Worldwide Pollution Control Association

Duke Energy Seminar
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Concord, NC

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Agenda

- **Catalyst 101**
  - Catalyst Basics
  - Catalyst Types
  - Catalyst Modules
  - Design Considerations

- **Catalyst Management**
  - Catalyst Activity Monitoring
  - Wash, Regenerate, or New
  - SCR Housekeeping
  - Plant Operation Considerations
    - Operation below the catalyst $T_{\text{min}}$
SCR Basics

- **SCR = Selective Catalytic Reduction**

- Propose is to reduce NOx from flue gas.

- A reducing agent, most commonly ammonia (NH₃), is injected into the flue gas as a reducing agent.
  - The NH₃ is mixed into the gas stream, sometimes using mixing plates.
  - The mixed gas then passes through the catalyst layers where the NH₃ reacts with NOx on the catalyst surface and in the pores to form N₂ and H₂O vapor.

Flue Gas: NOx, SOx, CO₂, O₂

N₂, H₂O, O₂, SO₂, (SO₃)
SCR Basics

High Dust
- SCR upstream of air preheater / ESP.
- High concentration of fly ash in exhaust, > 1,000 mg/Nm³.
- Catalyst with a plate pitch > 5.0 mm.

Low Dust
- SCR after ESP and before air preheater.
- Low concentration of fly ash in the exhaust < 500 mg/Nm³.
- Catalyst with a plate pitch < 5.0 mm.
Types of SCR Catalyst

- Plate
  - Rolled
  - Coated
- Honeycomb
  - Extruded
  - Coated
- Corrugated
  - Composite
  - Hybrid

Composition: Titania catalyst support with Vanadium as principal active component, with other promoters, including Tungsten
Plate-type Catalyst

Manufacture
- Stainless steel carrier, ceramic material rolled on.
  - TiO$_2$, V-oxide/W-oxide as the active catalytic material. Active materials rolled on with ceramic material or coated on later.
  - Other promoters used, Mo-oxide.
- Notches (corrugations) formed into plates to provide separation.
- Inserted in element boxes with variable spacing to set pitch: 60 to 90 plates.
- Variable plate height: 450 to 625 mm

Application
- Both low dust and high dust configuration.
Honeycomb Catalyst

Manufacture
- Homogeneously extruded ceramic with square-opening cell structure.
  - TiO$_2$, V-oxide/W-oxide as the active catalytic material. Active materials extruded with ceramic material or coated on later.
- Variable block height: 1,200+ mm.

Application
- Both low dust and high dust configuration.
Corrugated Catalyst

Manufacture
- Plate carrier is corrugated to provide plate separation. It is fused with TiO₂ and fibers.
- A controlled pore volume is generated.
- V-oxide/W-oxide as the active catalytic material are impregnated generating a homogeneous ceramic.
- A full plate hardening promoter is added.
- Monolith inserted in element boxes.
- Variable plate height: 200 to 550 mm

Application
- Both low dust and high dust SCR.
Catalyst Advantages

Plate
- Low pressure loss

Honeycomb
- High active surface area per unit volume

Corrugated
- High active surface area per unit volume
- Low $\text{SO}_2$-oxid. per unit activity
Catalyst Pitch

Plate Pitch = center to center line form one plate/wall to the next

Plate-type structure
- Flexible plates
- Rectangular opening
- Wall thickness: 0.6 to 0.8 mm
- Pitch: 5 to 7 mm

Honeycomb structure
- Rigid
- Square openings
- Wall thickness: 0.4 to 0.9 mm
- Pitch: 2 to 9.2 mm

Hybrid plate-type structure
- Rigid
- Corrugated openings
- Wall thickness: 0.4 to 1.1 mm
- Pitch: 2 to 12 mm
# Pitch Selection vs. Dust Load

