Bromine Injection Technology Demonstrations at Plant Miller for removing vapor phase mercury

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President
Vosteen Consulting, GmbH

12th ICESP
International Conference of Electrostatic Precipitation
Nuremberg, Germany
9th of May, 2011 - 13th of May, 2011
Southern Company “Owned”

Total 42,514 MW

- **N** Nuclear (3,759 MW)
- **S** Steam (21,587 MW)
- **CC** Combined Cycle (8,359 MW)
- **CT** Combustion Turbine (3,992 MW)
- **H** Hydro (2,815 MW)
- **PA** Power Purchase Agreements (2,002 MW)
Regulations Update in the US

In the U.S., Power Plants Emit:

- 60% of the SO₂
- 60% of the arsenic
- organics, dioxins/furans, and others
- 13% of the NOₓ
- 30% of the nickel
- 20% of the chromium
- 50% of the mercury
- over 50% of many acid gases

Sources: NEI Trends Data (2009) and IPM (2010) (SO₂, NOₓ); Proposed toxics rule modeling platform, based on inventory used for 2005 NATA (Hg); Inventory used for 2005 NATA (other toxics)
Fate of Power Plant Mercury

Coal Hg “100” (arbitrary units)

Boiler

Hg 100

ESP

Hg 70-95%

FGD

Gypsum 10-80%

Fly Ash 5-30%

Hg < 0.1%

Hg 15 - 60% out stack

97% into sediments

0.03% to methylmercury

3% water column

0.03% to methylmercury

97% into sediments

Energy to Serve Your World®
Under the Clean Air Act Section 112: Hazardous Air Pollutants for PC Units
As proposed on March 16th 2011

<table>
<thead>
<tr>
<th></th>
<th>Hg</th>
<th>Total PM</th>
<th>HCl</th>
<th>Organics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Existing Unit</td>
<td>1.0 lb / TBtu</td>
<td>0.03 lb / MMBtu</td>
<td>0.0020 lb / MMBtu</td>
<td>Work Practice Standard</td>
</tr>
<tr>
<td>(&gt; 8300 Btu / lb)</td>
<td>(0.008 lb / GWh)</td>
<td>(0.3 lb / MWh)</td>
<td>(0.020 lb / MWh)</td>
<td></td>
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<tr>
<td></td>
<td></td>
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<td></td>
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<tr>
<td>Existing Unit</td>
<td>4.0 lb / TBtu</td>
<td>0.03 lb / MMBtu</td>
<td>0.0020 lb / MMBtu</td>
<td>Work Practice Standard</td>
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<tr>
<td>(&lt;8300 Btu / lb)</td>
<td>(0.01 lb / GWh)</td>
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<td>(0.020 lb / MWh)</td>
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</tr>
<tr>
<td>New Unit</td>
<td>0.000010 lb / GWh</td>
<td>0.050 lb / MWh</td>
<td>0.30 lb / GWh</td>
<td>Work Practice Standard</td>
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<tr>
<td>(&gt; 8300 Btu / lb)</td>
<td></td>
<td></td>
<td></td>
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</tr>
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<td></td>
<td></td>
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<tr>
<td>New Unit</td>
<td>0.040 lb / GWh</td>
<td>0.050 lb / MWh</td>
<td>0.30 lb / GWh</td>
<td>Work Practice Standard</td>
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<tr>
<td>(&lt; 8300 Btu / lb)</td>
<td></td>
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<td></td>
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</tr>
<tr>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

30 day rolling averages
Removal Needed to Meet Limit

Cumulative, % less than

Mercury in coal, lbs/TBtu

91% Removal

97% Removal

1999 ICR data for subbituminous coals
Three (3) forms of mercury: elemental, oxidized & particulate

Percentage depends on flue gas constituents

- Oxidized Hg (soluble)
  - caught in WFGD with SO₂
- Elemental Hg (insoluble)
  - not captured in WFGD
  - other means of capture needed
- Particulate Hg (1% - 2%)
  - captured in ESP / FGD
Hg Control Approaches

