals and their effects
  - Case studies
  - Mitigation strategies
- Advanced passivation technologies

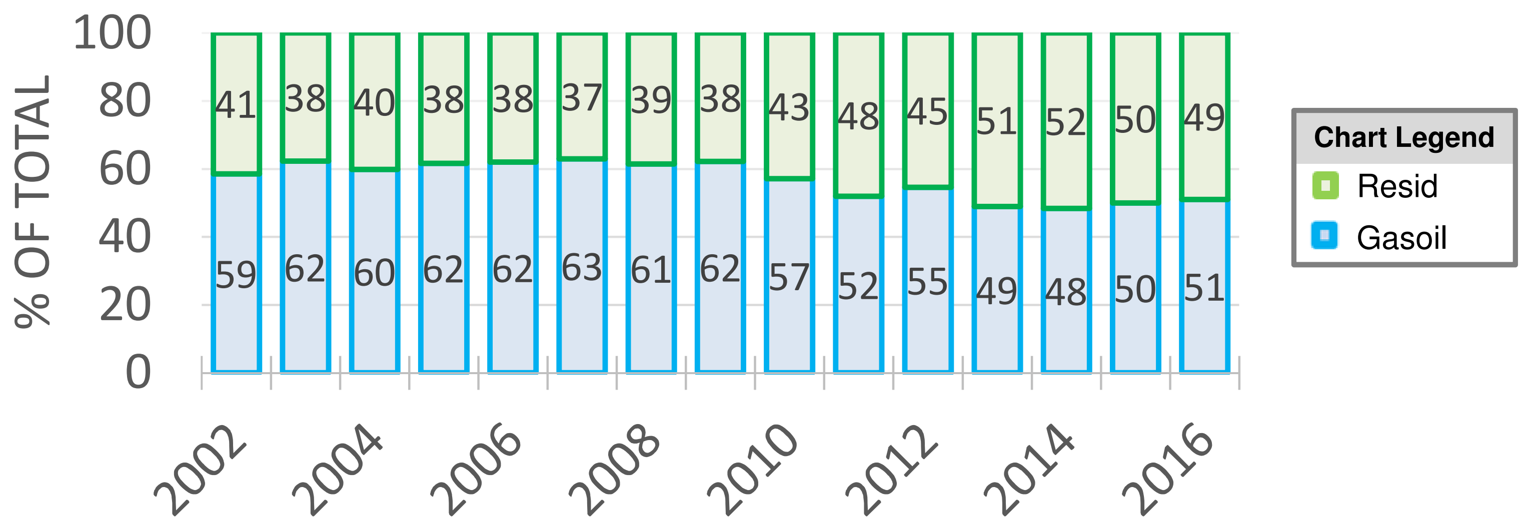
Diverse FCC Feeds

- Residue-containing and tight oil feeds have become much more prevalent in FCC
- Resids typically contain high Ni, V, CCR, N
- Tight oils typically contain high Fe, Ca, Na

Oil Quality Variability from One Field

Feed Property	Global Average	Global Minimum	Global Maximum
API	24.0	10.4	31.7
CCR, wt%	1.5	0.02	8.87
Ni, ppm	2.3	0	13
V, ppm	2.7	0	15
Fe, ppm	4.8	0	35
Na, ppm	1.3	0	6
Basic N, ppm	377	5	1058

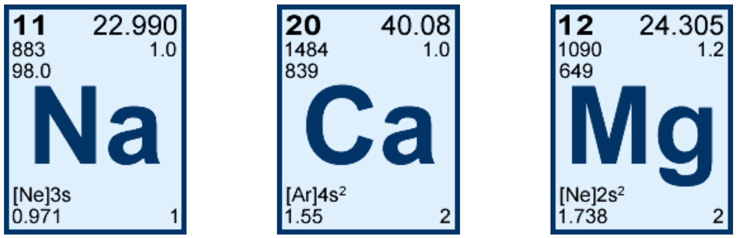
Gasoil-Resid Unit Split



- Resid >3000 ppm ecat Ni + V; Gasoil <3000 ppm ecat Ni + V
- Globally, more units are processing resid with the average moving from ~40% resid in the early 2000s, to today ~50%

Feedstock Contaminant Effects

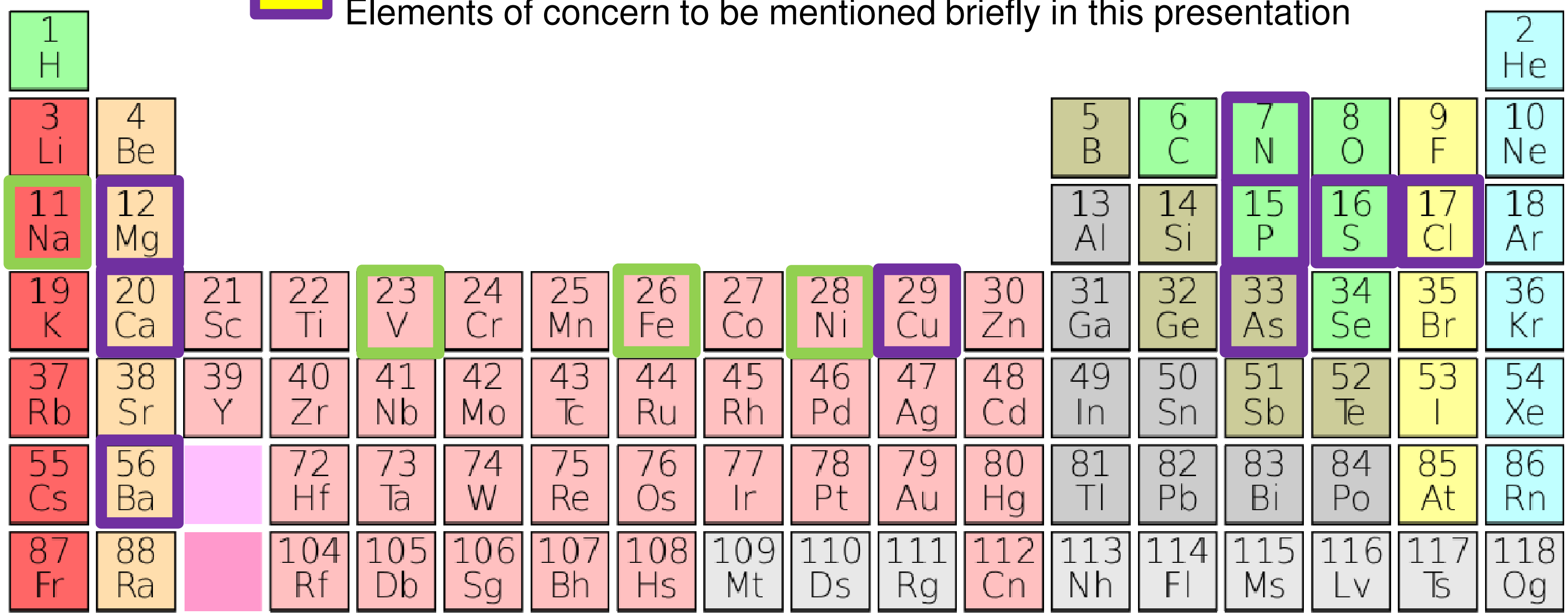
- **Why do we care about metal contaminants?**
- Metal contaminants are harmful to the catalyst and can cause unwanted reactions in the FCCU
- The metals deposit on the circulating catalyst and cause competing chemistries to the desired reactions
- Salts (Na, Ca, Mg) act as a base and attack the acid sites on the catalyst, lowering activity and conversion



