Test and Commercial Operating Results of Bromine Based Mercury Control at Coal-Fired Power Stations in USA

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http://www.vosteen-consulting.de

44. Kraftwerkstechnisches Kolloquium 2012, Congress Center Dresden,
Agenda

- Introduction: BBA today and 10 years ago
- EPA’s MATS as issued on December 21, 2011
- US Coals (Mercury, Chlorine, Bromine, Sulfur)
- Southern Company – Wet Mercury Capture at Plant Miller
- Alstom Power – Wet Mercury Capture at Plant WE Plaesant Prairie
- Dry Mercury Capture
- US EPRI Balance of Plant Report August 2012
- Outlook (Cooperation Vosteen/STEAG/AE&E)
- Conclusions
Precombustion Bromide Addition to Coal or Boiler Bromide Addition (BBA) – Today a main topic at any large US Conference on Air Pollution Control

Session C2 at EUEC 2012 in Phoenix AZ:

“Hg Control Demonstrations & Bromine”
sponsored and chaired by Vosteen Consulting GmbH
Today > 54 US Power Stations are applying Precombustion Bromide Addition commercially
Electric Power Research Institute (EPRI) at Mega Symposium in Baltimore, August 21 – 23, 2012

Source: Katherine Dombrowski, Katie Arambasick (URS), Ramsay Chang (EPRI), Corey Tyree (Souther Company): “Balance of Plant Effects of Bromide Addition for Mercury Control”, paper # 93, Power Plant Air Pollutant Control MEGA Symposium, Baltimore MD, August 21-23, 2012
Mercury-Related Chemistry in Waste Incineration and Thermal Process Flue Gases

Air Quality (VI) Conference, Arlington, VA, Sept. 2003

Bromine > 25 times more effective for Hg\textsuperscript{met} oxidation than chlorine, in waste incineration as well as in coal combustion

(BAYER patent applications pending worldwide)

KNX™ Coal Additive –
Addition on coal conveyor belt

Coal Conveyor (shown in black)

Injection Spray Header

KNX™ Additive Storage Tank

Metering Pump

ALSTOM
KNX™ Coal Additive – drums and pumps in a full scale test
Western Utilities
Plant D

KNX™ Storage & Feed System

Storage ~30,000 gallons
Other Mid-West Utilities
Typical KNX™ System

Storage ~6500 gallons

Feed ~3.3 gph / pump
## KNX™ Commercial Operations

### We Energies
- **Pleasant Prairie Station**
  - 2 x 610 MW
  - PRB
  - SCR + CSESP + WFGD

### Mid-West Utilities
- **Unit A**
  - 1 x 380 MW
  - PRB
  - ACI + CSESP
- **Unit B**
  - 1 x 330 MW
  - PRB
  - CSESP
- **Unit C**
  - 1 x 511 MW
  - PRB
  - ACI + CSESP

### Western Utilities
- **Plant D**
  - 2 x 384 MW
  - PRB
  - HSESP + WFGD
- **Plant E**
  - 3 x 750 MW
  - Bt
  - HSESP + WFGD

### Montana Dakota Utilities
- **Lewis & Clark Station**
  - 1 x 45 MW
  - Lignite
  - ACI + MC + WS

**Total Operating**
- 3254 MW
### EPA's List „NEEDS 4.10 MATS“ - Page 1 of 11

**Plant Name** | **ORR/PL Address** | **City** | **County** | **State** | **Latitude** | **Longitude** | **Coal Capacity** (MM) | **Oil Capacity** (MM) | **Total Capacity** (MM) | **COAL**** | **Oil**** |
---|---|---|---|---|---|---|---|---|---|---|---|
Bally | 3 Commonwealth Ave | East Penn | Montgomery | Pennsylvania | 40.0933 | -75.8108 | 2,360 | 2,300 | 2,360 | | |
Charles R. Brown | 36 Commonwealth | East Penn | Monroe | Pennsylvania | 40.0933 | -75.8108 | 2,360 | 2,300 | 2,360 | | |
Colette | 12000 High Place | Columbia | Howard | Maryland | 38.9051 | -76.8709 | 1,680 | 1,650 | 1,680 | | |
E & K. Davis | 12000 High Place | Columbia | Howard | Maryland | 38.9051 | -76.8709 | 1,680 | 1,650 | 1,680 | | |
Gordon | 7300 King Place | Columbia | Howard | Maryland | 38.9051 | -76.8709 | 1,680 | 1,650 | 1,680 | | |
Gordon | 12000 High Place | Columbia | Howard | Maryland | 38.9051 | -76.8709 | 1,680 | 1,650 | 1,680 | | |
Greene County | 15 High Place | Columbia | Howard | Maryland | 38.9051 | -76.8709 | 1,680 | 1,650 | 1,680 | | |
James R. Miller | 12000 High Place | Columbia | Howard | Maryland | 38.9051 | -76.8709 | 1,680 | 1,650 | 1,680 | | |
Kidd Creek | 12000 High Place | Columbia | Howard | Maryland | 38.9051 | -76.8709 | 1,680 | 1,650 | 1,680 | | |
Kidd Creek | 12000 High Place | Columbia | Howard | Maryland | 38.9051 | -76.8709 | 1,680 | 1,650 | 1,680 | | |
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**Utility Macht Rule** -> **EPA’s MATS as drafted**, Table 3 for EGUs firing high and low rank coals (excerpt)

