Cat Cracker Seminar
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Royal Sonesta Hotel
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CAT-14-102 **Evaluating Equilibrium Catalyst (Ecat) Data**

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Sample Shipment Safety

Ecat sample shipment is a routine activity, but there are multiple examples of receipt of dangerously packaged shipments

Work with your catalyst vendors to understand recommended shipment packaging and safety instructions

Objectives

Brief review of Ecat properties

Demonstrate different ways to view catalyst data

Review specific case studies

Active participation

What are the Key Features of FCC catalyst?

Optimized **SURFACE AREA**

\+

Tailored **PORE SIZE DISTRIBUTION**

\+

Tailored **ACIDITY**

→ **ACTIVITY & SELECTIVITIES**

Proper **PARTICLE SIZE DISTRIBUTION**

\+

Other Physical Properties

→ **FLUIDIZATION & RETENTION**

What Types of Tests are Run on Ecat Samples?

Activity/Selectivity Tests

- MAT or ACE cracking at standard conditions
- Determines Activity and Selectivities

Parameters to track from these tests

- Activity
- Gas Factor
- H2 Yield
- Coke Factor
- Single point ACE yields

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What Types of Tests are Run on Ecat Samples?

Chemical Composition Tests

- XRF or ICP testing for complete chemical analysis
- Carbon analysis
- Determines contaminant metals profile
- Often useful for tracking catalyst turnover

Parameters to track from these tests

- Carbon content
- Ni
- V
- Na
- Re2O3
- Al2O3
- MgO
- P2O5
- Sb
- All Trace Chemical Contaminants (CaO, K2O, Pb, etc.)

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What Types of Tests are Run on Ecat Samples?

Physical Property Tests

- Surface area
- Apparent bulk density (ABD)
- Pore volume
- Particle size distribution
- Umb/Umf
- Others

Parameters to track from these tests

- **Surface areas: total, zeolite, and matrix**
- **Unit Cell Size**
- **ABD and pore volume**
- **0-40, 40-80, and >105 micron fraction (particle size)**
- **U_{mb}/U_{mf}**

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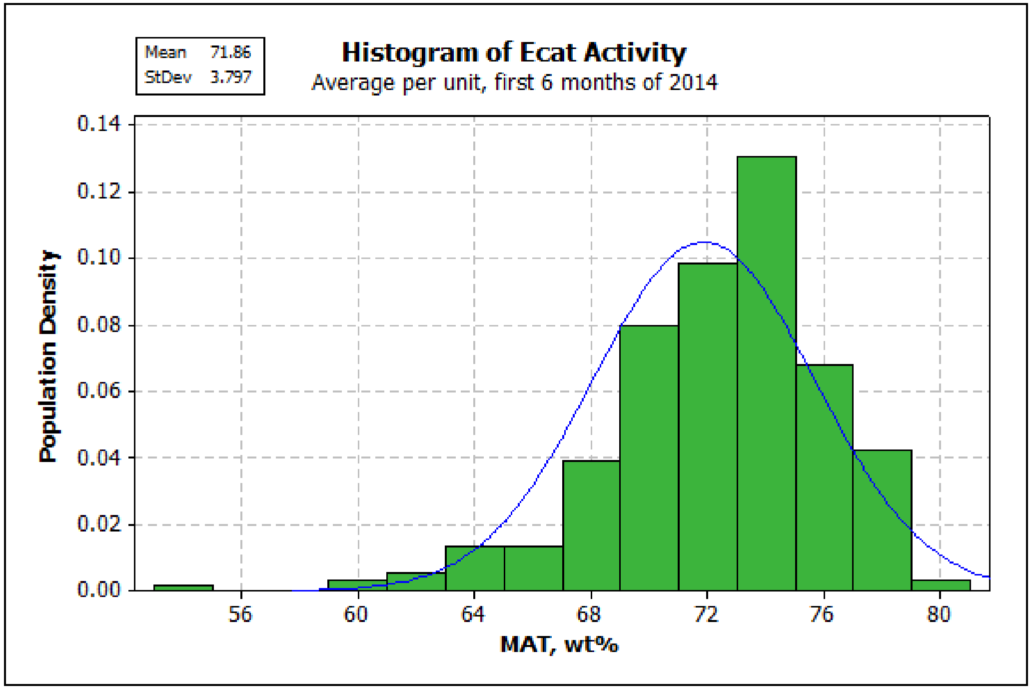
Ecat Activity

Defined as Conversion (100 – LCO (wt%) – Slurry (wt%)) as measured in a microscale test unit (fixed cat to oil).

Kinetic Conversion = [Conv] / (100 – [Conv])

Tested after carbon is burned off catalyst



85% of North American FCC's are represented in the distribution

Factors that Impact Activity

Fresh catalyst additions

Metals contamination

- Vanadium
- Alkali metals (Na, K)
- Alkaline earths (Ca)

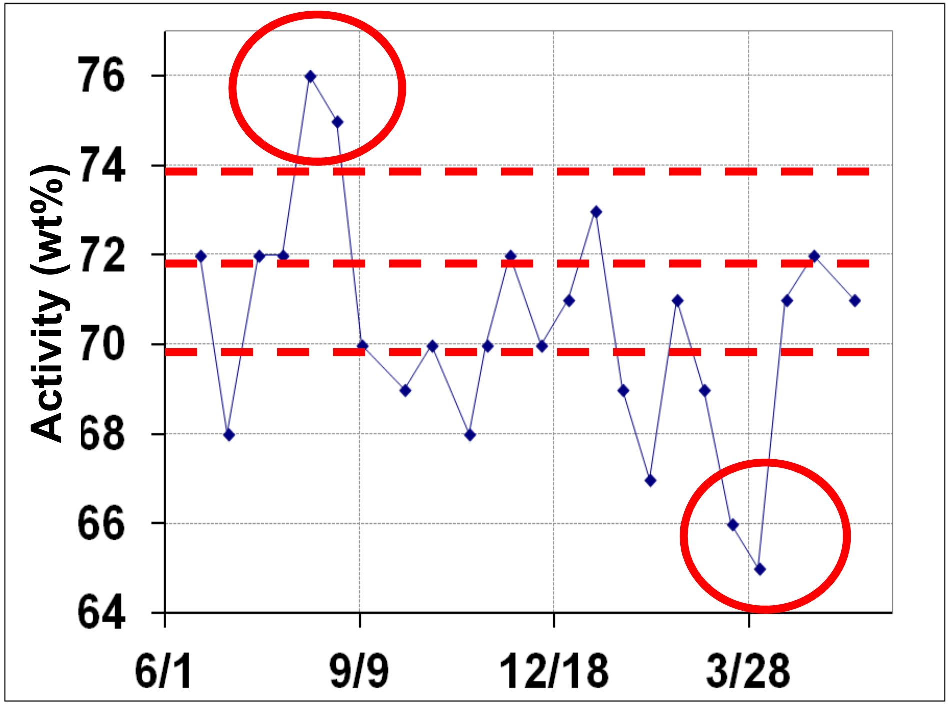
Catalyst reformulation

- Activity per unit of surface area
- Incorporation of a vanadium trap
- Zeolite input

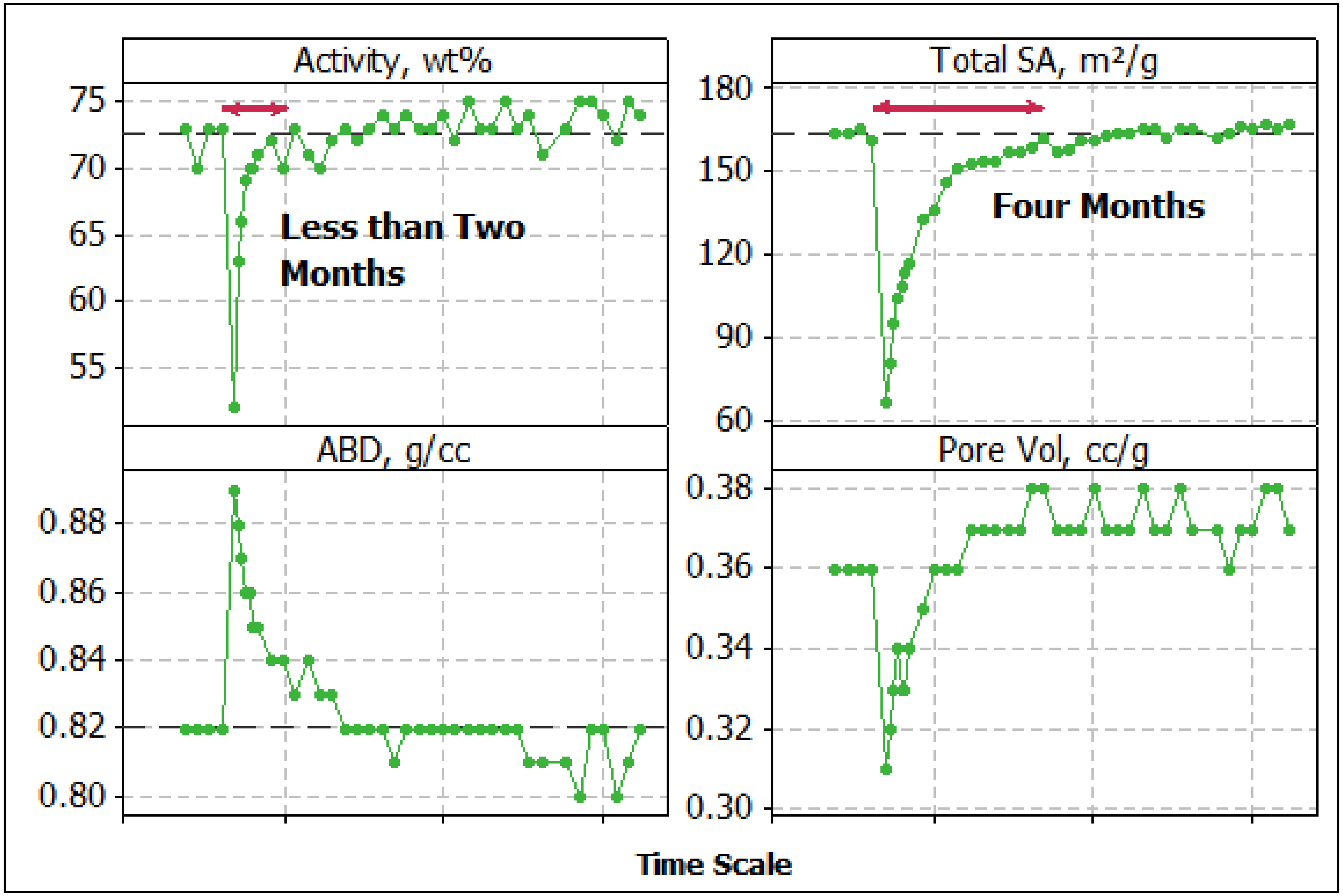
Unit severity

- Mode of operation (Full vs. Partial)
- Thermal/Hydrothermal deactivation

Re2O3 or other stabilization compounds



Activity Recovers Quicker than Bulk Properties



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Activity Testing - Selectivities

Gas factor (GF)

- Molar hydrogen-to-methane ratio from the ACE unit

Hydrogen yield (H2 Yield)

- Hydrogen yield measured in SCFB from the ACE unit

Coke factor (CF)

- Ratio of the ACE coke yield (wt%) to the kinetic activity

- Factors that impact GF, H2 Yield, and CF
- Catalyst formulation & design
- Contaminant metals (Ni, V, Cu, Fe, etc.)
- Metals tolerance of the fresh catalyst
- Antimony (Sb) injection

Full yield profiles can also be tracked via Ecat ACE testing

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Contaminant Impacts on FCC Catalysts

Zeolite Dealumination / Zeolite Destruction

- Vanadium
- Sodium
- Calcium
- Potassium

Destruction of Exterior Surface / Pore Structure

- Sodium
- Iron
- Calcium

Dehydrogenation Catalysts

- Nickel
- Iron
- Vanadium
- Molybdenum
- Copper

Common Sources of Metals

- Organic Complexes in Crude Oils
- Additives in Crude extraction
- Entrained metals from other catalytic processes
- Tramp metals (Iron)
- Non-Desalted Crude (Sea Water)
- Lube Extracts
- Purchased Ecat
- Micro-sized mineral particulates in feed (often seen in Shale Oil)

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Dealumination of Zeolite / Zeolite Destruction