<table>
<thead>
<tr>
<th>Dust Load</th>
<th>Plate Pitch</th>
<th>Honeycomb Pitch</th>
<th>Corrugated Pitch</th>
</tr>
</thead>
<tbody>
<tr>
<td>gr/dscf</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt; 2</td>
<td>5.0 mm</td>
<td>6.7 mm (22 cell)</td>
<td>5.8 mm</td>
</tr>
<tr>
<td>2 to 6</td>
<td>5.5 mm</td>
<td>7.4 mm (20 cell)</td>
<td>7.2 mm</td>
</tr>
<tr>
<td>6 to 10</td>
<td>6.0 mm</td>
<td>8.2 mm (18 cell)</td>
<td>8.3 mm</td>
</tr>
<tr>
<td>10 to 12</td>
<td>6.2 mm</td>
<td>9.2 mm (16 cell)</td>
<td>9.3 mm</td>
</tr>
<tr>
<td>&gt; 12</td>
<td>6.5 mm</td>
<td>NA</td>
<td>&gt; 9.3 mm</td>
</tr>
<tr>
<td>12 to 16</td>
<td>6.5 mm</td>
<td>NA</td>
<td>10.3 mm</td>
</tr>
<tr>
<td>16 to 20</td>
<td>6.5 mm</td>
<td>NA</td>
<td>12 mm</td>
</tr>
</tbody>
</table>
Catalyst Modules

- Catalyst elements arranged in and one steel frames.
  - Plate – 2 levels of 8 element boxes
  - Honeycomb – 72 monoliths
  - Corrugated – 2 to 3 levels of 8 element boxes.

- Standardized cross-section module
  - Possible to interchange corrugated and plate element boxes in most modules.

- Possible to interchange catalyst types within reactor

- Module height varies with catalyst monolith height
Catalyst Design Considerations

- **Performance Requirements**
  - NOx reduction (80 – 95%) and operating life (8,000 to 24,000 hours).
  - NH3 slip allowed, 2 to 5 ppm.
  - SO2 oxidation allowed, 0.1 to 1.0% per initial catalyst charge.
  - Pressure drop limit, usually 1 to 1.5” wc per layer.

- **Flue Gas Operating Conditions**
  - NOx concentration
  - Fuel characteristics
  - Fly ash concentration

- **SCR Reactor**
  - Initial catalyst charge
  - Reactor size – layers, catalyst depth, modules per layer
  - Plant configuration – high or low dust, AIG only, AIG/Mixers
Catalyst Management Goals

- Maintain target NOx reduction while maintaining NH₃ slip below required limits.
- Maintain catalyst active at the highest level for the longest period of time with the lowest economic impact.
- Replace lost catalyst activity by utilizing either washed, regenerated, or replaced catalyst potential.
- Conform catalyst activity potential replacement to plant outage schedule and budgetary constraints.
- Prevent excessive SO₂ conversion and pressure loss.
Catalyst Management Plan (CMP)

- Schedule for
  - SCR inspection and cleaning
  - AIG tuning
  - catalyst activity sampling
  - maintaining SCR catalyst potential
- Process for adding, replacing, and cleaning the catalyst
- With the above tailored to fit required NOx performance and outage schedule requirements for your unit and company.
Activity Monitoring

- When?
  - Once a year is typical

- Where?
  - Each layer
  - Area of highest dust loading

- How?
  - Bench or pilot scale

- Conditions?
  - Standard or unit specific, makes no differences as long as $k_o$ is known at test conditions.
  - Activity testing at different temperatures can indicate deactivation mechanism.
What Reduces Catalyst Activity?

Constituents from Fossil Fuel Combustion

- Vapors
  - Mg, Na, K, SO₂, As, etc.
- Molten Ash Droplets
- Solid Particles
Catalyst Deactivation

Masking: blocking catalyst surface

Fouling: physical pore blockage

Physical - ash and other solid particles
Catalyst Deactivation

- Chemical poisons that physically mask, foul and plug the catalyst surface and pores.
  - Arsenic – vapor phase condensation ($\text{As}_2\text{O}_3$).
  - Ammonium bisulfate (ABS) condensation.
  - Calcium - oxide ($\text{SO}_4$).
  - Vanadium sulfate.
Catalyst Deactivation

