Agenda

- SCR Catalyst Basics
  - Background on SCR catalyst and design considerations
  - Provides basis for relevance of Catalyst Management
- Catalyst Management
SCR Catalyst Basics
Quick Review of SCR Basics

- **SCR** = Selective Catalytic Reduction
- Purpose is to reduce NO\textsubscript{x} (NO & NO\textsubscript{2}) from combustion exhaust
- Ammonia (NH\textsubscript{3}) is injected into flue gas as reducing agent. Flue gas passes through catalyst layers installed in a reactor
- NH\textsubscript{3} reacts with NO\textsubscript{x} on the catalyst surface to form nitrogen and water vapor

\[
\begin{align*}
4\text{NO} + 4\text{NH}_3 + \text{O}_2 \xrightarrow{\text{Catalyst}} 4\text{N}_2 + 6\text{H}_2\text{O} \\
2\text{NO}_2 + 4\text{NH}_3 + \text{O}_2 \xrightarrow{\text{Catalyst}} 3\text{N}_2 + 6\text{H}_2\text{O}
\end{align*}
\]

Flue Gas: NO\textsubscript{x}, O\textsubscript{2}, SO\textsubscript{2}

NH\textsubscript{3}

N\textsubscript{2}, H\textsubscript{2}O, O\textsubscript{2}, SO\textsubscript{2}(SO\textsubscript{3})
SCR Configuration in Power Plants

High Dust
- SCR upstream of air preheater and ESP
- High concentration of fly ash in exhaust
- Catalyst with higher pitch required

Low Dust
- SCR between ESP and air preheater
- Low concentration of fly ash
- Catalyst with smaller pitch can be suitable
Catalyst Types

Plate  Honeycomb  Corrugated
Plate-type Catalyst

Composition
- Stainless steel carrier, ceramic material rolled on
- TiO₂, V-oxide/W-oxide/Mo-oxide as the active catalytic material
- Notches (corrugations) formed into plates to provide separation
- Inserted in element boxes with variable spacing: 60 to 90 plates
- Variable plate height: 450 to 625 mm

Advantages
- Ideal for high dust configurations
- Plugging resistance
- Low pressure loss
Honeycomb Catalyst

Composition
- Homogeneously extruded ceramic with square-opening cell structure
- TiO$_2$, V-oxide and W-oxide as the active catalytic material
- Variable block height: 1200+ mm
- 8 to 14 cpsi for coal-fired applications

Advantages
- Ideal for low/no dust applications
- High active surface area per unit volume
Catalyst Pitch

**Pitch = center to center distance from one plate/wall to the next**

**Plate-Type Structure**
- Flexible plates
- Rectangular Openings
- Pitch: 5 mm to 7 mm

**Honeycomb Structure**
- Rigid structure
- Square openings
- Pitch: 6.7 mm to 9.2 mm
Pitch Selection vs Dust Load

<table>
<thead>
<tr>
<th>Dust Load gr/dscf</th>
<th>Plate Pitch</th>
<th>Honeycomb Pitch</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;2</td>
<td>5.0 mm</td>
<td>6.7 mm (22 Cell)</td>
</tr>
<tr>
<td>2 – 6</td>
<td>5.5 mm</td>
<td>7.4 mm (20 Cell)</td>
</tr>
<tr>
<td>6 – 10</td>
<td>6.0 mm</td>
<td>8.2 mm (18 Cell)</td>
</tr>
<tr>
<td>10 – 12</td>
<td>6.2 mm</td>
<td>9.2 mm (16 Cell)</td>
</tr>
<tr>
<td>&gt;12</td>
<td>6.5 mm</td>
<td>NA</td>
</tr>
</tbody>
</table>
Catalyst Modules

- Catalyst elements arranged in steel frames
- Plate – 2 levels of 8 element boxes
- Honeycomb – 72 monoliths
- Standardized cross-section
- Possible to interchange catalyst types within reactor
- Module height varies with catalyst height
Catalyst Design Considerations

- **SCR Reactor**
  - Initial catalyst charge or reload
  - Reactor size – layers, modules per layer
  - Plant configuration – high dust / low dust

- **Flue Gas Operating Conditions**
  - Operating Temperature
  - Fuel Characteristics
  - Fly ash concentration

