Fuel Impacts on SCR Catalysts is "Hot Topic" on June 30, 2011

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Initial Considerations

- **Coal is the largest operating expense for a power plant**
  - SCR catalyst is often considered the sacrificial expense for burning less expensive or not the original designed coal.

- **For SCR System Performance**
  - Fly-ash loading
  - Pressure drop
  - DeNOx performance
  - Ammonia slip
  - Plugging
  - Flue gas temperature
  - Sulfur content in coal & SO₂ conversion
  - Poisons & blinding agents (e.g. As, Ca, Na, K, P ...)
  - Next planned outage
**SCR Catalyst Overview**

- **Catalyst Cell**
- **Honeycomb Element**

- Visible surface ~ 400 m²/m³
- Catalytic surface at 65 m²/g
- 30 million m²/m³
Fuel Related Catalyst Deactivation
Mechanism: Physical

- Catalyst plugging
  - Alkali and alkaline earth metals act as “flux” to reduce ash fusion temperature → large particle ash or LPA
  - LPA build-up cuts flow through catalyst channels
  - Fly-ash also can build up to block channels
  - Direct reduction in available catalyst surface
  - Easily detected (reversible via regeneration process)
Effect of SCR Pluggage

Difficult to Accurately Predict System Performance when Pluggage is Primary Decay Mechanism

Operating Hours

- Catalyst Deactivation
- Catalyst Deactivation with Pluggage
Plugging is Reversible

Before

Corrugated

Honeycomb

Plate

After
- Visible surface ~ 400 m²/m³
- Catalytic surface at 65 m²/g
- 30 million m²/m³
Fuel Related Catalyst Deactivation
Mechanisms: Physical

- Pore mouth blinding
  - Silica & aluminosilicate particles block access at pore mouths.
  - Silica deposition as “glass” \([-\text{SiO}_2\text{-}]_n\) blocks catalyst access at pore mouths.
  - CaO in fly ash reacts with SO$_3$ to form CaSO$_4$ (gypsum) or CO$_2$ to form CaCO$_3$ (calcium carbonate).
  - A common form of activity loss (reversible via regeneration).
NOx Reduction Reaction Mechanism

Gas phase adsorption to surface

\[
\text{NH}_3 + \text{NO} \rightarrow \text{N}_2 + \text{H}_2\text{O} + \frac{1}{2} \text{O}_2
\]

Gas phase reaction with adsorbed species

Na\(^+\) or K\(^+\) exchange with H\(^+\) blocks required

Bronsted acid

Lewis acid
SCR Catalyst Deactivation
Mechanism: Chemical Poisons

- **Alkaline metal poisoning (Na, K)**
  - Formation of metal salt complexes reduces $V_2O_5$ activity
  - Alkaline metal adsorption changes surface Bronsted/Lewis acid balance (reversible via regeneration)

- **Phosphorous poisoning**
  - High phosphorous coals fired in “reducing environment” (low NOx burners) generated PX$_3$ species that actively poison $V_2O_5$ (reversible via regeneration)

- **Arsenic poisoning**
  - Gaseous arsenic ($As_2O_3$) condenses in catalyst pores
  - Further oxidation to solid $As_2O_5$ to permanently plugs pore mouths
  - Combines with vanadium to form inactive V-As species
  - Mitigation by high-Ca coal or addition of limestone ($CaCO_3$)
  - $CaO + As_2O_3 + H_2O$ forms solid calcium arsenate trihydrate
  - Distinct chemical signature (reversible via regeneration)

- **Some heavy metals, i.e. chromium, cannot be easily removed**
Deactivation & Regeneration: Honeycomb Catalyst

Major deactivation modes:

- Pore blinding / masking by silica
- Arsenic poisoning
- Iron
- Sodium

XRF measured amount (As in ppm/1,000)

- SiO2 (S)
- SiO2 (B)
- Fe2O3 (S)
- Fe2O3 (B)
- Na2O (S)
- Na2O (B)
- As (S)
- As (B)

Surface sodium below XRF detection limits
Deactivation & Regeneration: Corrugated Catalyst

- **SiO₂**
- **Al₂O₃**
- **Fe₂O₃ (Surface)**
- **Fe₂O₃ (Bulk)**
- **Na₂O**
- **As (Surface)**
- **As (Bulk)**

Iron, sodium and arsenic below detection limits -- true value may be 0...