- Poisons that chemically bond to the active site.
  - Arsenic – vapor phase condensation (As$_2$O$_3$)
  - Alkali Metals – Na, K
  - Phosphorous – P$_2$O$_5$

- Flue gas vapors that deplete active metals.
  - HCl / HF
  - H$_2$SO$_4$, (acid dew point)
Relative Activity Loss

- Activity, $k_t/k_o$, decreases with time from 1.0 (exponentially decaying model).
- Decay depends on SCR configuration and design.
- Decay depends also on fuel, flue gas dust loading, flue gas composition along with ash composition.
- Deactivation usually takes place from the top down.
- Compare catalyst activity loss with chemical analysis.
Typical Relative Activity Loss

<table>
<thead>
<tr>
<th>Application – High Dust</th>
<th>Time, hr</th>
<th>Relative Activity, $k_t/k_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Eastern Bituminous firing</td>
<td>24,000</td>
<td>0.70 – 0.75</td>
</tr>
</tbody>
</table>

**Activity over Time**

- **Layer 2 Catalyst**
- **Layer 3 Catalyst**

*Red Line - Catalyst Design Activity required for 90% Reduction*
## Typical Relative Activity Loss

<table>
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<tr>
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<th>Time, hr</th>
<th>Relative Activity, $k_l/k_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRB firing</td>
<td>16,000</td>
<td>0.65 – 0.70</td>
</tr>
<tr>
<td>Lignite firing</td>
<td>16,000</td>
<td>0.50 – 0.55</td>
</tr>
<tr>
<td>Bituminous with 10 – 20% bio-fuels co-firing</td>
<td>24,000</td>
<td>0.70 – 0.75</td>
</tr>
<tr>
<td>Bio-fuels firing</td>
<td>10,000</td>
<td>0.30 – 0.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Application - Low Dust</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>24,000</td>
<td>0.85 – 0.95</td>
</tr>
</tbody>
</table>
Activity Monitoring

- Determine
  - relative activity compared to fresh catalyst
  - deactivation rate of catalyst
- Predict when reactor potential (Po) reaches minimum level
- Adjust CMP as required.

Relative Catalyst Activity Prediction

Expected Catalyst Replacement

2+1 beds - Base

![Graph showing relative catalyst activity and NH3-slip over operating hours.](image)
CMP Actions / Options

- Plant could water wash – removes ash particles from catalyst surface / pores and some poisons.
CMP Actions /Options

- **Plant Water Washing (Pros)**
  - Can be done in situ and many times
  - Many times, so far (9) times on the same catalyst charge
  - Restores catalyst activity
    - Amount depends on application and poisons
    - Relative activity experience after cleaning
      - Bituminous – 0.80 to 0.90
      - PRB – 0.90 to 1.0
      - Bio-fuels - 0.90 to 1.0

- **Plant Water Washing (Cons)**
  - No guarantee on restored activity, performance or service life
  - Service life is limited (In situ cleaning results in less activity gain)
  - Could remove active metals over time if not careful
Plant Water Washing Results

Bituminous - High Dust

- DI Water
- Warm DI Water
- 0.05 M Acid Solution

PRB – High Dust

- Sample 1
- Sample 2
- Sample 3

Catalyst Activity

Before washing □ After washing
CMP Actions / Options

- **Regeneration – offsite chemical treatment**
  - Remove chemically bonded poisons – As and others
  - Replace active catalytic promoters

- **Regeneration (Pros)**
  - Can restore catalyst activity to near new levels
  - Lower cost than new catalyst??

