Boiler Bromide Addition -
A Survey On Bromine Based Mercury Abatement
From Flue Gases at Coal Combustion and Waste Incineration Plants

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2010 AICHE Spring Meeting
San Antonio, TX, March 21 - 25, 2010
Session 14: Mercury and Other Trace Elements in Fuel:
Emissions, Control, Measurement
Agenda

- Introduction
- Industrial Process Development in 2000 - 2002
- Complementary Bench Scale Laboratory Tests in 2002 - 2006
- Fundamental Insights Presented at AQ (IV) in September 2003
- Mercury and Inherent Halogens in US Coals
- Large Scale Applications in Power Generation
  - at Coal-fired Units with Wet Flue Gas Cleaning
- Outlook - Bromide Distribution - BOP
Mercury-Related Chemistry in Waste Incineration and Thermal Process Flue Gases

Bernhard W. Vosteen, Vosteen Consulting GmbH, Cologne (Germany)
Richard Ullrich, WastePro Engineering Inc., Kennett Square, PA

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 world wide)

Bromine Based Mercury Abatement

German Patent DE 10 233 173
(assigned to CURRENTA GmbH & Co. OHG)

European Patent EC 1 386 655
(assigned to CURRENTA GmbH & Co. OHG)

Patents granted also in Australia, Canada, Korea, Japan, USA, Southafrica,
Licensees of Vosteen 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
2500 MWe in commercial application since 2010

Electric Power Research Institute, Palo Alto/CA, USA,
Limited R&D License for the States

Southern Company Services, Inc.
Birmingham/AL, USA,
License for units owned by Southern Company
Preferred approach towards new patents - promising even in case of no inventive height
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... speaking about Hazardous Waste Combustion in 2000

BAYER AG - CURRENTA GmbH & Co. OHG, Germany
Hazardous Waste Combustion (HWC)
(4 plants with 30,000.. 80,000 Nm³/h dry)
of CURRENTA GmbH & Co OHG in Leverkusen, Dormagen and Uerdingen

Process Development with CURRENTA GmbH & Co OHG
(Project leader: Prof. Vosteen)
Spiking Mercury

Continuously and Discontinuously

Pump HgCl$_2$ diluted

Injection-lance

at top of after burning chamber
100 ... 20,000 µg/Nm$^3$ dry

at bottom of after burning chamber
500,000 ... 80 Mio µg/Nm$^3$ dry

„Hg-bombs“ -> „Hg-clouds“
Hg oxidation by bromine (HWC)

Hg oxidation by chlorine (HWC)

Hg\textsubscript{met}/Hg\textsubscript{total} in the boiler flue gas versus its Cl\textsubscript{total} or Br\textsubscript{total} content
How to prevent emission peaks caused by “hidden mercury”? 

with courtesy of Dr.-Ing. Rico Kanefke

Source: Dr.-Ing. Rico Kanefke, CURRENTA GmbH & Co. OHG |
Large Scale Tests at Slag Tap Boiler of Bayer AG - Currenta in Uerdingen (Germany) in 2001 and 2002

Analysis of dry Mercury Capture by Adsorption at ESP Flyash / UBC

Fly ash samples for fractional laboratory analysis

Source: Vosteen, Nolte et al.: „Chlorine- and bromine-enhanced Hg sorption on ESP fl 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) during test runs in April, 2002 with and without fire side bromide addition to boiler

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)
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Study of Gas Phase Bromination
with Prof. Heinz Koeser and Prof. Bernhard Vosteen at Martin-Luther University Halle-Wittenberg

- Dosing of highly diluted Br₂
- Thermostated Annular Gap Reactor
- Dosing of Hg(0)
- Hovacal Evaporator for HBr
- Dosing of Hg²⁺
- CEMs for Hg(0) and Hg_{total}

Annular Gap Reactor: \( d = 28 \text{ mm} \)
Gas Mixing and Gas Analyzer Station
Prof. Heinz Koeser and Prof. Bernhard Vosteen
at Martin-Luther University Halle-Wittenberg (Germany)
Elemental mercury (100 μg/Nm³ dry) brominated by Br₂ at 150 °C and 450 °C in humidified air (20 vol.-% H₂O, 21 vol.-% O₂) without SO₂ present.
Elemental mercury (100 $\mu$g/Nm$^3$ dry) brominated by Br$_2$ at 150 °C and 450 °C in humidified air (20 vol.-% H$_2$O, 21 vol.-% O$_2$) without SO$_2$ and with SO$_2$ present.
Comparison with Tests at HWC (Vosteen, Kanefke in 2000):
NaBr added at 1100 °C, with 2200 mg SO₂/Nm³ dry

Elemental mercury (100 μg/Nm³) brominated by Br₂ and HBr at 150°C - 650 °C in humidified air (20 vol.-% H₂O, 21 vol.-% O₂) without SO₂ and with SO₂ present
Study of Catalysed Mercury Oxidation
Sandra Straube (2004)
with Prof. Heinz Koeser and Prof. Bernhard Vosteen
at Martin-Luther University Halle-Wittenberg

\[0 - 2000 \mu g \text{ Hg/Nm}^3\]
commercial SCR-DeNO\textsubscript{X} catalysts
\[0 - 0.53 - 2.5 - 4.5 \text{ Ma.-\% } V_2O_5\]

crashed

ca. 15 g ... 31 g
4 x 4 channels
6.5 ... 13 cm long

2 x 0.5 g
Honeycomb catalyst
4 x 4 canals, 12.5 cm long
2.5 weight-% V₂O₅, AV = 10 m/h