- New: 10.0
- Deactivated: 17.0
- Regenerated: 11.4

XRF measured concentrations (As in ppm/1,000)
Coal General Characteristics

- Lignite and sub-bituminous coals
  - High in alkali and alkaline earth metals: Na, K, Ca, Mg
  - High in silicates, alumina, aluminosilicates, phosphates and Hg
  - Low in sulfur and halogen

- Bituminous coals
  - High in sulfur, iron, arsenic, “heavy metal” pyrites (metal sulfides)
  - Low in calcium and alumina

- Biomass
  - High in alkali (Na, K) and phosphates

- Pet coke
  - Enriched in vanadium and heavy metals – chromium, cadmium
Coal Resource Classification System (U.S. Geological Survey)

- **High-ash coal:** > 15 percent total ash (as-received basis)
- **Medium-ash coal:** 8 percent to 15 percent ash
- **Low-ash coal:** < 8 percent total ash

- **High-sulfur coal:** > 3 percent or more total sulfur
- **Medium-sulfur coal:** 1-3 percent total sulfur
- **Low-sulfur coal:** < 1 percent total sulfur
# Coal Sulfur Content

<table>
<thead>
<tr>
<th>Region</th>
<th>No. Samples</th>
<th>Organic % S</th>
<th>Pyritic % S</th>
<th>Total % S</th>
</tr>
</thead>
<tbody>
<tr>
<td>N. Appalachian</td>
<td>227</td>
<td>1.00</td>
<td>2.07</td>
<td>3.01</td>
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<tr>
<td>S. Appalachian</td>
<td>35</td>
<td>0.67</td>
<td>0.37</td>
<td>1.04</td>
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<tr>
<td>E. Midwest</td>
<td>95</td>
<td>1.63</td>
<td>2.29</td>
<td>3.92</td>
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<tr>
<td>W. Midwest</td>
<td>44</td>
<td>1.67</td>
<td>3.58</td>
<td>5.25</td>
</tr>
<tr>
<td>Western</td>
<td>44</td>
<td>0.45</td>
<td>0.23</td>
<td>0.68</td>
</tr>
</tbody>
</table>

## Sulfur Content Range (% w/w)

<table>
<thead>
<tr>
<th>Rank</th>
<th>0 - 0.07</th>
<th>0.08 – 1.0</th>
<th>1.1 – 3.0</th>
<th>≥ 3.1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthracite</td>
<td>95.6</td>
<td>0.6</td>
<td>2.9</td>
<td></td>
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<tr>
<td><strong>Bituminous</strong></td>
<td><strong>14.3</strong></td>
<td><strong>15.2</strong></td>
<td><strong>26.2</strong></td>
<td><strong>44.3</strong></td>
</tr>
<tr>
<td>Sub Bituminous</td>
<td>66.0</td>
<td>33.6</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>Lignite</td>
<td>77.0</td>
<td>13.7</td>
<td>9.3</td>
<td></td>
</tr>
<tr>
<td>U.S. Average</td>
<td>46</td>
<td>19</td>
<td>15</td>
<td>20</td>
</tr>
</tbody>
</table>
The “Glue” That Blinds: SO$_3$

- Reacts with alkaline earth metal oxides to form masking and blinding agents – CaSO$_4$

- Reacts with NH$_3$ to form sulfates (e.g. NH$_4$HSO$_4$)
  - Temperature range 350°F to 450°F when molar concentration of SO$_3$ exceeds molar concentration of NH$_3$ plugs air heater
  - Temperature range of 530°F to 620°F may condense in SCR and plug / blind (defines minimum operating temperature)

- Reacts with vanadium from pet-coke combustion to form vanadyl sulfate
  - Deposit at high levels on SCR catalyst – 20% or more
  - Increase in SO$_2$ to SO$_3$ oxidation rate
  - Slows increase in rate of DeNOx activity loss until pores are blocked then activity drops rapidly
<table>
<thead>
<tr>
<th>Fuel Type</th>
<th>Primary Deactivation Elements</th>
<th>Expected Activity @ 16,000 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>Petcoke</td>
<td>Heavy metals</td>
<td>K/K₀ &gt; 0.80</td>
</tr>
<tr>
<td>Sub-bituminous Coal - Powder River Basin</td>
<td>Calcium (Ca) and Phosphorus (P)</td>
<td>K/K₀ = 0.65 – 0.85</td>
</tr>
<tr>
<td>Bituminous Coal</td>
<td>Arsenic (As)</td>
<td>K/K₀ = 0.60 – 0.75</td>
</tr>
<tr>
<td>Lignite</td>
<td>Sodium (Na) &amp; Potassium (K)</td>
<td>K/K₀ = 0.60 – 0.70</td>
</tr>
<tr>
<td>Biomass</td>
<td>Phosphorus (P), Potassium (K), Sodium (Na)</td>
<td>K/K₀ = 0.45 – 0.55</td>
</tr>
<tr>
<td>Municipal Solid Waste (MSW)</td>
<td>Heavy metals, halogens, Potassium (K), Sodium (Na)</td>
<td>K/K₀ &lt; 0.50</td>
</tr>
</tbody>
</table>
Consult your SCR Catalyst Manager to model fuel change impacts on catalyst life and system performance.

Less expensive coal generally “trumps” more frequent catalyst replacement; but total economics and system performance must be evaluated.

Most important factors to determine catalyst type, formulation and geometry:

- Ash content
- Sulfur content
- Arsenic & calcium content
- Operating temperatures
- Flue gas velocity