<table>
<thead>
<tr>
<th>Subcategory</th>
<th>Filterable particulate matter</th>
<th>Hydrogen chloride</th>
<th>Mercury</th>
</tr>
</thead>
<tbody>
<tr>
<td>Existing - Unit not low rank virgin coal</td>
<td>3.0E-2 lb/MMBtu (3.0E-1 lb/MWh)</td>
<td>2.0E-3 lb/MMBtu (2.0E-2 lb/MWh)</td>
<td>1.2E0 lb/TBtu (1.3E-2 lb/GWh)</td>
</tr>
<tr>
<td>Existing - Unit designed low rank virgin coal</td>
<td>3.0E-2 lb/MMBtu (3.0E-1 lb/MWh)</td>
<td>2.0E-3 lb/MMBtu (2.0E-2 lb/MWh)</td>
<td>1.1E1 lb/TBtu (1.2E-1 lb/GWh)</td>
</tr>
<tr>
<td>New - Unit not low rank virgin coal</td>
<td>7.0E-3 lb/MWh</td>
<td>4.0E-4 lb/MWh</td>
<td>2.0E-4 lb/GWh</td>
</tr>
<tr>
<td>New - Unit designed for low rank virgin coal</td>
<td>7.0E-3 lb/MWh</td>
<td>4.0E-4 lb/MWh</td>
<td>4.0E-2 lb/GWh</td>
</tr>
</tbody>
</table>

**Range about: 1.4 µg/dscm @ 6 % O₂**

**Mercury Limit lowered by the Factor 65**

**Range about: 22 ng/dscm @ 6 % O₂ CRAZY!**

**Beyond the Floor range for mainly TX Lignites:**

*about: 4.1 µg/dscm @ 6 % O₂*

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## Actual Status of the Mercury and Air Toxics Standards (MATS) as 30 day-Rolling-Averages

<table>
<thead>
<tr>
<th>Subcategory</th>
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<th>Mercury</th>
<th>Übersetzung</th>
</tr>
</thead>
<tbody>
<tr>
<td>Existing – Unit not low rank virgin coal</td>
<td>3.0E-2 lb/MMBtu (3.0E-1 lb/MWh)</td>
<td>2.0E-3 lb/MMBtu (2.0E-2 lb/MWh)</td>
<td>1.2E0 lb/TBtu (1.3E-2 lb/GWh)</td>
<td>1,4 µg/m³ i.N. tr. bei 6 Vol.-% O₂</td>
</tr>
<tr>
<td>Existing – Unit designed for low rank virgin coal</td>
<td>3.0E-2 lb/MMBtu (3.0E-1 lb/MWh)</td>
<td>2.0E-3 lb/MMBtu (2.0E-2 lb/MWh)</td>
<td>4.0E0 lb/TBtu (4.0E-2 lb/GWh)</td>
<td>4,1 µg/m³ i.N. tr. bei 6 Vol.-% O₂</td>
</tr>
<tr>
<td>New – Unit not low rank virgin coal</td>
<td>7.0E-3 lb/MWh</td>
<td>4.0E-4 lb/MWh</td>
<td>2.0E-4 lb/GWh</td>
<td>22 ng/m³ i.N. tr. bei 6 Vol.-% O₂</td>
</tr>
<tr>
<td>New – Unit designed for low rank virgin coal</td>
<td>7.0E-3 lb/MWh</td>
<td>4.0E-4 lb/MWh</td>
<td>4.0E-2 lb/GWh</td>
<td>4,1 µg/m³ i.N. tr. bei 6 Vol.-% O₂</td>
</tr>
</tbody>
</table>

lb/MMBtu = pounds pollutant per million British thermal units fuel input; lb/TBtu = pounds pollutant per trillion British thermal units fuel input; lb/MWh = pounds pollutant per megawatt-hour electric output (gross); lb/GWh = pounds pollutant per gigawatt-hour electric output (gross).