• Hg Co-Benefit Control
  – Two Step Process
  – Hg oxidation (SCR or other)
  – Hg Sequestration in FGD sump

• Adsorption Processes
  – Sorbent Injection (Activated Carbon)
    o ESP Applications (40% - 90%)
    o Baghouse Operations (80% - 90%)

• Other Processes
  – MERCAP™
  – MERSCREEN™
  – Fixed Structures
Hg Oxidation Technology

- Occurs as a byproduct of the NO$_x$ to N$_2$ reduction process
- Competes with same sites as NH$_3$ + NO$_x$ reaction sites
- Special Hg Oxidation SCR catalyst formulations available
- Halogen contents of the coal
  - Coal Cl + Br enhance oxidation
  - Halogen (Cl, Br, I) can be added to promote oxidation further
Precombustion Bromide Addition (VOSTEEN-Technology)

as covered by the valid

Patents granted also in
Australia, Canada, Europe, Germany, Japan, Korea, South Africa
Bromine vs. Chlorine

Source: B. W. Vosteen et al., US patent 6,878,358 B2, there Figure 6 on mercury speciation tests at Hazardous Waste Combustion Unit (HWC)
Bromine Enhanced Hg-Oxidation

Relevant global reactions

\[ 4 \text{HBr} + \text{O}_2 \leftrightarrow 2 \text{H}_2\text{O} + 2 \text{Br}_2 \]  
Bromine-Deacon-Reaction

\[ \text{SO}_2 + \text{Br}_2 + \text{H}_2\text{O} \leftrightarrow \text{SO}_3 + 2 \text{HBr} \]  
Bromine-Griffin-Reaction

\[ \text{SO}_2 + \text{Br}_2 + 2 \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4 + 2 \text{HBr} \]  
Bromine-Bunsen-Reaction

\[ \text{SO}_2 + \frac{1}{2} \text{O}_2 \leftrightarrow \text{SO}_3 \]  
SO\textsubscript{2}/SO\textsubscript{3}-Konversion

\[ \text{Hg} + \text{Br}_2 \leftrightarrow \text{HgBr}_2 \]  
direct Hg-Bromination

Bromine highly effective in Hg-oxidation because \( \frac{\text{Br}_2}{\text{Br}_{\text{total}}} \rightarrow 1 \)

SO\textsubscript{2} is not consuming Br\textsubscript{2} during boiler passage
Calcium Bromine Injection

- All Testing conducted @ Miller Unit 4 (4x700 MW)
- Inject CaBr$_2$ 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

Alabama Power Company
J.H. Miller Station Units 1, 2, 3 and 4
## Typical Fuel Analysis at Miller

<table>
<thead>
<tr>
<th>Fuel Parameter</th>
<th>Value (dry basis, except where noted)</th>
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<tbody>
<tr>
<td>Heating Value</td>
<td>12,056 Btu/lb</td>
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<tr>
<td>Carbon</td>
<td>70.3 wt.%</td>
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<tr>
<td>Hydrogen</td>
<td>5.0 wt.%</td>
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<tr>
<td>Nitrogen</td>
<td>0.9 wt.%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>17.3 wt.%</td>
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<tr>
<td>Ash</td>
<td>6.1 wt.%</td>
</tr>
<tr>
<td>Sulfur</td>
<td>0.38 wt.%</td>
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<tr>
<td>Moisture (as received)</td>
<td>27.3 wt.%</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.047 ppm</td>
</tr>
<tr>
<td>Chloride</td>
<td>19.5 ppm</td>
</tr>
<tr>
<td>Bromide</td>
<td>&lt;1.3 ppm</td>
</tr>
</tbody>
</table>
Method of Injection

52% solution of CaBr$_2$
Injection at Coal Feeder

52% solution of CaBr₂

2006 10 12
Phase I: Measurement Locations

Boiler → SCR → Air Heater → Cold Side ESP → Stack

- Hg SCEM M26a
- Hg SCEM M17
- Hg SCEM Appendix K
- Ontario Hydro M26a

Bromide Injection

Coal Mill → Fan

SOUTHERN COMPANY

Energy to Serve Your World™
Phase I: Test Plan

- 14 Days of Testing
  - Baseline
  - Parametric
  - Continuous Bromide Injection
  - Oxidation in boiler and SCR