Elements of Concern

Elements of high concern to be discussed in this presentation

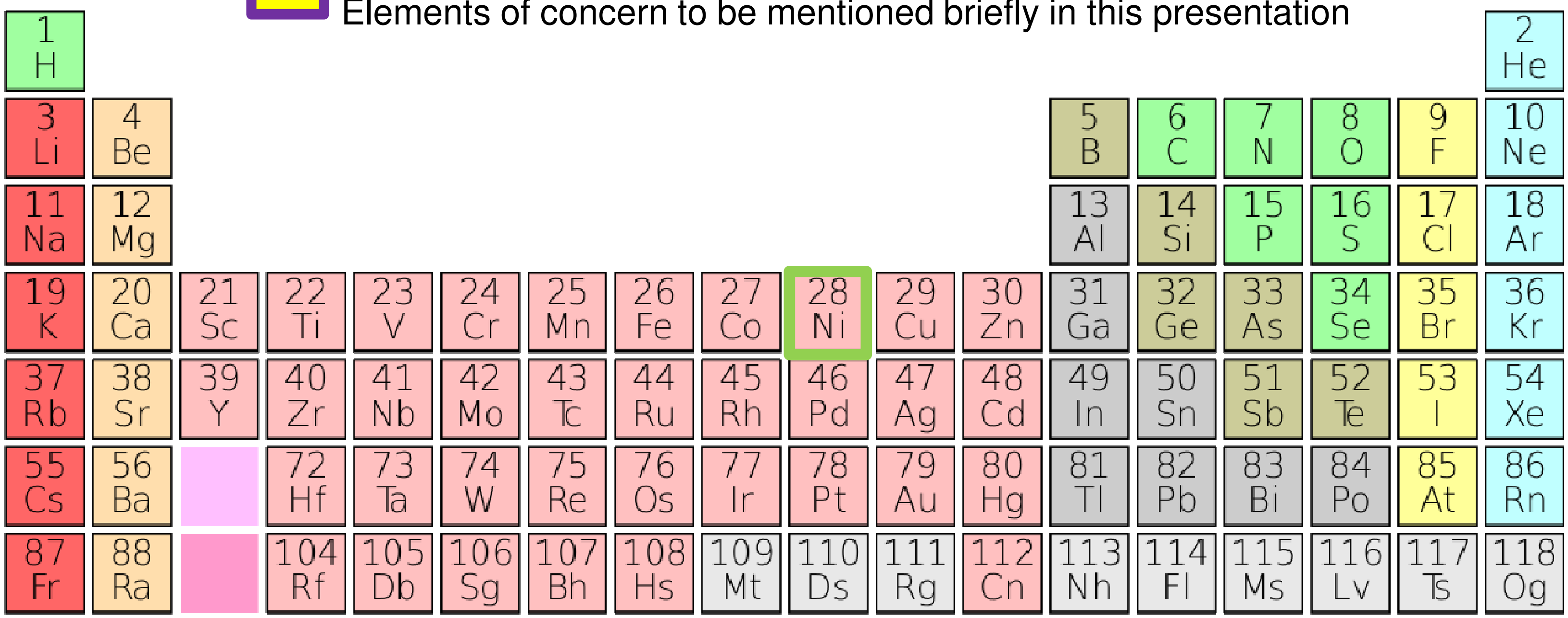
Elements of concern to be mentioned briefly in this presentation



Elements of Concern: Nickel

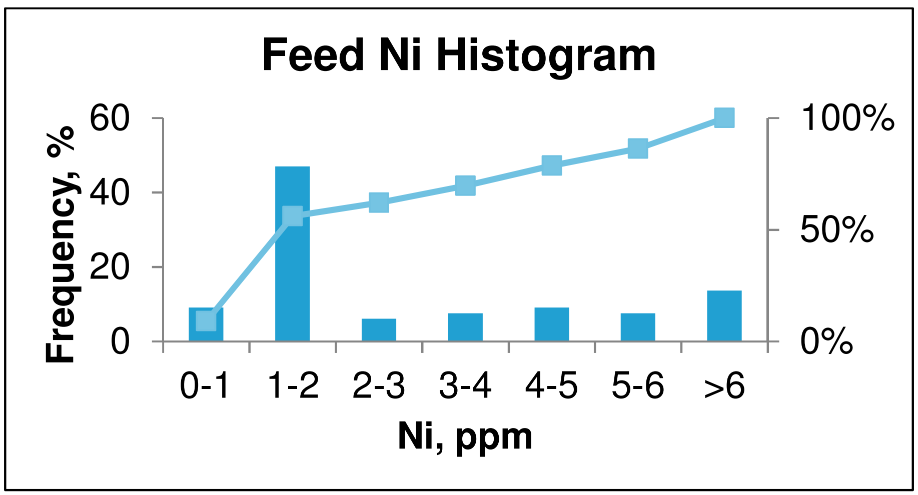
Elements of high concern to be discussed in this presentation

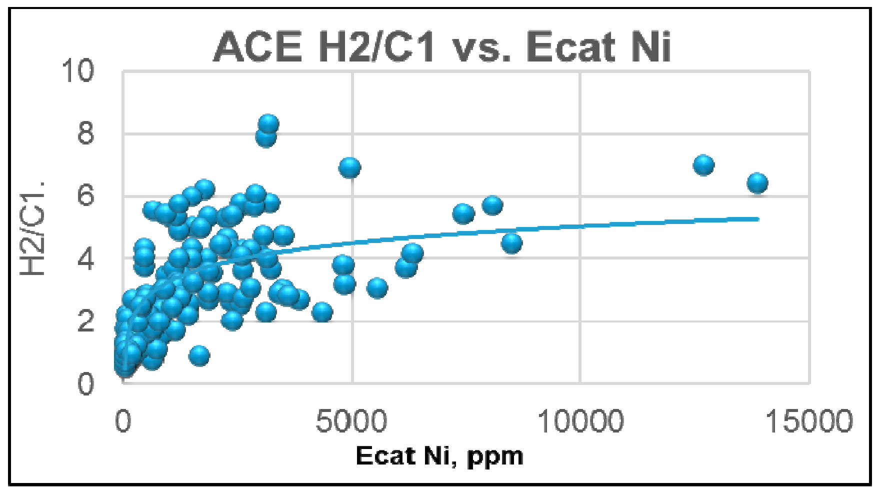
Elements of concern to be mentioned briefly in this presentation



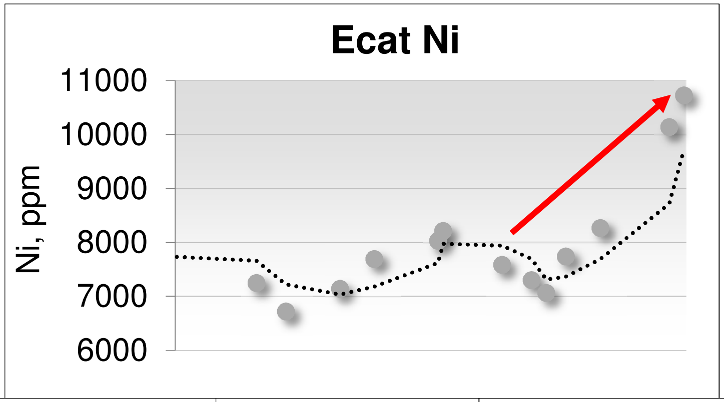
Nickel Sources & Effects

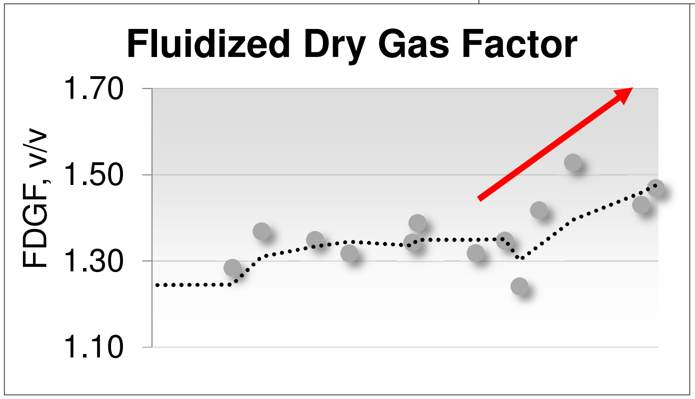
- Ni comes in with the feed and deposits on catalyst particles
  - Undergoes redox cycles
  - Nickel oxides do not migrate
- Catalyst activity is not significantly affected
- Ni acts as a dehydrogenation catalyst

