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Catalyst Losses and Troubleshooting

REFCOMM GALVESTON 2019

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Why are catalyst losses a problem?

- Almost **all** FCC units have experienced a catalyst loss problem!
- Main causes of elevated catalyst losses include:
  - Cyclone Problems
  - Catalyst Attrition

High catalyst losses can eventually lead to a unit shutdown due to:

- Erosion and/or pluggage in the slurry circuit
- Erosion of the flue gas equipment
- Environmental violation
- Catalyst circulation instability or inability to fluidize
- Excessive catalyst additions to maintain inventory

Catalyst Balance

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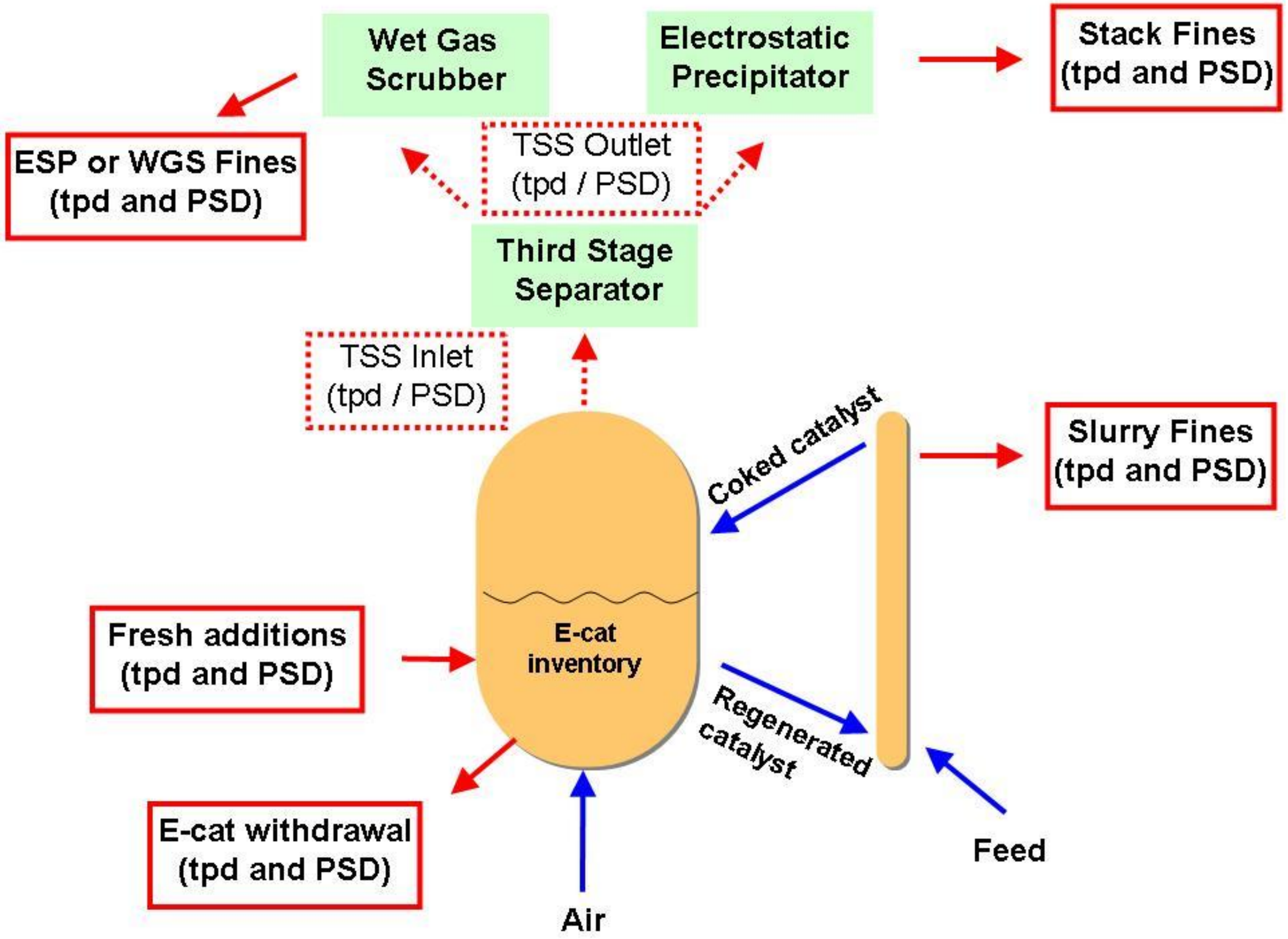
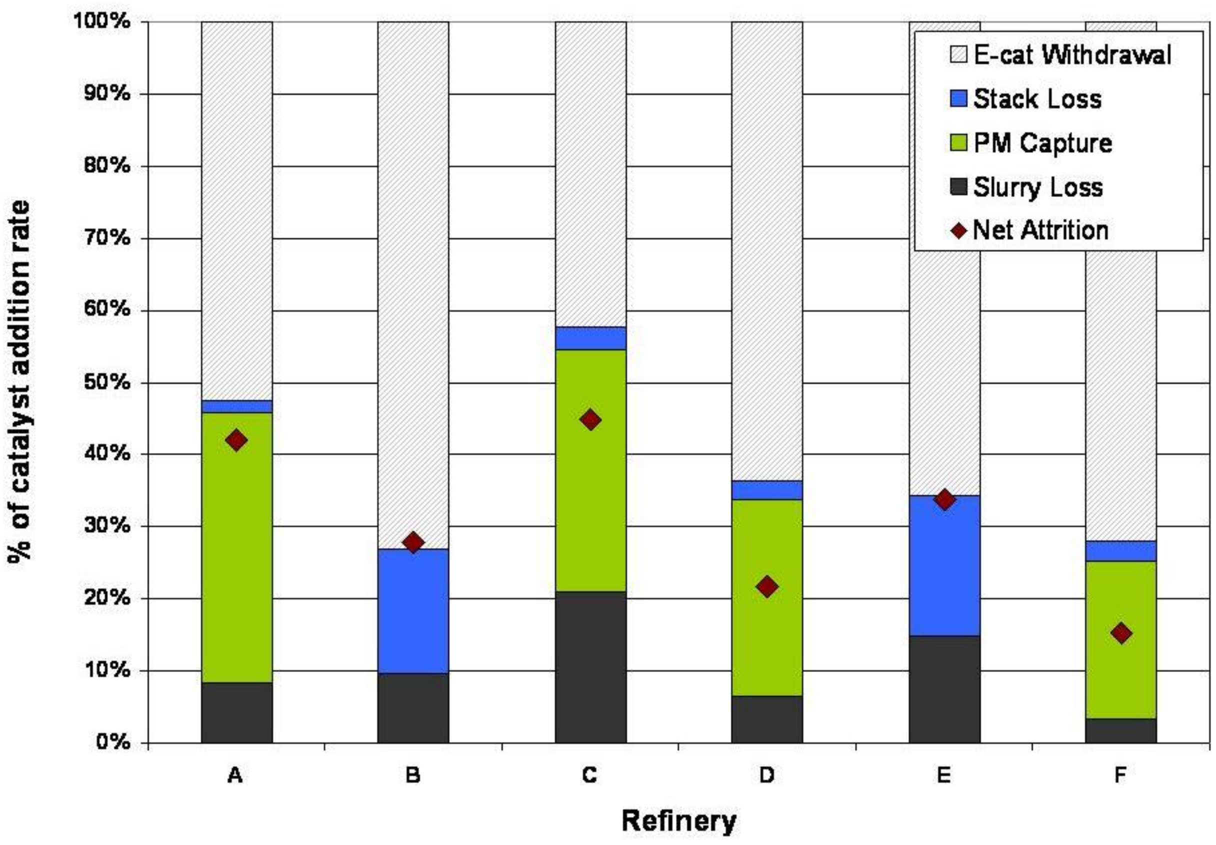
FCCU Data Collection Complete Catalyst Material Balance



