SCR Operations and FGD Additives for Hg Control
Agenda

• Impacts of SCR operations on mercury
• SCR and catalyst management
  o NO$_x$ / NH$_3$
  o Pluggage and poisons
• Retrofitting SCR for improved operation
• Managing Hg as catalysts degrade
• Redox-Hg FGD additives
• Conclusions
SCR
Primary: \( \text{NO}_{(g)} \rightarrow \text{N}_2{(g)} \)
Secondary: \( \text{Hg}^0 \rightarrow \text{HgX}_2 \) (\( X = \text{Cl}, \text{Br}, \text{I} \))

wet FGD
\( \text{HgX}_2{(g)} \rightarrow \text{HgX}_2{(aq)} \)
SCR Operation Parameters and Influences on Hg

- **Load profile**
  - Baseload vs. load cycling
- **Ash loading/particle size distribution**
- **Flow stratification**
- **% transition metals in catalyst (e.g. V, W, Mo)**
  - Can also increase SO$_2$ to SO$_3$ conversion rate
- **Catalyst poisons**
  - Particulate, CaSO$_4$, As, Se, Na, K
SCR Operations: Major O&M Cost Factors

- Catalyst changes/regeneration/rejuvenation
  - Driven by performance degradation
    - NO\textsubscript{x} reduction
    - Hg\textsuperscript{0} oxidation
  - Catalyst pluggage/poisoning
    - Catalyst washes

- SO\textsubscript{2} to SO\textsubscript{3} conversion rates
  - Increased SO\textsubscript{3} emissions may require sorbent injection

- Minimum operation temperature (MOT)
  - Driven by ABS formation and performance
  - Decrease SO\textsubscript{3} through sorbent injection upstream of SCR
    - TIFI Mg(OH)\textsubscript{2}, limestone, hydrated lime, sodium sorbents
**SCR Catalyst Design**

1) **NO\(_x\) reduction**
   - \(4 \text{ NO}(g) + 4 \text{ NH}_3(g) + \text{O}_2(g) \xrightarrow{\text{catalyst}} 4 \text{ N}_2(g) + 6 \text{ O}_2(g)\)
   - \(2 \text{ NO}(g) + 2 \text{ NO}_2(g) + 4 \text{ NH}_3(g) \xrightarrow{\text{catalyst}} 4 \text{ N}_2(g) + 6 \text{ H}_2\text{O}(g)\)

2) **Hg\(^0\) oxidation**
   - \(\text{Hg}^0(g) + 2 \text{ HCl}(g) + \frac{1}{2} \text{ O}_2(g) \xrightarrow{\text{catalyst}} \text{HgCl}_2(g) + 2 \text{ H}_2\text{O}(g)\)

3) **SO\(_2\) oxidation**
   - \(\text{SO}_2(g) + \frac{1}{2} \text{ O}_2(g) \xrightarrow{\text{catalyst}} \text{SO}_3(g)\)

**Goal:** Maximize reaction (1) and (2), minimize reaction (3)
Hg^0 Oxidation Impact Factors: NH_3, H_2O, O_2

- O_2 and H_2O significantly impact Hg oxidation activity
  - These have minimal impacts on NO_x reduction/SO_2 oxidation

Reference: Bertole, C.; Reinhold 2015 NO_x-Combustion Round Table; Richmond, Va.
Hg⁰ Oxidation Impact Factors : HCl

- Hg⁰ oxidation activity decreases with increasing temperature and increasing NH₃ concentrations
- NH₃ and HCl compete for active sites on catalyst

Reference: Bertole, C.; Reinhold 2015 NOₓ-Combustion Round Table; Richmond, Va.
Hg$^0$ Oxidation Impact Factors: $V_2O_5$ Content and Temperature

- Load cycling significantly impacts Hg$^0$ oxidation.
- Higher $V_2O_5$ improves Hg$^0$ oxidation and NO$_X$ reduction.
  - Must be balanced with SO$_2$ oxidation.