Vanadium

- Deactivates by destroying zeolite surface area and reducing activity
- Forms vanadic acid in the regenerator (H_3VO_4)
- Rule of Thumb: 500 ppm (V + Na) lower catalyst activity by ~ 1 number
- Range: 70 –7800 ppm (includes SOx reducing additive V)
- Average: 1974 ppm (includes SOx reducing additive V)
- More severe activity loss in full burn units (more oxidizing environment in regenerator)

Alkali metals and alkaline earths

- Form eutectics with elements in fluid cracking catalyst which can fuse at regenerator conditions, causing negative yield impacts
- Harmful effects are magnified when regenerator severity is increased

Sodium (Na), wt%

- Range: 0.09 – 1.42 wt%
- Average: 0.27 wt%

Calcium (CaO), wt%

- Range: 0.02 – 2.28 wt%
- Average: 0.15 wt%

Potassium (K_2O), wt%

- Range: 0.02 – 0.37 wt%
- Average: 0.07 wt%

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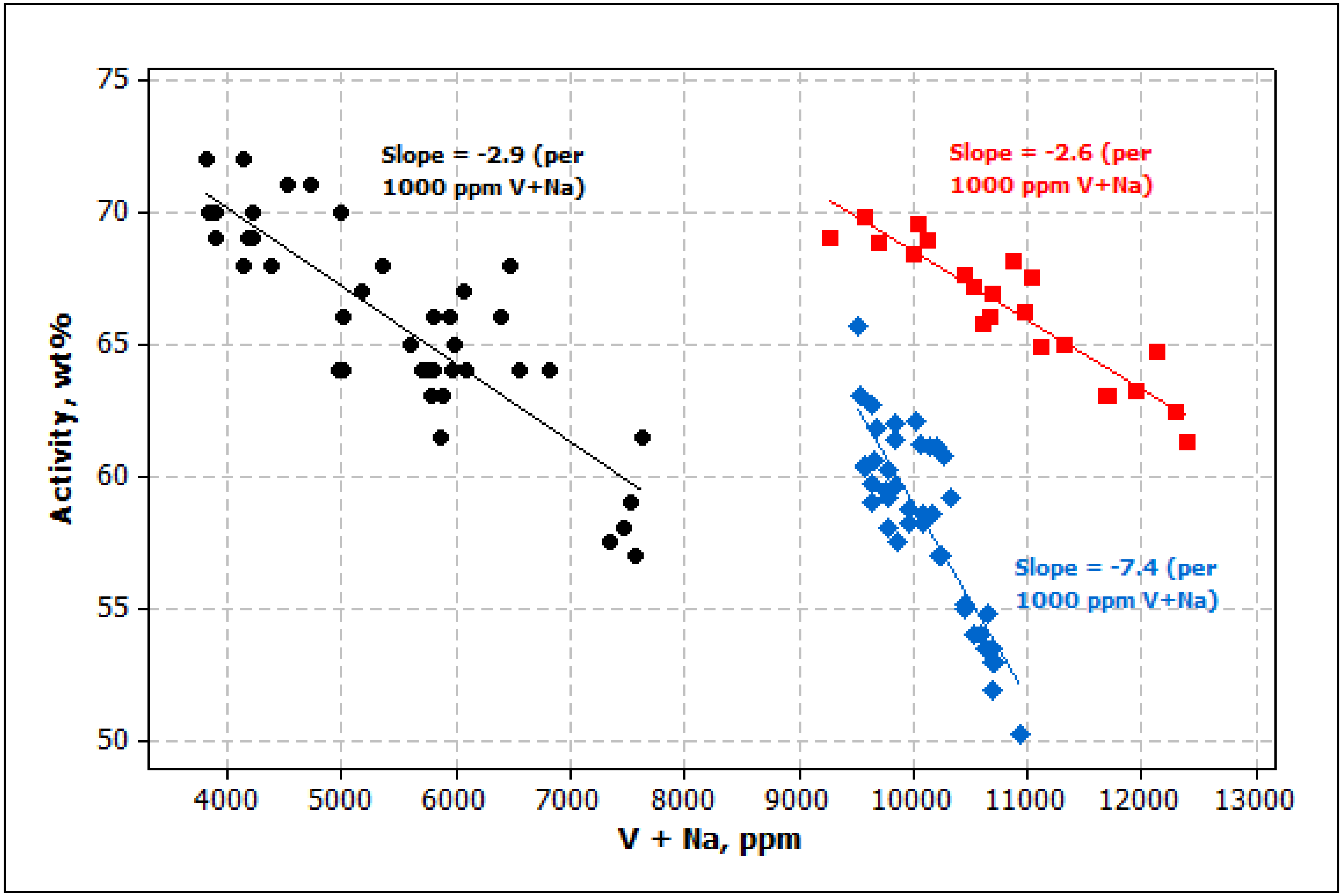
Each FCCU Responds Uniquely to Contamination



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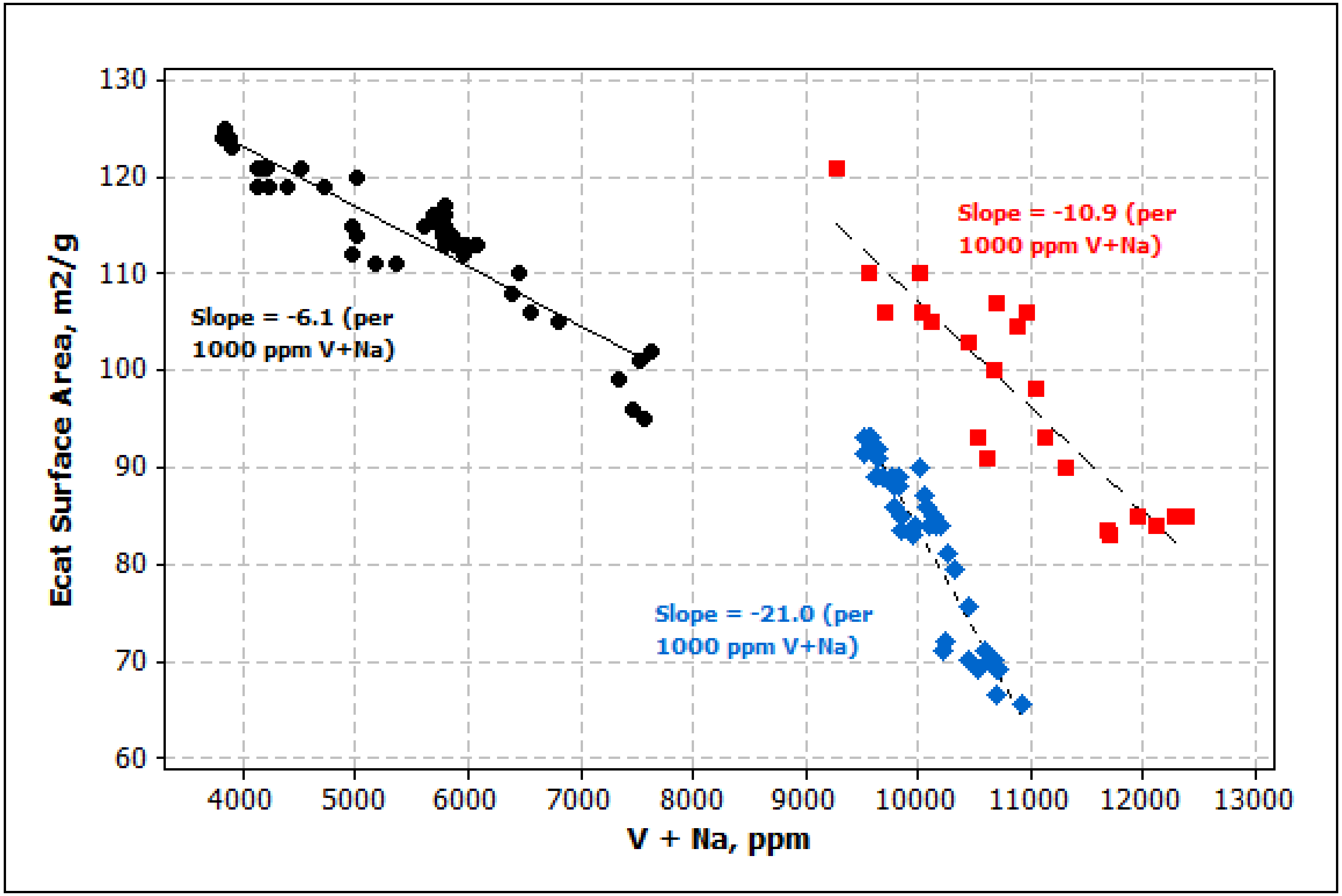
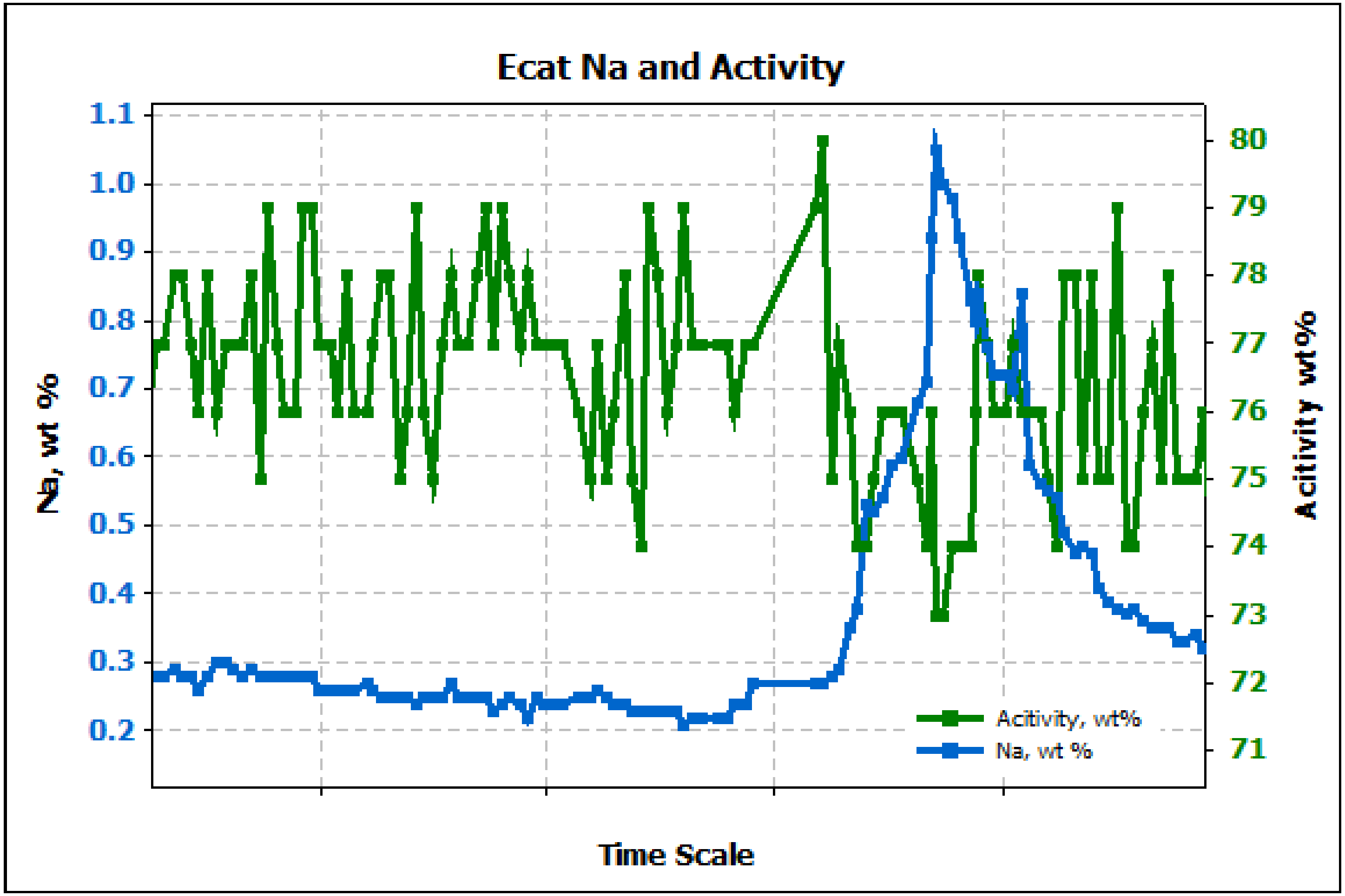
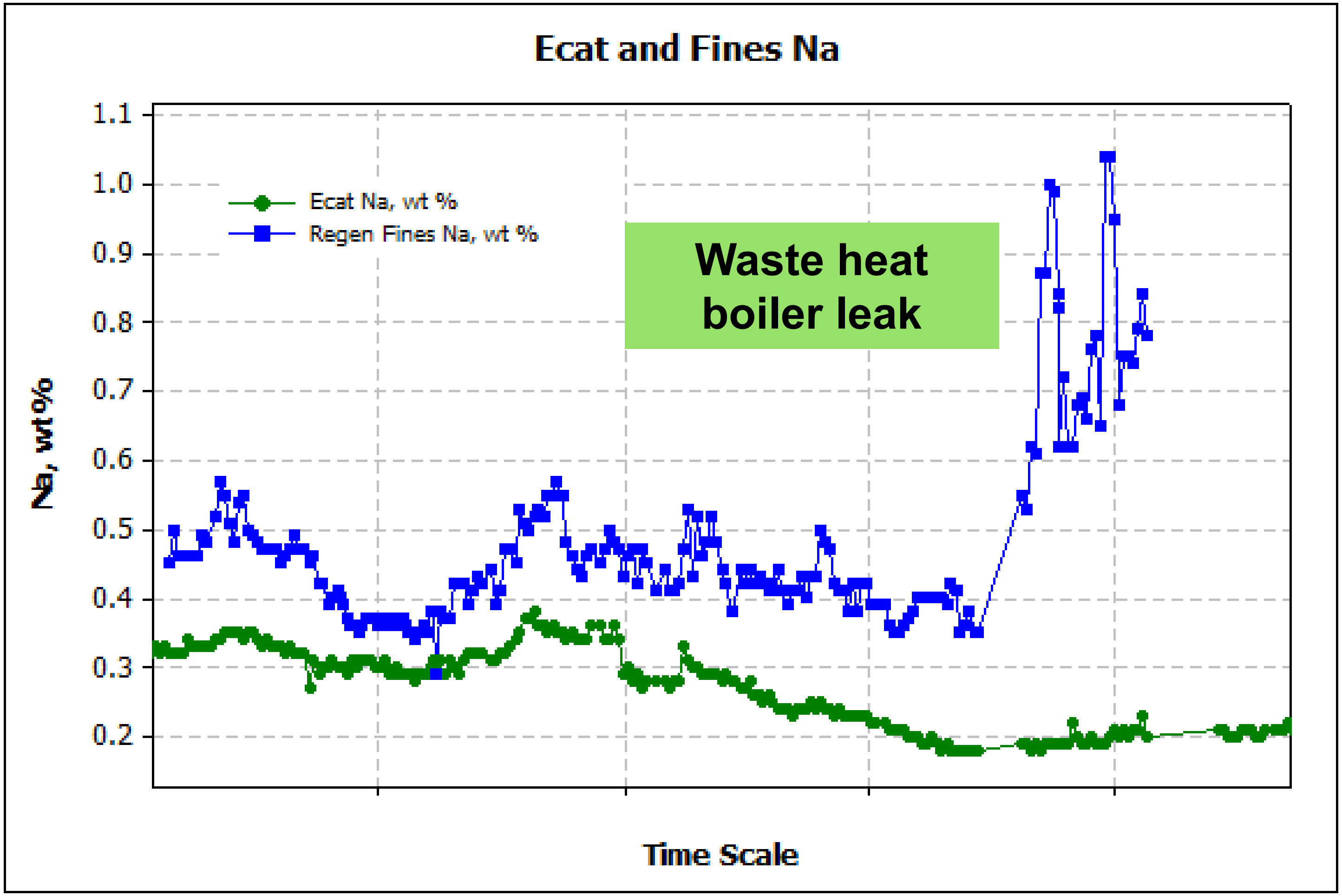
Each FCCU Responds Uniquely to Contamination