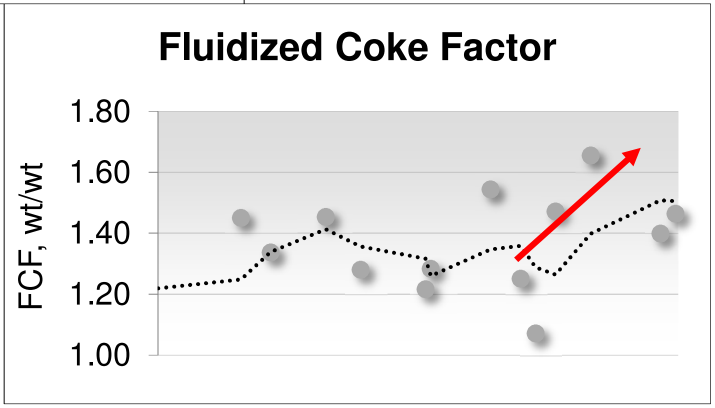




Nickel Effects
Case Study

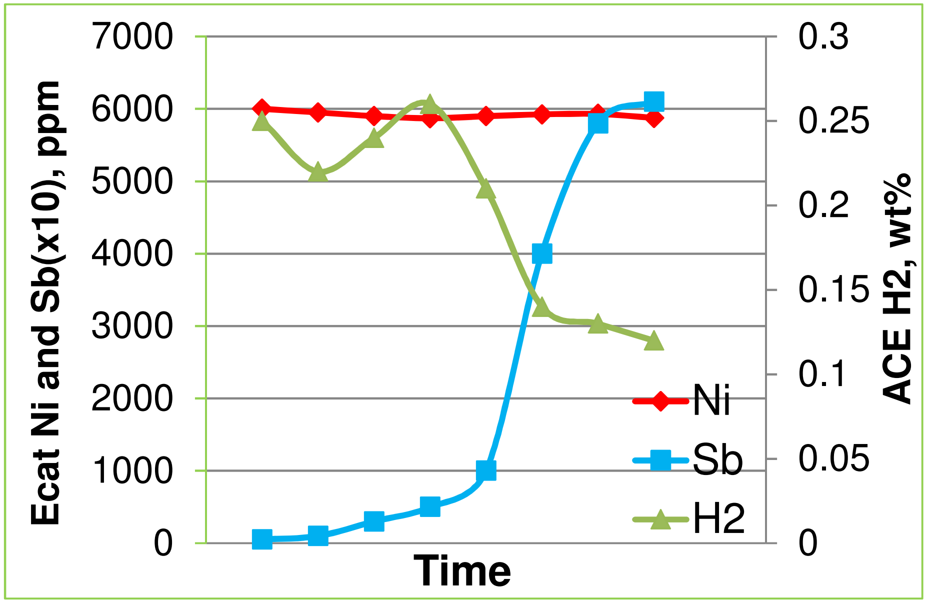






Nickel Mitigation Strategies

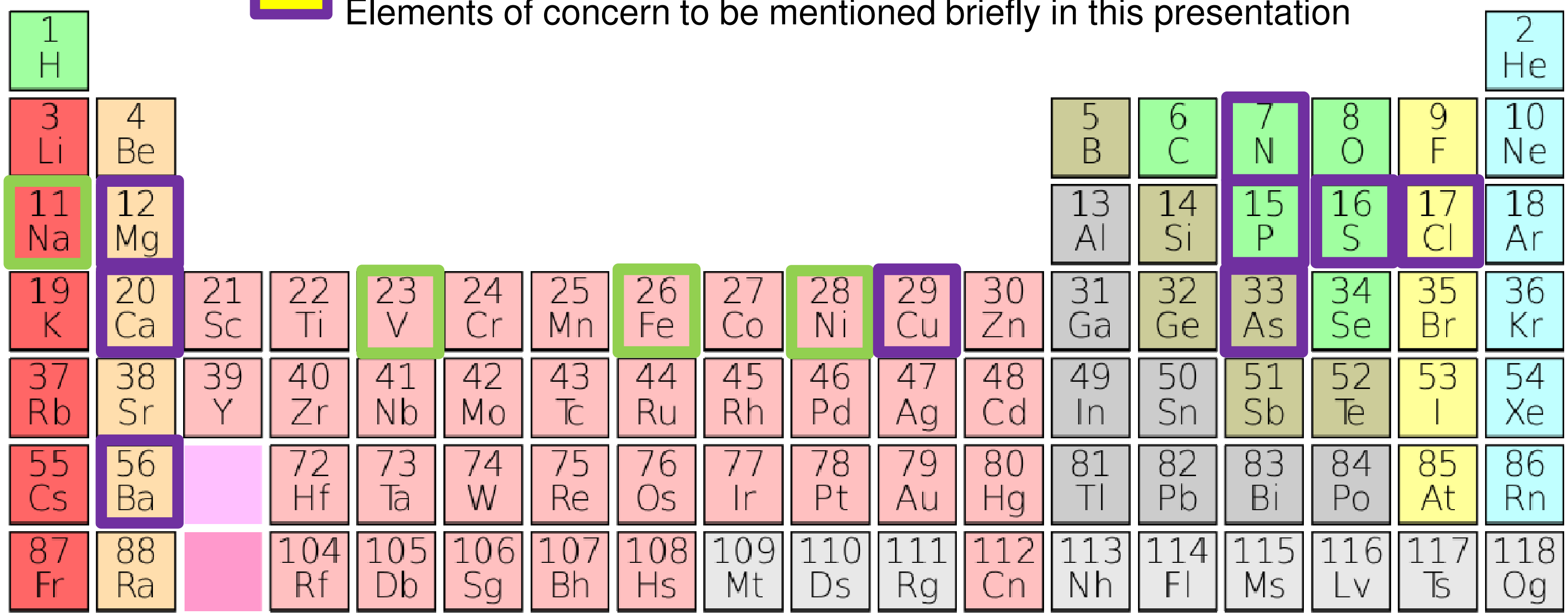
- Typically, Ni becomes a concern >800 ppm on the ecat
- Some refiners use antimony (Sb) injection to passivate Ni
  - Can increase NOx emissions
  - Can increase bottoms fouling
- A more permanent solution is to use catalyst with specialty alumina (such as Flex-Tec)
  - Ni deposits on alumina and becomes passivated



Elements of Concern

Elements of high concern to be discussed in this presentation

Elements of concern to be mentioned briefly in this presentation



Elements of Concern: Vanadium

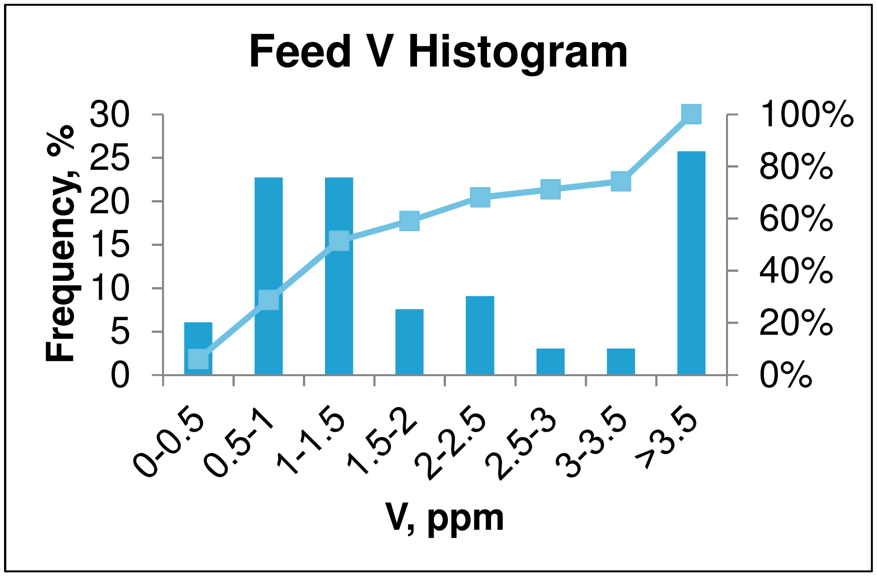
Elements of high concern to be discussed in this presentation