Reference: Bertole, C.; Reinhold 2015 NO$_X$-Combustion Round Table; Richmond, Va.
Hg\textsuperscript{0} Oxidation Impact Factors

- Halogens are critical to high Hg\textsuperscript{0} oxidation across SCR
  - Catalysts alone do not significantly oxidize Hg\textsuperscript{0}
- NH\textsubscript{3} can significantly inhibit Hg\textsuperscript{0} oxidation activity
  - Proper flow distribution is critical to minimize local high NH\textsubscript{3} concentrations

Reference: Bertole, C.; Reinhold 2015 NO\textsubscript{X}-Combustion Round Table; Richmond, Va.
Impact of Catalyst Aging

Mercury oxidation over SCR is based on many conditions and is transient

Reference: Repp, D.; WPCA Mercury Seminar, October 2012, Birmingham, AL
Hg$^0$ Oxidation Impact Factors

- Hg$^0$ oxidation performance degrades with:
  - Usage/life (linear decline)
  - Load cycling (variable, temperature, flow rate)
  - NH$_3$ concentration (linear)
  - H$_2$O and O$_2$ (variable)

- Catalyst management dampens variability

- Wet scrubber additive can be used to dampen variability
  - Capture Hg$^0$ and Hg$^{2+}$
  - Cost effective and can be done on-demand
SCR Consulting Services

SCR Consulting Services

- Fuel Change Analysis
- Catalyst Life Cycle Analysis
- Cleaning/Regeneration & Assessments
- Catalyst Testing
- Reactor Inspections
- SCR System Operations Monitoring
- AIG Tuning

SCR / Catalyst O&M Planning

- Environmental Compliance
- Optimized SCR Solutions
- Budget Planning
- SCR Operations Planning
Program Attributes

• **FTEK does NOT:**
  - Produce or manufacture catalyst
  - Regenerate catalyst
  - Rejuvenate catalyst

• **FTEK does:**
  - Optimize SCR Operation
  - Investigates ways to prolong life of existing catalyst
  - Helps client with planning and budgeting

• 28 years and more than 80,000 MW of Experience

• All SCR performance related know-how is in house
SCR and Reactor Inspections
Reactor Inspections – Ash Pluggage

Top Catalyst Level (6.7 mm Pitch)

<table>
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<tr>
<th>Location</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<th>7</th>
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<td>90-100%</td>
<td>50-60%</td>
<td>50-60%</td>
<td>50-60%</td>
<td>100%</td>
<td>100%</td>
<td>70-80%</td>
<td>40-50%</td>
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<td>50-60%</td>
<td>50-60%</td>
<td>80-90%</td>
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<td>C</td>
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Top Catalyst Level (8.2 mm Pitch)

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<tr>
<td>B</td>
<td>5-10%</td>
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Pluggage Levels:
- < 10% Pluggage
- 10% to 20% Pluggage
- 20% to 40% Pluggage
- 40% to 70% Pluggage
- 70% to 100% Pluggage

Unburned Carbon
Popcorn Ash / LPA
Fly Ash Piles (>1 ft)
Ammonia Injection Grid Tuning

- Utilizing fixed measurement grid for NO\textsubscript{X} measurements and DCS data regarding SCR system operations results
- Tuning objective = ±15 to 25 ppm outlet NO\textsubscript{X} dependent on AIG and gas path configuration
- Providing comprehensive tuning report
- AIG tuning services since 1999
  - 100+ AIGs tuned
  - 10+ (> 20,000 MW) of catalyst management programs
Reporting and Analysis

AIG Tuning and Balancing - Representative AIG Tuning Result

Pre-tuning Baseline

Post-tuning Baseline
Catalyst Testing

- Independent review
- Use 3rd Party Lab for Testing
- Review, analyze, and interpret testing results
- Use results to identify a Catalyst Management Strategy

![Catalyst Deactivation graph]

Exposure to Flue Gas, hours

Catalyst Activity Ratio K/Ko

Design/Expected Deactivation

Expected Activity (16000 Hours)
Common Challenges
Temperature and Flow (Mal)Distribution

- The economizer outlet temperature on PRB units can exceed 800 °F (427 °C) when the boiler becomes dirty.
- Imperative to minimize the temperature distribution before the AIG with modeling.
GSG™ Graduated Straightening Grid