- Need complete material balance and PSD of each catalyst stream
- Assumption that unit is under steady state

Catalyst Losses in Six FCCUs



- 27-58% of total catalyst addition is lost to the slurry or out the flue gas train.
- Reducing losses allows a refiner to lower catalyst addition rates
- Net Attrition is a rough measure to assess how much of the cat losses are due to attrition.

$$\frac{\sum_{i=1}^{6}\left|m_{i\_ecat} + m_{i\_losses} - m_{i\_fresh}\right|}{2}$$

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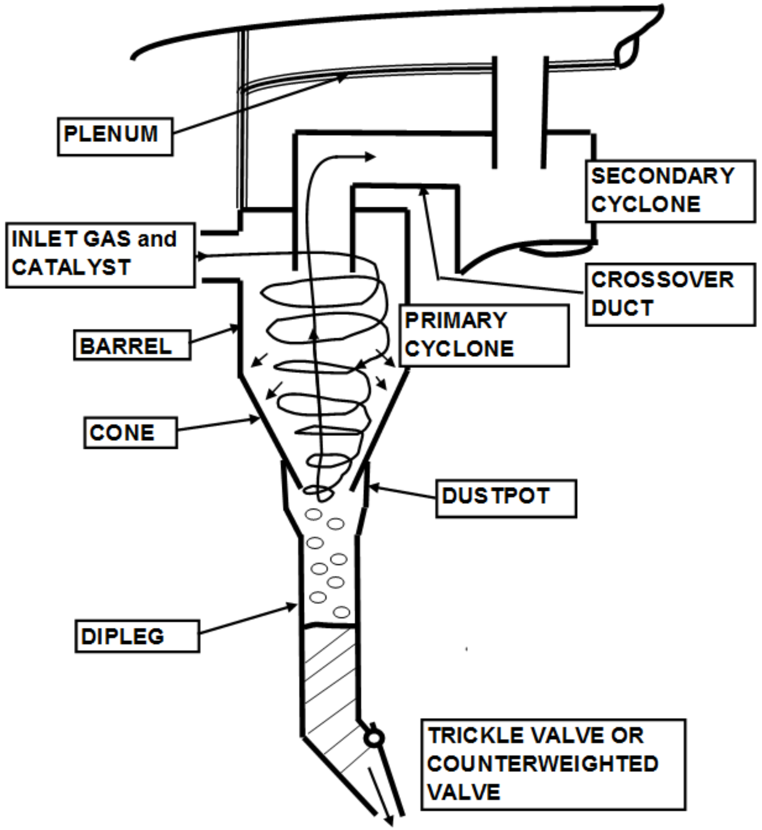
Cyclone Fundamentals

Why are Cyclone Fundamentals Important?

- Cyclones are the primary cause of mechanical concern leading into turnarounds, with **40%** of refiners anticipating cyclone repairs.
- According to an industry survey, cyclone problems account for what percentage FCC unit unplanned shutdowns!!

12%



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Cyclone Operation

- Recovery Efficiency of Two-Stage Cyclone System is high at over 99.99 %
  - Goal of **99.997+%**
- Velocity is a key operating parameter for cyclone performance:
  - **Collection efficiency** increases with velocity and then reaches a point where it drops off due to catalyst re-entrainment
  - **Catalyst attrition** to microfines occurs within cyclones and increases with velocity

Primary Cyclones	Design Maximum
Inlet Velocity	65 ft/s
Outlet Velocity	150 ft/s
Secondary Cyclones	**Maximum**
Inlet Velocity	75 ft/s
Outlet Velocity	175 ft/s

Commonly Accepted Cyclone Design Velocities

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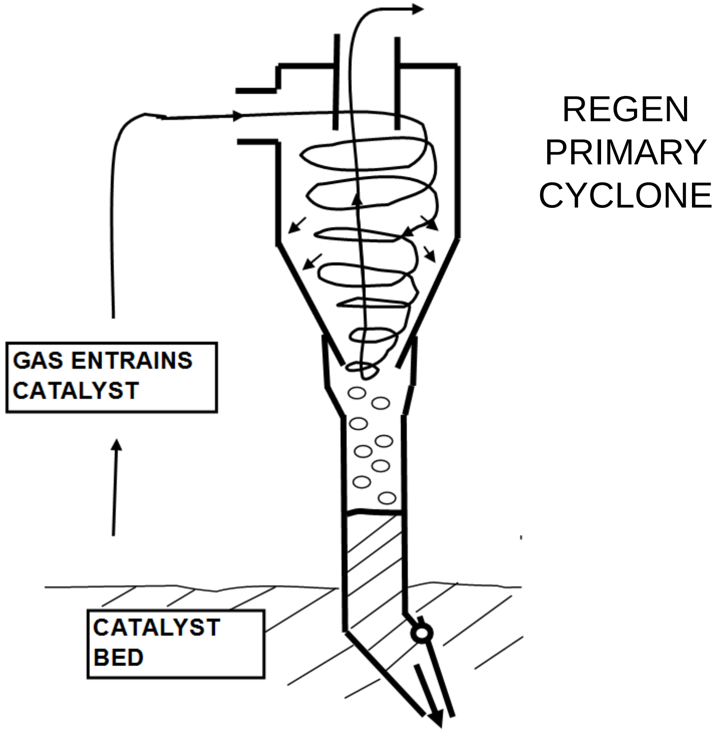
Cyclone Problems