- Various Hg Measurements
  - Sorbent traps
  - Speciating sorbent traps
  - SCEM (4 locations)
    - SCR Inlet
    - SCR Outlet
    - Air Heater Outlet
    - ESP Outlet
  - Ontario Hydro

<table>
<thead>
<tr>
<th>Day in Oct 2006</th>
<th>Activity</th>
<th>Halogen Concentration (ppm Br in coal)</th>
<th>SCEM (4 locations)</th>
<th>C-at ESP inlet</th>
<th>Sorbent Traps in ESP outlet</th>
<th>C-at ESP outlet</th>
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<tr>
<td>2</td>
<td>Travel to host site; Safety orientation</td>
<td></td>
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<tr>
<td>3</td>
<td>Equipment setup</td>
<td></td>
<td></td>
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<tr>
<td>4</td>
<td>Equipment setup</td>
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<tr>
<td>5</td>
<td>Equipment setup</td>
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<td>6</td>
<td>Baseline measurements</td>
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<td>C</td>
<td>3</td>
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<td>3</td>
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<td>C</td>
<td>3</td>
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<td>9</td>
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<td>C</td>
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<td></td>
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<td>10</td>
<td>Parametric calcium bromide injection</td>
<td>328</td>
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<td>3</td>
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<td>11</td>
<td>Parametric calcium bromide injection</td>
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<td>C</td>
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<td>12</td>
<td>Parametric calcium bromide injection</td>
<td>71</td>
<td>C</td>
<td>2</td>
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<td>13</td>
<td>Continuous calcium bromide injection (pump failed)</td>
<td>30.23</td>
<td>C</td>
<td>2</td>
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<td>14</td>
<td>Continuous calcium bromide injection</td>
<td>0</td>
<td>C</td>
<td></td>
<td></td>
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<tr>
<td>15</td>
<td>Continuous calcium bromide injection</td>
<td>8.9, 17.7, 7.0</td>
<td>C</td>
<td>6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>Continuous calcium bromide injection</td>
<td>7.0, 3.3</td>
<td>C</td>
<td>3</td>
<td></td>
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<tr>
<td>17 - month</td>
<td>Continuous calcium bromide injection</td>
<td>9.0</td>
<td>C</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>17 - after</td>
<td>Continuous calcium bromide injection</td>
<td>9.0</td>
<td>C</td>
<td>3</td>
<td>1</td>
<td></td>
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<td>18</td>
<td>Continuous calcium bromide injection</td>
<td>86</td>
<td>C</td>
<td>3</td>
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<td>19</td>
<td>Equipment Teardown</td>
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<td>20</td>
<td>Teardown Travel</td>
<td></td>
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</table>
The Results from Phase I - as measured at Miller Unit 4 in 2006 by URS (Katherine Dombrowski) - were some years later used for the verification of a sophisticated "predictive model", see Dr. S. Niksa et al.: "The Process Chemistry of Br Addition to Utility Flue Gas for Hg Emission Control", Energy Fuels 2010, 24, 1020 – 1029, there Figure 8 (Left Panel)

Figure 8. (Left panel) Comparisons among (●) measured and (solid curve) predicted Hg\(_2\) level at the SCR inlet and at the SCR outlet (○, dashed curve) for various Br loadings on coal. (Right panel) (●) Measured and predicted \(\chi_{Hg}\) across the SCR.
Miller Phase II Testing

- 6 week test program
- Conducted February 2008
- Key issues
  - Confirm Phase I Results
    - SCR (with & without)
    - SCR inlet, outlet. ESP outlet, FGD outlet
  - Confirm Hg removal across FGD
    - Investigate FGD chemistry (Hg, Br, Cl interactions)
    - Determine ultimate Hg fate
      - Liquid vs. particulate

MHI 2.5MW Pilot DCFS
At Gulf Power Plant Crist today
Phase II: Results Summary

• Role of the SCR in improving Hg oxidation
  – w/o SCR: 234 ppm Br to achieve >95% Hg oxid.
  – w/ SCR (no NH₃): 28 ppm Br for ~99% Hg oxid.