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Existing Units
High Rank Coals as Hard Coal

Existing Units
Low Rank Coal as Lignite *)

New Units
High Rank Coal
Again under revision by EPA since June 2012

*) beyond the floor limits - more stringent than the MATS floor
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5000 samples - evaluated by Vosteen Consulting
with courtesy of Prof. Dr. Belkin,
Febr. 20, 2010

NCRDS CHEMICAL DATA
Only low mercury coals?  
(e.g. PRB with 0.1 ppm Hg dry)  

What about the other coals - in the long run?

5000 samples - evaluated by Vosteen Consulting  
with courtesy of Prof. Dr. Belkin,  
Febr. 20, 2010
5000 samples - evaluated by Vosteen Consulting
with courtesy of Prof. Dr. Belkin,
Febr. 20, 2010

- CL IN PPM ON DRY, WHOLE-COAL BASIS
5000 samples - evaluated by Vosteen Consulting
with courtesy of Prof. Dr. Belkin,
Febr. 20, 2010

- BR in PPM on dry, whole-coal basis
5000 samples - evaluated by Vosteen Consulting
with courtesy of Prof. Dr. Belkin,
Febr. 20, 2010

Source: Allan Kolker and Jeffrey C. Quick, U.S. Geological Survey and Utah Geological Survey:
“Geologic Controls on Halogens in Coal”, MEC 9 - Mercury Emissions from Coal, St. Petersburg (Russia), May 2012
5000 samples - evaluated by Vosteen Consulting
with courtesy of Prof. Dr. Belkin,
Febr. 20, 2010

*S IN % ON DRY, WHOLE-COAL BASIS

[S chart with data points and regions labeled Central Appalachian, Northern Appalachian, Southern Appalachian, Powder River Basin]
Halogen Proportions in Coal

- Figure shows U.S. county-average Cl and Br contents (USGS data).
- Bromine is typically 1-4% of Cl content on a weight concentration basis.
- Iodine contents are typically ≤ Br.
- Fluorine is ≤ Cl.

Low Halogen Coals as Subbituminous PRB Coal and Lignite and as imported coals from Columbia, also fired in USA

Rank Dependence of Halogen Contents

Results show U.S. county-average Cl and Br contents with ASTM coal rank and origin. Cl data from 1999 EPA ICR; Br results from USGS (Kolker and Quick, 2012 in review).

Source: Kolker and Quick, 2012, in review

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Removal Needed to Meet Limit

Source: M. S. Berry and B. W. Vosteen: „Bromine Injection Technology Demonstrations at Plant Miller for Removing Vapor Phase Mercury“, 12th ICESP in Nuremberg, May 2011
Calcium Bromide Injection

- All Testing conducted @ Miller Unit 4 (4x700 MW)
- Inject CaBr₂ onto coal (equivalent Bromide per coal: 0 ppm – 350 ppm)
- Three Phases
  - Phase I: Measurement Only
  - Phase II: Pilot FGD removal
  - Phase III: 90 Days (full-scale)
  - 2006; 2008 & 2010
- Hg Oxidation w & w/o SCR
- Verify Removal via FGD
- Balance of Plant Impacts

Source: M. S. Berry and B. W. Vosteen: “Bromine Injection Technology Demonstrations at Plant Miller for Removing Vapor Phase Mercury “, 12th ICESP in Nuremberg, May 2011
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License granted in 2008 to WE Power Stations Pleasant Prairie (2 x 600 MWe Units with SCR, ESP, WFGD in commercial operation since January 1st, 2010)

2 x 600 MWe Base Load (24 hours/day)

PRB coal
2 x 315 tons/hour
0.11 ppm Hg

KNX (as CaBr$_2$)
25 ppm Br on coal

H$_{\text{total}}$ at stack
$< 1 \mu\text{g/dscm}$
(both units)
Power Station WE Pleasant Prairie with SCR, ESP, WFGD
25 ppm Br per Coal only, SCR in service with NH₃
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BAYER/Currenta GmbH& Co oHG in Uerdingen: PC-fired Boiler (100 MW\textsubscript{therm})
Co-Combustion of Industrial Sewage Sludges

Multi-stage APC System – APC Type: dry/wet

Source: Vosteen, Nolte et al.: „Chlorine- and bromine-enhanced Hg sorption on ESP fyl ash from a coal-fired slag-tap boiler and on cement raw meal“, VDI Seminar 431802, September 29 - 30, 2003 in Duesseldorf (Germany)
Fire side bromide addition (internal bromination) is improving Hg-adsorption at fly ash UBC by the factor 2.5

Sorption isothermes of the ESP-fly ash of high LOI (22.3 % UBC)