- **Performance Requirements**
  - Amount of NO\textsubscript{x} to reduce and operating life
  - NH\textsubscript{3} slip allowed, 2 ppm standard
  - SO\textsubscript{2} oxidation allowed
  - Pressure drop limit, < 1.0” wc per layer
Required Reactor Potential

- Minimum catalytic potential required to achieve desired DeNO$_x$ and NH$_3$ slip rates for given operating period

\[ \text{RP} = \frac{k_t}{AV} \]

- Catalyst deactivates with time, \( k_0 \rightarrow k_t \) (time at end of life)

- Fresh catalyst activity, \( k_0 \), depends on
  - Catalyst formulation \( \rightarrow V_2O_5 \)
  - Temperature
  - Flue gas composition – H$_2$O, O$_2$, SO$_2$

- Iterative process to determine required AV and k
Catalyst Deactivation Mechanisms

Masking:
Macroscopic blockage of catalyst surface by cemented fly ash

Plugging:
Microscopic blockage of pore system by small fly ash particles

Poisoning:
Deactivation of active sites by chemical attack
Catalyst Poisons

- Arsenic – vapor phase $\text{As}_2\text{O}_3$
- Phosphorus – $\text{P}_2\text{O}_5$
- Alkali metals – Na, K
Relative Activity, $k_t/k_0$

- Initially ($t=0$), $k_t/k_0 = 1.0$
- $k_t/k_0$ decreases with time (exponentially decaying model)
- Characteristic of SCR configuration, fuel, deactivation mechanisms.
- Obtained from catalyst activity monitoring
- Have $k_t \rightarrow k_0$ or have $k_0 \rightarrow k_t$

<table>
<thead>
<tr>
<th>Application</th>
<th>time, hr</th>
<th>$k_t/k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Low dust config</td>
<td>16000</td>
<td>0.80 - 0.85</td>
</tr>
<tr>
<td>Bituminous firing</td>
<td>16000</td>
<td>0.70 - 0.75</td>
</tr>
<tr>
<td>PRB firing</td>
<td>16000</td>
<td>0.65 - 0.70</td>
</tr>
<tr>
<td>Lignite firing</td>
<td>16000</td>
<td>0.50 - 0.55</td>
</tr>
</tbody>
</table>
Effects of Sulfur in Fuel

- SO$_2$ oxidation, undesired side reaction in SCR catalyst
  \[ 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 \]
- Rate depends on T and catalyst formulation
- Occurs in the bulk mass of catalyst material

SO$_3$/H$_2$SO$_4$ aerosols cause the “Blue Plume”

- SO$_3$ reacts with NH$_3$ to form ammonium bisulfate (ABS) and ammonium sulfate (AS)
  \[
  \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4 \quad (\text{ABS}) \\
  \text{NH}_4\text{HSO}_4 + \text{NH}_3 \rightarrow (\text{NH}_4)_2\text{SO}_4 \quad (\text{AS}) \\
  2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow (\text{NH}_4)_2\text{SO}_4 \quad (\text{AS})
  \]
- AS is dry, powdery compound
- ABS is sticky, viscous compound that can plug catalyst and foul other equipment
SO₂ Oxidation – Influence of V₂O₅

- Relative Activity
- Relative Oxidation Rate

\( k_{\text{NOx}} \)

\( k_{\text{SOx}} \)

V₂O₅ content [wt-%]
Minimum Operating Temperature, ($T_{\text{min}}$)

- Minimum temperature for NH$_3$ injection
- Of particular concern for low load operation and firing fuels containing sulfur
- Operating above $T_{\text{min}}$ prevents AS/ABS formation
- $T_{\text{min}}$ depends on SO$_3$, NH$_3$, H$_2$O in flue gas
- Must stop NH$_3$ injection when operating below $T_{\text{min}}$
Catalyst Management Goals

- Maintain target NO$_x$ reduction of the SCR system
- Control NH$_3$ slip below required limit
- Replace activity potential lost to catalyst deactivation
- Optimize use of catalyst activity potential
- Conform catalyst replacements to plant outage schedule
- Conform to plant budgetary constraints
- Maximize operating life between catalyst replacements
- Prevent excessive pressure loss
Catalyst Management Plan (CMP)

- Schedule for maintaining SCR catalytic potential for NO\textsubscript{x} reduction
- Process of adding, replacing, cleaning catalyst
- Tailored to fit unit performance based on activity monitoring
CMP, 2 + 1 Example