Example: Na Impact on Catalyst Activity



Usefulness of Ecat and Fines Analysis



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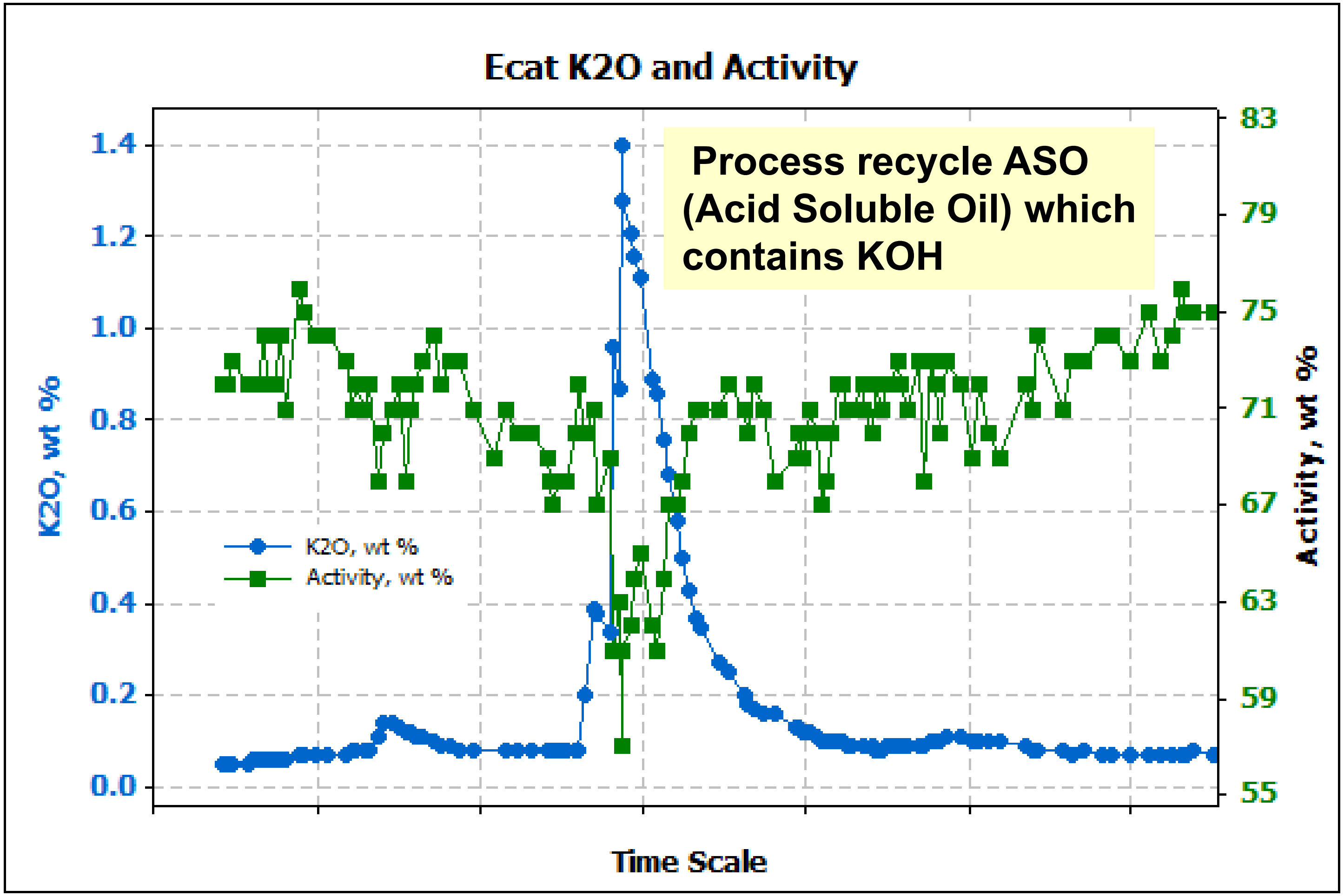
Potassium Contamination



Destruction of Exterior Surface/Pore Structure

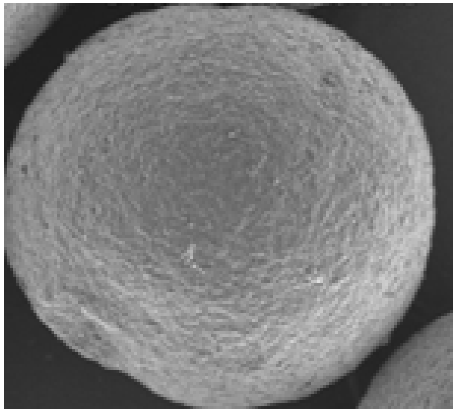
Ecat Iron (Fe) = Fresh Catalyst Fe + Added Fe

- Fe is naturally present in the clay used to manufacture catalyst, but this Fe does not negatively impact unit performance
  - Fe in clay may vary with catalyst supplier and formulation
- From secondary crude recovery processes and more recently in Tight Oils
- Coats catalyst surface – can cause severe conversion loss by blocking access to sites
- Fe acts as reverse SOx reducing additive
  - Fe reacts with H2S in the riser to form FeS, which in the regenerator is oxidized and eventually released as SOx
- Watch for a drop in ABD
- Range: 0.23 – 1.47 wt%
- Average: 0.52 wt%

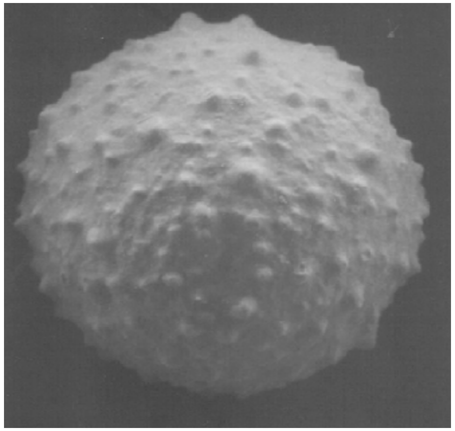
Calcium (CaO)

- Frequently found with Fe in Tight Oils
- Forms a eutectic with Fe and alumina that can fuse and form nodules on the catalyst particles

Normal Ecat



Contaminated Ecat



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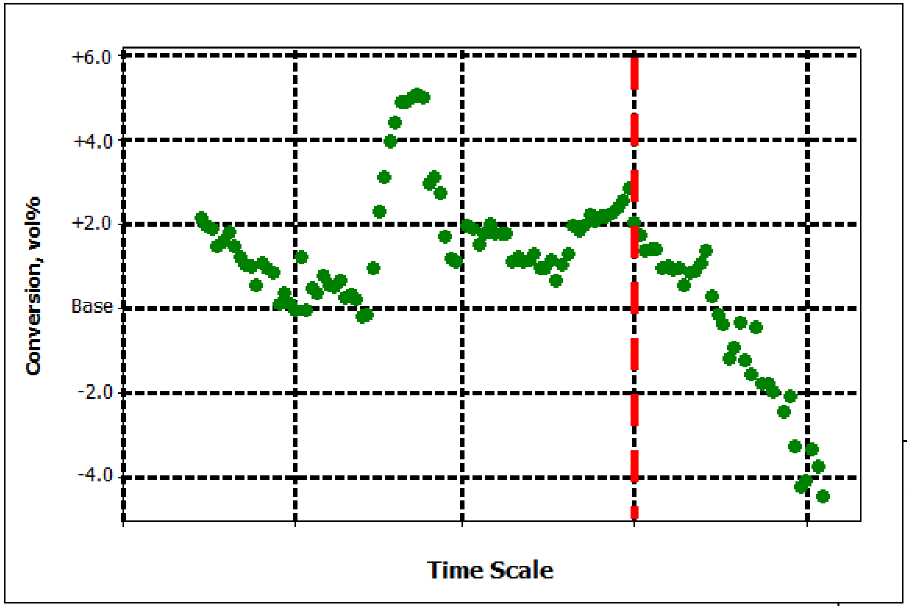
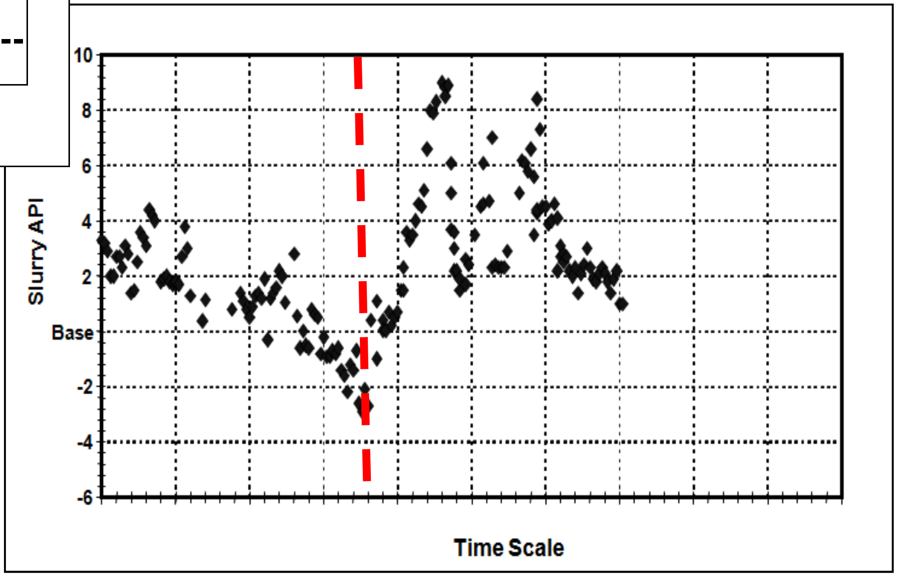
Case Study: Troubleshooting Conversion Loss