Elements of concern to be mentioned briefly in this presentation

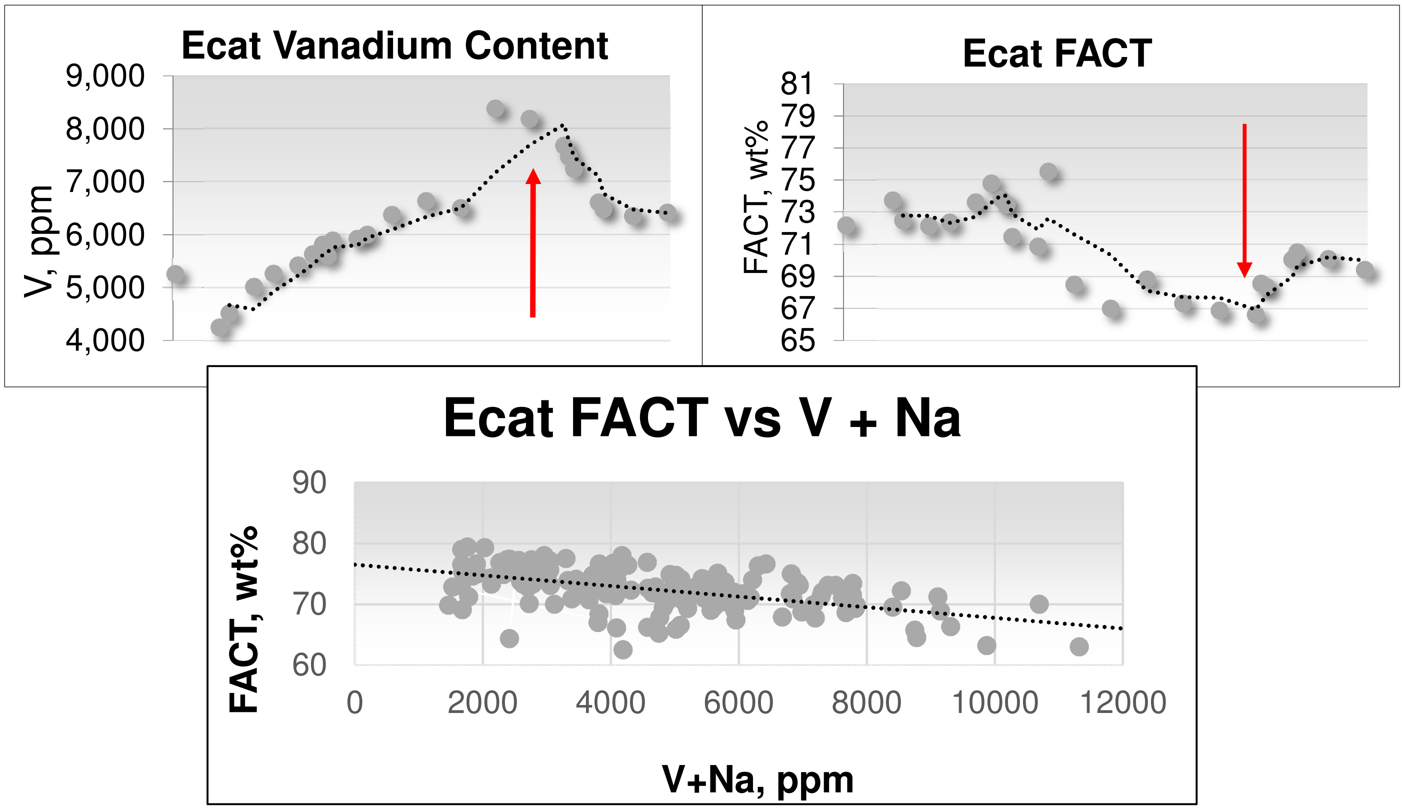
1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Ms	116 Lv	117 Ts	118 Og

Vanadium Sources & Effects

- Vanadium comes in with the feed and deposits on the catalyst particle
- V is converted into an oxide
  - V is very mobile – can migrate from **particle to particle** & **within the particle**
- Destroys zeolite, especially in the presence of high Na
- V causes significant reduction in activity and has some dehydrogenation activity



Vanadium Effects
Case Study



Vanadium Mitigation Strategies

- Typically, V becomes a concern >1500 ppm on ecat
- Refiners can use a V-trap additive to passivate
  - Can be REO, Ca, or Ca/Mg based
  - Can be added separately or blended into the catalyst formulation
- Because the effect of V is exaggerated with high Na, use a low-Na fresh catalyst
- Increase catalyst additions or use purchased catalyst to flush out the V in the circulating inventory

Elements of Concern

BASF We create chemistry

Elements of high concern to be discussed in this presentation

Elements of concern to be mentioned briefly in this presentation

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Ms	116 Lv	117 Ts	118 Og

Elements of Concern: Sodium

BASF
We create chemistry

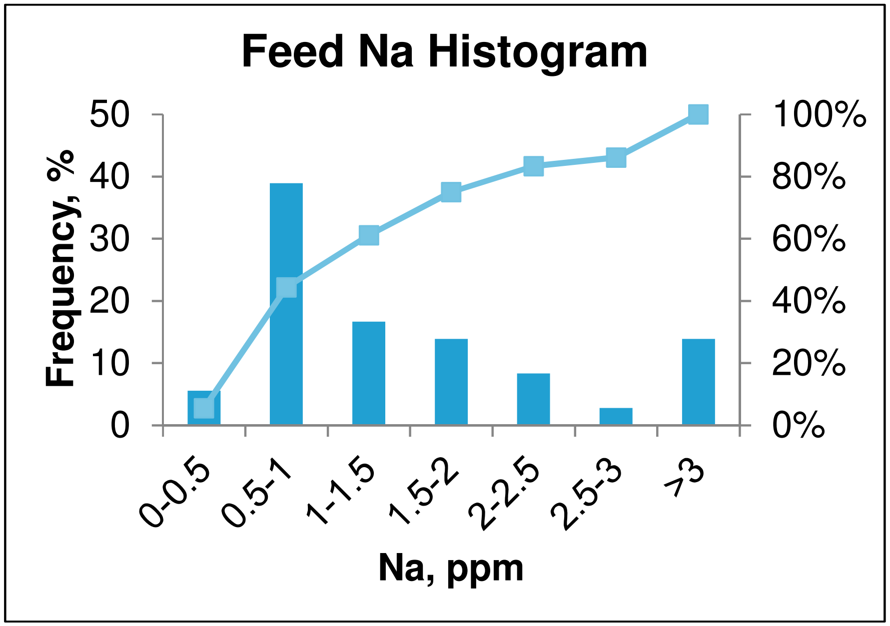
Elements of high concern to be discussed in this presentation

Elements of concern to be mentioned briefly in this presentation

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Ms	116 Lv	117 Ts	118 Og

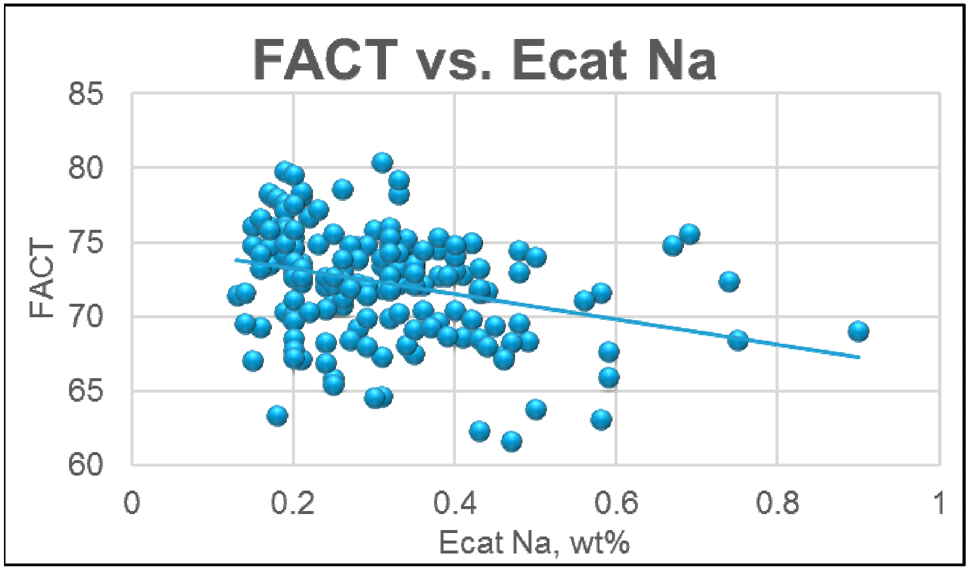
Sodium Sources

- Sodium comes from various sources:
  - Fresh catalyst – typically between 0.15-0.3 wt%
  - Feed – deposits on the surface of catalyst particle
    - Does not migrate within the particle or to other particles



