Catalyst Losses and Troubleshooting

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May 2019
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
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.

\[
\sum_{i=1}^{6} \left| m_{i_{\text{ecat}}} + m_{i_{\text{losses}}} - m_{i_{\text{fresh}}} \right| \frac{2}{2}
\]
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!!

DID YOU KNOW? 12%
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

### Commonly Accepted Cyclone Design Velocities

<table>
<thead>
<tr>
<th>Primary Cyclones</th>
<th>Design Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Velocity</td>
<td>65 ft/s</td>
</tr>
<tr>
<td>Outlet Velocity</td>
<td>150 ft/s</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Secondary Cyclones</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Inlet Velocity</td>
<td>75 ft/s</td>
</tr>
<tr>
<td>Outlet Velocity</td>
<td>175 ft/s</td>
</tr>
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</table>
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
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
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
Mechanical Problems

Dipleg hole

PHOTOS SOURCE: Quartis

Dipleg obstruction

Coke build on outlet tube

Dustbowl refractory loss
Catalyst Attrition
### Mohs Scale of Hardness

<table>
<thead>
<tr>
<th>HARD</th>
<th>Soft</th>
<th>Hardness of Some Common Objects</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 Diamond</td>
<td>5 Apatite</td>
<td>Specialty Alumina 8</td>
</tr>
<tr>
<td>9 Corundum</td>
<td>4 Fluorite</td>
<td>Silica (SiO2) 7</td>
</tr>
<tr>
<td>8 Topaz</td>
<td>3 Calcite</td>
<td>Mullite 6-7</td>
</tr>
<tr>
<td>7 Quartz</td>
<td>2 Gypsum</td>
<td>6.5 Streak plate</td>
</tr>
<tr>
<td>6 Orthoclase Feldspar</td>
<td></td>
<td>Monolithic refractory 9</td>
</tr>
</tbody>
</table>

- **Hardness**
  - 5.5 Glass
  - Masonry nail
  - Knife blade
  - Zeolite 4.5 - 5
  - Calcined Kaolin 4.5
  - Speciality Alumina 3.5
  - 3.5 Copper wire or coin (penny)
  - 2.5 Fingernail
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
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

- **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

<table>
<thead>
<tr>
<th>Refinery</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>total attrition / cat adds</td>
<td>84%</td>
<td>36%</td>
<td>60%</td>
<td>25%</td>
<td>43%</td>
<td>16%</td>
</tr>
<tr>
<td>wt% Fracture</td>
<td>43 ± 13%</td>
<td>30 ± 9%</td>
<td>32 ± 9%</td>
<td>27 ± 7%</td>
<td>21 ± 5%</td>
<td>13 ± 5%</td>
</tr>
<tr>
<td>wt% Abrasion</td>
<td>53 ± 14%</td>
<td>64 ± 13%</td>
<td>65 ± 11%</td>
<td>71 ± 8%</td>
<td>75 ± 7%</td>
<td>86 ± 5%</td>
</tr>
<tr>
<td>wt% SPT</td>
<td>4 ± 2%</td>
<td>6 ± 4%</td>
<td>3 ± 2%</td>
<td>2 ± 1%</td>
<td>4 ± 2%</td>
<td>1 ± 1%</td>
</tr>
</tbody>
</table>
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
Identifying the Problem
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?
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)](image-url)
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):

![PSD Graph](chart.png)
Solving the Problem
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
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
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
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.