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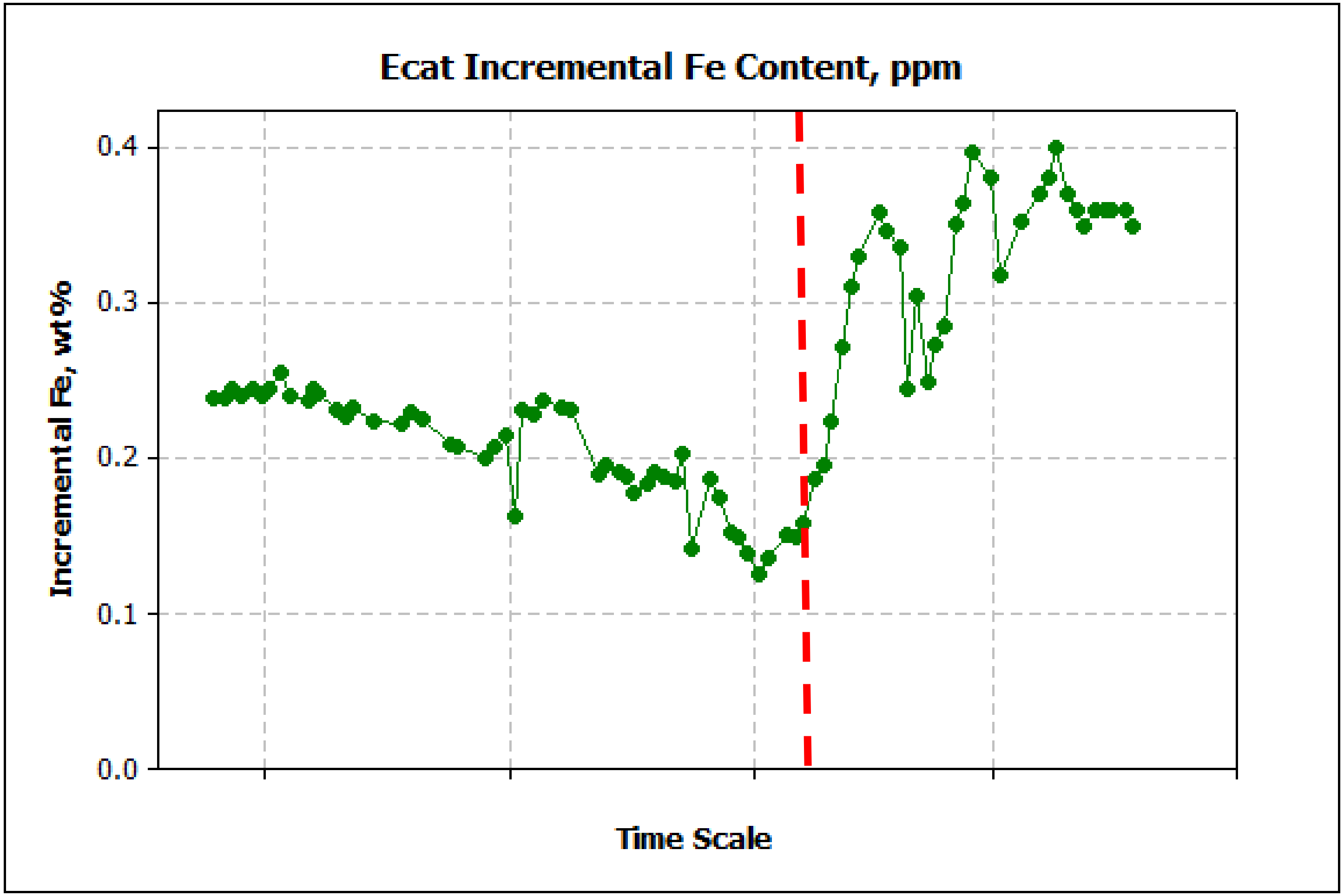
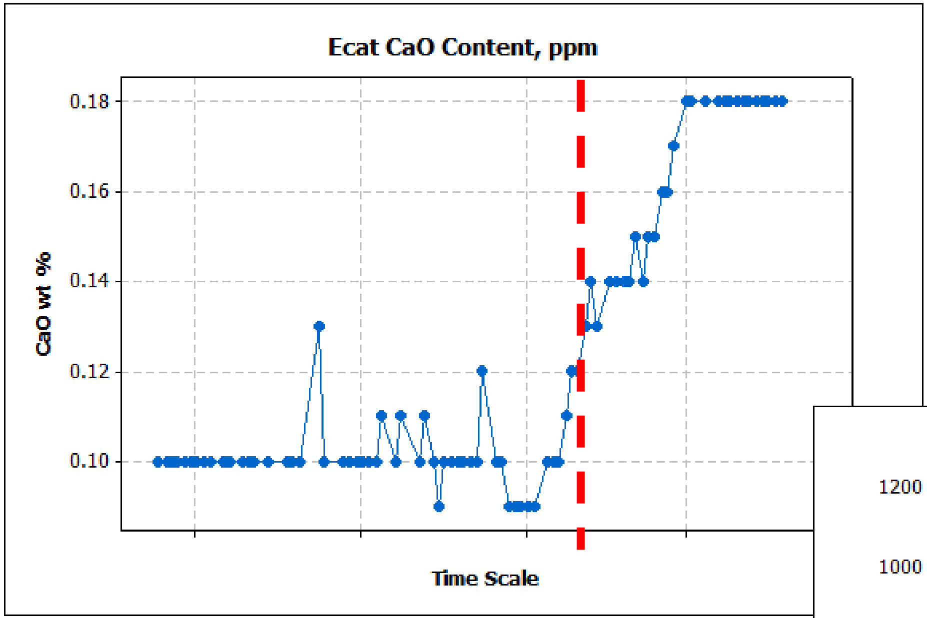
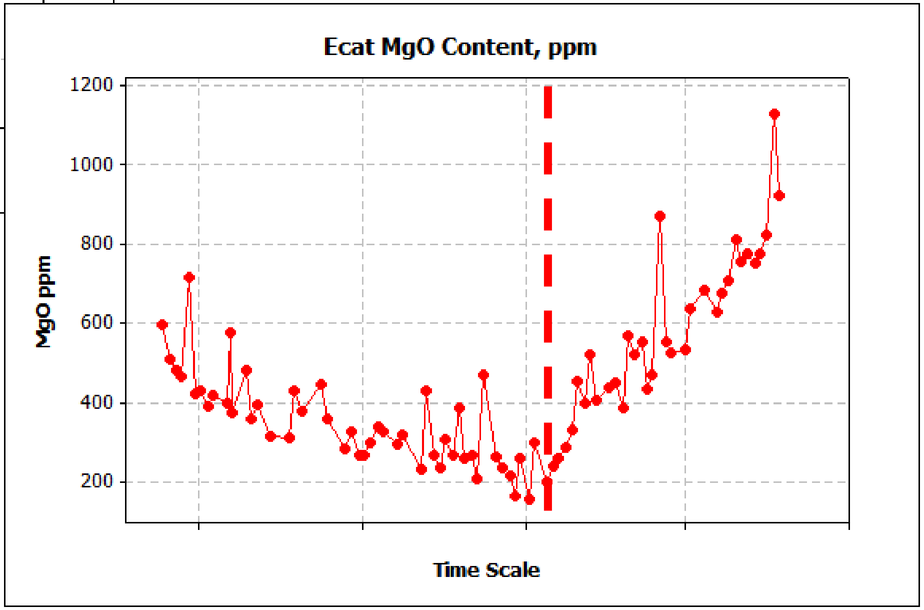
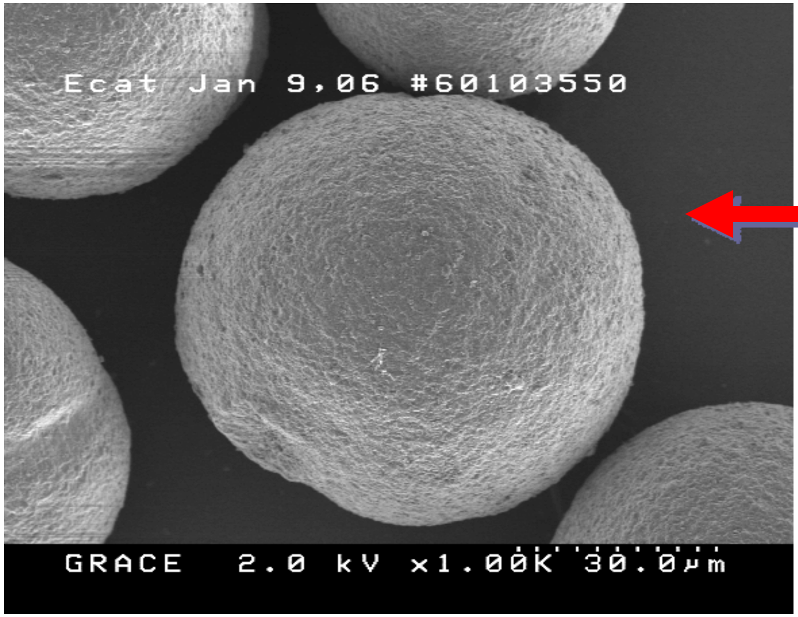


