Reinhold Environmental Ltd.

2008 NOx-Combustion Round Table & Expo Presentation

February 4-5, 2008 in Richmond, VA
Quick Review of SCR Basics

- SCR = Selective Catalytic Reduction
- Purpose is to reduce NO\(_x\) (NO & NO\(_2\)) from combustion exhaust
- Ammonia (NH\(_3\)) is injected into flue gas as reducing agent. Flue gas passes through catalyst layers installed in a reactor
- NH\(_3\) reacts with NO\(_x\) on the catalyst surface to form nitrogen and water vapor

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

Flue Gas: NO\(_x\), O\(_2\), SO\(_2\)

NH\(_3\)

N\(_2\), H\(_2\)O, O\(_2\), SO\(_2\)(SO\(_3\))
1. External diffusion of \( \text{NH}_3 \) to catalyst surface
2. Internal diffusion of \( \text{NH}_3 \) into the catalyst pore
3. \( \text{NH}_3 \) adsorption on the active centers
4. NO diffusion from gas phase to adsorbed \( \text{NH}_3 \)
5. Reaction of NO and \( \text{NH}_3 \) to \( \text{N}_2 \) and \( \text{H}_2\text{O} \)
6. Desorption from \( \text{N}_2 \) and \( \text{H}_2\text{O} \) to catalyst surface
7. Diffusion of \( \text{N}_2 \) and \( \text{H}_2\text{O} \) into gas phase
SCR Applications

- Waste Incineration Plants
- Heavy Duty Vehicles
- Greenhouses
- Wood-Fired Boilers
- Power Plants
- Gas Turbines
- Marine Engines
- Stationary Engines GEN SETS

NOx Control
**SCR Configuration in Power Plants**

### High Dust
- SCR upstream of air preheater and ESP
- Catalyst with higher pitch required

### Low Dust
- SCR between ESP and air preheater
- Catalyst with lower pitch can be suitable

### Tail End
- Mostly in Europe, none in US(?)
- SCR at the end after air preheater
- Flue gas reheating required
Geometry Selection: Plate-Type Catalyst

Composition
- Stainless steel carrier, ceramic material rolled on
- TiO₂, V-oxide/W-oxide/Mo-oxide as the active catalytic material
- Variable plate-spacing: 60 to 100 plates per element box
- Variable plate height: 450 to 700 mm

Advantages
- Most suitable for high dust configurations
- Thermal and mechanical resistance
- Low pressure loss
- Low SO₂/SO₃ conversion rate
Geometry Selection: Honeycomb Catalyst

Composition

- Homogeneously extruded ceramic
- TiO$_2$, V-oxide and W-oxide as the active catalytic material
- Variable monolith height: 250 mm – 1000 mm
- 10 to 100 cells per square inch (cpsi)

Advantages

- Most suitable for low/no dust applications
- Operating temperature range: 340° F - 800° F
- High active surface area per unit volume
Geometry: Structure & Pitch

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

Honeycomb Structure
- Rigid structure
- Square openings
- Pitch: 3 mm to 8 mm

Pitch = center to center distance from one plate/wall to the next
Pitch Selection vs Dust Load

<table>
<thead>
<tr>
<th>Catalyst Type</th>
<th>High Dust</th>
<th>Low Dust</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plate</td>
<td>5 mm – 7 mm</td>
<td>&lt;5 mm</td>
</tr>
<tr>
<td>Honeycomb</td>
<td>8 mm</td>
<td>4 mm – 5 mm</td>
</tr>
</tbody>
</table>
Geometry Selection: Module Structure

- Catalyst elements arranged in steel-frame modules
- Standardized cross-section
- Module height can vary as required
- Possible to interchange catalyst types within reactor
- Modules can be customized to customer requirements
Catalyst Design Approach

- Starting Point
  - New SCR reactor vs existing SCR reactor
  - Initial catalyst charge or reload
  - SCR reactor layout - # of layers, # of modules per layer
  - SCR configuration – high dust / low dust

- Desired operating period, 16000/24000 hrs

- Understand performance requirements
  - DeNOx, amount of NO\textsubscript{x} to reduce, 70 - 90%
  - SO\textsubscript{2} oxidation allowed, <0.5% per catalyst layer
  - NH\textsubscript{3} slip allowed, 2 ppm standard (5 ppm for low S fuel)
  - Pressure drop limitations, 0.5 - 1.0” WC

- Determine catalyst activity required at end of operating period (EOL)

- Specify appropriate catalyst to do the job: Volume, element height, pitch
Details of the Design Process

- $\eta_{NOX} = f\{k_{NOX} (EOL), \text{area velocity (AV), NH}_3/NO_x \text{ ratio (} \alpha )\}$

- Calculate maximum AV (gas flow per total active surface area)

- Select pitch $\Rightarrow$ sets the catalyst specific area, $A_{spec} = \text{area/volume}$

- Determine required volume

- Adjust volume as necessary to fit the application

- Determine $SO_2$ oxidation rate, pressure drop

$$Vol_{cat} = \frac{V_{FG}}{AV*A_{spec}}$$
$k_{NOx}$ of Fresh Catalyst, $k_0$

- $k_0$ depends on
  - Temperature
  - Composition of active, catalytic material $\Rightarrow V_2O_5$
  - $H_2O$, $O_2$, flue gas flow rate

- $k_0$ data and correction factors are obtained from controlled experiments
Catalyst Activity vs Temperature

