Worldwide Pollution Control Association

IL Regional Technical Seminar
August 3-4, 2010

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WPCA

90% Mercury Removal – Control Technologies

Amy Evans – Marsulex Environmental Technologies
Ken Jeffers – Johnson Matthey Catalysts
Don Stowe – Babcock Power
Greg Bielawski – The Babcock & Wilcox Company

WPCA Regional Seminar
Springfield, Illinois
August 3, 2010
Man-made Sources of Mercury in the Environment – 2006

- Fossil Fuel Combustion (Primarily Coal) 67%
- Cement Industry 10%
- Non-Ferrous Metal Production 10%
- Pig Iron & Steel Production 7%
- Caustic Soda Production 5%
- Mercury Production 3%
- Gold Production 1%
- Waste Disposal 1%
- Other 1%
- Other 1%
- Other 1%
- Other 1%
- Other 1%
- Other 1%
What we do know?

- Federal Mercury MACT Standard
  - 3/16/2011 To be proposed
  - 11/16/2011 Final rule
Houston Astrodome

A Hypothetical Example

- Dome filled with 30 billion ping-pong balls
- 30 black mercury balls
- Find and remove 27 balls for 90% Hg capture
 Lessons learned in the past

- **1970’s & 1980’s**
  - Sulfur dioxide
    - 500-3000 ppm SO₂
    - Early systems
      - 70%-85% capture
      - Very poor availability

- **1980’s & 1990’s**
  - NOx
    - 200-600 ppm
    - Early systems
      - low capture rates
      - High ammonia slip

- **2000’s**
  - Mercury
    - ~1 ppb
Coal Mercury Concentration

1999 coal production, ICR 2 data, by county

Chlorine in Coal

Chlorine (ppm, dry)

- <100
- 100 - 250
- 250 - 500
- 500 - 1,000
- 1,000 - 2,000
- 2,000 - 4,450

http://ugs.utah.gov/emp/mercury/index.htm
Mercury Speciation by Fuel Type

Flue Gas Speciation

- Bituminous
- Subbituminous
- Lignite

Elemental Hg vs. Oxidized Hg

Influences on Hg Speciation

- Gas Composition (i.e., Chloride)
- Unburned Carbon (UBC)
- Catalysts (i.e., SCR, Ash, Boiler Metals)

2000 Data per NETL at 2002 EPRI Workshop

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Power Plant “Co-benefits”
Reduce Stack Mercury Emissions
Mercury Control Options

- **MercPlus™ (Hg+) System**
- **Pulverizer**
- **Boiler**
- **SCR**
- **Air Heater**
- **SO₃ Sorbent Injection**
- **Dry FGD**
- **PAC Injection**
- **TOXECON**
- **TOXECON II**
- **ESP**
- **Wet FGD**
- **PJFF**
- **Absorption Plus (Hg)™ System**
90% Mercury Removal – SCR Effects

Ken Jeffers – Johnson Matthey Catalysts

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Hg Oxidation across SCR Catalyst

WPCA Illinois Technical APC Seminar
Springfield, IL
August 3, 2010

Ken Jeffers
SCR Applications Engineer
Introduction – Mercury Emission Control from Coal-fired Sources

- Hg speciation
  - $H^0$ – elemental mercury
  - $Hg^{2+}$ – oxidized mercury
  - Total – $Hg^T$ includes $Hg^0$, $Hg^{2+}$, $Hg^P$
  - Strong influence on speciation by Cl/Br in flue gas

- Basic Capture/Removal Methods
  - Activated Carbon Injection, baghouse – $Hg^0/Hg^{2+}$
  - Novel Sorbents, baghouse – $Hg^0/Hg^{2+}$
  - Capture in wet-FGD – $Hg^{2+}$ (water soluble, easier to absorb)

- Hg oxidation is a co-benefit of SCR catalyst
  - ***SCR catalyst does not capture or remove Hg***
  - Challenging as Hg is in trace amounts ~ ppb, µg/Nm$^3$
  - $Hg^{2+}$ can re-emit to $Hg^0$ downstream of SCR
Reactions of Hg in SCR Catalyst

Desired Reactions – Hg oxidation
• Hg + 2 HCl + ½ O₂ → HgCl₂ + H₂O
• Hg + SO₃ + ½ O₂ → HgSO₄

Side Reactions
• 2 HCl + ½ O₂ → Cl₂ + H₂O
• Hg + Cl₂ → HgCl₂

Undesired Side Reactions
• Cl₂ + SO₂ + H₂O → 2 HCl + SO₃, inhibition of Cl₂ formation
• 3 HgCl₂ + 2 NH₃ → 3 Hg + 6 HCl + N₂, reduction of Hg by NH₃
• HgCl₂ + SO₂ + H₂O → Hg + 2 HCl + SO₃, reduction of Hg by SO₂
Key Variables for Hg Oxidation in SCR Catalyst