- Improves flue gas velocity distribution without increasing cost, complexity, or compromise on performance
- Minimizes angle at which ash particles enter catalyst, near perfectly vertical flow into catalyst
- Innovative design allows for
  - Higher flue gas velocity, improved operating and financial performance via longer catalyst life and reduce downtime
  - Reduction in time required to tune ammonia injection grid
  - Higher flue gas velocity translates into smaller cross-section and less pressure drop, lower capital

Typical Arrangement

GSG Arrangement
Minimum Operating Temperature (MOT)

- Desire to decrease load below MOT, driven by financial savings
  - Temperature below which catalyst reactivity declines below guarantee level
- ABS (NH₄HSO₃) forms at $T < \sim 650 \, ^\circ\text{F}$ and can condense on catalyst layers
  - $T_{\text{formation}}$ depends on NH₃ and SO₃ concentrations
  - MOTs typically range from 600 °F to 625 °F
- Flow and temperature can be stratified across catalyst;
- Sorbents can be injected ahead of SCR to capture SO₃, and limit ABS-related pluggage
  - CaO + SO₃ → CaSO₄ (insoluble particulate)
  - MgO + SO₃ → MgSO₄ (water soluble particle)
Reducing MOT with TIFI Mg

- Mg(OH)$_2$ reagent fed into furnace just prior to primary superheater
  - Slag/fouling control
  - Mg(OH)$_2$(slurry) → MgO(s) + H$_2$O(g) + SO$_3$(g) → MgSO$_4$(s)

- Captures furnace- and SCR-generated SO$_3$
- Efficient reaction = low NSRs = cost-effective

Approximate Residence Times
- SCR Inlet: 4.5 sec
- SCR Outlet: 6.5 sec
- APH Inlet: 8.0 sec
Reducing MOT Through SO$_3$ Capture: O&M Impact

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<td>Off-peak power price</td>
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<td>Unit generation variable cost</td>
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<td>Design minimum load</td>
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<td>New minimum load</td>
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<td>Off-peak period (hrs/day)</td>
<td>7.5 hours</td>
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<td>Off-peak days (days/week)</td>
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<td>Savings from minimum load decrease (350 days/yr)</td>
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<td>Fuel Tech TIFI$^\text{TM}$ Mg(OH)$_2$ Program</td>
<td>($750,000)</td>
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<tr>
<td>Net Annual Savings</td>
<td>$2,408,000</td>
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La Cygne U1
SCR Retrofit Project Summary

• Fuel Tech provided KCP&L Computational Fluid Dynamics (CFD) modeling and design services for the La Cygne Unit 1 SCR
  o 815 MW B&W cyclone boiler with OFA and SCR
  o Second oldest WFGD installation in the country
• Installed in 2007 with a “3+1” catalyst layer configuration
  o Plagued with excess fly ash accumulations
  o Original design allowed for extensive ash buildup/plugging in back of reactor which increased velocities elsewhere causing catalyst erosion
• Project Goals:
  o Improve flow and velocity distribution
  o Eliminate recirculation areas in the reactor hood
Before – Ash Pluggage
Baseline Results – Velocity Profile

High and low spots from the turning vanes are helped by the straightening grid and perforated plate but still *yield a poor distribution into the 1st catalyst layer.*

Vectors near vanes show recirculation areas where potential ash fallout can occur.
Final Results – Velocity Profile

Flow shadows from large truss reduced with new design

Uniform flow vectors; no recirculation
Finished Product

No ash buildup after months of operation
La Cygne Statistics

- Baseline catalyst inlet velocity profile – 17.5% RMS
  - % within +/- 15% of average = 57.9%
  - % within +/- 30% of average = 88.6%

- Final Catalyst Inlet Velocity Profile – 9.4% RMS
  - % within +/- 15% of average = 90.8%
  - % within +/- 30% of average = 98.8%

- Unit in Operation since November 2012
  - Lower rise in dP and reduced fan power
  - Short outage inspections show clean reactor
  - Reduced ash pluggage aids reactor potential and decreases deactivation
  - Lengthened catalyst life and reduced costs
  - Reduced vacuuming and rejuvenation
  - Lower ammonia use and slip (reduced FGD foaming)
### FTEK SCR Experience – Partial List