Cyclone Flooding

- Catalyst level in a cyclone dipleg adjusts to overcome bed backpressure and cyclone pressure drop
- Reactor cyclones diplegs can be submerged or discharge into the dilute phase
- **Cyclone flooding can occur when:**
  - Catalyst loading exceeds dipleg capacity
  - Dipleg catalyst level backs up into the dust hopper/cone
  - Excessive Regen Dense Bed Level or Reactor Stripper Level
  - Excessive Catalyst Circulation Rate/Velocity



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Dipleg Malfunction

- **Plugged/Restricted Diplegs = Cyclone Flooding**
  - Mechanical or Catalyst/Chemical/Coke Deposits
    - Regen: Fe and Ca in the feed
    - Reactor: High levels of Sb & poor feed vaporization
    - De-fluidized or wet/oil soaked catalyst
    - Refractory spalling
    - Trickle or Flapper Valve stuck closed/restricted

- **Unsealed Diplegs = Gas Leakage up the dipleg**
  - Disruption of the cyclone system, catalyst re-entrainment
    - Catalyst level too low in Regenerator Dense Bed or Reactor Stripper, un-submerging diplegs (if sealed normally)
    - Trickle Valve or Flapper Valve sealing plate lost or stuck in an open position
    - Sealing plate erosion and subsequent hole through

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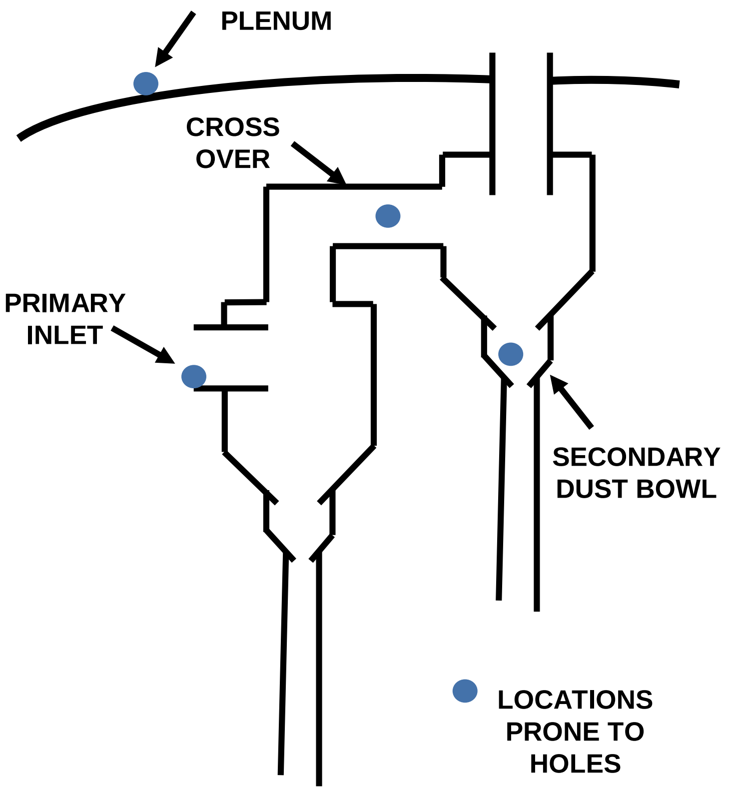
Holes in the Cyclone System

- Cyclone holes result in vapor leakage from the dilute phase and disruption/bypassing of the cyclone system
- Catalyst erosion of refractory/metal at high velocities
  - Holes almost always get bigger once formed and show a gradual increase in catalyst losses
  - Erosion more commonly seen in secondary cyclones where velocities are higher
- Cracks may be caused by thermal cycling
  - Plenum head and cyclone/dip legs cracks can be seen, especially on metal reaching end of life