- Flue gas Chlorine concentration (HCl/Cl\textsuperscript{−})
  - Influences speciation at SCR inlet \(\rightarrow\) high Cl, increases Hg\textsuperscript{2+} in Hg\textsubscript{T}
  - 50+ ppm HCl in flue gas \(\rightarrow\) 80 – 90%+ Hg oxidation
  - Similar effect for 5+ ppm Bromine
  - Lower oxidation rates for low Cl fuels (PRB, low Cl bituminous)
- Flue gas Temperature \(< 700 \, ^\circ F\) favorable for Hg oxidation
- Ammonia competes for active sites in catalyst and inhibits Hg oxidation
  - NH\textsubscript{3}-NO\textsubscript{x} reaction favored in top catalyst layer(s)
  - Hg oxidation favored in lower catalyst layers as NH\textsubscript{3} is depleted
  - Filling spare catalyst layers good for Hg oxidation
Hg Oxidation in Catalyst – General Effect of Cl

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Hg Oxidation in Catalyst – General Effect of NH₃

Reproduced by permission from Effects of Chlorine and other Flue Gas Parameters on SCR Catalyst Mercury Oxidation and Capture, EPRI, Palo Alto, CA 2009. 1020591
Hg Oxidation in Catalyst – Effects of Temperature and Cl

Hg = 1015 µg/Nm³

Hg_{ges} = 10 – 15 µg/Nm³
Thank You!

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1121 Alderman Drive, Suite 204
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www.jmcatalysts.com
90% Mercury Removal – Activated Carbon

Don Stowe – Babcock Power

WPCA Regional Seminar
Springfield, Illinois
August 3, 2010
90% Mercury Capture;
Can we get there?

Don Stowe, Consultant – Babcock Power

www.babcockpower.com
No Single Answer
Each unit is site specific

- Fuel
- Boiler type
- Plant layout
- Background Hg Capture (high LOI ash)
- Existing APC devices (co-benefits)
Similar Patterns Found to Hold for Hg Capture by Activated Carbon
(Most data from tests <1 month)

- WC, FF or TOXECON
- WC, ESP
- LSEB, ESP
- HSEB, ESP

| WC = Western Coal |
| LS = Low Sulfur  |
| HS = High Sulfur |
| EB = Eastern Bituminous |

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Co-Benefits

- **SCR**
  - Reasonable job of oxidizing Hg
  - Also Oxidizes SO$_2$ to SO$_3$
- **Wet FGD**
  - Good job of capturing oxidized Hg
- **Spray dryer/Fabric filter**
- **CDS technology**
Easy Answer is NOT the best answer

- Install baghouse/PAC injection
  - Most expensive
    - $80-130/KW capital investment
    - Additional parasitic load
  - Not practical at many installations
    - Space constraints
    - Fan capacity
What do we know?

- PAC extremely effective for capturing oxidized Hg
- PAC does poorer job of capturing elemental Hg
- PRB flue gas predominantly elemental Hg
- SO$_3$ proven to “poison” PAC
Carbon has the adsorption capacity
- Fixed bed data – Hg loading up to 10%
  - 100,000 µg/g
- Typical real world adsorption
  - 20-40 µg/g

Challenge is kinetics (assure Hg contacts carbon)
Hg Adsorption
Fixed Bed
Commercial PAC

HgCl$_2$

mg Hg ret/g PAC

Typical reaction time $\leq$ 1 sec.

Source: UK CAER
Criteria for success

- Oxidation of Hg (bromine)
  - Coal blending
  - Furnace injection of oxidant
  - PAC/Br blends
- Elimination of “poisons” (SO3)
  - Trona/Hydrated Lime/Magnesium Oxide
    - Pre-blended PAC/alkali
    - Upstream alkali injection
- Selection of most cost effective carbon
  - Pore size critical parameter
  - Low ash
  - Low moisture
Other possible means of improvement

- Reduce carbon particle size
  - Finer grind
    - Material handling issues
    - ESP “blow-by”
  - On site micronizing
    - Expensive / high maintenance

- Increase residence time
  - Install baghouse (Toxicon)

- Improve dispersion/mixing
  - CFD
  - Physical Modeling
  - Install mixing device
Babcock Power Capabilities

- Design/engineer PAC dosing systems
  - CFD
  - Physical flow modeling
  - Delta Wing static mixer
- Low cost lignite based carbon – HOK
  - Bromine impregnated
  - Sulfur impregnated
  - Alkali impregnated
Effect of Delta-Wing®
Delta Wing
Full Scale Installation

[Image of a construction site with metal framework and cranes in the background.]
A6

800 mw
duct between X and Y
dimensions -
gas flow-

Author, 7/29/2010
The road to success

- Every unit is site specific
- Remove carbon “poisons” – SO3
- Oxidize Hg
- Put PAC in contact with oxidized Hg
  - Physical modeling
- Evaluate low cost PAC
PAC Evaluation