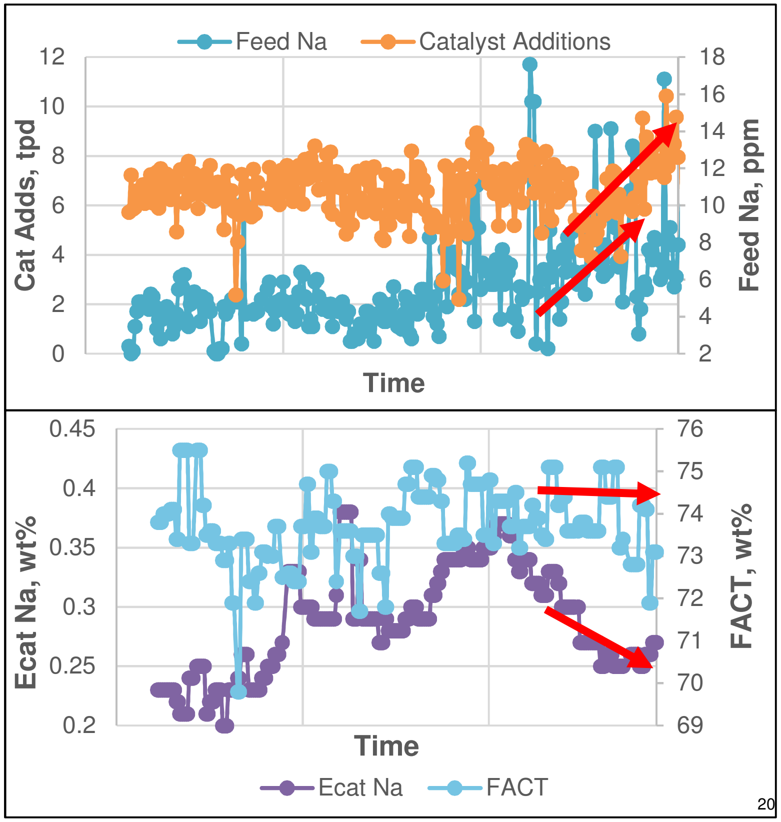
Sodium Effects

- Na acts as a permanent catalyst poison
  - Neutralizes acid sites
  - Also forms a **low melting point eutectic** with vanadium to lower ecat activity and conversion
  - Activity loss exaggerated when ecat V and regen temps are also high
- Ca and K have similar effects



Sodium Mitigation Strategies

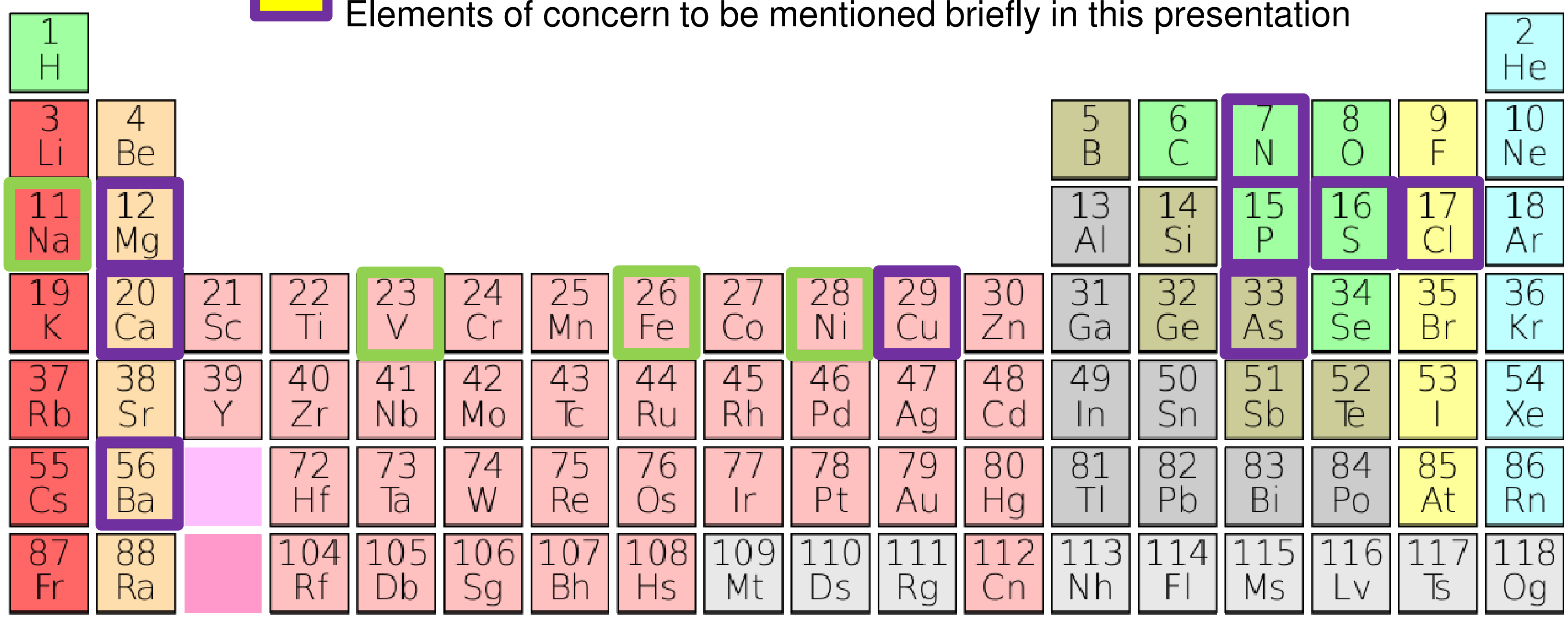
- Employ low-Na fresh catalyst
- Improve and optimize desalter operation – remove Na from the feed
- Increase catalyst additions or use purchased catalyst to flush Na out of circulating inventory
- Increase fresh catalyst activity to combat activity loss from Na



Elements of Concern

Elements of high concern to be discussed in this presentation

Elements of concern to be mentioned briefly in this presentation

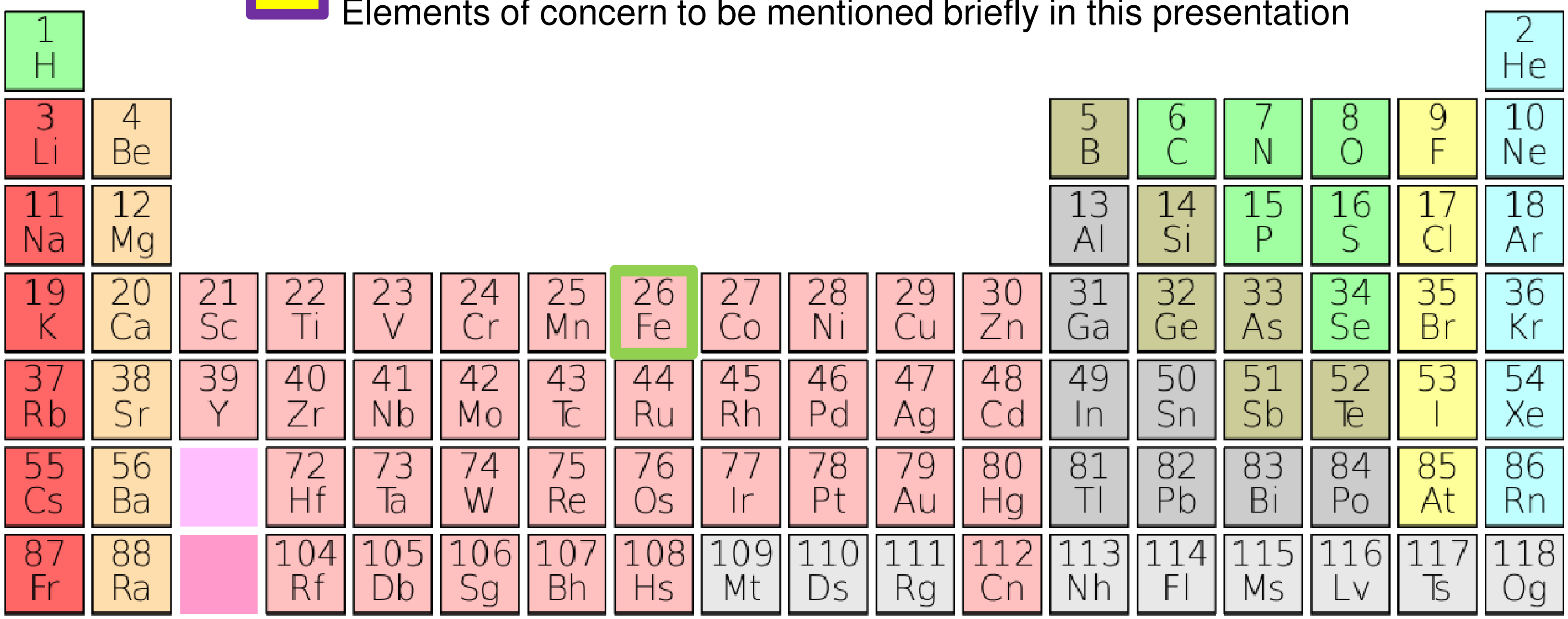


Elements of Concern: Iron

BASF
We create chemistry

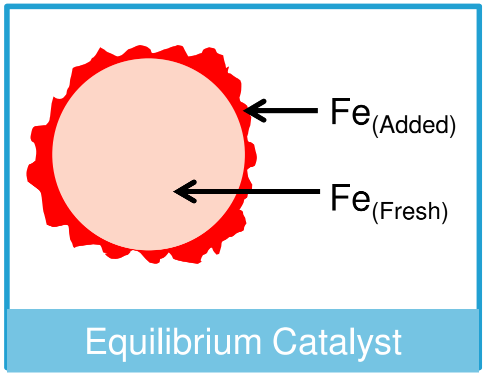
Elements of high concern to be discussed in this presentation