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Mechanical Problems

Dipleg hole

Dipleg obstruction

Dustbowl refractory loss

Trickle valve erosion

Coke build on outlet tube

PHOTOS SOURCE: Quartis

Catalyst Attrition

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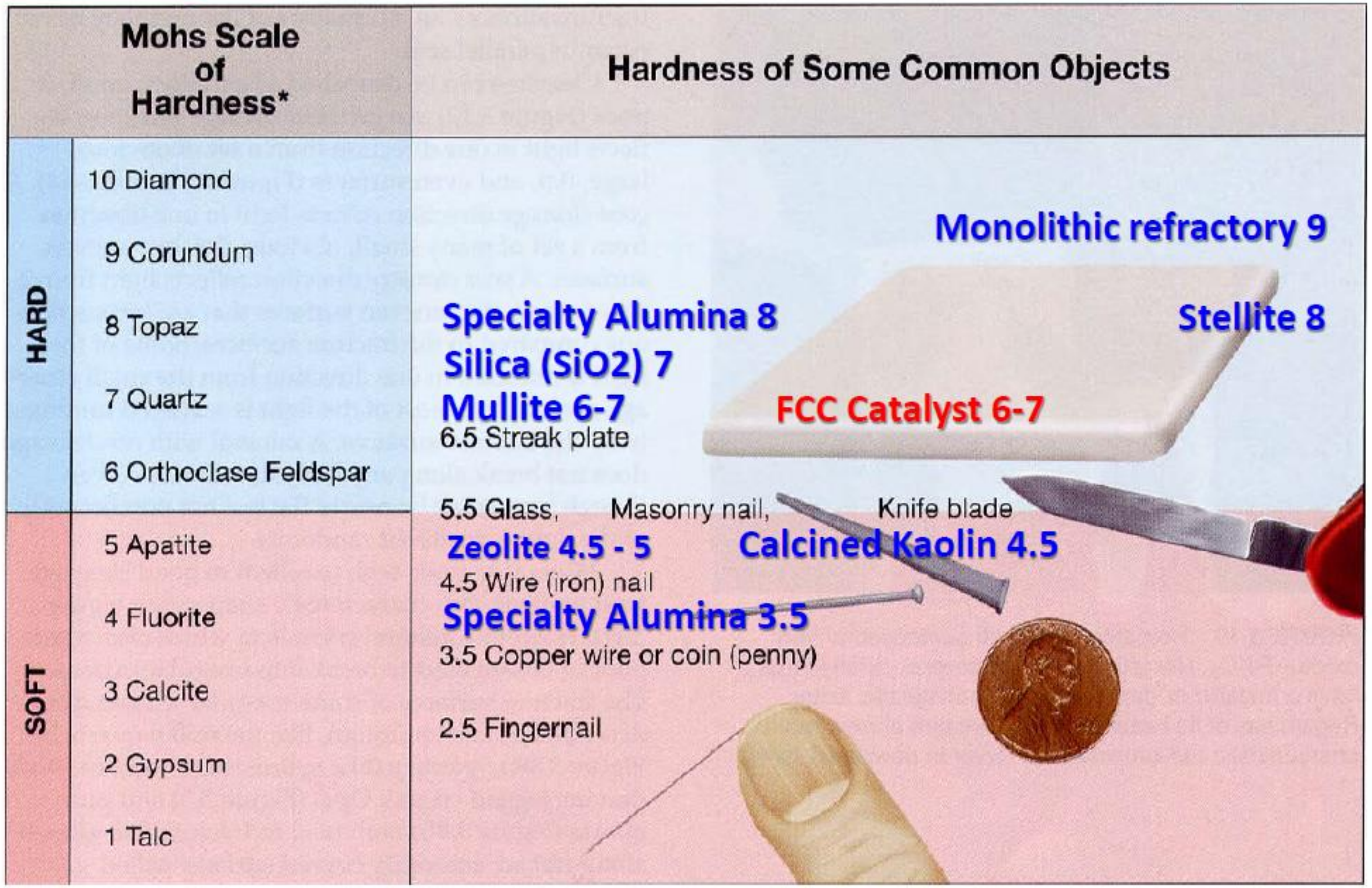
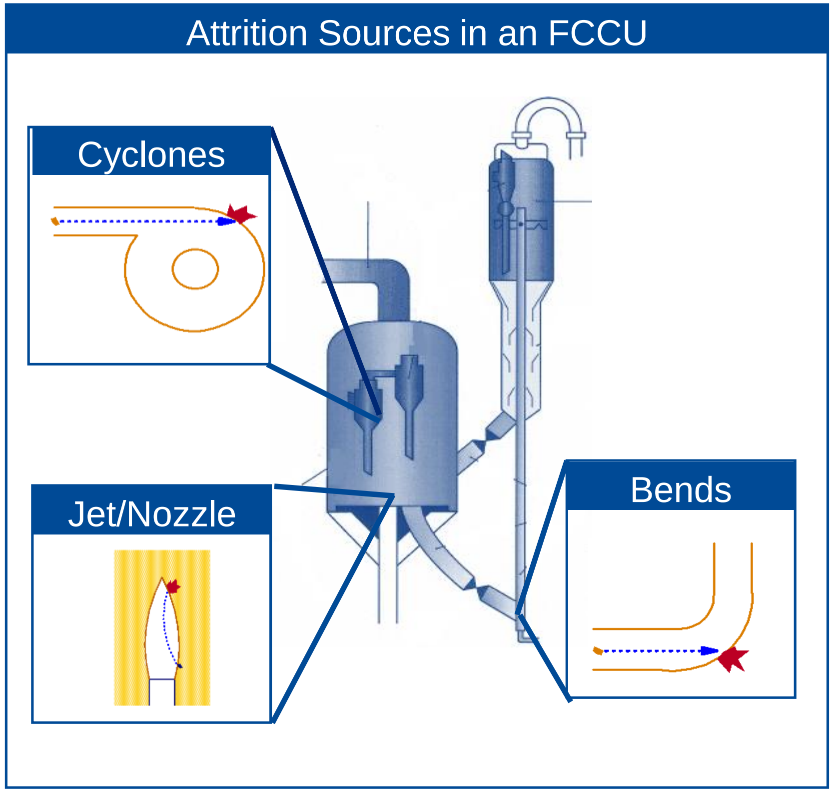
Attrition ≠ Hardness



Causes of Attrition

- **Excessive velocities**
  - Feed injectors, air grid, cyclones operating above design guidelines
- **Higher catalyst loading to cyclones**
  - Entrainment to regenerator cyclones
  - Primary (particle-particle) vs secondary (particle-wall) cyclones
- **Catalyst properties and management**
  - Unsuitable fresh catalyst attrition properties for severe units



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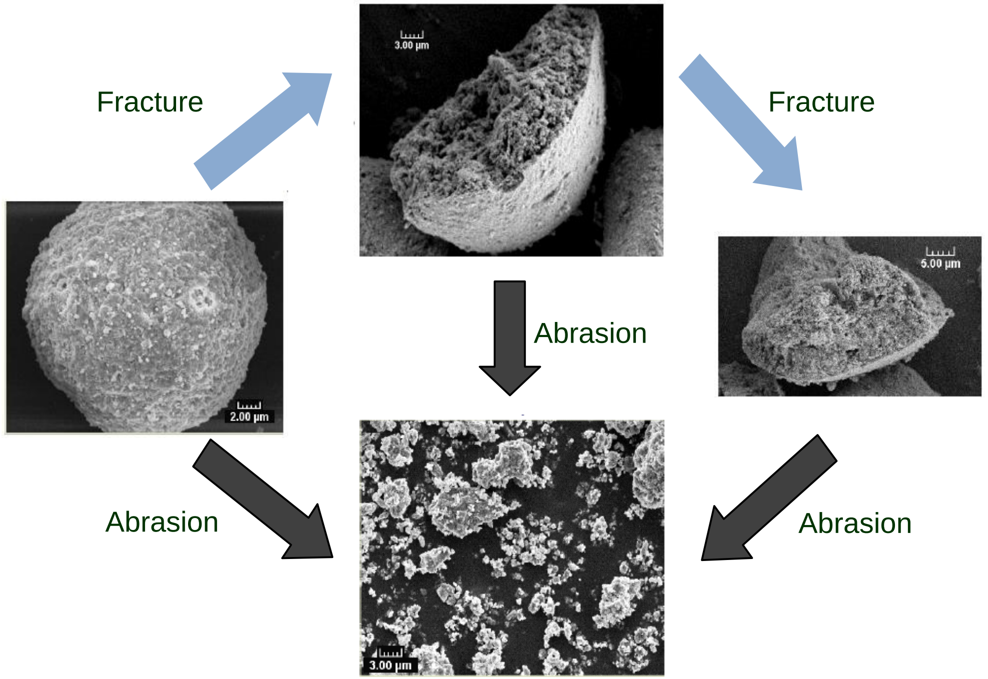
Catalyst Attrition Mechanisms

Catalyst breaks into smaller particles by fracturing and abrasion

- Large mass of catalyst impacts cyclone refractory walls
- Jets of oil/steam/air cause catalyst particles to collide against each other
- Excessive jet velocities from the air or steam distributors (>300 ft/s) and catalyst loadings to the cyclones can generate micro-fines



Attrition Properties of 6 FCCUs

Refinery	A	B	C	D	E	F
total attrition / cat adds	84%	36%	60%	25%	43%	16%
wt% Fracture	43 ± 13%	30 ± 9%	32 ± 9%	27 ± 7%	21 ± 5%	13 ± 5%
wt% Abrasion	**53 ± 14%**	**64 ± 13%**	**65 ± 11%**	**71 ± 8%**	**75 ± 7%**	**86 ± 5%**
wt% SPT	4 ± 2%	6 ± 4%	3 ± 2%	2 ± 1%	4 ± 2%	1 ± 1%

