Bromine Enhanced Dry Mercury Capture

Bernhard W. Vosteen, Vosteen Consulting GmbH
Tim C. Hartmann, ALSTOM Power Inc.

http://www.vosteen-consulting.de

9th Mercury Emissions from Coal International Experts Workshop (MEC9)
May 22 – 23, 2012, Sankt Petersburg
Agenda

- Dry APCS Design and MATS Emission Limits for Coal-Fired EGUs
- Multi-Stage APC Systems as in Waste Incineration?
- Dry Capture of \( Hg_{ion} \) and \( Hg_{met} \) at UBC and AC
- Conclusions
RWE-RheinBraun: Industrial CFB Boiler (270 MW$_{\text{therm}}$) in Berrenrath

Co-combustion of lignite coal and communal sewage-sludge since 1999, ACI in form of HOC Injection (lignite derived PAC)

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

Source: Wirling et al., RWE-RheinBraun, 2001
EPA’s MATS Rule (February 16, 2012),
Table 3 for EGUs firing high 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><strong>Existing - Unit not low rank virgin coal</strong></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><strong>Existing - Unit designed low rank virgin coal</strong></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>1.1E+1 lb/TBtu (1.2E-1 lb/GWh)</td>
</tr>
<tr>
<td><strong>New - Unit not low rank virgin coal</strong></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><strong>New - Unit designed for low rank virgin coal</strong></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: 1.5 µg/dscm @ 5% O₂
Mercury Limit lowered by the Factor 65
Range about: 25 ng/dscm @ 5% O₂
CRAZY!
II. Conclusion

EPA has authority under Clean Air Act (“CAA”) to reconsider the final Hg standards. Here, there is substantial evidence that one of the Hg limits for new sources is not practicably measurable and thus compliance cannot be reasonably assured. Compliance of new sources with the Hg emission limits in the MATS Rule is obviously of central relevance to the operation of the rule and intrinsic to both the rational implementation of the CAA and compliance with Executive Orders for significant rulemakings. EPA should therefore promptly grant partial reconsideration of the MATS Rule and undertake expedited procedures to finalize a substantially higher level for Hg for new sources of 3.0E-3lb/GWh when utilizing non-low rank virgin coal.

Range about:

0.35 µg/dscm
@ 5 % O₂

ACHIEVABLE
BAYER/Currenta GmbH & Co oHG in Uerdingen: PC-fired Boiler (100 MW_{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 fly 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

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)
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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Design of the KNX™ Application System

- Typical - CaBr₂ in 52 wt% water solution
- Adjustable pumps and hosing
- Spray header with nozzles or feeder drip
- Control box
Alstom KNX™ Injection skid

- 5 metering pumps provide up to 8.5 gal/hr CaBr2 solution for 1-5 separate coal feeders
- 110 VAC
- Easy to use “bucket check” cylinder for flow checks.
- Plastic tubing connections

Shown on pickup truck bed
Coal Additives and Brominated AC on a PRB Unit with only an ESP

Sharon Sjostrom: “Mercury Control for PRB and PRB/Bituminous Blends”, presented at EUEC, Tucson/Arizona, January 24, 2006
KNX™ Testing with Holcomb DFGD, 350 MWe, PRB coal
Sharon Sjostrom: "Mercury Control for PRB and PRB/Bituminous Blends“, presented at EUEC, Tucson/Arizona, January 24, 2006
# KNX™ Commercial Operations

## We Energies

<table>
<thead>
<tr>
<th>Location</th>
<th>Capacity</th>
<th>Fuel Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pleasant Prairie Station</td>
<td>2 x 610 MW</td>
<td>PRB, SCR + CSESP + WFGD</td>
</tr>
</tbody>
</table>