Source: Vosteen, Nolte et al.: „Chlorine- and bromine-enhanced Hg sorption on ESP flyash from a coal-fired slag-tap boiler and on cement raw meal“, VDI Seminar 431802, September 29 - 30, 2003 in Duesseldorf (Germany)
Sharon Sjostrom: „Mercury Control for PRB and PRB/Bituminous Blends“, presented at EUEC, Tucson/Arizona, January 24, 2006
Sharon Sjostrom: “Mercury Control for PRB and PRB/Bituminous Blends“, presented at EUEC, Tucson/Arizona, January 24, 2006
Mer-Cure™ System Technology

The patented Mer-Cure™ process uniformly injects freshly treated sorbent upstream of the air preheater.
Alstom’s Mer-Cure™ & KNX™

Portable Mer-Cure™ Test Trailer

Synergistic Effect of KNX™ & Mer-Cure™

500 MW PRB with Particulate Scrubber

55% incremental performance improvement
**Colstrip Power Station Units U1 – U4 (2,200 MWe) fired with PRB coal from the Rosebud Mine**

<table>
<thead>
<tr>
<th></th>
<th>U1</th>
<th>U2</th>
<th>U3</th>
<th>U4</th>
<th>Site Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Hg lb/TBtu</td>
<td>0.48</td>
<td>0.69</td>
<td>0.95</td>
<td>1.01</td>
<td>0.84</td>
</tr>
</tbody>
</table>

Figure 9: U1 (310 MWe net) Total Stack Hg vs. Oxidizer and PAC Injection Rates

Figure 10: U3 and U4 (740 MWe net) Total Stack Hg vs. Oxidizer and PAC Injection Rates

Overall site average for the months of February through May 2010:

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Hg Emissions Limits

- **Section 45**: 40% Hg reduction
- **State regulations**: vary by state
- **MATS (Non-Lignite Coal)**: 1.2 lb/Tbtu
- **MATS (Lignite)**: 4.0 lb/Tbtu

**For MATS compliance:**
Halogen Addition must be coupled with FGD and/or with ACI

Source: Katherine Dombrowski, Katie Arambasick (URS), Ramsay Chang (EPRI), Corey Tyree (Souther Company): “Balance of Plant Effects of Bromide Addition for Mercury Control”, paper # 93, Power Plant Air Pollutant Control MEGA Symposium, Baltimore MD, August 21-23, 2012
(1) EPRI Study (Status August 2012)

Air Heater (AH) Corrosion

- 16 units in the survey with > 1 year operating time
- 12 of these units reported no corrosion issues
- 4 BBA units reported air heater corrosion
  - One unit: BBA + ACI; low AH outlet gas temperatures
  - One unit: operated BBA for 3 years without AH corrosion; lower operating loads in the past year
  - Two units: old air heater baskets
- 4 Br-ACI units reported AH corrosion
  - Units operated at low AH outlet temperatures
  - Units did not experience severe corrosion previous to the implementation of ACI

Source: Katherine Dombrowski, Katie Arambasick (URS), Ramsay Chang (EPRI), Corey Tyree (Souther Company): “Balance of Plant Effects of Bromide Addition for Mercury Control”, paper # 93, Power Plant Air Pollutant Control MEGA Symposium, Baltimore MD, August 21-23, 2012
(2) EPRI Study (Status August 2012)

Conclusions

- Widespread deployment of BBA in past year
- Documentation of Hg oxidation performance needed for certain unit configurations
- More operating experience and testing needed to characterize Br BOP effects and safe operating windows
  - AH, duct, ESP corrosion
  - FGD corrosion
- Unknown regulatory implications for effluents
  - Bromide ion, Hg, Se

Source: Katherine Dombrowski, Katie Arambasick (URS), Ramsay Chang (EPRI), Corey Tyree (Southern Company): “Balance of Plant Effects of Bromide Addition for Mercury Control”, paper # 93, Power Plant Air Pollutant Control MEGA Symposium, Baltimore MD, August 21-23, 2012
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Großtechnische Versuchsreihen
Kraftwerk Nord, Überblick Messtechnik

Abbildung 1: Quecksilberanteil (massenbezogen) im Unterlauf in Abhängigkeit vom Zyklontyp

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- The KNX™ technology has been successfully operated for over 2 years.

- The effectiveness of CaBr$_2$ and its rapid response to fuel Hg variations has been demonstrated in wet and dry APC systems.

- The combination of pre-combustion bromide addition and normal non-brominated activated carbon injection (ACI) reliably controls Hg emissions with variable load and fuel Hg content.

- Many “free riders”
Questions please?
Preferred approach towards new patents - promising even in case of no inventive height