Relative Reactor Potential

Operating Time (h)

NH₃ slip (ppm)

Minimum potential for DeNOx, NH₃ slip requirements
Activity Monitoring

- Routine catalyst activity testing
- Once per year (typically)
- Pull samples from each installed catalyst layer
- Determine relative activity compared to fresh catalyst
- Determine rate of catalyst deactivation
- Predict when reactor potential reaches minimum level
- Verify or adjust CMP schedule
CMP Actions

- Install new catalyst

- Onsite (in situ) Cleaning – removing fly ash/LPA buildup
  - Vacuuming
  - Air blowing
  - Shaking/vibration
  - Water washing

- Rejuvenation – onsite or offsite washing/chemical treatment
  - Remove ash/particles from catalyst pores
  - Remove water soluble poisons

- Regeneration – offsite chemical treatment
  - Remove chemically bonded poisons – As, P
  - Replace active catalytic material
# Pros/Cons for CMP Options

<table>
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<tr>
<th>CMP Action</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
<tbody>
<tr>
<td>New Catalyst (Catalyst Supplier)</td>
<td>Longest operating life&lt;br&gt;Performance guarantees</td>
<td>Highest Cost Option</td>
</tr>
<tr>
<td>Cleaning (by Owner)</td>
<td>Low(est) cost option&lt;br&gt;Can be done in situ</td>
<td>Lowest activity restoration&lt;br&gt;Limited extension of life</td>
</tr>
<tr>
<td>Rejuvenation (Service Supplier)</td>
<td>Lower cost than new catalyst&lt;br&gt;Can be done onsite</td>
<td>Does not restore to “new” activity, limited life extension&lt;br&gt;Performance guarantees?</td>
</tr>
<tr>
<td>Regeneration (Service Supplier)</td>
<td>Lower cost than new catalyst&lt;br&gt;Can restore to “new” activity</td>
<td>Done offsite, may need spare catalyst&lt;br&gt;May increase SO₂ conversion&lt;br&gt;Performance guarantees?</td>
</tr>
</tbody>
</table>
Considerations for CMP Options

- CMPs are unit-specific

- Economic Trade-offs: New vs Regen
  - Lower cost for Regen, shorter operating life
  - Higher cost for New, longer operating life
  - Spare catalyst layer on-hand may be required to replace catalyst removed for regen
  - Catalyst supplier offers performance guarantees for new catalyst
  - Does regen supplier offer guarantees for Regen’d catalyst?

- Consider which options conform best to plant outage schedule
  - Cleaning/rejuvenation may not extend catalyst life to next outage
  - Consider operation with lower DeNO$_x$, higher NH$_3$ slip
  - Consider impact to plant emission standards
Catalyst Mixing

- Standardized module structure – catalyst mixing is possible and common
  - Multiple catalyst types in reactor
  - New and regen’d
  - Multiple suppliers

- Consider tooling requirements
  - Lifting, transport tooling for unloading/loading
  - Sealing systems

- Performance Guarantees from new supplier (other than initial)
  - Layer guarantees – geometry, durability, activity, SO₂ conversion, pressure drop – based on fuel and flue gas characteristics
  - System guarantees – DeNOₓ, NH₃ slip, operating life – based on total reactor potential → requires info about existing catalyst
Required Info for Existing Catalyst

- Geometry
  - Catalyst type
  - Volume
  - Specific area, m²/m³

- Activity Trends
  - Fresh catalyst, initial activity – k₀
  - Relative/absolute activity after exposure to flue gas
  - Age of catalyst at time of testing

- Above info used to . . .
  - Calculate existing reactor potential
  - Determine rate of deactivation
  - Develop CMP
Plant Operation Considerations

- Control Ash buildup
  - Sootblowers/Sonic horns
  - Cleaning/vacuuming during outages

- Uniform NH$_3$/NO$_x$ distribution
  - AIG Tuning
  - Maintain NH$_3$ injection nozzles

- Limit injecting NH$_3$ below Tmin
  - Short time operation OK (< 8 hr, 100 hr/yr)
  - Period below Tmin must be followed by higher Temp operation (>350 °C for 8 hours)

- Effects of Operating changes on SCR performance
  - Fuel changes
  - Economizer modification
Thank You!

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