<table>
<thead>
<tr>
<th>Owner</th>
<th>Plant</th>
<th>Size, MW</th>
<th>Firing Method</th>
<th>Sub-Contract/Support To</th>
<th>Year of Service</th>
<th>Types of SCR Services Provided</th>
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<td>AECI</td>
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<td>600</td>
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<td>C, F</td>
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**Types of SCR Services Provided:**

A) SCR Consultation  
B) SCR Process Design  
C) SCR Arrangement and Component Design  
D) SCR Catalyst Design  
E) SCR Specification Preparation and Review  
F) SCR Physical Flow and CFD Model Design  
G) SCR Startup, Troubleshooting, Tuning and Optimization  
H) SCR Catalyst Management  
I) Other: AIG Tuning, reactor inspection, catalyst specification review, etc.
SCR Operation and Mercury Oxidation

Changes in SCR operating conditions can adversely affect the expected co-benefit on mercury (Hg) oxidation. Unexpected increases in elemental mercury (Hg\(^0\)) entering the wet FGD system will immediately increase the total stack mercury (Hg), thus jeopardizing the MATS 30-day rolling average for mercury compliance.

<table>
<thead>
<tr>
<th>SCR Condition</th>
<th>Effect on Mercury Oxidation</th>
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<tr>
<td>NH(_3) (ammonia) Slip</td>
<td>- Excess NH(_3) inhibits Hg(^0) oxidation across catalyst</td>
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<tr>
<td>Increasing SCR exit gas temps</td>
<td>- Reverts portion of Hg(^{2+}) back to Hg(^0)</td>
</tr>
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</table>
| Increased SO\(_2\) to SO\(_3\) conversion | - Degrades Hg capture by PAC  
- ABS fouling                     |
| Ash plugging or ash path issues | - Blinds catalyst active sites = degraded Hg\(^0\) oxidation                  |
| Catalyst Aging                | - Hg\(^0\) oxidation decreases as catalyst reaction sites are consumed. Potential of Hg\(^0\) to stack increases. |

What options do you have?
Redox-Hg in wFGD
Redox-Hg Technology Overview

Redox Technology Group, LLC, (d/b/a Redox Solutions) is an Indiana-based chemical manufacturer specializing in the development and synthesis of highly reactive, insoluble inorganic sulfide solutions marketed under the brand names Redox-Hg and FerroBlack®.

These reagents are ideal for the treatment of aqueous, gaseous, or solid media contaminated with heavy metals such as:

- Oxidized Mercury (Hg²⁺)
- Elemental Mercury (Hg⁰)
- Selenite (Se⁴⁺)
- Arsenic (As)
- Hexavalent chromium (Cr⁶⁺)
- Copper (Cu)
- Nickel (Ni)
Product Advantages

**Colloidal suspension:**

- Ferrous sulfide particles sometimes referred to as “mackinawite or “amorphous ferrous sulfide”
- pH range from 10.0 to 13.0 and ORP from -600 to -1,200 mV.

**Multiple pollutant removal mechanisms:**

- Dissolution / precipitation
- Occlusion / mixed crystal formation / physical entrapment
- Surface adsorption
- Electron Transfer / Electron “Hopping”