Case Study: Troubleshooting Conversion Loss

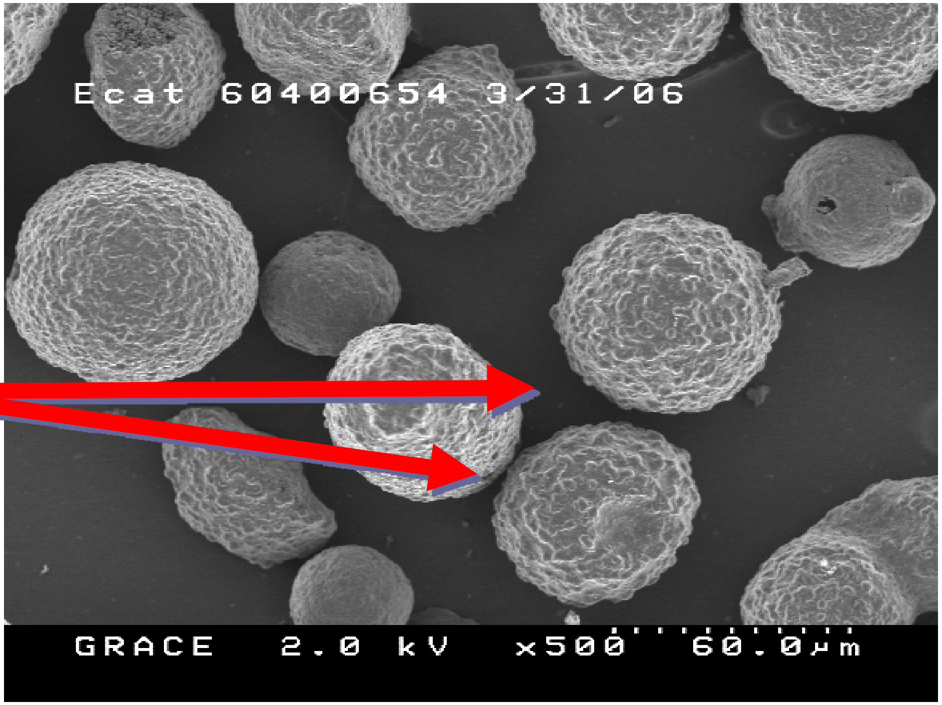




Troubleshooting Conversion Loss – SEM



Added Fe = 0.15 wt%
CaO = 0.1 wt%
No Evidence of Fe Nodules

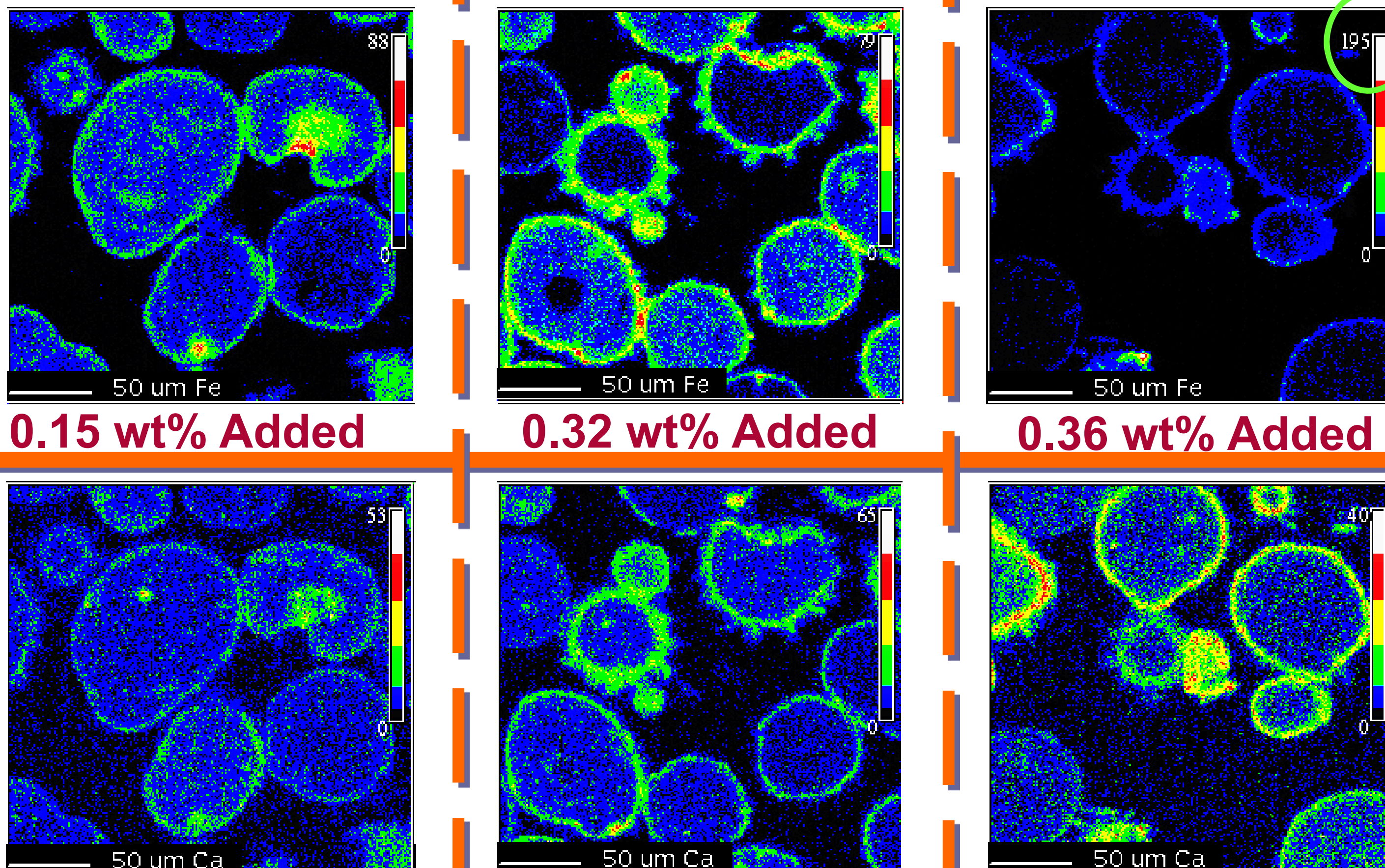


Added Fe = 0.36 wt%
CaO = 0.18 wt%
Serious poisoning evident

Troubleshooting Conversion Loss – EPMA

Fe

Ca



0.15 wt% Added

0.32 wt% Added

0.36 wt% Added

Lower apparent intensity due to larger scale

0.1 wt%

0.18 wt%

0.18 wt%

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Dehydrogenation Catalysts

Nickel (Ni) / Copper (Cu)

- Strong dehydrogenation catalyst
- Significant increase in coke and gas
- Does not cause catalyst activity to decline for most units
- Nickel passivators such as Sb are used when high nickel content feeds are charged to the unit

Nickel (Ni), ppm

- Range: 26 – 16,372 ppm
- Average: 1,587 ppm

Copper (Cu), ppm

- Range: 7 – 400 ppm
- Average: 38 ppm

Molybdenum (Mo), ppm

- Present in some hydrotreated oils
- Very strong dehydrogenation agent
- May slowly climb as hydrotreaters near end of run, or spike if contaminated feed is purchased

Vanadium, ppm

- Acts at about ¼ the dehydrogenation effect of Ni

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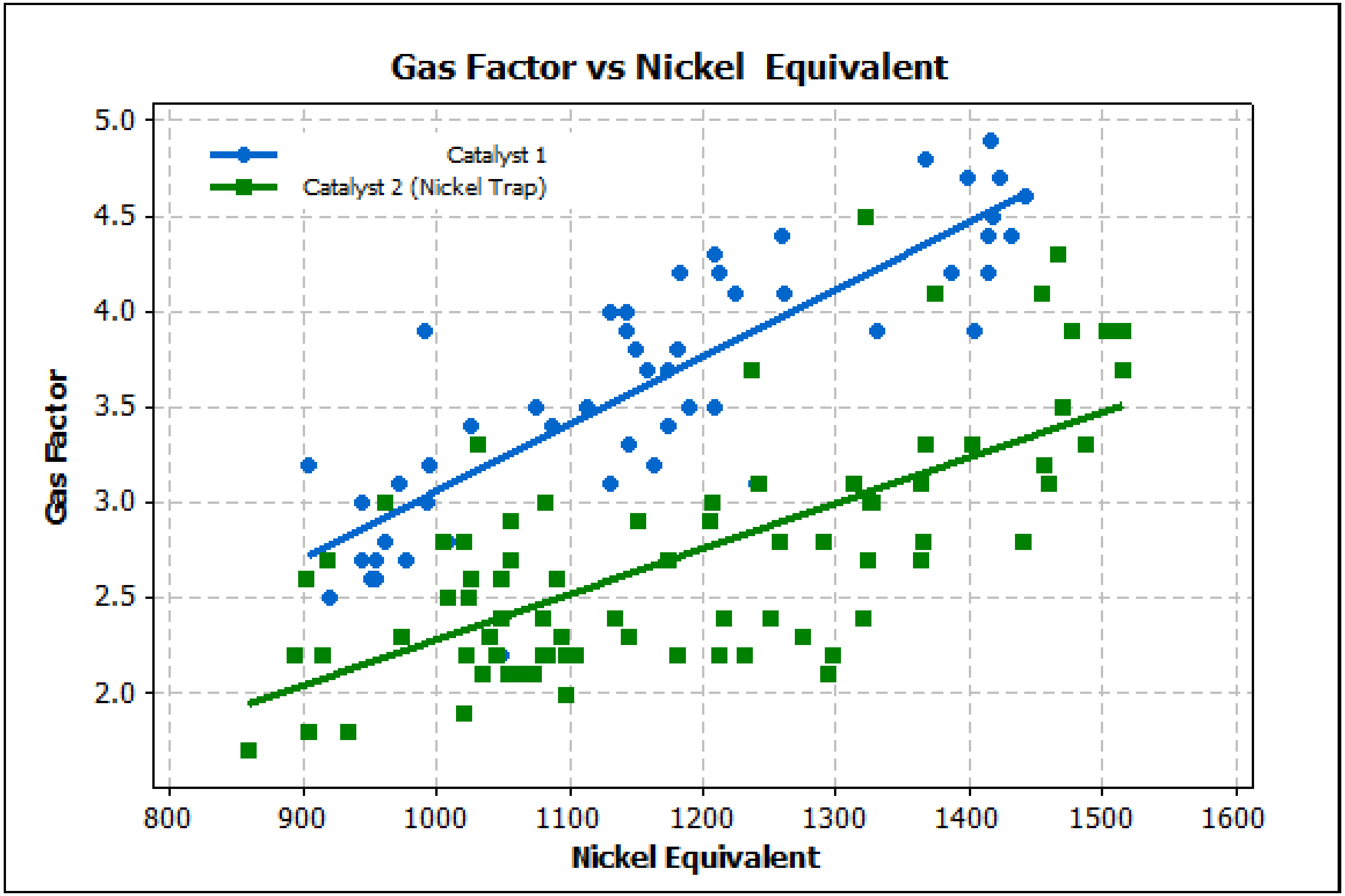
Case Study: Nickel Trap



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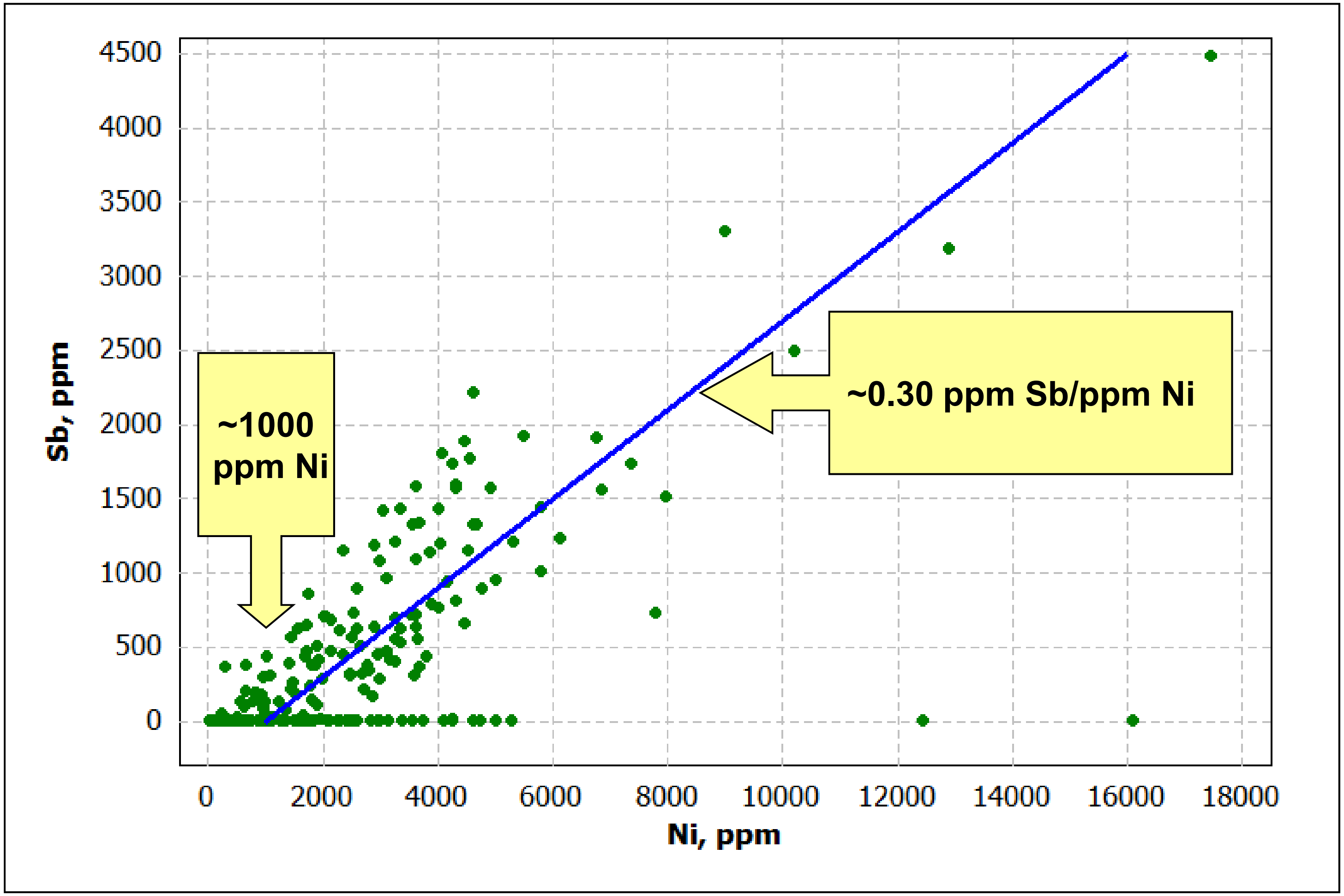
Antimony Passivates Ni



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Temporary Catalyst Deposit - Carbon