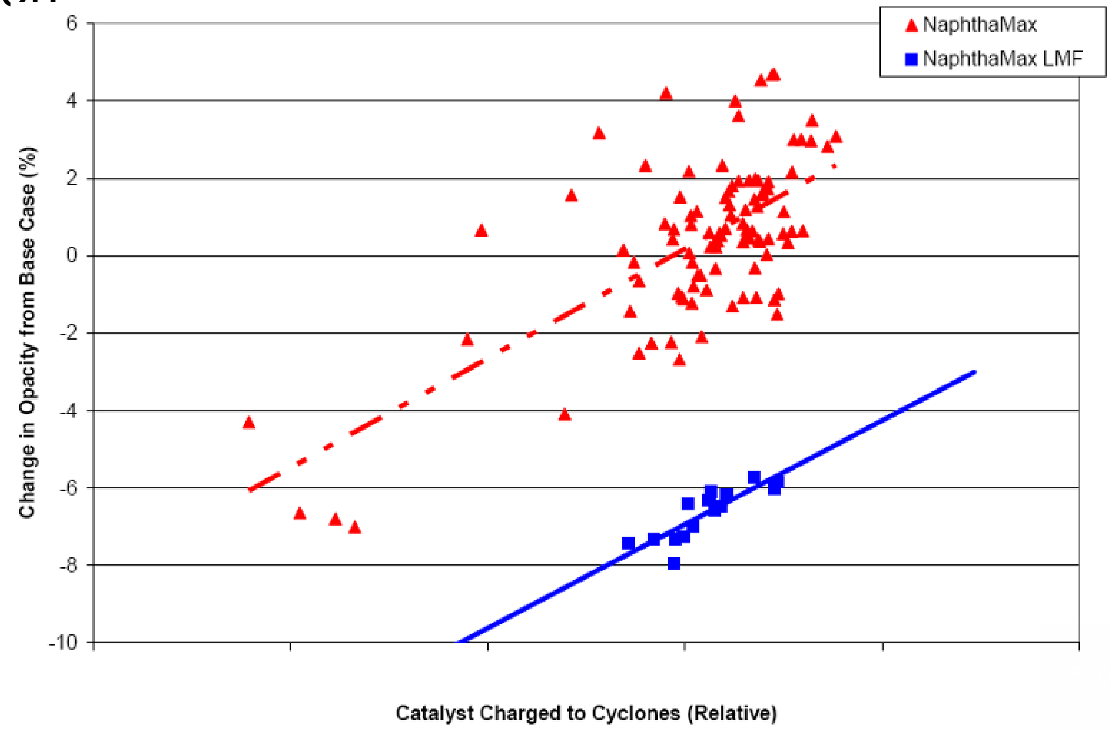
- ***Abrasion* is most important in 5 out of 6 FCCUs**
- **Total attrition accounts for all attrition transitions, even those that occur through several size bins**
- **Refinery A shows fracture and abrasion to both be important. This unit also shows the highest total attrition**

Catalyst Attrition Properties

- Minimizing micro-fines is particularly important for low stack opacity
  - Micro-fines are 0.5-2.5 micron material
  - Minimize abrasion to minimize microfines generation

Attrition is just one aspect of catalyst design and formulation

- A low catalyst attrition may be needed in some cases due to local emission limits
- Often a lower attrition requires a compromise on other aspects of catalyst performance
- Discuss the attrition requirements of your FCC catalyst with your catalyst supplier



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Identifying the Problem

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Step #1: Base Line Monitoring

GOOD BASELINE MONITORING IS ESSENTIAL!!

- Early indication of a problem and potentially minimizes ***risk***
- Troubleshoot ***before*** emissions limits are exceeded
- Potentially ***prevents costly*** equipment repairs
- Provides time to ***ask for help!***

CRITICAL MONITORING PARAMETERS

- **Catalyst Balance:**

  Catalyst Addition (fresh + additive + purchased ECAT) = Regen Losses + Reactor Losses + Withdrawals
- **PSD Samples:**

  ECAT weekly, Slurry Fines and Regenerator Fines monthly (Scrubber, ESP, 3rd Stage), Fresh catalyst and additives COAs
- **Solids Removal Rate:**

  Slurry Ash * Slurry Rundown Rate; Scrubber TSS * Purge Rate; Stack Opacity * Flue Gas Rate
- **Reactor/Regenerator Vessel Level trends on regular basis**

Step #2: Identify Losses

REACTOR

- Slurry Ash or BS&W increase
- Slurry Fines and/or ECAT PSD shift
- Increase in DP in Slurry PAR circuit
- Decrease in Delta T in Reactor Overhead Line (extreme case)
- Reactor/Regenerator Inventory Balance shift

REGENERATOR

- Stack Opacity increase
- ESP Fines Collection increase
- Scrubber TSS increase
- Scrubber Fines and/or ECAT PSD shift
- Reactor/Regenerator Inventory Balance shift

Step #3: Investigation

- Review **operating conditions:** have there been any changes? Verify catalyst balance calculations? Pressure survey changes?
- **Review the nature of the losses:**
  - ***Gradual increase*** → Attrition or cyclone hole
  - **Step change** → Mechanical failure or operating problem
  - **Intermittent** → Operating close to cyclone flooding limit
- **Take additional samples and review historical results:** ECAT and Fresh Catalyst
- **Verify Instrumentation:** Regen Level/Pressures, Reactor Level/Pressures
- **Check potential attrition sources:** Have fresh catalyst properties changed? Did the unit recently start up? Are all valves in the correct position and RO's in place? ***WALK THE STRUCTURE!***
- **Review inspection history:** Has a similar problem occurred in the past?