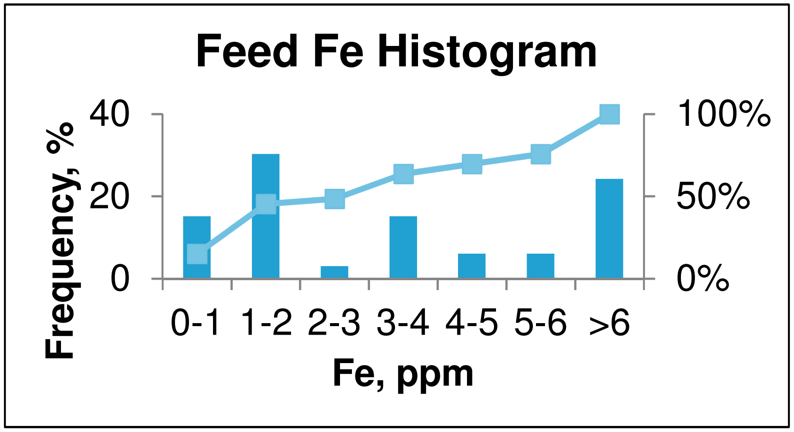
Elements of concern to be mentioned briefly in this presentation



Iron Sources

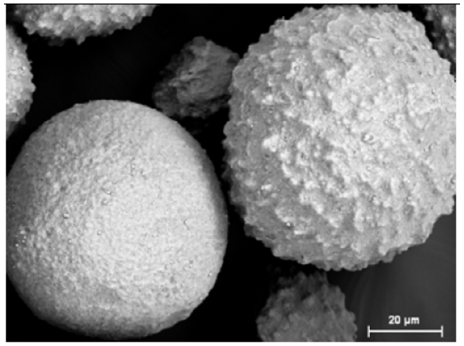
- Fe comes from various sources:
  - Fresh catalyst – typically between 0.25-0.75 wt%
    - Incorporated within the silica/alumina framework → does NOT impact surface accessibility or side chemical reactions
  - Organic Fe from the feed
  - Inorganic Fe from equipment corrosion
- Refiners should focus on "Added Fe" which deposits on the catalyst surface
- $Fe_{(Added)} = Fe_{(Ecat)} - Fe_{(Fresh)}$





Iron Effects

Physical Effects



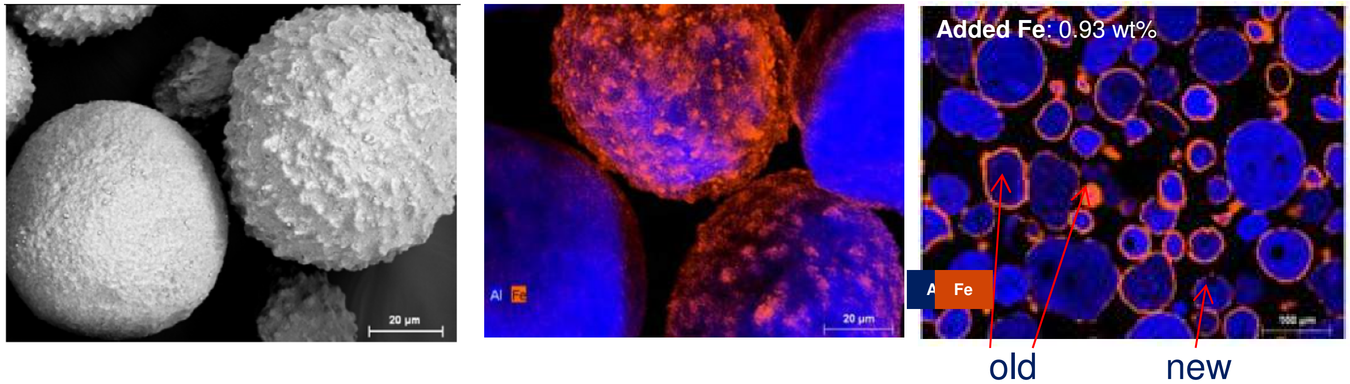
- Surface **nodule** formation, which has been reported to cause catalyst **circulation** issues
- **Vitrification** on catalyst surface, loss in surface area
- Severe poisoning leads to surface blockage and reduced **conversion** and high slurry yield with non-BASF catalyst
  - Slurry density becomes unusually light due to uncracked feed

Iron Effects

Chemical Effects

- **Dehydrogenation**: some refiners have reported increased H_2 make
- Transfers S from reactor to regenerator for increased **SOx**
- Acts as a **CO promoter**: can be an issue in partial-burn units

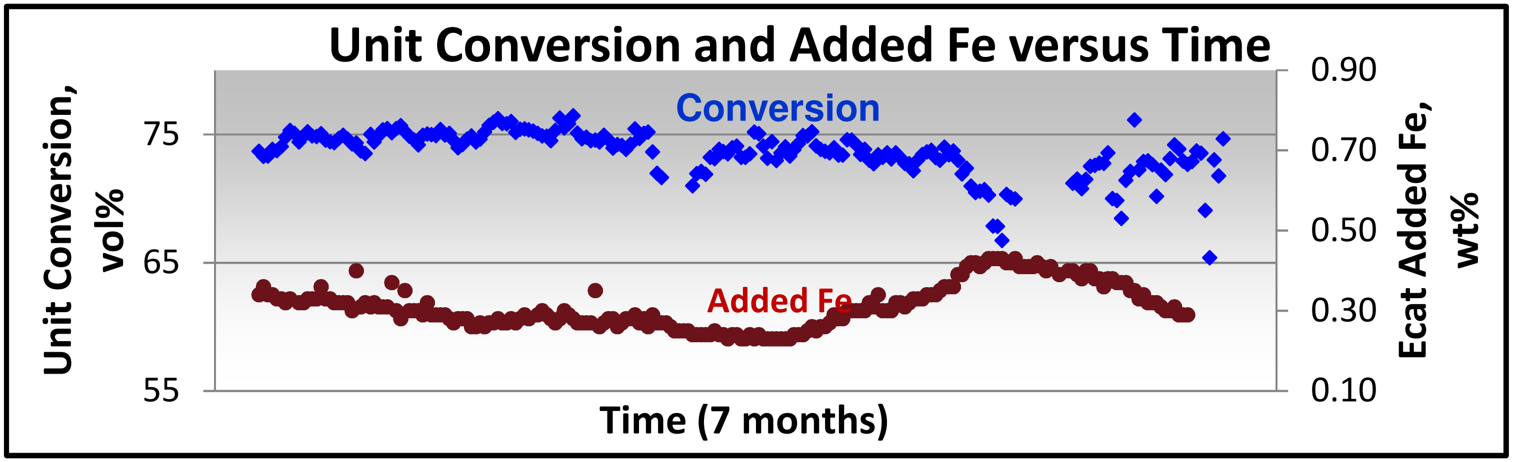
Iron Imaging: Iron deposits on the surface of the catalyst



- Fe deposits on the catalyst surface, with formation of very clear surface nodules.
- Old and new catalyst particles can be easily distinguished
- Dissimilar iron coating on each catalyst → indicative of limited mobility from one catalyst particle to another.