Carbon on regenerated catalyst (CRC)

- Measured on the Ecat to determine the efficiency of the regenerator
- Full combustion units typically operate below 0.15 wt%
- Partial burn units typically operating 0.1-0.4 wt%
- Range: 0.01 – 1.2 wt%
- Average: 0.11 wt%

Factors that impact carbon

- Regenerator temperature
- Regenerator design
- Mode of operation (Full vs. Partial)
- Air distribution
- Low excess O_2
- Residence time

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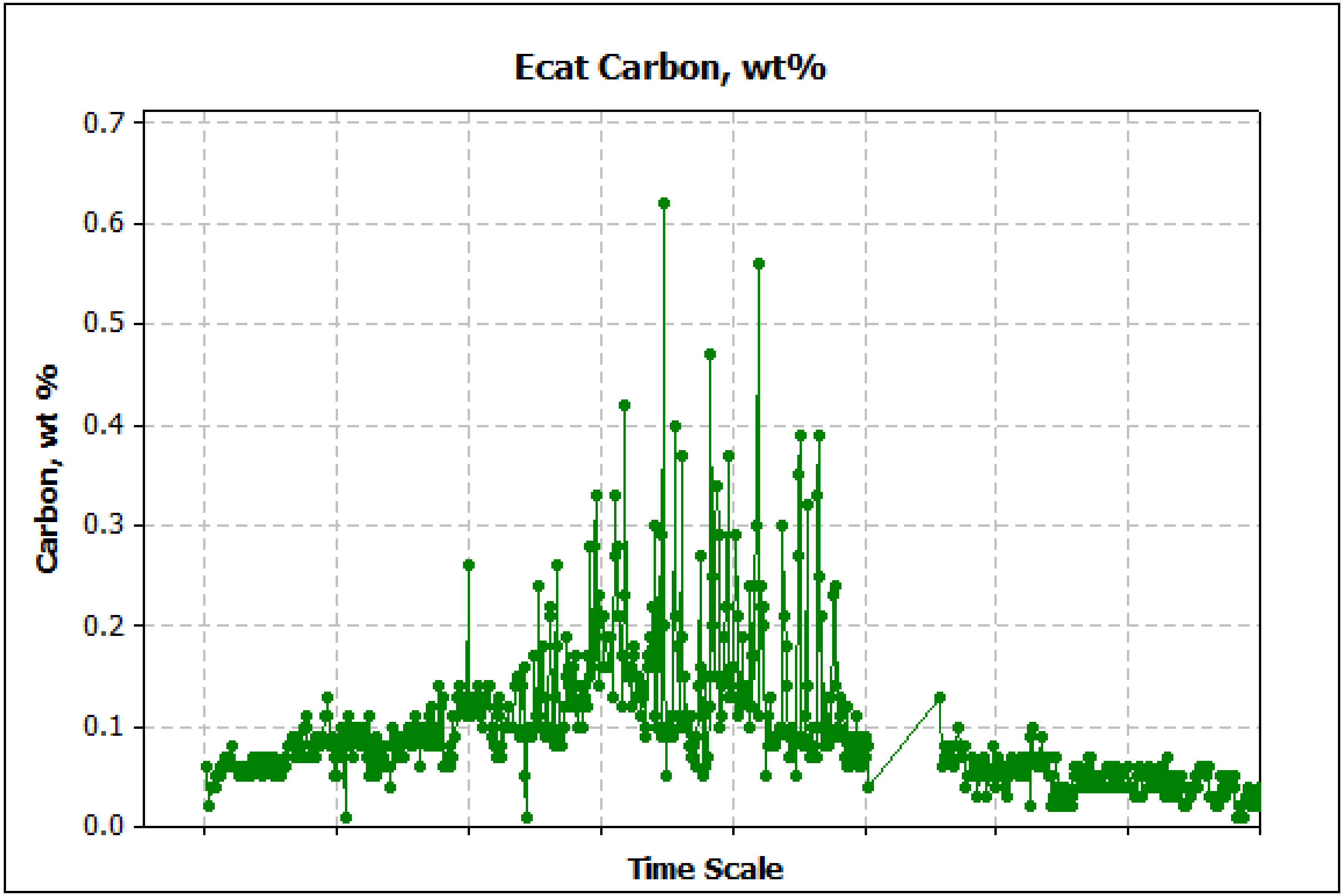
Case Study: High CRC



Particle Size Distribution

Ecat 0-40µ

- Used to determine cyclone efficiency and to identify attrition sources
- Range: 0 - 20µ wt%
- Average: 4µ wt%

Ecat 40-80µ

- Most important fraction for catalyst fluidization
- Range: 24 - 57µ wt%
- Average: 44µ wt%

Ecat APS, µm

- Used to determine cyclone efficiency and track both retention and fluidization properties
- Range: 67 – 109 µm
- Average: 81.8 µm

Factors that impact Particle Size Distribution

- Unit catalyst retention (cyclone performance)
- 0-40µ on fresh catalyst
- Attrition sources
- Fresh cat add rates
- Purchased Ecat adds & quality
- Fresh catalyst attrition mechanism

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Case Study: Catalyst Retention

FCCU background

- Gas Oil service
- Typical catalyst additions: 3 TPD

Problem: Catalyst Loss

- Adding 5-7 TPD to maintain regenerator bed level

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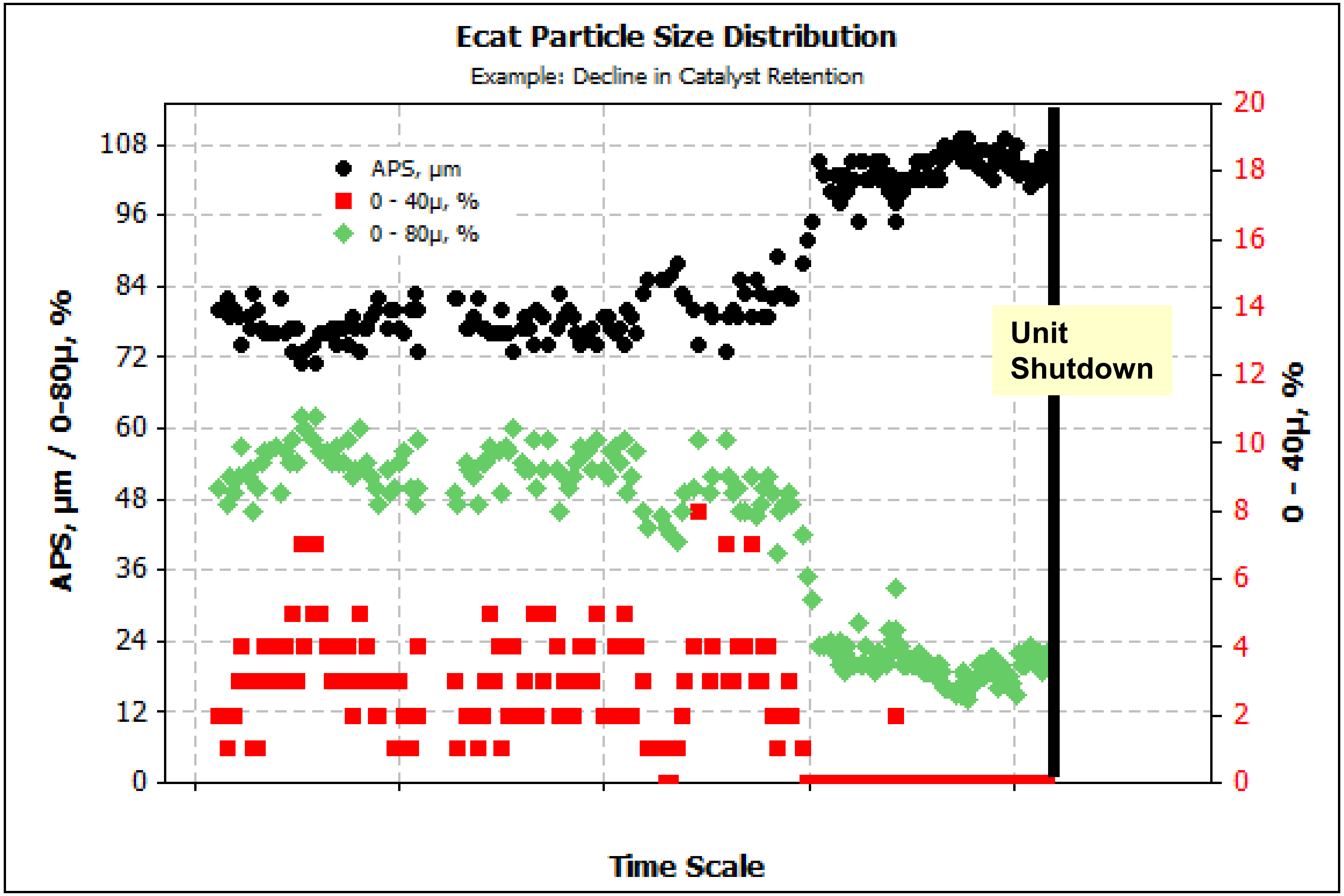
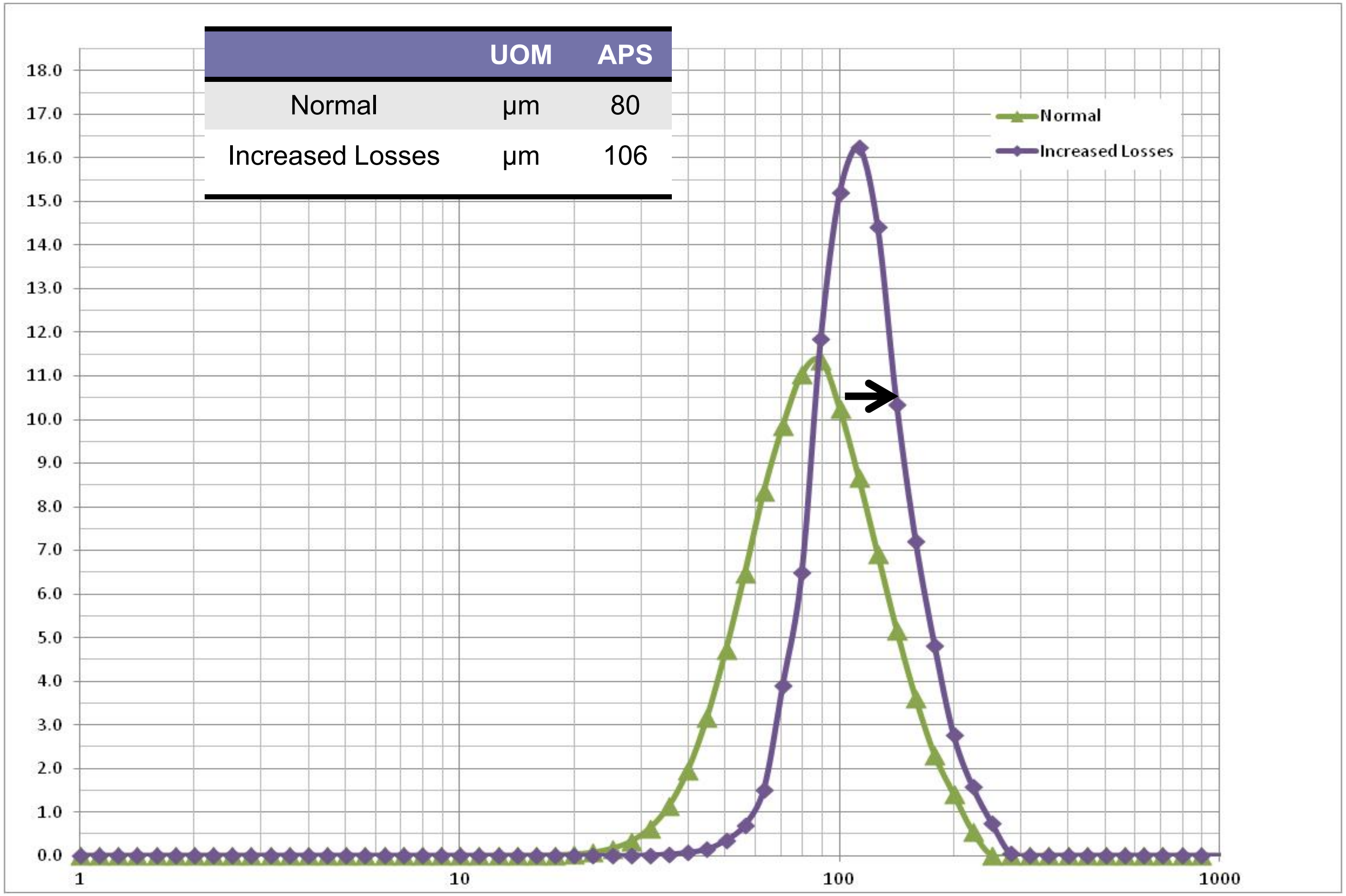
Case Study: Catalyst Retention