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Step #3: Investigation

- **Review operating data to check for a deviation from normal/original design:**
  - Sudden vessel pressure loss
  - Regenerator bed de-fluidization due to low air rate
  - Capacity creep, increased feed rate
  - Verify instrumentation, especially levels and pressures
- **Reactor cyclone flooding may be caused by:**
  - High velocity (higher feed rate, more gas, lower pressure etc.)
  - High cat circulation rate
  - High stripper level
  - Plugged/Restricted dipleg
- **Regenerator cyclone flooding may be caused by:**
  - Excessive catalyst entrainment to cyclones from bed due to high bed velocity, higher bed level, lower pressure, lower density catalyst
  - High cyclone velocity (increased air rate, lower pressure etc.)
  - Plugged/Restricted dipleg

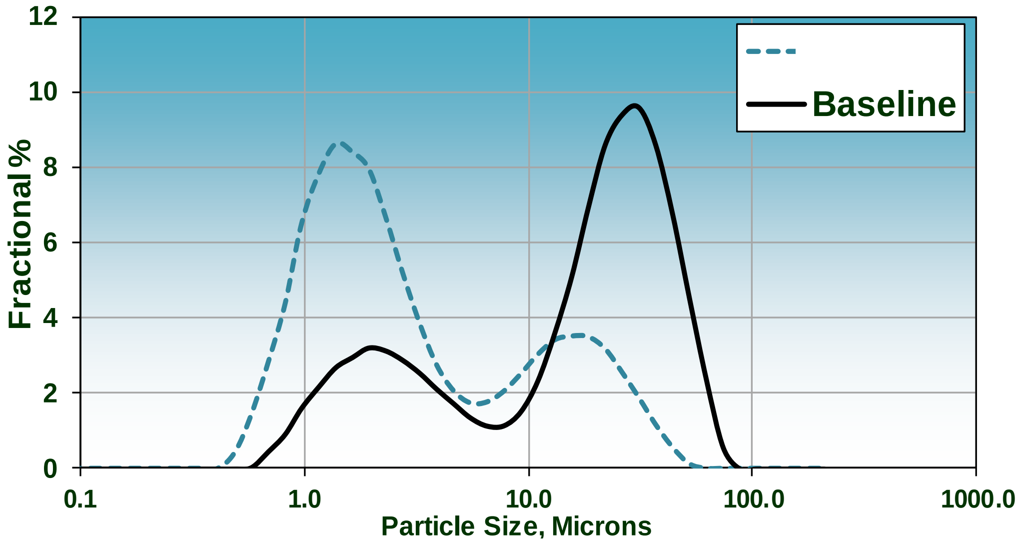
Step #4: Identifying the Problem

Fines analysis is the most useful source of data for identifying the type of loss problem!

Attrition Problem

- Gradual increase in losses
- Increased losses on **both** the Reactor or Regenerator side
- Fines will have an abnormally large peak at around **1-2 microns**
- Change in ECAT PSD showing a **increase** in fines
- PSD of Scrubber/ESP/3rd Stage/Slurry sample shows an increase in **fines** fraction

PSD of losses (Slurry Fines, 3rd Stage Fines, ESP):



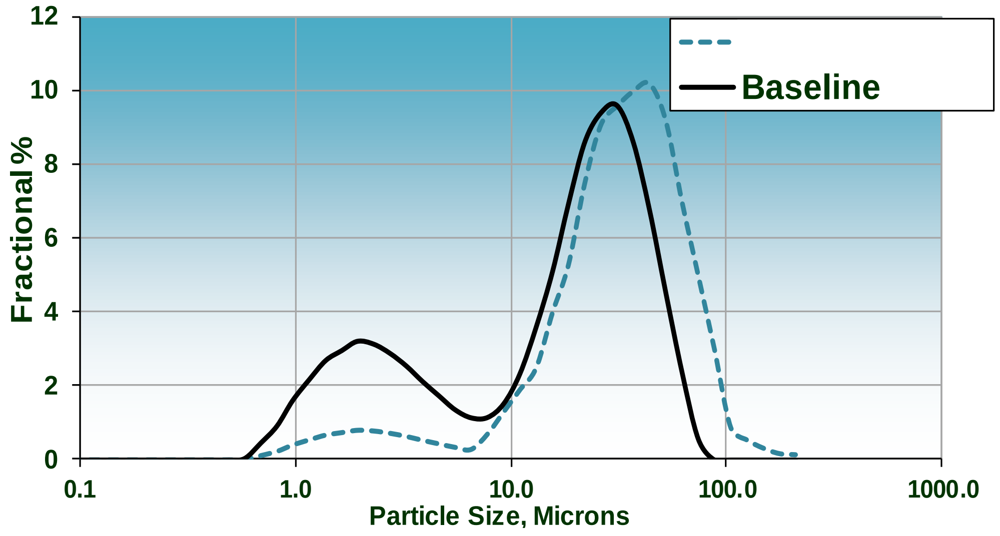
Step #4: Identifying the Problem

Fines analysis is the most useful source of data for identifying the type of loss problem!

Blocked Dipleg or Loss of Efficiency

- A step change, gradual increase, or intermittent losses from **either** the reactor or regenerator side.
- Fines will have a large than normal peak around **30-50 microns** depending on the type of cyclone problem
- Attrition peak will be **small.**
- Change in ECAT PSD showing a **decrease** in fines
  - Normal: 10 wt% < 40 µ, APS 65 µ
  - Cyclone: 6 wt% < 40 µ, APS 72 µ
- PSD of Scrubber/ESP/3rd Stage/Slurry sample shows an increase in **coarse** fraction

PSD of losses (Slurry Fines, 3rd Stage Fines, ESP):



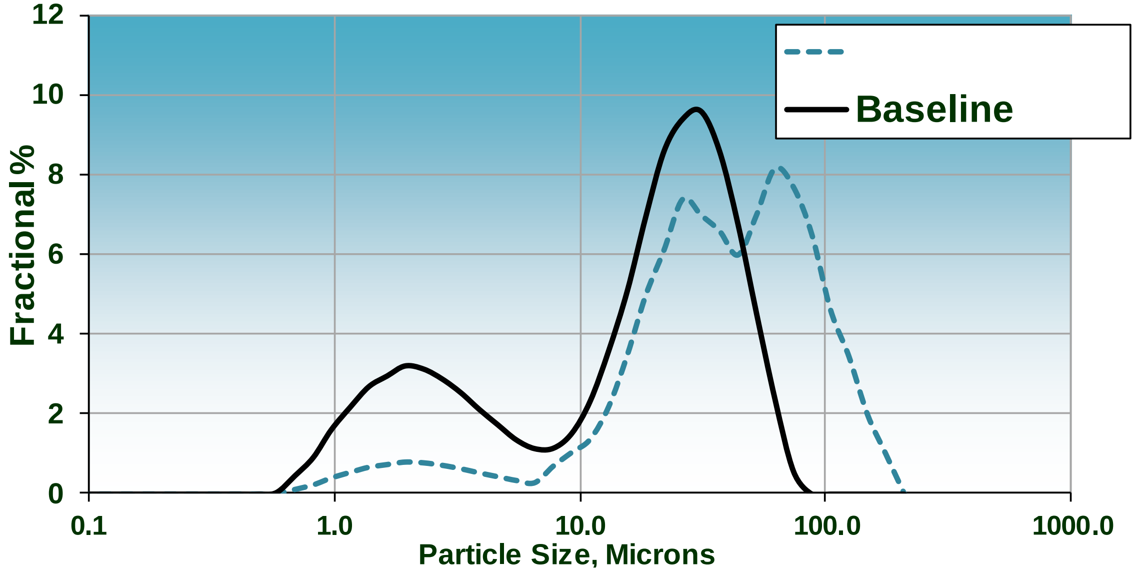
Step #4: Identifying the Problem

Fines analysis is the most useful source of data for identifying the type of loss problem!