• Six-day Injection at 25 ppm Br to coal
  – Hg oxidation at FGD inlet: 97%
  – Removal across FGD:
    • Oxidized Hg: 95% removal
    • Total Hg: 93% removal
    • No re-emissions
    • FGD outlet Hg: 0.4 to 0.9 µg/dNm³ @ 3% O₂

• Three-day Injection at 50 ppm Br to coal
  – Hg oxidation at FGD inlet: 98%
  – FGD outlet Hg: 0.3 to 0.6 µg/dNm³ @ 3% O₂
Phase II: Testing Results

Total Mercury Measurements at the FGD Inlet and Outlet Locations at 25 ppm Injection

- 2.2 gph to treat 700 MW unit

95% and 90% efficiencies are indicated on the graph.
Phase III: Full-Scale Testing

- Full-scale MHI Advatech FGD added Spring 2010
- HAPS MACT compliance evaluation
- Testing conducted to determine 30 day rolling average
- Goal: Hg emissions < 0.8 lb / TBtu
- SCR in service for entire test program
- CaBr$_2$ injection at ~20 ppm for 79 day period
Phase III: Full Scale Testing

Plant Miller 2010 Long Term Bromide Addition 20 ppm (dry, coal)
Mercury Concentration Trend (corrected for dry gas and 3% O2)
(FULL VIEW)
Phase III: Full Scale Testing

Br per coal at Unit 4 (ppm)

Hg at Unit 3 w/o Br (lb/TBtu)

Hg at Unit 4 with Br (lb/TBtu)

Source: M. B. Berry and B. W. Vosteen: “Bromine Injection Technology Demonstrations at Plant Miller for Removing Vapor Phase Mercury“, ICESP XII Conference in Nuernberg (Germany), May 9 – 13, 2011
### Phase I, II & III
Native Coal Halogen Content

<table>
<thead>
<tr>
<th>Test Date</th>
<th>Br (ppm)</th>
<th>Cl (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fall 2006</td>
<td>5.8</td>
<td>13.4</td>
</tr>
<tr>
<td>Spring 2008</td>
<td>&lt;1.0</td>
<td>25.8</td>
</tr>
<tr>
<td>Fall 2010</td>
<td>&lt;1.3 – 3.2</td>
<td>19.5</td>
</tr>
</tbody>
</table>
Phase III: Br Concentration in FGD

![Graph showing Br Concentration in FGD](image-url)
## Phase III: Summary

<table>
<thead>
<tr>
<th></th>
<th>Unit 3 without Bromine</th>
<th>Unit 4 with Bromine</th>
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<tbody>
<tr>
<td><strong>DAILY AVERAGES</strong></td>
<td></td>
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<tr>
<td>79 Day Hg Emission Average</td>
<td>2.950</td>
<td>0.337</td>
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<tr>
<td>(lb/TBTU)</td>
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<tr>
<td>79 Day Standard Deviation</td>
<td>0.778</td>
<td>0.200</td>
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<tr>
<td>(lb/TBTU)</td>
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<tr>
<td><strong>30 DAY ROLLING AVERAGE</strong></td>
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<tr>
<td>Frequency (&lt;0.35 lb/TBTU)</td>
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<td>45</td>
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<tr>
<td>Frequency (&lt;0.5 lb/TBTU)</td>
<td>0</td>
<td>49</td>
</tr>
<tr>
<td>Frequency (&lt;1.0 lb/TBTU)</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Frequency (&lt;2.0 lb/TBTU)</td>
<td>0</td>
<td>0</td>
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<tr>
<td>Frequency (&lt;3.0 lb/TBTU)</td>
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<td>0</td>
</tr>
<tr>
<td>Frequency (&lt;4.0 lb/TBTU)</td>
<td>49</td>
<td>0</td>
</tr>
</tbody>
</table>

