Catalytic Emissions control for coal and gas power plants

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APGTF Workshop- “Power generation (coal, gas, and biomass) under increasingly stringent emissions regulations”

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JM – Divisions and Products

- Stationary Emissions Control business is a subdivision of the larger Emission Controls business

Stationary Emissions Control (SEC)

Power Industry
- Catalyst and Equipment
  - Coal Plant SCR
  - Gas Turbine SCR and CO
  - Engine SCR

Oil, Gas, Marine, and Locomotive Industry
- Catalyst and Equipment
  - Modulex 3-Way & 2-Way Converters for Gas Compression and Oil Pumps
  - HAPs Converters
  - Selective Catalysts Reduction (SCR)

Industrial Manufacturing
- Catalysts
  - PTA
  - VOC
  - NOx Abatement
  - Selective Catalytic Reduction (SCR)
Targeted Pollutants

- Oxides of Nitrogen (NOx)
- Particulate Matter (PM)
- Carbon Monoxide (CO)
- Unburnt Hydrocarbons (HC)
- SEC pollutants (Hg, SO$_3$, SO$_2$, ...)

[Chemical structures of the pollutants]
Catalysts and Catalytic Systems for Emission Control

<table>
<thead>
<tr>
<th>Honeycomb Catalysts</th>
<th>Plate Catalysts</th>
<th>SCR Systems</th>
<th>Pellets</th>
<th>Oxidation Catalysts</th>
<th>DPF Filtration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Several pitches for applications such as WtE gas turbine, and engine, etc.</td>
<td>High dust applications coal fired power plants</td>
<td>System soln inc. reactor, catalysts, dosing &amp; controls</td>
<td>Removal of NOx or organic compounds</td>
<td>Removal of CO odor &amp; VOCs</td>
<td>Removal of Particulate Material from Diesel Engines</td>
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- The majority of our products focus on the Selective Catalytic Reduction of NOx using NH₃ as the reductant
Three main reactions of interest

1) \[ 4\text{NO} + 4\text{NH}_3 + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \] Maximize

2) \[ \text{SO}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{SO}_3 \] Minimize

3) \[ \text{Hg} + 2\text{HCl} + \frac{1}{2}\text{O}_2 \rightarrow \text{HgCl}_2 + \text{H}_2\text{O} \] Maximize

Undesired Parallel Reactions

\[ \text{NH}_3 + \text{SO}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4\text{HSO}_4 \]

\[ \text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4\text{Cl} \]

\[ 4\text{NH}_3 + 5\text{O}_2 \rightarrow 4\text{NO} + 6\text{H}_2\text{O} \]

\[ \text{SO}_3^{2-} + \text{Hg}^{2+} \rightarrow \text{HgSO}_3 + \text{H}_2\text{O} \rightarrow \text{Hg} + \text{HSO}_4^- + \text{H}^+ \]
Typical SCR Emissions Control in a Coal Power Plant
Hg is one of the most volatile of all the heavy elements and is known for its toxicity particularly in the form of methylmercury.

In the US, MATS regulations are currently enforced and existing plants are limited to 1.2 lbs Hg/TBtu(coal) and 4.0 lbs Hg/Tbtu(lignite) for a 30 day average.¹

In Europe the BAT conclusions of the LCP BREF should be adopted in 2017. All LCP permits in Europe will have to be updated accordingly within 4 years after publication of BAT conclusions. Only the higher end of the BAT-AEL range is legally binding at EU level.

Generally preferred technology for Hg removal is “co-benefits”, in which Hg⁰ is oxidized over the SCR catalyst to Hg²⁺ which is then adsorbed in the downstream sulfur scrubber. Europe appears to be following the US lead in terms of technology approach.

In light of this, a power generation facility intending to rely on the Hg oxidation properties of an SCR catalyst will need to ensure that property is reliably predicted under actual operating conditions.

Advanced Hg oxidation catalysts are available and several different applications are being considered (Lignite vs. Hard coal).
Challenges for Hg oxidation over SCR catalysts in Coal Power Plants

• Accurately measuring Hg oxidation under simulated power plant conditions in the lab and correlating activity measurements of the catalyst to performance in a plant or to third party tests. Hg concentrations are typically in the ppb level of the flue gas!

• Maximize Hg oxidation while maintaining the same SO\textsubscript{x} and NO\textsubscript{x} activity, particularly in the following tough conditions (equilibrium limited):
  1. Low halogen content
  2. High temperature
  3. High H\textsubscript{2}O content & Low temperatures (Lignite plants, which typically don’t have SCR catalysts installed)

• Understand how the operating conditions affect Hg oxidation activity of SCR catalysts so that better Hg oxidation guarantees can be made and Utilities have more operational flexibility

• Understanding and minimizing the deactivation mechanisms (Plate/HC erosion, posions, etc) of these SCR catalysts both for Hg and for SCR.

<table>
<thead>
<tr>
<th>Example Conditions</th>
<th>Sub-/Bituminous plants</th>
<th>Lignite plants</th>
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<tbody>
<tr>
<td>T (°C)</td>
<td>320-420</td>
<td>170-200</td>
</tr>
<tr>
<td>LV (Nm/s)</td>
<td>1.7-2.2</td>
<td>1.0-2.2</td>
</tr>
<tr>
<td>AV (Nm/h)</td>
<td>13-20</td>
<td>7-9</td>
</tr>
<tr>
<td>SO\textsubscript{2} conc (ppm)</td>
<td>400-3000</td>
<td>400-2000</td>
</tr>
<tr>
<td>NO\textsubscript{x} conc (ppm)</td>
<td>0-550</td>
<td>0-140</td>
</tr>
<tr>
<td>NH\textsubscript{3} conc (ppm)</td>
<td>0-500</td>
<td>-</td>
</tr>
<tr>
<td>HCl conc (ppm)</td>
<td>15-110</td>
<td>0-15</td>
</tr>
<tr>
<td>Inlet Hg (mg/Nm\textsuperscript{3})</td>
<td>5-45</td>
<td>10-20</td>
</tr>
<tr>
<td>O\textsubscript{2} (%)</td>
<td>2.5-6</td>
<td>3.5</td>
</tr>
<tr>
<td>H\textsubscript{2}O (%)</td>
<td>6-12</td>
<td>18-24</td>
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In addition to our standard NOx and SOx testing facilities, JM has a dedicated lab for Hg oxidation research and has been involved with Hg oxidation since early 2000s.