Case Study: Catalyst Retention

	UOM	APS
Normal	µm	80
Increased Losses	µm	106



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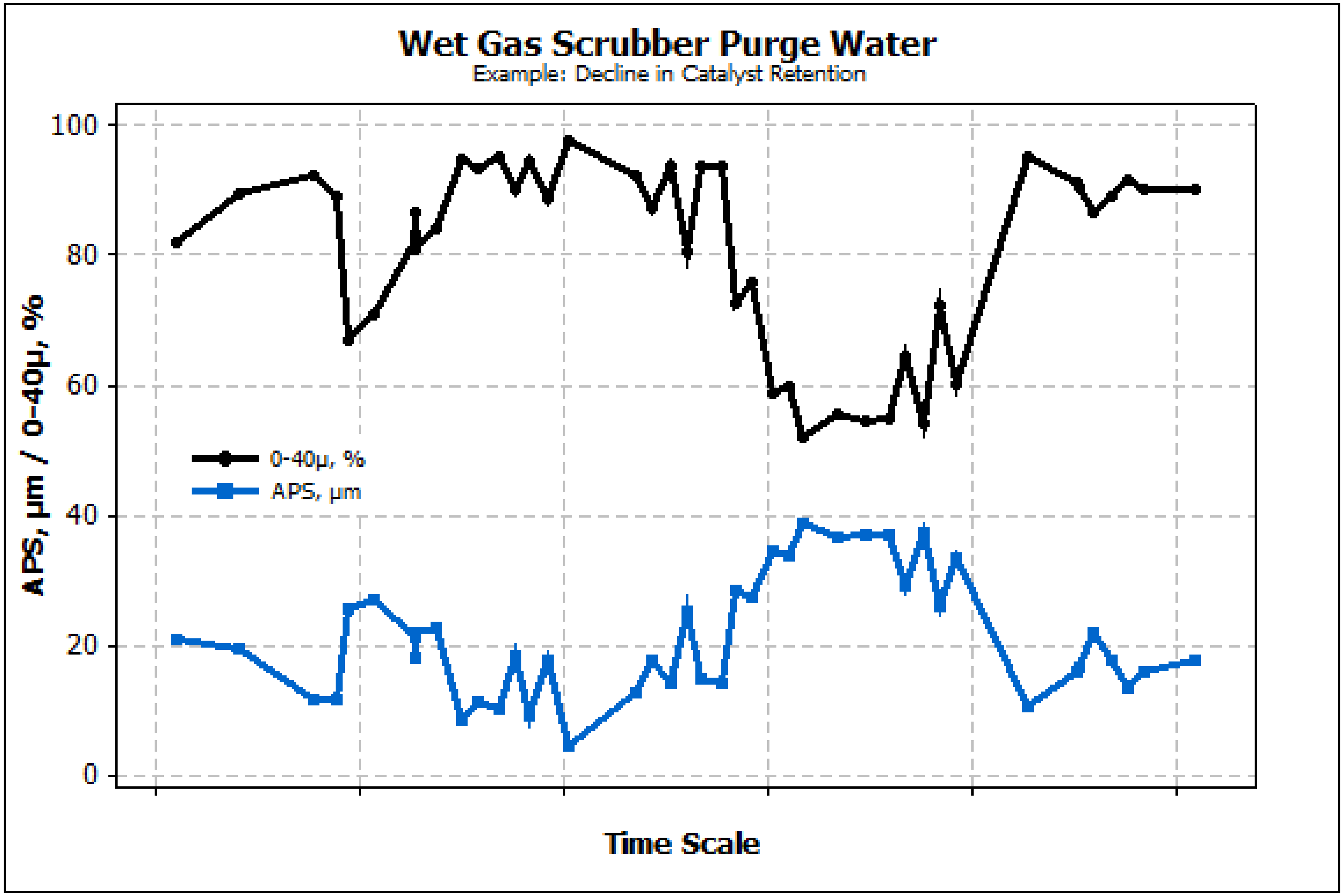
Case Study: Catalyst Retention



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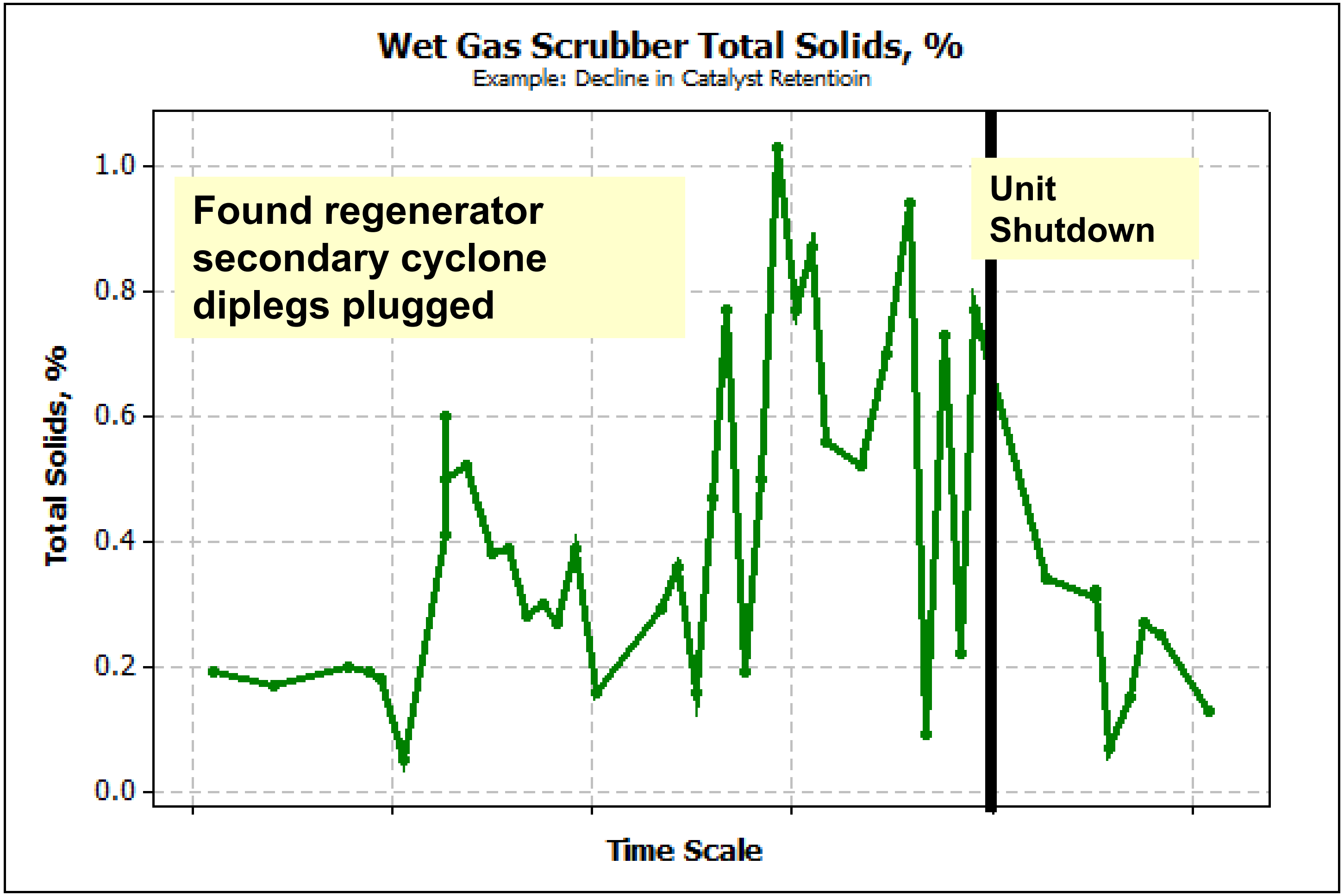

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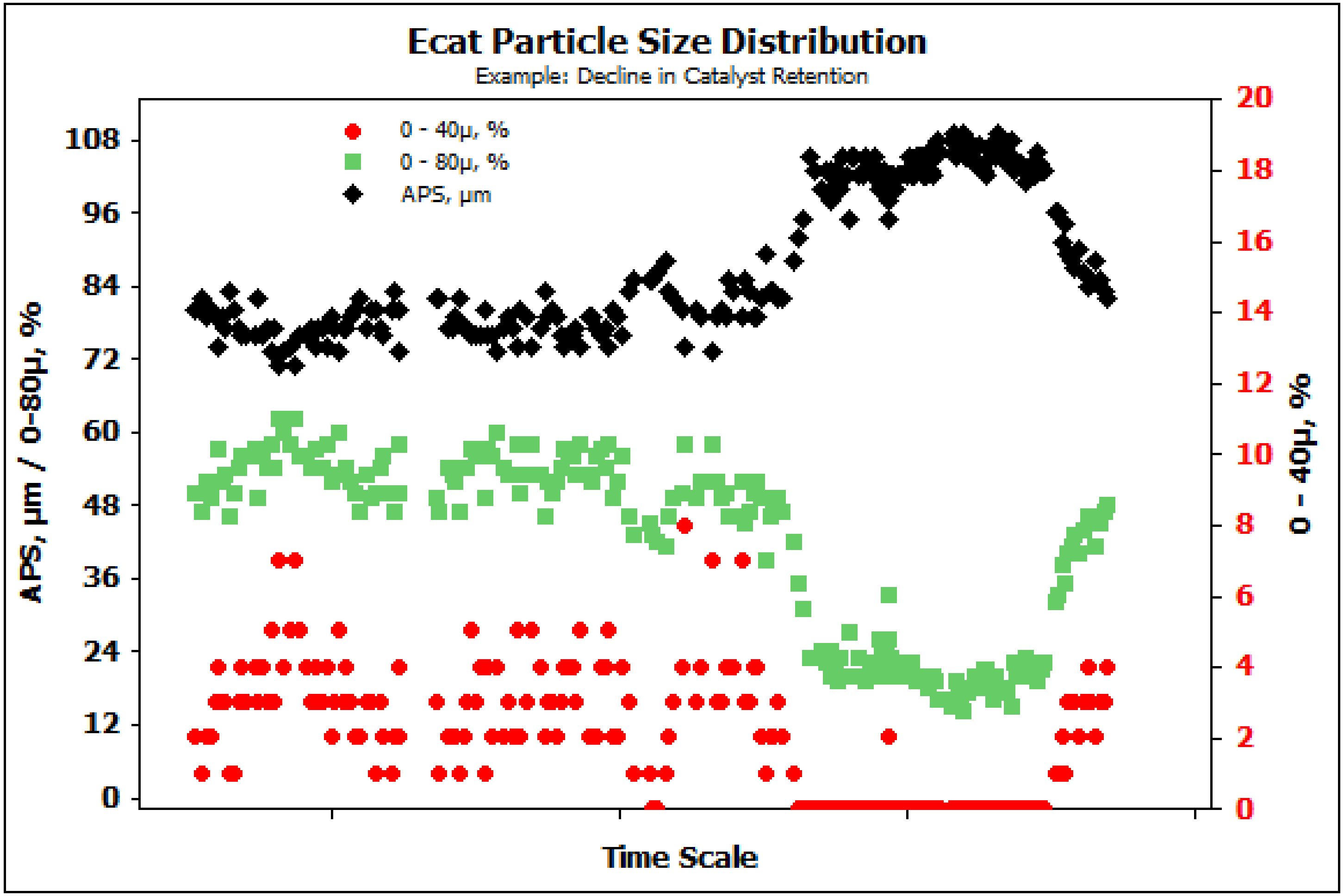
Case Study: Catalyst Retention



Fluidization

Umb/Umf (fluidization factor)

- Calculated number used to determine the fluidization capabilities of an Ecat
- Higher values represent an inventory with better flow characteristics.
- The value of a “good” Umb/Umf is unit dependent
- Number is valuable to units that struggle with catalyst circulation issues

Factors that impact Umb/Umf

- 0-45
- APS

$$\frac{U_{mb}}{U_{mf}} = \frac{2300 \times \rho_g^{0.126} \times \mu^{0.523} \times e^{(0.716F)}}{D_p^{0.8} \times g^{0.934} \times (\rho_p - \rho_g)^{0.934}}$$

