REINHOLD ENVIRONMENTAL Ltd.

2014 NOx-Combustion Round Table & Expo Presentations

Latest Developments in SCR Catalyst Mercury Oxidation

Christopher Bertole
Cormetech, Inc.
2014 Reinhold NOx-Combustion Round Table
Presentation Overview

• **Background**
  – SCR Co-Benefits for Hg Removal
  – General Plant Hg Control Strategy

• **COMET™ (Cormetech Oxidized Mercury Emissions Technology)**
  – COMET™ Introduction
  – Key Differences between Hg and NOx Control
  – Catalyst Management and Case Study 1
  – Characterization, Modeling, Advanced Hg Ox Catalyst
  – Catalyst Management and Case Study 2

• **Summary**
SCR Co-Benefits for Hg Removal

1. Elemental
2. Oxidized
3. Particle bound

Hg + 2HCl + ½O₂ → HgCl₂ + H₂O
Hg + 2HBr + ½O₂ → HgBr₂ + H₂O
General Plant Hg Control Strategy
Site Specific. Includes All or Some Components.

**Coal Type and Combustion**
- Hg Content
- Cl and Br Contents
- Added Cl and/or Br
- LOI in Fly Ash
- Boiler Load Profile

**GOAL**
MATS Limit
Hg < 1.2 lbs/Tbtu

**SCR Co-Benefits**
- **SCR:**
  - Hg$^0$ Oxidation Activity
  - HCl and HBr
  - Temperature
  - Gas Composition
  - Seasonal Impacts
- **WFGD:**
  - Hg$^{2+}$ Net Capture Efficiency
  - Hg$^0$ Reemission

**ACI & DSI + ESP or FF**
- **ACI:**
  - Hg Capacity
  - Temperature
  - SO$_3$ Concentration
  - HCl and HBr
  - Sorbent Injection Rate
- **DSI:**
  - SO$_3$ Mitigation
- **ESP or FF:**
  - ACI, DSI Capture
  - Ash Capture (Hg on LOI)

**Strategy:** Utilize all or some of these components to deliver a robust control plan for MATS compliance. Currently installed APCE can influence selection.

**APH**
- Passive; small amount of Hg Oxidation
Presentation Overview

• Background
  – SCR Co-Benefits for Hg Removal
  – General Plant Hg Control Strategy

• COMET™ (Cormetech Oxidized Mercury Emissions Technology)
  – COMET™ Introduction
  – Key Differences between Hg and NOx Control
  – Catalyst Management and Case Study 1
  – Characterization, Modeling, Advanced Hg Ox Catalyst
  – Catalyst Management and Case Study 2

• Summary
COMET™
An Integrated Approach to Solutions

- Understand needs & options.
- Define SCR Hg oxidation requirement.
- Evaluate multiple scenarios.
- Develop management plans.
- Select catalyst type:
  - Standard, or
  - COMET™ Advanced Hg Ox Catalyst
- Set SCR performance guarantees.

- Use COMET™ modeling technology.
- Test catalyst samples in lab (fresh, field).
- Evaluate against available field data.
- Select catalyst type:
  - Standard, or
  - COMET™ Advanced Hg Ox Catalyst
- Set SCR performance guarantees.

Micro & Bench Activity Testing

Modeling

Field Results
Presentation Overview

• **Background**
  – SCR Co-Benefits for Hg Removal
  – General Plant Hg Control Strategy

• **COMET™** (Cormetech Oxidized Mercury Emissions Technology)
  – COMET™ Introduction
  – Key Differences between Hg and NOx Control
  – Catalyst Management and Case Study 1
  – Characterization, Modeling, Advanced Hg Ox Catalyst
  – Catalyst Management and Case Study 2

• **Summary**
Key Differences for Hg vs. NOx
SCR is One Component of Overall System for Hg

• **DeNOx**
  - Performance requirements for the SCR are typically well defined due to the sole role of the SCR for NOx reduction

• **Hg**
  - Multiple system units are involved in Hg control → SCR performance requirements are not typically as well-defined as for NOx reduction
Key Differences for Hg vs. NOx
More Factors Influence Hg Oxidation

DeNOx
– Key Factors
  • NOx inlet
  • Efficiency
  • Slip
  • Temperature
  • O₂, H₂O, SO₂ (lower impact)
  • SO₂ conversion (formulation)
  • Fuel → contaminants → K/Ko
  • Reactor condition

Hg
– Key Factors
  • Hg oxidation → Performance Threshold
  • NOx inlet
  • Efficiency
  • Slip
  • Layer position (NH₃)
  • Halogen (Fuel or additive)
  • Temperature
  • CO, hydrocarbons
  • O₂, H₂O, SO₂ (can be larger impact)
  • SO₂ conversion (formulation)
  • Fuel → contaminants → K/Ko
  • Reactor condition
Key Differences for Hg vs. NOx
Hg Ox Catalyst Potential, K/AV

- **Hg Oxidation** $K_{HgOx}$/AV defines:
  - Capacity for X% Hg oxidation

- **Activity**, $K_{HgOx}$, **depends on**:
  - Catalyst composition and age
  - Flue gas conditions (+HCl, HBr, NH$_3$, CO, SO$_2$, HC)

- **AV** = Area Velocity = (Gas Flow) / (Total GSA)

- First order rate equation can be applied for Hg oxidation tests, **but be careful**!