- Ultimate answer by testing
  - Lbs/hr required x $/lb
- Data suggest most brominated perform similarly as well as non-brominated
- Ineffective measuring sticks
  - BET surface area
  - Bromination method
Hg-Breakthrough curves (detail) \((60 \text{ m}^3/(\text{m}^2\cdot\text{h}), 150 ^\circ\text{C}, 1030 \text{ mbar})\)
Thank You
90% Hg Removal with Wet or Dry FGD Systems
by
Greg Bielawski

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B&W’s Wet FGD
Mercury Control Options

CaCl$_2$ Injection (if needed)
PAC Injection (if needed)

FGD Injection (if needed)
Industry Challenges

- Hg re-emission in WFGDs
- PAC poisoning when burning high sulfur coal
Absorption Plus (Hg)™ System for Enhanced Mercury Capture

- Proprietary technology prevents mercury re-emission from Wet FGD
- Removes and retains over 95% of oxidized mercury in FGD
- Mercury removed with solids from FGD system
- Cost effective reagent
Wet FGD Reagent Feed System

Injection Skid

Feed Location
E.ON America’s Mill Creek Unit 4
Louisville, KY

- 2007 DOE/EERC Phase III Mercury Testing
- B&W Wet FGD additive Absorption Plus(Hg)™
- Mill Creek burns *high sulfur* bituminous coal
- Air quality control system consists of SCR + ESP + Wet FGD
E.ON. Mill Creek
Mercury Control Tools
E.ON Mill Creek WFGD Outlet

B&W WFGD Additive

Absorption Plus @ 60 gph

Hg° re-emission

Mercury Concentration, µg/dsm³

7/11/07 0:00 7/11/07 4:00 7/11/07 8:00 7/11/07 12:00 7/11/07 16:00 7/11/07 20:00 7/12/07 0:00
Powdered Activated Carbon Storage and Feed System

PAC Storage Silo

Feed System

Injection System
Industry Challenges

Hg re-emission in WFGDs

PAC poisoning when burning high sulfur coal
Influence of $\text{SO}_3$ on Mercury Removal with Activated Carbon
Dry Sorbent Injection (DSI) Technology Overview

- DSI = Dry Sorbent Injection
- DSI is based on dilute phase pneumatic conveying technology
- Major components are:
  - Truck/rail unloading
  - Silo
  - Weigh hopper/Rotary feeder
  - Transport Air Blowers
  - Reagent milling (optional)
- Not a new technology
  - Used for SO₂ since 1980s
- Current applications for SO₂, SO₃, HCl and Hg
- B&W mobile test unit available
Texas Genco, Parish Plant – Sub-bituminous Coal

- 650 MW SCR / FF / Wet FGD
- Low Chlorine PRB Coal
- Limestone Wet FGD for SO$_2$ Control
MercPlus™ Fuel Additive for Low Halogen Coals

- Injected onto coal in coal feeders
- Increases oxidation of elemental mercury
- Co-benefits Hg removal with FGD
- Reduces or eliminates PAC consumption
- May allow use of standard PAC versus more costly brominated PAC
- Typical payback less than one year by reducing PAC consumption
Additive Injection Skid and Tank
Total Mercury Removal Across Wet FGD Scrubber

- **CaCl$_2$ Only**
- **Wet FGD Additive Alone**
- **CaCl$_2$ and Wet FGD Additive**

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<th>200 ppm</th>
<th>400 ppm</th>
<th>500 ppm</th>
<th>600 ppm</th>
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<th>22 gph</th>
<th>200 ppm+9 gph</th>
<th>400 ppm+29 gph</th>
<th>500 ppm+4 gph</th>
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**B&W’s Dry FGD**  
**Mercury Control Options**

- CaCl₂ Injection (if needed)
- Coal Preparation
- PAC Injection
- SDA
- FF or ESP
MercPlus™ Fuel Additive for Low Halogen Coals

- Injected onto coal in coal feeders
- Increases oxidation of elemental mercury
- Co-benefits Hg removal with FGD
- Reduces or eliminates PAC consumption
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- Typical payback less than one year by reducing PAC consumption
Powdered Activated Carbon Storage and Feed System

PAC Storage Silo  Feed System  Injection System
Black Hills Power – Wygen 1 Sub-bituminous Coal

- Nominal 80 MW Unit
- Wyodak Mine Coal
- B&W Opposed Wall-Fired Boiler
- SCR
- B&W SDA and PJFF
Wygen 1 Mercury Controls
Wygen 1 Parametric Mercury Tests

- Total Hg Removal (%)

- Baseline
- Baseline
- 230 ppm
- 400 ppm
- 690 ppm
- 2 lb/Macf
- 5 lb/Macf
- 230 ppm + 2 lb/Macf
- 400 ppm + 2 lb/Macf

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Thank You!