This Semi-Bench reactor system is unique since it can nearly match both the LV and AV in SCR reactors on typical coal power plants. It also has the ability to investigate the effects of lesser components in the flue gas such as CO, NO\textsubscript{2}, and HBr.
Some of the Hg Oxidation developments at JM

- Developed a detailed model of the Hg oxidation performance of our SCR catalysts under a variety of operational conditions, which allows utilities to predict Hg oxidation performance.
- Developed advanced SCR catalysts with enhanced activity (Hg and NOx)
- Heavily involved in the development of Hg oxidation protocols for both the US and European markets
- Involved in several field trial applications for our catalysts (Europe & USA).
- Published mechanistic investigations on Hg oxidation over SCR catalysts
Emissions control for gas turbines typically involve a CO and SCR catalyst installed in a HRSG.

There are strict emissions regulations from these units for CO, VOC, NOx, and NH$_3$.

Some of the main concerns regarding emission control on Gas Turbines are:

- Emissions at low temperature
- Frequent start-ups/shut downs (Operational flexibility)
- Low load operations
- Pressure drop across the catalysts
- Catalyst deactivation
- Cost

Diagram: Heat Recovery Steam Generator (HRSG)

- HRSG Tubes
- Ammonia Injection Grid
- HRSG Tubes

Diagram: Exhaust from Turbine

Diagram: CO Catalyst and SCR Catalyst

Diagram: Grid and Exhaus from Turbine
Typical Catalyst products for Gas Turbines

**Oxidation Catalyst**
- Typically used for CO and VOC oxidation on gas and Diesel engines
- Typically 200 CPSI
- Custom Block sizes that are fully brazed for strength
- Thin walls for low pressure drop
- Contains Precious Metals such as Pt

**SCR HC Catalysts**
- Typically used for the reduction of Nox with NH₃ as reductant
- High activity & specific surface area
- Variable length and number of cells
- Typical: 140 cpsi & 200 – 400 mm length
- Homogeneously extruded ceramic with square-opening cell structure
- TiO₂, V-oxide/W-oxide
JM’s New Products for Gas Turbine Emission Control

- Advanced Oxidation Catalyst
  - Improved activity (particularly at low temperatures)
  - Sulfur resistance

- Advanced SCR Catalyst
  - Thin wall geometry for lower pressure drop

Today we will focus on this development

- Ammonia Slip Catalysts (ASC)
  - Ammonia slip control
  - Catalyst volume reduction for low pressure drop
SCR-ASC Has a Number of Potential Advantages

SCR-ASC Advantages
- Reduced Volume, delta P
- High NOx Conversion, Low NH$_3$ slip
- CO Oxidation Functionality

SCR-ASC System

Standard System
Pt Based Ammonia Slip Catalyst Selective to NOx

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

Non-Selective Ammonia Slip Catalyst

\[ \text{NH}_3 = 20\text{ppm}, \text{O}_2 = 15\%, \text{H}_2\text{O} = 8\%, \text{CO}_2 = 3\%, \text{Balanced by N}_2 \]
New Ammonia Slip Catalyst Selective to $N_2$

$NH_3 = 30\text{ppm}$, $O_2 = 15\%$, $H_2O = 8\%$, $CO_2 = 3\%$, Balanced by $N_2$

Selective Ammonia Slip Catalyst

$NH_3 + O_2 \rightarrow N_2 + H_2O$

Temperature (°C)

Concentration (ppm)
Conclusions

• JM has several new technologies to help utilities deal with the increasingly stricter emissions controls legislation on both coal and gas turbine power plants.

• These technologies allow these plants to be emissions compliant and still economically competitive with other forms of power generation.

• JM has worked with many utility operators world-wide to develop standard or unique solutions that allow them to achieve their emissions limits.

Questions?
Background Slides
Engine SCR (Diesel or Natural Gas)
References
Waste-to-Energy

Incinerator Kristiansand, N
- 120 000 t/a municipal waste
- Low-dust
- Reduction rate NO$_x$ > 95%
- Ammonia slip < 5 mg/m$^3$

Incinerator Hameln, N
- 140 000 t/a municipal waste
- Low-dust
- Reduction rate NO$_x$ > 88%
- Ammonia slip < 3.8 mg/m$^3$

Incinerator EVI Europark, D
- 365 000 t/a municipal waste
- Low-dust
- Reduction rate NO$x$ > 90%
- Ammonia slip < 5 mg/m3
EON, Ratcliffe, UK

- 4 x 520 MW
- World-Market Coal
- Reduction rate NO$_x$ > 85 %
- Ammonia slip < 2 ppm

Studstrupværket, DK

- 2 x 350 MW
- Coal and Straw
- Reduction rate NO$_x$ > 90 %
- Ammonia slip < 2 ppm

NUON, Amsterdam, NL

- 660 MW
- World-Market Coal
- Reduction rate NO$_x$ > 90 %
- Ammonia slip < 1 ppm