  → *This K value is strongly condition dependent!*

\[
\frac{K_{HgOx}}{AV} = -\ln\left[1 - \eta_{HgOx}\right]
\]

\[
\eta_{HgOx} = \text{fraction of } Hg^0 \text{ oxidation}
\]
### Key Differences for Hg vs. NOx

**SCR Catalyst Design Approach**

**Historical:**
Catalyst is formulated to achieve DeNOx requirements, while meeting SO\(_2\) oxidation constraints.

<table>
<thead>
<tr>
<th>K/AV Needs (NO(_x))</th>
<th>SO(_3) Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Life</td>
<td>Visible Plume</td>
</tr>
<tr>
<td>NO(_x) Removal</td>
<td>Corrosion</td>
</tr>
<tr>
<td>NH(_3) Slip</td>
<td>Mitigation Cost</td>
</tr>
</tbody>
</table>

**Moving Forward:**
Catalyst is formulated to achieve DeNOx and Hg oxidation requirements, while meeting SO\(_2\) oxidation constraints.

<table>
<thead>
<tr>
<th>K/AV Needs (NO(_x), Hg)</th>
<th>SO(_3) Costs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Life</td>
<td>Visible Plume</td>
</tr>
<tr>
<td>NO(_x), Hg Removal</td>
<td>Corrosion</td>
</tr>
<tr>
<td>NH(_3) Slip, Halogens</td>
<td>Mitigation Cost</td>
</tr>
</tbody>
</table>

---

2014 Reinhold NOx-Combustion Round Table
Charlotte, North Carolina
SCR Catalyst Design
Understand Needs and Options

• Hg in Coal

• Halogen in coal

• Define how much Hg oxidation is needed by the SCR, and assess vs. what can be achieved
  – DeNOx and SO₂ oxidation targets
  – Temperature and gas composition
    • Hg, NOₓ, NH₃, O₂, H₂O, HCl, HBr
  – Catalyst selection
    • Standard Catalyst
    • COMET™ Advanced Hg Oxidation Catalyst
  – Benefit and capability for halogen addition
  – Need for ACI (+ DSI) trim
Key Factor: Hg in Coal
(Affects % Removal Needed for 1.2 lb/TBTU emission)

Source: Utah Geological Survey

% Removal Required @ 1.2 lb/TBTU

- 40%-70%
- 70%-80%
- 80%-87%
- 87%-92%
- 92%-96%
- 96%-98%

Lbs / trillion (10^{12}) BTU
- 2 - 4
- 4 - 6
- 6 - 9
- 9 - 15
- 15 - 30
- 30 - 52
- coal province

2014 Reinhold NOx-Combustion Round Table
Charlotte, North Carolina
SCR Catalyst Design
Understand Needs and Options

- Hg in Coal
- **Halogen in coal**
- Define how much Hg oxidation is needed by the SCR, and assess vs. what can be achieved
  - DeNOx and SO₂ oxidation targets
  - Temperature and gas composition
    - Hg, NOx, NH₃, O₂, H₂O, HCl, HBr
  - Catalyst selection
    - Standard Catalyst
    - COMET™ Advanced Hg Oxidation Catalyst
- Benefit and capability for halogen addition
- Need for ACI (+ DSI) trim
Key Factor: Chlorine in Coal
(Affects SCR Catalyst Potential for Hg Oxidation)

If coal halogen content is low, option to augment with added Cl or Br to improve SCR catalyst Hg oxidation.