**Redox-Hg continues to operate when other additives are ineffective**
How Does Redox-Hg Work?

• Minimum solubility
  o FeS ↔ Fe^{2+} + S^{2-} or FeS + H^+ ↔ Fe^{2+} + HS^-
  o Hg^{2+} + S^{2-} ↔ HgS↓
• Adsorb and holds metals at the particle surface
  o ≡FeS + Hg^{2+} ↔ ≡FeS–Hg^{2+} (surface adsorption)
  o 2[≡Al(OH)_{3}] + Hg^{2+} ↔ 2[≡Al(OH)_{3} ]−Hg^{2+} (surface adsorption)
• Electron transfer and hopping
  o Ability to oxidize Hg^0 on the particle surface (Hg^0 + 2 Fe^{3+} ⇔ Hg^{2+} + 2 Fe^{2+})
• Stable to oxidation vs. competition
  o Minimally soluble particles release reactive sulfides over time
  o Other soluble sulfides (e.g. NaHS, polymers, etc.) are prone to oxidation of reactive sulfides to inert SO_3^{2-} and SO_4^{2-}
    ▪ Diminished reactivity over time = more chemical required
In wFGD, Fe$^{2+}$ oxidizes to Fe$^{3+}$, cation vacancies develop to maintain overall charge balance. Cation vacancies (negatively-charged holes) promote positively-charged metals adsorption.
Direct Removal of Elemental Hg (Hg⁰): Simulated wFGD

- Bench-scale tests specifically targeted Hg⁰
- Batch reactor with continuous Hg⁰ gas feed was treated with single dose of Redox-Hg
- Results were consistent with initial field trials
- Reagent added as % of total scrubber liquor volume

### Redox-Hg Removal of Hg⁰ in Simulated Wet Scrubber Module

![Graph showing Hg⁰ removal over time with different reagent concentrations.](image_url)

- 0.01% Redox HgRPC
- 0.025% Redox HgRPC
Direct Removal of Hg\textsuperscript{0} in wFGD

- On-demand Redox-Hg injection into wFGD captures Hg\textsuperscript{0} going into the scrubber during “upset” conditions.
- Redox-Hg controls Hg re-emission that may contribute to total stack mercury until “normal” SCR operations are restored.
Rapid Response to Stack Hg Emissions

- Recent emergency response to Hg emission concern
- Total injection of 1 tote (300 gallons)
- B&W Spray Tower, single 1 MM gallon absorber
Redox-Hg: Rapid Response to Stack Hg

300 gallon tote injected into wFGD (0.027% v/v) over 30 to 45 minute span
AEP Cardinal Station: 650MW BIT SCR CESP WFGD (JBR type scrubber)
Feed Modes

• Rapid response allow Redox-Hg to be used in several modes:
  
  o Batch mode
    ▪ 0.03% – 0.1% (v/v) to reduce scrubber Hg content
  
  o Continuous feed mode
    ▪ 1-10 gph to maintain ORP and scrubber Hg content to prevent stack emissions
Impact of ORP on Mercury Emissions

- At low ORP (< 100 mV) and high ORP (> 300 mV)
  - Emissions at stack increase

- Forced oxidation, low ORP – little Hg remains in liquor
  - Re-emission typically minimal or none
- Forced oxidation, high ORP – most of Hg remains in liquor
  - Significant re-emission levels likely

Mercury Adsorption – Speciation in wFGD

wFGD liquor samples collected from the outlet of the slurry recirculation pumps

Redox-Hg Injection started

Shift dissolved Hg into particulate form for removal with scrubber solids
Total Metals Management: Injection Locations

1. Wet Scrubber Additive (Hg⁰, Hg⁺², As, Se⁺⁴, ORP Control)
2. Waste water treatment (alternative to organo-sulfides)
3. Immobilization of mobile metals (TCLP and Total) in fly ash
4. In-situ control of metals in landfill seeps
5. Landfill leachate treatment
Advantages of Redox Reagents

- Fast-acting mercury control option
  - Start-up, SCR bypass, ORP excursions, or other events that higher Hg stack emissions
- Lowers Hg$^0$ across the scrubber and total stack mercury emissions by greater than 95%
  - Doesn’t impact quality of fly ash or gypsum
- Effective over a wider pH (4.5 to 7.0) and ORP (-200 to +600mV) ranges than traditional soluble sulfides and works within existing scrubber conditions
- Eliminates the potential of leachable heavy metals in solids and ash
- Additional co-benefits:
  - Lower chemical consumption in WWTPs for heavy metals removal
  - Inhibits selenium oxidation in wFGD slurry (e.g. selenite (Se$^{+4}$) to selenate (Se$^{+6}$))
  - Removal of selenite (Se$^{+4}$) from the scrubber liquor and waste water
  - Reducing total dissolved mercury (Hg), arsenic (As) and selenium (Se) in ash pond water