Fe Effects
Case Study #1

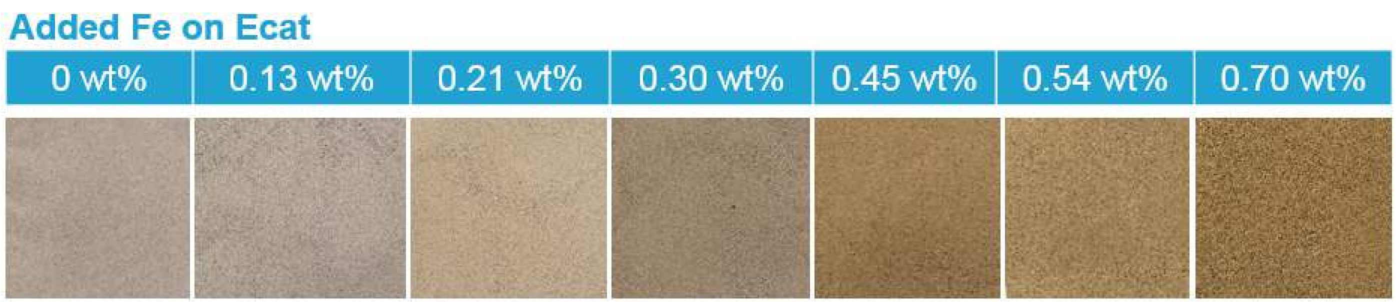
- Resid unit in Middle East
  - Using non-BASF catalyst
  - Feed API: 16 – 19
  - Ecat Ni: 6200 ppm; Ecat V: 5100 ppm
- Added Fe increased from 0.23 to 0.43 wt%
- Resulted in a conversion loss of **4 vol%**



Fe Effects
Case Study #2

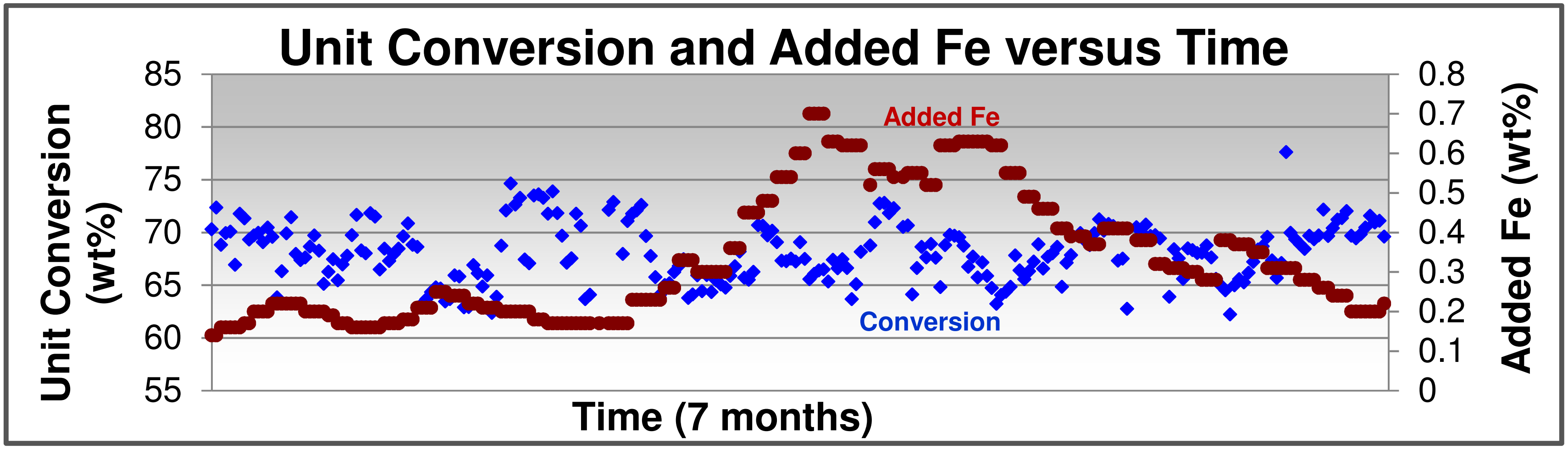
BASF
We create chemistry

- R2R unit in Asia Pacific
  - Feed API: 21 – 26
  - Ecat Ni: 2200 ppm
  - Ecat V: 2000 ppm
- Long history of using BASF catalyst since 2002
- Refiner started processing high-Fe feed
- Ecat Fe increased up to 1.3 wt% (or Added Fe of 0.7 wt%)
- Noticed change in color of the ecat around ~0.2 wt% added Fe



Fe Effects
Case Study #2

- Added iron increase from 0.15 to 0.70 wt% with no loss in unit conversion
- During the same period, other contaminants (Ni, V) decreased / stayed same

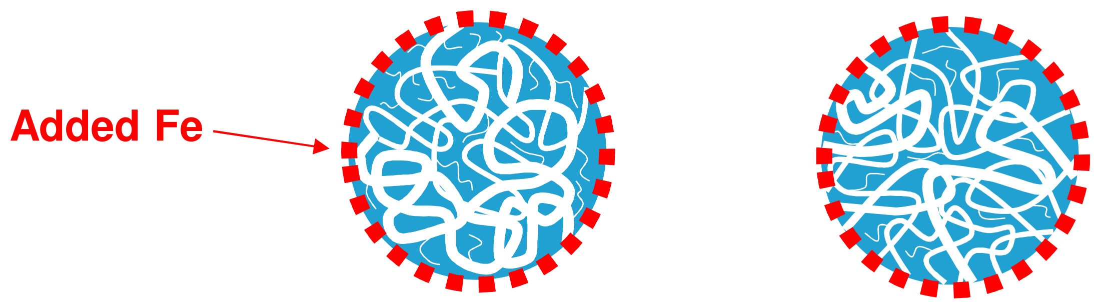


Result: No detrimental impact on unit conversion and yields at significantly high Added Fe

Iron Mitigation Strategies

BASF
We create chemistry

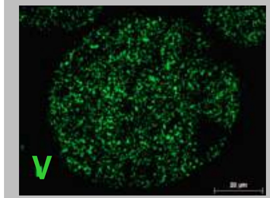
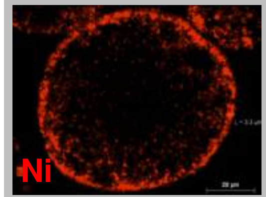
- Employ fresh catalyst with optimized surface porosity
- Increase catalyst additions or use purchased catalyst to flush Na out of circulating inventory



Surface Pores	Minimal	Optimized
Diffusion of feed	poor	excellent
Threshold to added Fe	Low (e.g. 0.3 wt%)	High (e.g. >1.5 wt%)
Resulting liquid yield	low	high

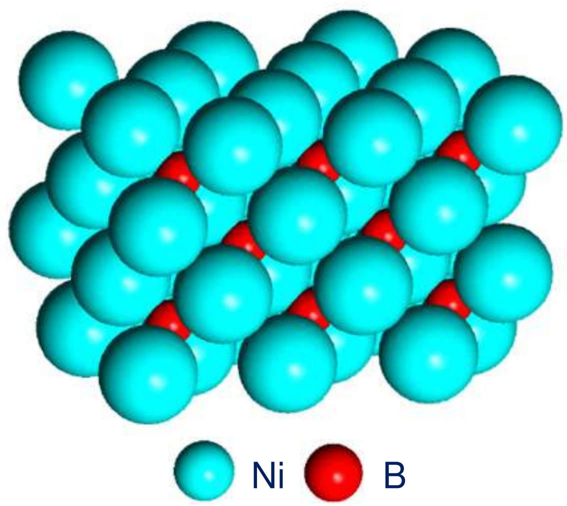
Mitigation strategies should make sense!

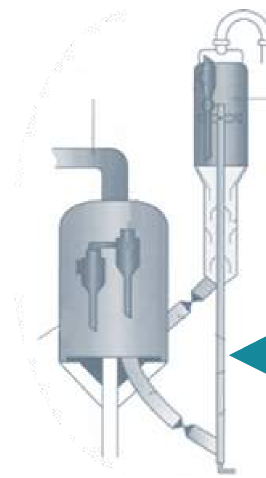
- Design of the catalyst passivation technology: passivator mobility should complement metal's mobility

Metal	Metal mobility	Passivator mobility	Passivator technology
	Mobile	Immobile	REO or separate particle
	Immobile	Immobile Mobile	Specialty Alumina Boron Based Technology

Mitigation Strategies – Boron-Based Technology (BBT)

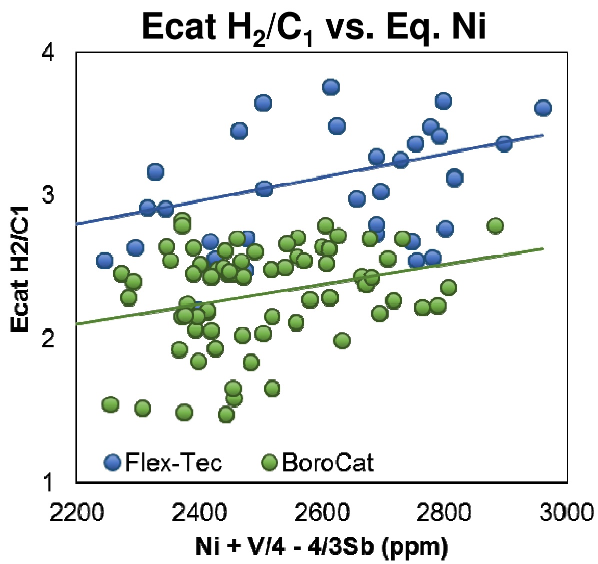
- New BASF catalyst technology designed to passivate Ni
- Boron is mobile under FCC conditions and migrates to Ni on the catalyst