## Mid-West Utilities

<table>
<thead>
<tr>
<th>Unit</th>
<th>Capacity</th>
<th>Fuel Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit A</td>
<td>1 x 380 MW</td>
<td>PRB, ACI + CSESP</td>
</tr>
<tr>
<td>Unit B</td>
<td>1 x 330 MW</td>
<td>PRB, CSESP</td>
</tr>
<tr>
<td>Unit C</td>
<td>1 x 511 MW</td>
<td>PRB, ACI + CSESP</td>
</tr>
</tbody>
</table>

## Western Utilities

<table>
<thead>
<tr>
<th>Location</th>
<th>Capacity</th>
<th>Fuel Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plant D</td>
<td>2 x 384 MW</td>
<td>PRB, HSESP + WFGD</td>
</tr>
<tr>
<td>Plant E (Pending)</td>
<td>3 x 750 MW</td>
<td>Bit, HSESP + WFGD</td>
</tr>
</tbody>
</table>

## Montana Dakota Utilities

<table>
<thead>
<tr>
<th>Location</th>
<th>Capacity</th>
<th>Fuel Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lewis &amp; Clark Station</td>
<td>1 x 45 MW</td>
<td>Lignite, ACI + MC + WS</td>
</tr>
</tbody>
</table>

## Total Operating

| Total Operating | 3254 MW |

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Mer-Cure™ System Technology

The patented Mer-Cure™ process uniformly injects freshly treated sorbent upstream of the air preheater.

ALSTOM
Photo 1: Portable Mer-Cure™ Test Trailer

Source: Richard LaFlesh et al., Megasymposium 2011, paper #91
Synergistic Effect of KNX™ + Mer-Cure™

500 MW PRB with Particulate Scrubber

- Baseline
- Mer-Cure @ 1 lb/MACF
- Mer-Cure & KNX

55% incremental performance improvement
Photo 3: Upper Silo Section Transport

Source: Richard LaFlesh et al., Megasymposium 2011, paper #91
Figure 10: U3 and U4 (740 MWe net)
Total Stack Hg vs. Oxidizer and PAC Injection Rates

Source: Richard LaFlesh et al., Megasymposium 2011, paper #91
Demonstration Testing at Colstrip

The Colstrip Power Plant, east of Billings, Montana, operates four coal-fired generating units capable of producing a total of up to 2,100 megawatts of electricity. PPL is the operator and part owner of the Colstrip facility. Units 1 and 2 began commercial operation in 1975 and 1976, and Units 3 and 4 started in 1984 and 1986. Units 1 and 2 each have about 310 MWe net of generating capacity. Units 3 and 4 each have about 740 MWe net of generating capacity.

The Colstrip facility is the second largest coal-fired project west of the Mississippi. Colstrip Units 1 and 2 are Controlled Circulation®, radiant reheat, and tangentially-fired pulverized-coal boilers manufactured by Combustion Engineering. The units are also equipped with two Ljungstrom® air pre-heaters and three plumb-bob venturi scrubber modules for SO₂ and particulate control.

Colstrip Units 3 and 4 are tangentially-fired units manufactured by Combustion Engineering, with two Ljungstrom air preheaters and eight plumb bob venture scrubber modules for SO₂ and particulate controls.

Source: Richard LaFlesh et al., Megasympoisum 2011, paper #91
**NID™ Flue Gas Desulphurization System**

The NID™ system is a Dry Flue Gas Desulphurization (DFGD) process that is based on the reaction between SO₂ and Ca(CH₃COO)₂ in humid conditions. The humidified mixture of hydrated lime and reaction product is injected into the NID system absorber and cools the inlet flue gas by evaporation. The cooled flue gas then flows to the dust collector, preferably a Fabric Filter (FF) or an Electrostatic Precipitator (ESP), where the particles in the flue gas are removed and recycled back through the NID FGD system.