* Unit 4 data includes controlled shutdown and uncontrolled start-up with bromine injection
Br effects on Concrete

• 2006 Testing: Appeared that Br affected concrete 28 day strength
  – USA Ready Mix 4000 psi / 28 day design
  – All Class C ash sold at plant (1200 ton/day)

• Summer 2007 Lab Study showed no effect on concrete
  – Same USA Ready Mix Design

• Research Program w/ Gallet & Associates

• Testing Series Conducted
  – 3d, 28d & 56d strength testing
  – Set-time

<table>
<thead>
<tr>
<th>Date</th>
<th>Br Injection Concentration (ppmv)</th>
<th>Br Ash Concentration (ppm)</th>
<th>Concrete Set Time</th>
<th>28 Day Concrete Strength (psi)</th>
<th>Baseline difference (%)</th>
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</thead>
<tbody>
<tr>
<td>10/6</td>
<td>0</td>
<td>Not detected</td>
<td>315</td>
<td>5975</td>
<td>NA</td>
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<tr>
<td>10/10</td>
<td>10</td>
<td>43.5</td>
<td>300</td>
<td>4690</td>
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</tr>
<tr>
<td>10/11</td>
<td>5</td>
<td>4.0</td>
<td>315</td>
<td>5010</td>
<td>-16.2</td>
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<tr>
<td>10/12</td>
<td>2</td>
<td>4.8</td>
<td>270</td>
<td>4915</td>
<td>-17.7</td>
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</tbody>
</table>
Financial Driver at Miller (4 x 700 MW)
Technology Alternatives

**Fabric Filter**
- Capital cost: $600 Million
  - FF, ACI system, fans, etc
- O&M costs
  - ACI @ 500 lb PAC/hour: $1.875 Million / yr
  - Bag replacements: $1.1 Million/yr
  - Fan and aux. power: 5.1 MW

**Vosteen Technology**
- Capital cost: $1 Million
- O&M costs
  - Bromine @ 25 ppm on coal: $1.2 Million / yr
Hg Co-benefits

Coal Fired Boiler → SCR → Air Heater → Cold Side ESP → FGD Scrubber → Stack

additives

Hg Co-benefits + Fabric Filter + ACI (TOXECON)

Coal Fired Boiler → SCR → Air Heater → Cold Side ESP → TOXECON → FGD Scrubber → Stack

additives
• R&D Conducted over three (3) phases illustrating that precombustion calcium bromide injection was successful at oxidizing mercury
• Combination precombustion CaBr$_2$ addition + high-dust SCR provides high Hg oxidation at very low bromine injection rates
• Long term testing revealed emissions well below the EPA proposed 1.0 lb / TBtu limit for existing boilers (HHV $> 8300$ lb/ TBtu)
• Application of technology could reduce compliance cost significantly
  – FF + ACI: $600M$ capital with $1.875M$ / yr carbon costs
  – Bromine : $1M$ capital with $1M$ / yr bromine costs
Technology as Tested

Licensees of Vosteon Consulting GmbH in North America

ALSTOM Power - Environmental Control Systems, Knoxville/TN, USA,

**KNX™ Mercury Control Technology**
as Tradename of ALSTOM Power Inc.
Exclusive license for USA and Canada

Michael J. Rini, John Buschmann, Leif Lindau

Electric Power Research Institute,
Palo Alto/CA, USA,

Limited R&D License for the States

George R. Offen, Ramsay Chang

Southern Company Services, Inc.
Birmingham/AL, USA,
License for units owned by Southern Company

Larry S. Monroe, Mark S. Berry et. al.
Similar Results at WE Energies
4P Pleasant Prairie (2 x 600 MW)

KNX Test Results
25 ppm Br on Coal

Stack Total Hg (µg/m³)
Unit Load (gross MW)

7/29/08  8/5/08  8/12/08  8/19/08  8/26/08  9/2/08  9/9/08
Questions