Temperature, F

\[ \text{NH}_3 + \text{O}_2 \rightarrow \text{NO}_x \]

(Side reaction at higher T)

Temperature, F

kNOx, m/h

High V2O5, Med V2O5, Low V2O5
$k_{NOx}$ – Influence of Water and $O_2$
T, \(V_2O_5\), \(H_2O\), \(O_2\), flow rate \(\rightarrow k_0\)

Catalyst deactivates over time \(\rightarrow k_t\)?
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

- Alkali metals – Na, K
- Alkaline earth metals – Ca
- Arsenic – vapor phase As$_2$O$_3$
- Phosphorus – P$_2$O$_5$
**k_{NOx} Deactivation Model – Relative Activity, k_t/k_0**

- $k_t/k_0$ decreases exponentially with time.
- Proportionality constant, $\lambda$
  - Characteristic of SCR configuration, fuel, deactivation mechanisms.
  - Obtained from catalyst activity testing.

\[ k_t/k_0 = e^{-\lambda t} \]

<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>0.85</td>
</tr>
<tr>
<td>Bituminous firing</td>
<td>16000</td>
<td>0.70</td>
</tr>
<tr>
<td>PRB firing</td>
<td>16000</td>
<td>0.65</td>
</tr>
<tr>
<td>Lignite firing</td>
<td>16000</td>
<td>0.50</td>
</tr>
</tbody>
</table>
T, $V_2O_5$, $H_2O$, $O_2$, flow rate $\rightarrow$ $k_0$

$k_0 \rightarrow$ Deactivation Model $\rightarrow$ $k_{t=EOL}$
SO₂ to SO₃ Oxidation, k₅₆₉₉₉

- Undesired side reaction in SCR catalyst
  \[ 2\text{SO}_2 + \text{O}_2 \rightarrow 2\text{SO}_3 \]
- Occurs in the bulk of catalyst material (in the walls)
- \(k_{SOx}\) depends on \(V_2O_5\) and Temperature
- “Blue Plume” is a result of SO₃/H₂SO₄
- SO₃ reacts with NH₃ to form ammonium bisulfate (ABS) and ammonium sulfate (AS)
  \[
  \begin{align*}
  \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{NH}_4\text{HSO}_4 \text{ (ABS)} \\
  \text{NH}_4\text{HSO}_4 + \text{NH}_3 & \rightarrow (\text{NH}_4)_2\text{SO}_4 \text{ (AS)} \\
  2\text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} & \rightarrow (\text{NH}_4)_2\text{SO}_4 \text{ (AS)}
  \end{align*}
  \]
- AS is dry, powdery compound that can pass through SCR catalyst
- ABS is sticky, viscous compound that can plug catalyst and corrode downstream equipment – example: air preheater
SO$_2$ Oxidation – Influence of V$_2$O$_5$

![Graph showing the influence of V$_2$O$_5$ content on SO$_2$ oxidation rate and activity](image)
SO₂ Oxidation – Influence of Temperature

![Graph showing the influence of temperature on SO₂ oxidation rate with different V₂O₅ concentrations.](image-url)

- **V₂O₅ = 1.2%**
- **V₂O₅ = 0.6%**

Temperature, F

kSOₓ

500 600 700 800
Minimum Operating Temperature, MOT (Tmin)

- Minimum temperature for continuous SCR operation
- Of particular concern for low load operation and firing fuels containing sulfur
- Operating above Tmin prevents AS/ABS formation
- Tmin depends on SO₂/SO₃, NH₃, H₂O in flue gas
- Must stop NH₃ when operating below Tmin

![Tmin vs SO₃ inlet graph](image_url)

- NOₓ in 250 ppm, 88% DeNOₓ, NH₃ Slip 2 ppm
- Tmin vs SO₃ inlet (ppm wet) for different H₂O levels (12%, 10%, 8%)
- Tmin (F) on the y-axis
- SO₃ inlet (ppm wet) on the x-axis
Catalyst Design is an Iterative Process

**Design Inputs**
- DeNOx criteria - % of NOx to remove
- Operating period – 16,000/24,000 hr
- Flue gas flow conditions
  - Flow rate
  - Temperature
  - Pressure
  - Composition (NOx inlet, O2, H2O, SO2/SO3)
- Allowable NH3 slip
- Catalyst geometry/composition

**Considerations**
- Reactor configuration/space, flow distribution
- Coal type/specs, ash load
- Catalyst deactivation
- SO2 to SO3 oxidation
- Allowable pressure drop

**Design Outputs**
- Catalyst volume
- Catalyst activity
- SO2 to SO3 oxidation rate
- Pressure drop
- Design margin (safety factor)
Catalyst Management Plan (CMP)

- **2+1 layer example:** initial load 2 layers, L3 empty
- **Minimum potential to meet DeNOx, NH3 slip requirements**
- **Add L3**
- **Replace L1**
- **Replace L2**
- **Replace L3**

<table>
<thead>
<tr>
<th>Operating Time [h]</th>
<th>Activity Potential k/k₀ [%]</th>
<th>NH₃ Slip [ppmv]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>140</td>
<td>12</td>
</tr>
<tr>
<td>20000</td>
<td>120</td>
<td>10</td>
</tr>
<tr>
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<td>100</td>
<td>8</td>
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<tr>
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<td>2</td>
</tr>
<tr>
<td>120000</td>
<td>20</td>
<td>0</td>
</tr>
</tbody>
</table>
Thank You

Ken Jeffers