✓	U_{mb}	= Minimum Bubbling Velocity, m/s	✓	F	= 0-45 μm Fraction in Catalyst
✓	U_{mf}	= Minimum Fluidization Velocity, m/s	✓	μ_g	= Gas viscosity, kg/ms
			✓	D_p	= Mean Particle Diameter = m
			✓	$\rho_{p,g}$	= Particle and Gas Properties, kg/m^3
			✓	g	= Gravitational Constant = 9.8 m/s^2

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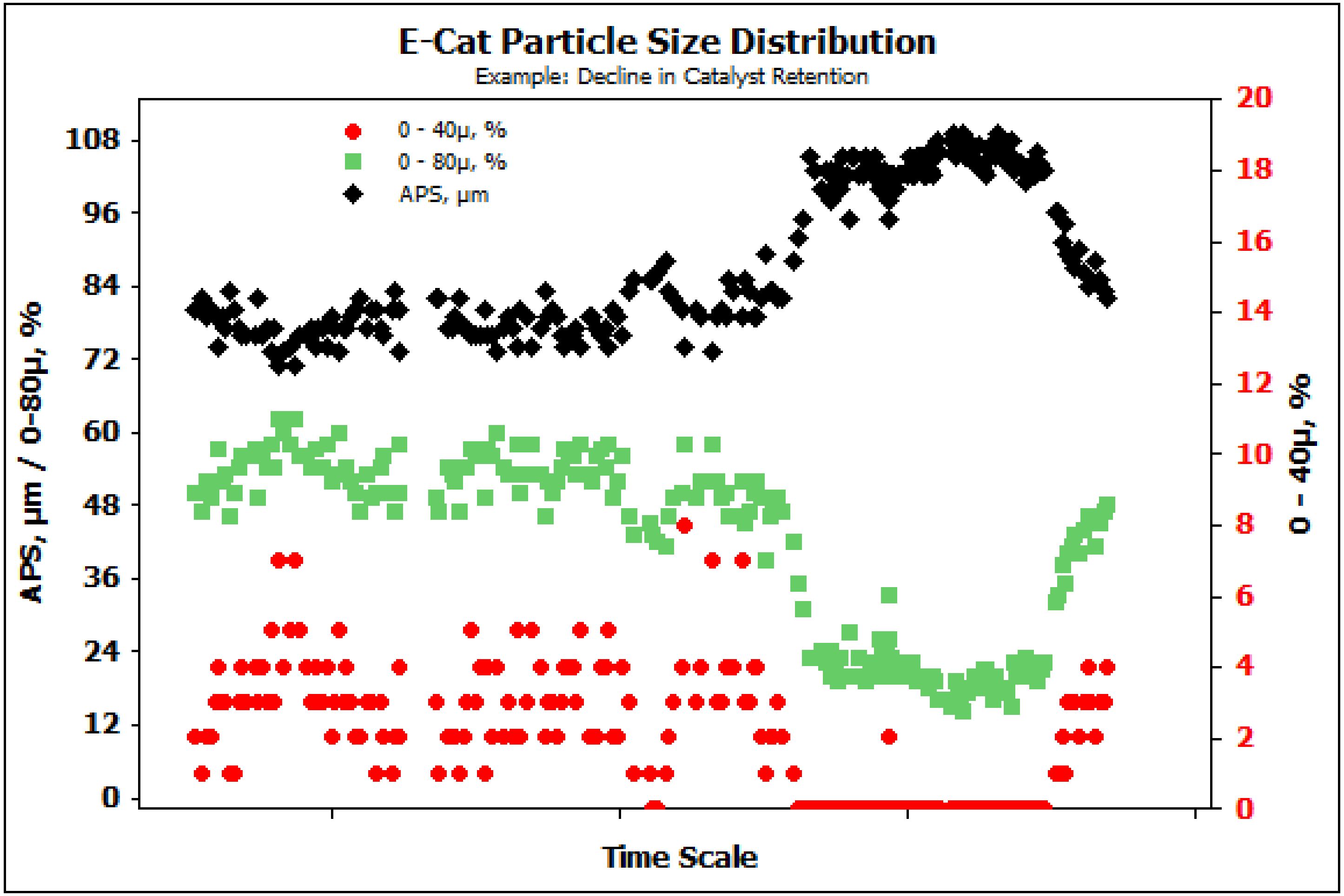
Case Study: Catalyst Retention



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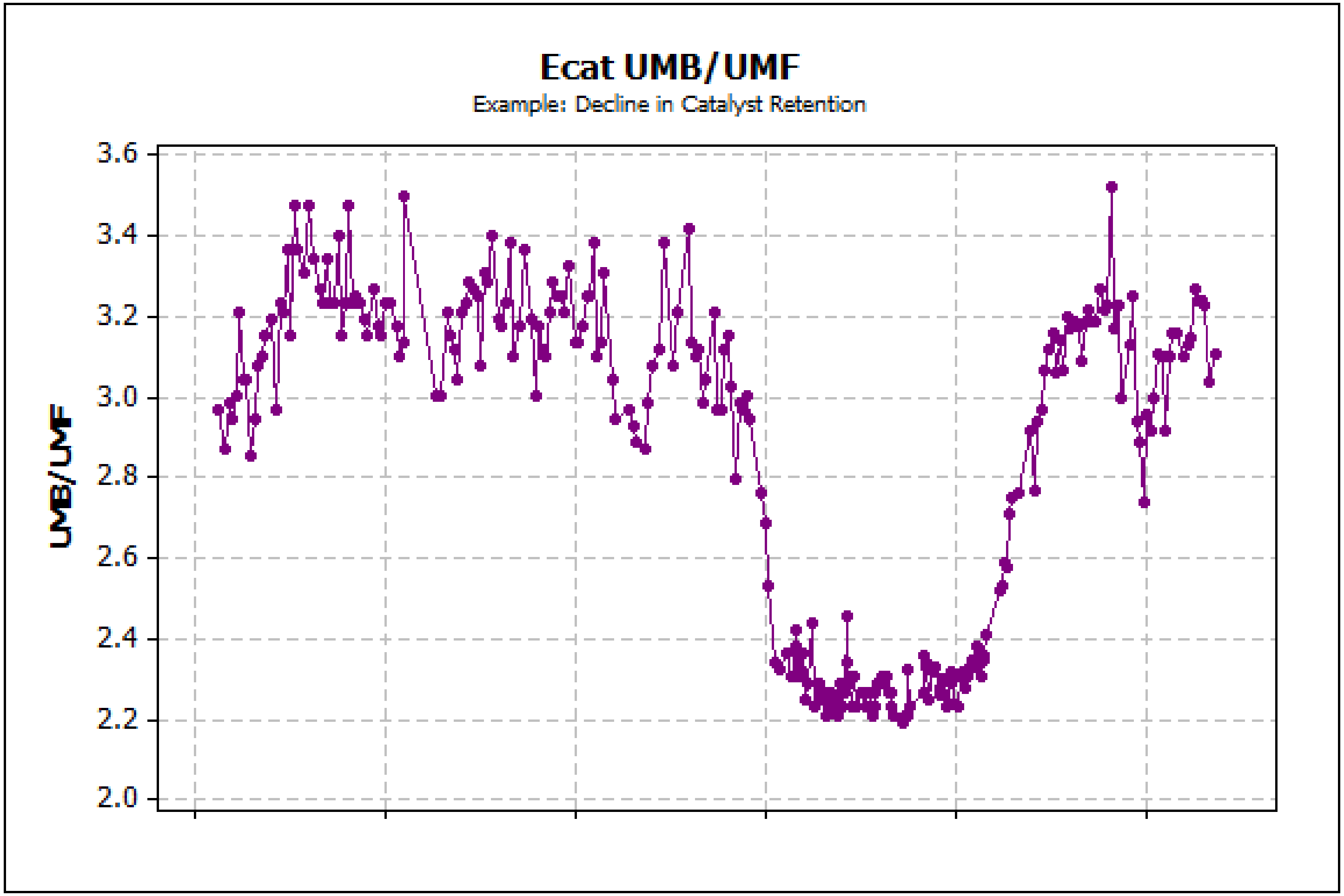

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Tracking Additive Performance – Ecat vs. Fines

SOx reducing additive effect:

- MgO
- Vanadium
- Re_2O_3

NOx reducing additives can effect:

- Cu
- Re_2O_3

ZSM5 additive effect:

- P_2O_5
- Increases in C3 and C4 olefins and gasoline octane at the expense of cat gasoline
- Increases volume gain

CO Promoter:

- Noble metal based – not typically measurable in Ecat
- May make NO_x if used in high concentrations

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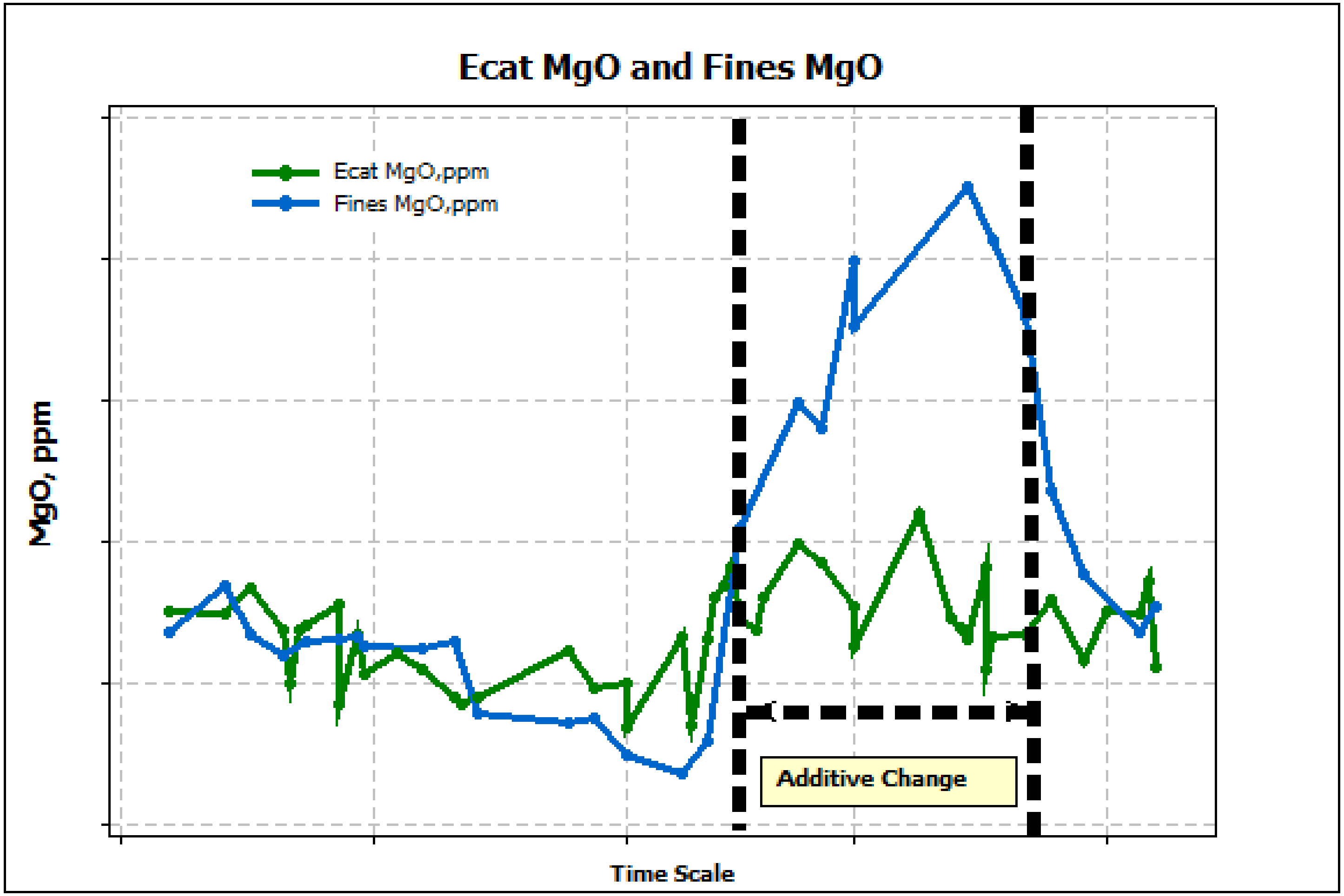
Usefulness of Ecat and Fines Analysis



Conclusion

Ecat, fines, and fresh catalyst analysis are pieces of the puzzle that can be used in troubleshooting FCCU problems

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