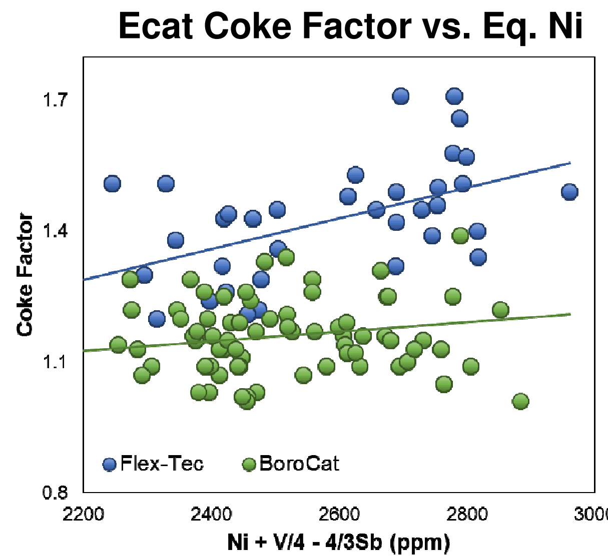




B deters Ni from being reduced to a more detrimental state in the riser

BOROCAT™ Reduces Hydrogen and Coke in the FCCU





- BoroCat™: lower hydrogen, lower coke, higher liquid products
- Catalyst architecture modifications allow for dramatic alleviation of constraints

Mitigation Strategies Summary

BASF
We create chemistry

28 58.70
Ni
Nickel

Nickel

- Employ catalyst incorporated with specialty alumina
- Boron-based technology
- Antimony (Sb) injection

23 50.94
V
Vanadium

Vanadium

- Employ catalyst designed for high V – high REO, stable zeolite
- Employ low-Na fresh catalyst
- Incorporate V-trap additive

11 22.99
Na
Sodium

Sodium

- Employ low-Na fresh catalyst
- Efficient and optimized desalter operation

26 55.85
Fe
Iron

Iron

- Employ catalyst with optimized surface porosity
- Use of purchased catalyst to lower ecat Fe

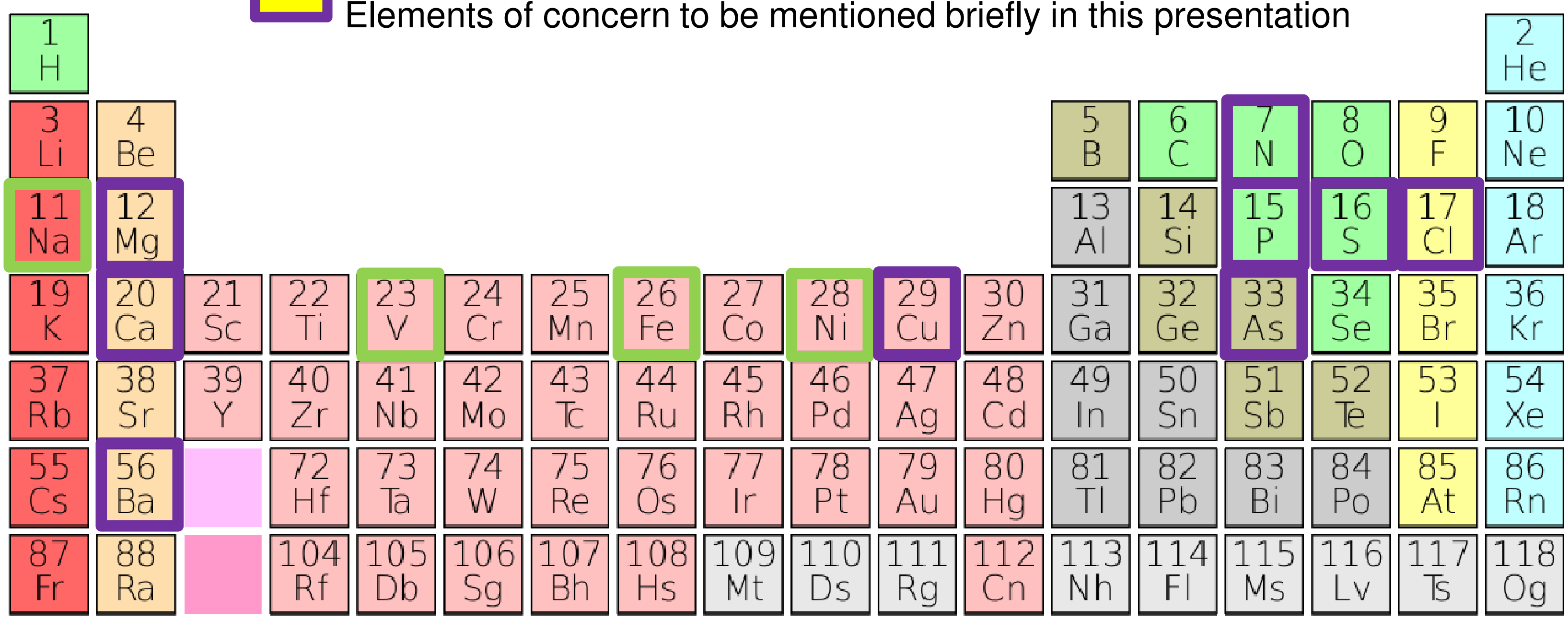
Mitigation Strategies Summary

Feed Metal	Deposition Method	Primary Effect	Secondary Effect	What to Watch for in the Unit	Solutions
Vanadium	Deposits evenly and migrates in the regenerator	Permanent catalyst poison	Dehydrogenation agent	• Increased H_2 and coke production • Decreased catalyst activity	• V-trap additive • Flush catalyst
Sodium	Deposits evenly and does not migrate	Permanent catalyst poison	Forms eutectic with V	• Decreased catalyst activity	• Flush catalyst • Catalyst change • Optimize desalter operation
Nickel	Deposits and binds on the outside of the particle. Does not migrate	Dehydrogenation agent (creates coke and H_2)	--	• Increased H_2 and coke production	• Antimony injection • Catalyst change • Flush catalyst
Iron	Deposits and binds on the outside of the particle. Low mobility between particles	Creates nodules on the surface of the particle at very high levels	Dehydrogenation agent CO promotion Transfers S from reactor to regenerator	• Circulation issues and lower ABD • Over-promotion in partial burn units • Slightly increased SO_x emissions	• Flush catalyst • Catalyst change

Additional Feed Contaminants

BASF
We create chemistry

Elements of high concern to be discussed in this presentation
Elements of concern to be mentioned briefly in this presentation



Additional Feed Contaminants

Elements of high concern to be discussed in this presentation

Elements of concern to be mentioned briefly in this presentation

1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba		72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra		104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Nh	114 Fl	115 Ms	116 Lv	117 Ts	118 Og

Additional Feed Contaminants

Calcium

- Comes in with feed or some V-trap additives
- Neutralizes acid sites (less active than Na); can also plug pores in combination with high added Fe
- Use flush catalyst or employ catalyst with optimized surface porosity

Sulfur

- Comes in with feed
- No negative effects on conversion or yields
- Use hydrotreating or gasoline sulfur additives to remove for environmental purposes

Barium

- Used in some V-traps or chemicals for tight oil extraction
- Has no effect on catalyst activity or yields when REO is present

Arsenic

- Comes in with feed
- Volatile at FCC conditions and does not stay on the FCC catalyst
- Arsine (AsH3) does go out with the C3= stream which must be treated

Additional Feed Contaminants

Chlorine

- Comes with feed and poor desalter operation
- Re-disperses and reactivates “old” metals on the catalyst, especially Ni
- Use low-Cl catalyst or flush catalyst to remove from inventory

Phosphorus

- Used to stabilize zeolite – typically an indicator of ZSM-5 additive
- Can also be used in chemicals for tight oil extraction – no effect on activity

Copper

- Comes in with feed or NOx reduction additives
- Has 5x more dehydrogenation activity than Ni
- Use low-Cu promoter such as CONQUERNOX

(Basic) Nitrogen

- Comes in with feed and neutralizes acid sites, lowering conversion
- Temporary poison – burns off in the regenerator as coke

Summary: Metals Contamination in FCC

- Metals are continuing to rise as we see increased resid processing as a global trend
- Ni, V, Fe, and Na among the most detrimental, with Ca, K, Cu also of concern
- Catalytically: employ catalyst designed for high metal applications including metal passivators, REO, and optimized surface porosity
- Proper operational and catalytic mitigation strategies enable stable operation and profitability at the refinery

BASF

We create chemistry