Source: Utah Geological Survey

- 20-200 ppmw
- 2500-4500 ppmw

1999 coal production, ICR 2 data, by county

chlorine impact example

Source: Utah Geological Survey

2014 Reinhold NOx-Combustion Round Table
Charlotte, North Carolina
SCR Catalyst Design
Understand Needs and Options

• Hg in Coal
• Halogen in coal

• Define how much Hg oxidation is needed by the SCR, and assess vs. what can be achieved
  – DeNOx and SO₂ oxidation targets
  – Temperature and gas composition
    • Hg, NOx, NH₃, O₂, H₂O, HCl, HBr
  – Catalyst selection
    • Standard Catalyst
    • COMET™ Advanced Hg Oxidation Catalyst
  – Benefit and capability for halogen addition
  – Need for ACI (+ DSI) trim
Presentation Overview

• Background
  – SCR Co-Benefits for Hg Removal
  – General Plant Hg Control Strategy

• COMET™ (Cormetech Oxidized Mercury Emissions Technology)
  – COMET™ Introduction
  – Key Differences between Hg and NOx Control
  – Catalyst Management and Case Study 1
  – Characterization, Modeling, Advanced Hg Ox Catalyst
  – Catalyst Management and Case Study 2

• Summary
Catalyst Management for Hg

• Analogous to DeNOx…
  – With the caveats for $K_{HgOx}$ previously outlined

• Either DeNOx or Hg oxidation establishes the design minimum volume
  – Depends on the relative catalyst potential and performance requirements for each reaction

• Case Study 1 (next slides)
  – Situation: SCR at 70,000 hours operation requires catalyst action for DeNOx. How does consideration of Hg oxidation affect the catalyst action decision?
Case Study 1
w/ DeNOx Potential & Hg Oxidation

Catalyst Management Plan
(DeNox, NH3 Slip, Oxidized Hg)

Performance:
85% DeNOx.
Max NH₃ slip = 2 ppm.

C Cormetech
Comet™
Case Study 1
w/ DeNOx Potential & Hg Oxidation

Catalyst Management Plan
(DeNox, NH3 Slip, Oxidized Hg)

Target 80% Ox Hg EOL.
Action: Inject Halogen

Operating Hours

DeNOx Efficiency (%), SCR Outlet Oxidized Hg (%)
Case Study 1
w/ DeNOx Potential & Hg Oxidation

Target: 90% Ox Hg EOL.
Action: Initially change 2 layers to Max length COMET™ and repeat for layer 3
Case Study 1
w/ DeNOx Potential & Hg Oxidation

Target 90% Ox Hg EOL. Action: Initially change 2 layers to Max length COMET™ and inject Halogen

Catalyst Management Plan (DeNox, NH3 Slip, Oxidized Hg)
Presentation Overview

• **Background**
  – SCR Co-Benefits for Hg Removal
  – General Plant Hg Control Strategy

• **COMET™**(Cormetech Oxidized Mercury Emissions Technology)
  – COMET™ Introduction
  – Key Differences between Hg and NOx Control
  – Catalyst Management and Case Study 1
  – Characterization, Modeling, Advanced Hg Ox Catalyst
  – Catalyst Management and Case Study 2

• **Summary**
Lab Reactor Activity Testing

- Fresh catalyst characterization
- Model development
- Catalyst management and field catalyst audits
- Case study validations
MHI Semi-Bench Reactor
Reflects Years of Experience for Hg Ox Testing

- Collected Hg oxidation data for development, designs, deactivation studies, and quality assurance since 2002.
- Total system testing (fresh and deactivated) up to 4 layers

![Diagram of MHI Semi-Bench Reactor](image-url)

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Measurement Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hg and Hg$^{2+}$</td>
<td>Ontario Hydro Method</td>
</tr>
<tr>
<td>SO$_2$, SO$_3$, HCl, NH$_3$</td>
<td>Wet Chemical Analysis</td>
</tr>
<tr>
<td>NO$_x$, O$_2$</td>
<td>CEMs</td>
</tr>
</tbody>
</table>

Courtesy of: Mitsubishi Heavy Industries, Ltd.
Cormetech Micro-Reactor

- Versatile and fully-automated for efficient data collection. CEMS for Hg, NO\textsubscript{x}, SO\textsubscript{2}.
  - Allows us to measure Hg oxidation under a full range of conditions to develop catalysts and management strategies.
  - Capable of characterizing any catalyst type/vintage.

Cormetech participated in the first VGB Round Robin test series for Hg oxidation.
Cormetech Bench Reactor

• **Added Bench scale Hg oxidation test capability.**
  – Construction is complete
  – Validation testing is underway

• Full size element testing.
• Individual element and multi-layer testing.
• Any catalyst type or combination.
• Fresh or deactivated.
• HCl/HBr, O₂, H₂O, SO₂, SO₃, NOₓ, CO, HC.
Catalyst Performance Example
Lab Data Shown (Models were Developed from Lab Data).

Shows impact of temperature, HCl concentration, and molar ratio on Hg oxidation activity.

Layer Dependency: MR = 0.9 represents top layer
MR = 0.2 represents a lower layer
Layer Dependency
Influenced by Temperature and Halogen Level. Lab Data Shown.