Hole in Cyclone or Plenum

- A hole or plenum crack will often present as a gradual increase in losses from **either** the reactor or regenerator.
- ECAT fines (<45μm) will typically decrease, but can depend on the extent of the losses..
- Fines PSD will often show a **new peak** at around 70-80 microns.
- Check for a **gradual** increase in the relative size of the peak.

PSD of losses (Slurry Fines, 3rd Stage Fines, ESP):



Solving the Problem

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Path Forward - Attrition

High Velocity Jets

- Confirm that all ***RO's*** on aeration taps are in place (especially if there is a problem seen after TAR)
- ***Pressure survey*** almost always REQUIRED
- ***Verify DP*** across steam and feed rings
- Check ***torch oil*** nozzle steam
- Verify blast taps and emergency steams are ***closed***
- Problem may be due to a damaged steam sparger, feed injector, air distributor etc.
- Verify all material injected is ***dry***
- Verify ***N2 purges*** are closed where appropriate, especially after an outage
- Check flow rates and ***control valve output/position*** to see if any changes
- ***Majority*** of attrition problems are due to high velocity jets

Fresh Catalyst

- Get catalyst supplier involved ***immediately***
- ***Verify*** COA properties have not changed (PSD, bulk density, attrition index)
- Send fresh catalyst samples to separate labs for confirmation – this will take ***TIME***
- Very ***rare*** but worth checking

Excessive Circulation

- ***Sudden*** change in feed composition/drop in Regen temp
- Charge rate or reactor temperature ***increase***

Path Forward – Cyclone Problem

Cyclone Flooding - Plugged/Restricted Dipleg

- Losses will typically ***step change*** and stay consistent once equilibrium is reached
- Verify ***and reduce catalyst operating level*** if possible
    - *Unseal diplegs if possible*
- ***Pressure survey*** almost always REQUIRED
- Reduce charge rate/superficial velocity to ***reduce cyclone loading***
- ***Pressure bumping*** can sometimes clear a restriction
    - *Reduce operating level first*
    - *Reduce charge rate*
    - *4-5 psi pressure change*
    - *As quickly as practical*
    - *Proceed with* ***CAUTION***
- ***Thermal cycle*** (shutdown)

Cyclone/Dipleg Hole

- Can be ***difficult*** to verify
- Losses will increase ***gradually*** and get worse over time
- Fines PSD could look normal depending on hole location
- Pressure bumping will ***not help***
- Thermal cycling will likely make losses ***worse***
- ***Catalyst PSD adjustment*** will likely be necessary if losses are sustainable to prevent erosion of downstream equipment
- Some units can operate with a cyclone hole until an upset or pressure balance interruption

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Path Forward – Cyclone Problem

Cyclone Flooding – Poor Distribution

- Can be ***difficult*** to verify
- Losses will typically ***step change*** and stay consistent once equilibrium is reached
- ***Startup losses*** after major maintenance/revamp will be higher than expected
- Change Regen ***bed distribution***
  - Adjust Regen air grid DP, air flow rates if independently adjustable, ***reduce velocity***
  - Verify and ***reduce catalyst operating level*** if possible
- Pressure bumping could help ***temporarily***
- ***De-fluidized regions*** can migrate under a dipleg and look like a plugged dipleg

Unsealed Dipleg

- High ***startup*** losses (Regen side)
- ***Full range*** catalyst losses
- Catalyst fines will have a ***high C content*** due to low bed residence time
- Verify and ***raise operating level*** until dipleg(s) are covered
- ***Pressure bumping*** will make losses worse short term and will not help long term

Running with High Catalyst Losses

- **Conduct tests and planning**
  - Gamma scans for vessel and cyclone dipleg levels
  - Radioactive tracers for gas/catalyst flow distribution
  - Have an outage/repair plan ready to go

- **Reformulate**
  - Attrition resistant catalyst or adjusted PSD could reduce losses and maintain operation until TAR
  - Fines can be added to help circulation stability
  - Catalyst classification can help remove fines and/or coarse particles
  - Purchased ECAT can be used to maintain inventory levels

- **Mitigate**
  - Consider slurry settling aid and/or slurry recycle to manage slurry ash content and product quality
  - Monitor slurry PAR for fouling
  - Increase purge rate to lower Scrubber solids content and minimize erosion
  - Swap slurry and/or scrubber circulating pumps often
  - Recycle catalyst back from ESP/TSS
  - Adjust operating conditions, reduce charge/severity

Case Studies

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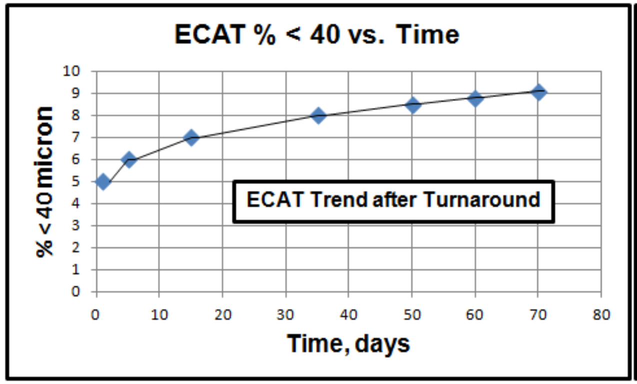
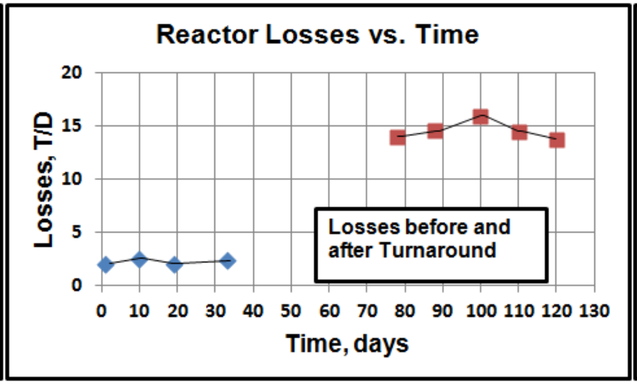
Case Studies