![Diagram of NID™ Flue Gas Desulphurization System](image-url)
Select Project Profiles – NID

Kiewit / Dominion – Brayton Point Unit 3

Location: Somerset, MA
Application: PC Boiler
Unit size: 660 MW (Net)
Scope: Design, Supply, and Represent
Fuel: Bituminous coal
Inlet Loading: 2.5 lb SO₂/MMBtu or 3,800 mg/Nm³
Gas Flow: 2,400,000 acfm or 4,100,000 m³/hr
Commercial: First Calendar Quarter 2013

Emissions:
SO₂: 98% removal
Filterable PM: 0.010 lb/MMBtu or 12 mg/Nm³
Reagent: Pebble Lime
Byproduct: Landfill
8 NID in parallel à 500,000 m³/h each

Kiewit / Dominion – Brayton Point Unit 3
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RMVA Köln of AVG mbH – Residual Waste Incineration Plant Cologne, 4 Parallel Units with Multi-Stage APC Systems each - in operation since 1998 (Designed by L&C Steinmueller, Gummersbach, in 1995)

Plant capacity 4 x 200,000 tonnes/year, 4 x 100,000 Nm³/hour (dry, @ 8 % O₂)
Hg concentration in boiler raw gas: 150- 200 ( ...1000) µg/Nm³/hour
Hg emission concentration (sorbent traps): „non detectable“ (Near Zero)
5 APC stages at each of the 4 parallel lines:

1. Ca(OH)$_2$-based Spray Dryer (100 % Evaporation: Closed Loop)
2. Wet HCl-Scrubber (Quench + 2 Stages at pH = 0 and pH = 0.5) with **100 % Hg Capture at Regenerative Ion Exchange Columns**
3. Wet SO$_2$-Scrubber (pH = 6, lime-based -> Gypsum)
4. SCR - DeNOx (including PCDD/F Destruction)
5. HOC-Polishing Filter (4 parallel Moving Beds à 150 tonnes HOC)

**Solid APC Byproducts (to be disposed off) - No Liquid Blow Down!**
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Multi-Stage WFGD and Entrained Flow Adsorber as Tail-End Unit

Sorbilate Injection, LUEHR Reactor with Ball-Rotor, LUEHR Flat Bag Filter and Recirculation System

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

Fixed Bed in Bypass behind Scrubber (R&D BAYER/Vosteen in August 1995)
Tests #1 - #5 in July – August 1995

- 40 %-points drop in $\text{Hg}_{\text{met}}$ Removal by Norit GL50 in case of missing Selfimpregnation

- 77 %-points drop in $\text{Hg}_{\text{met}}$ Removal in case of missing AC

(“Sand only“)
Selfimpregnation of Norit GL50 promotes $\text{Hg}_{\text{met}}$-Capture (1)

Bypass-Test # 2 at July 17th, 12:00 until July 18th, 5:30, 1995
Bed content: 340 g Sand + 1 g Norit GL 50, 9 g Ca(OH)$_2$

Test duration (hours)

Inlet: Hg species (µg/dscm)
Outlet: Hg species (µg/dscm)

$\text{Hg}_{\text{met}}$-Sorption obviously needs Selfimpregnation

While $\text{Hg}_{\text{ion}}$-Sorption doesn't need Selfimpregnation
Selfimpregnation of Norit GL50 promotes $Hg_{\text{met}}$-Capture (2)

Bypass-Test # 2 at July 17th, 12:00 until July 18th, 5:30, 1995
Bed content: 340 g Sand + 1 g Norit GL 50, 9 g Ca(OH)$_2$

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Hg$_{\text{ion}}$-Sorption:
Selfimpregnation not needed

Hg$_{\text{met}}$-Sorption
Obviously:
Selfimpregnation needed
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Conclusions

- Precombustion Bromide Addition enhances dry and wet mercury capture
- KNX + ACI complies with MATS Emission Limits for Existing EGUs
- KNX + ACI might also comply with the modified Emission Limits for New EGUs - as recently submitted to EPA by ICAC
- Tail-end APC systems behind wFGD need minimal „Selfimpregnation“ or external „Pre-impregnation“ (e.g. BPAC)
Questions please?