- Hg oxidation catalyst potential is a function of layer position, due to NH₃ inhibition
  - All catalyst layers still contribute to the overall Hg oxidation performance
- High halogen levels significantly reduce the NH₃ impact: more Hg ox from layer 1!
Parameter Impacts
(Temperature, Flow, Halogens)

- Highest temperature with highest flow (i.e. Full load) typically design condition
- Temperature impact more significant than for DeNOx and condition dependent
- Distribution of HCl content must be considered (may result in more than one design condition)
Parameter Impacts
(O₂, H₂O, CO)

- O₂, H₂O and CO have significant impact (much lower impact on DeNOx)
- Impact is condition dependent (CO for example)
- Distribution of these parameters should be considered in setting design conditions
Deactivation Studies

Hg oxidation deactivation generally correlates with DeNOx deactivation.

However, the extent of deactivation for the two reactions are not equivalent (Hg oxidation deactivation is influenced by test condition).
Deactivation Studies

- Measured $K/K_0$ for Hg oxidation is sensitive to operating conditions ($\text{NH}_3$, HCl, Temperature).

...An example from one unit (PRB)

- $Hg\ Ox$: $MR=0$
  - 400°C, $MR=0$, 10ppmHCl
  - 400°C, $MR=0$, 50ppmHCl

- $Hg\ Ox$: $MR=0.9$
  - 400°C, $MR=0.9$, 10ppmHCl
  - 400°C, $MR=0.9$, 50ppmHCl

- 400°C, $MR=0.9$ (DeNOx)
Advanced Hg Oxidation Catalyst

PRB Unit - Lab Testing Case Study: COMET™ -vs.- Standard
At same SO2 oxidation rate.

80% higher Hg ox Activity at design case!
(Range: 50% - 400%)
Presentation Overview

• **Background**
  – SCR Co-Benefits for Hg Removal
  – General Plant Hg Control Strategy

• **COMET™ (Cormetech Oxidized Mercury Emissions Technology)**
  – COMET™ Introduction
  – Key Differences between Hg and NOx Control
  – Catalyst Management and Case Study 1
  – Modeling, Advanced Hg Ox Catalyst, Characterization
  – Catalyst Management and Case Study 2

• **Summary**
COMET™
An Integrated Approach to Solutions

- Understand needs & options.
- Define SCR Hg oxidation requirement.

- Evaluate multiple scenarios.
- Develop management plans.
- Select catalyst type:
  - Standard, or
  - COMET™ Advanced Hg Ox Catalyst
- Set SCR performance guarantees.

- Use COMET™ modeling technology.
- Test catalyst samples in lab (fresh, field).
- Evaluate against available field data.

Micro & Bench Activity Testing

Modeling

Field Results

2014 Reinhold NOx-Combustion Round Table
Charlotte, North Carolina
Case Study 2
System Characterization and Options Analysis

- Evaluation of impacts to Hg oxidation and DeNOx performance for catalyst replacement options
- 4 layer system – replacement of first and last layer
  - Layer 1: Honeycomb A
  - Layer 2: Honeycomb B
  - Layer 3: Honeycomb B
  - Layer 4: Plate
- Layer 1 – replace with fresh catalyst
  - Layer was already purchased
- Options for Layer 4 replacement:
  - Regenerated honeycomb (from layer 1)
  - Fresh COMET™ catalyst
Case Study 2
System Characterization and Options Analysis

• Lab tested 7 samples of field and fresh catalyst
  – MR = 0, 0.2, 0.3
  – Over 60 tests completed.

• Validated lab data against model
  – Average absolute deviation within 3% across range of MR

• Field data in good agreement

• Options analyzed and management plan developed.

<table>
<thead>
<tr>
<th></th>
<th>Baseline</th>
<th>Option 1</th>
<th>Option 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer 4</td>
<td>Existing</td>
<td>Fresh Regen</td>
<td>Fresh COMET™</td>
</tr>
<tr>
<td>Hg Oxidation</td>
<td>40%</td>
<td>55%</td>
<td>70%</td>
</tr>
<tr>
<td>(System)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

– Higher oxidation can be achieved with additional COMET™ layers.
Summary

• **Hg oxidation is influenced by multiple factors**
  – Layer dependency
  – More factors in setting design conditions
  – Impacts of catalyst type & formulation

• **Cormetech has developed testing capabilities to characterize performance under all operating conditions**

• **COMET™**
  – *Testing and Modeling Technology* allows us to predict system performance and evaluate options for catalyst actions.
  – *Advanced Hg Oxidation Catalyst* can significantly improve SCR co-benefit for Hg oxidation.
  – Used in combination to provide [optimal solutions](#)

*can help you evaluate and meet Hg Emissions Goals*
Thank You!

Questions?

Christopher Bertole
Cormetech, Inc.
2014 Reinhold NOx-Combustion Round Table