Attrition



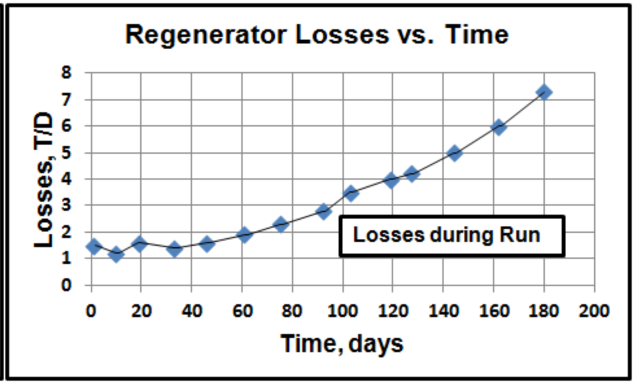
- Missing RO in torch oil nozzle steam purge line
- Catalyst attrition due to high velocity steam jet
- Double the fines content in the ECAT

Cyclone Plugging



- Refractory dropped from plenum roof and plugged a cyclone dipleg
- Losses to the main column, high slurry ash

Plenum Crack



- Cyclone plenum crack (aged plenum) opened during the run following a thermal cycle/unit shutdown
- Gradual increase in losses

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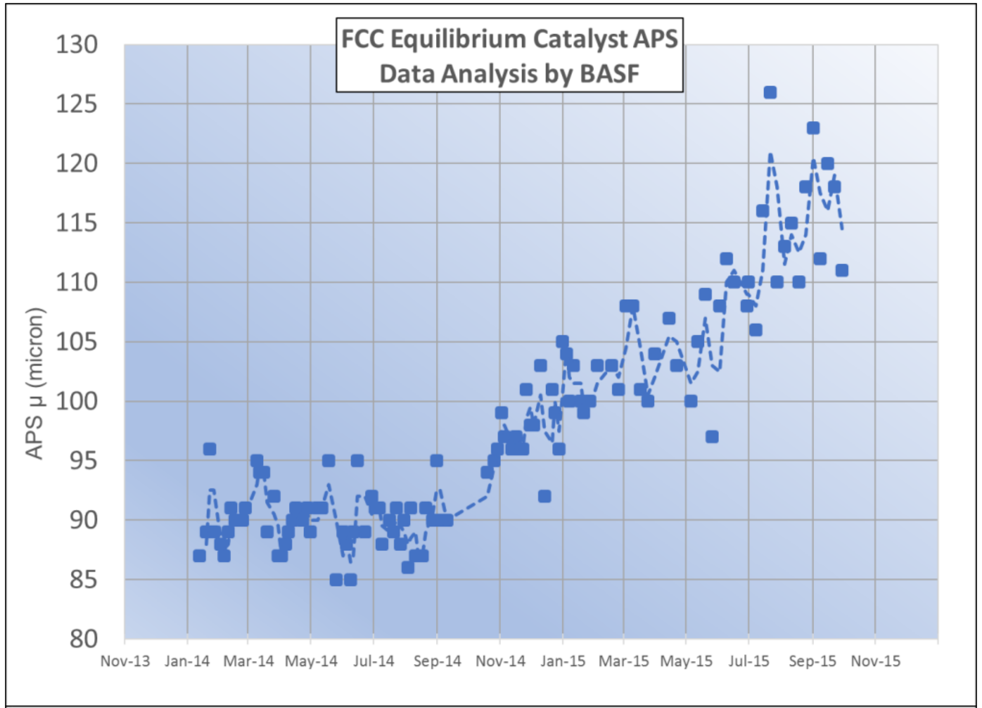
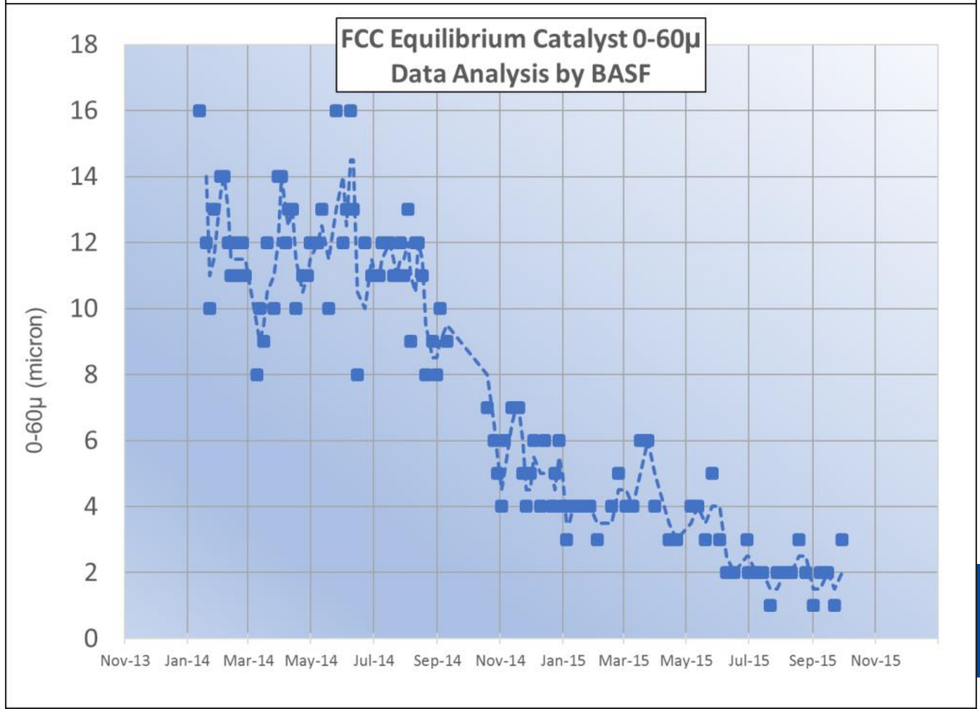
Case Study - Cyclone Holes

- **Loss Rate**
  - No initiating event
  - Gradual increase in losses over 1.5 years
  - Step change in losses following unplanned unit shutdowns
  - Multiple pressure bumps with no benefit
- **Catalyst Analysis**
  - ECAT APS increase from 90 to 125 µ
  - Scrubber fines APS increase
  - Slurry fines APS and total ash content decrease
- **Operational Impacts**
  - Reduced velocity and charge rate
  - Flue gas system erosion issues, circulation instability, loss of standpipe DP with immediate return of high DP
  - ECAT loading
  - Difficulty establishing DP in standpipes following a shutdown





Summary

- Catalyst losses can be very problematic and lead to operational issues or a unit shutdown
- Monitoring the unit and baseline operation is **key** to identifying the issue!
- Understanding cyclone fundamentals and catalyst attrition mechanisms are key to troubleshooting catalyst losses
  - **This can help prevent a unit shutdown by making the proper operational changes quickly**

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