- **Regeneration (Cons)**
  - Done offsite, may need spare catalyst
  - Reduces catalyst porosity (poison resistance could be lowered)
  - May increase SO$_2$ oxidation
  - Performance guarantees??
CMP Actions / Options

- Install New Catalyst

Pros
- Longest operating life
- Highest poison resistance
- Lowest SO$_2$ conversion per unit activity
- Performance and service life guarantees provided

Cons
- Highest cost option??
CMP Actions / Options

- Economic Trade-offs:
  - Washed vs. New
    - No guarantees of performance or service life.
    - Both performance / service life based on experience.
    - Cost savings achieved could be wiped out by a shorter operating life, lower performance and unexpected unit outages.
  - Regenerated vs. New
    - How will regenerated catalyst respond with reduced porosity?
    - Are performance and service life guarantees provided?
    - Will SO₂ conversion increase?
    - Cost savings achieved can be wiped by a shorter operating life, lower performance and one unexpected unit outage.
CMP Actions / Options - Bottom Line

- CMP are unit specific

- What needs to be considered is which option conforms best to your company’s / plant’s
  - NOx performance / compliance strategy
  - and outage schedule requirements.
Catalyst Mixing

- Catalyst mixing is possible and common
  - Standard module structure (not identical)
  - Multiple catalyst types in reactor
    - New (multiple suppliers), washed, regenerated

- Considerations
  - Lifting tools
  - Module sealing system

- Performance guarantees
  - Layer guarantees – activity, potential, deactivation, $SO_2$ oxidation, pressure drop, mechanical service life
  - Reactor guarantees – NOx reduction, $NH_3$ slip, operating life, $SO_2$ oxidation, pressure drop – req. information on existing catalyst
SCR Housekeeping

- Control ash build up
  - Inspect Soot blowers, Sonic Horns regularly.
  - Clean, air blow, and vacuum reactor during outages.
  - Remove excessive LPA from catalyst protective screens.
SCR Housekeeping

- Maintain NH$_3$/NOx distribution
  - Inspect injection nozzles regularly.
  - Control ash build up in, on and around mixer elements.
  - Tune AIG as required or at least annually.
  - Inspect SCR seals for NH$_3$ bypass.
SCR Housekeeping

- Maintain SCR ducts
  - Inspect Inlet duct, mixers, turning vanes, rectifier and catalyst at least annually.

- Control ash build up in ducts, turning vanes, rectifiers, etc.
Plant Operation Considerations

- SO$_2$ oxidation (slow reaction)
  - 2 SO$_2$ + O$_2$ → 2 SO$_3$ (Blue Plume)
  - Kinetically controlled, increases with vanadium content and flue gas temperature.
  - Low SO$_2$ conversion rates < 0.05 % with high catalyst activity and Poper layer, is possible.
  - Excessive Alkali metals and Fe deposits will increase SO$_2$ conversion.

- SO$_3$ reacts with NH$_3$ to form ammonium bisulfate (ABS) and ammonium sulfate (AS)
  - NH$_3$ + SO$_3$ + H$_2$O → (NH$_4$)$_2$HSO$_4$ (ABS)
  - NH$_3$ + NH$_4$HSO$_4$ → (NH$_4$)$_2$SO$_4$ (AS)
  - 2NH$_3$ + SO$_3$ + H$_2$O → (NH$_4$)$_2$SO$_4$ (AS)

- AS is a dry powdery compound
- ABS is sticky, viscous compound
Plant Operation Considerations

- Minimum Operating Temperature ($T_{\text{min}}$) for NH$_3$ injection
  - Concern for low load operation firing fuels containing sulfur
  - Depends on SO$_3$, NH$_3$, H$_2$O in the flue gas
  - Operation above $T_{\text{min}}$ prevents AS/ABS formation
Plant Operation Considerations

- NH₃ injection below the T_{min} is possible for a continuous and intermittent period.
- Duration depends on:
  - Catalyst
  - Fuel sulfur content
  - Flue gas temperature, SO₃, NH₃, and H₂O composition
  - NOx performance upon return
- Typically, for 8 hours below T_{min}, 8 hours above T_{min}
- No NH₃ injection at or below the bulk ABS dew point, approx. 40 degrees below T_{min}
Thank You!

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Reference – for Plate and Honeycomb catalyst information and pictures
1) Jeffers, Ken; “SCR Catalyst Management; WPCA/Ameren, ESP and SCR Seminar. Effingham, IL; August 20, 2008”