Laboratory tests with humid air, 160 μg Hg⁰/Nm³ dry and only 0.5 mg HBr/Nm³ added
(no NH₃ and no NOₓ)

In contrast to Hg-chlorination, only small influence of temperature and SO₂ on enhanced Hg-bromination at SCR catalyst
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Chlorine less effective in Hg-oxidation because \( \frac{Cl_2}{Cl_{total}} \ll 1 \)

(e.g. < 4 % in HWC and < 1 % in coal combustion)

SO\(_2\) is consuming Cl\(_2\) during boiler passage

Source: Vosteen et al.: „Mercury-Related Chemistry in Waste Incineration and Thermal Process Flue Gases“ (Poster)
Air Quality (VI) Conference, Arlington, VA, Sept. 2003
### Bromine Enhanced Hg-Oxidation

<table>
<thead>
<tr>
<th>Main global reactions</th>
<th>(hypothesis Vosteen)</th>
<th>Thermodynamics</th>
</tr>
</thead>
<tbody>
<tr>
<td>4 HBr + O₂ ↔ 2 H₂O + 2 Br₂</td>
<td>Bromine-Deacon-Reaction</td>
<td>Δ_r G &lt; 0</td>
</tr>
<tr>
<td>SO₂ + Br₂ + H₂O ↔ SO₃ + 2 HBr</td>
<td>Bromine-Griffin-Reaction *)</td>
<td>Δ_r G &gt;&gt; 0</td>
</tr>
<tr>
<td>SO₂ + ½ O₂ ↔ SO₃</td>
<td>SO₂/SO₃-Konversion</td>
<td>Δ_r G &lt; 0</td>
</tr>
<tr>
<td>Hg+ Br₂ ↔ HgBr₂</td>
<td>direct Hg-Bromination*)</td>
<td>Δ_r G &lt; 0</td>
</tr>
</tbody>
</table>

*) The reaction does not proceed in the upper boiler temperature range, but at temperatures < 100 °C, e.g. downstream in WFGD

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### Bromine highly effective in Hg-oxidation

because Br₂/Br_total → 1

SO₂ is not consuming Br₂ during boiler passage

Source: Vosteen et al.: „Mercury-Related Chemistry in Waste Incineration and Thermal Process Flue Gases“ (Poster)
Air Quality (VI) Conference, Arlington, VA, Sept. 2003
Vosteen’s Stoptemperature Method
- to describe kinetics in relation to equilibrium thermodynamics - is based on experiments

Closed Sulfur and Chlorine Balances

1) Balance including rotary kiln \( \rightarrow \) acid scrubber

\[
\begin{align*}
\Delta S &= 400 \text{ mg S/Nm}^3 \text{ dry} \\
&= 12.5 \text{ mmol S/Nm}^3 \text{ dry} \\
\Delta Cl_2 &= 12.5 \text{ mmol Cl}_2/Nm^3 \text{ dry} \\
&= 886 \text{ mg Cl}_2/Nm^3 \text{ dry}
\end{align*}
\]

\[3 \text{ wt. } % \text{ Cl}_2 \text{ of Cl}_2^{total}\]
\((\text{Cl}_2 \text{ resuppression in boiler via Griffin reaction})\)

Total intermediate Cl\(_2\) in boiler flue gas:
4 wt. % of Cl\(_2^{total}\)

\[1 \text{ wt. } % \text{ Cl}_2 \text{ of Cl}_2^{total}\]
(\(\text{Cl}_2\) absorption in alkaline scrubber)

\[\rightarrow 680 \text{ °C for Cl-Deacon}\]
\(< 380 \text{ °C for Cl-Griffin} \quad (\text{running until boiler exit})\)

Source: Vosteen et al.: „Mercury-Related Chemistry in Waste Incineration and Thermal Process Flue Gases“ (Poster)
Air Quality (VI) Conference, Arlington, VA, Sept. 2003
Halogenation of Mercury by Molecular Halogens (if present)

Evaluation of the Gibbs Free Energy of Reaction (based on Nist, data Chase)

Non-realistic assumptions lead far away from reality - though thermodynamic calculations behind may be correct.

Do not believe in any thermodynamical calculation, which you haven't falsified yourself - willingly or unwillingly.

Prof. Dr. Bernhard W. Vosteen, November 2009
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5000 samples - evaluated by Vosteen Consulting
with courtesy of Prof. Dr. Belkin,
Febr. 20, 2010

NCRDS CHEMICAL DATA

Powder River Basin

Northern, Central and Southern Appalachian
5000 samples - evaluated by Vosteen Consulting
with courtesy of Prof. Dr. Belkin,
Febr. 20, 2010

* HG IN PPM ON DRY, WHOLE-COAL BASIS

![Graph showing distribution of mercury concentration in U.S. coal samples](image)
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

* S IN % ON DRY, WHOLE-COAL BASIS

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**Centrally Appalachian**

**Northeastern Appalachian**

**Southern Appalachian**

**Pinedale River Basin**

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**US coal sample number #**
5000 samples - evaluated by Vosteen Consulting
with courtesy of Prof. Dr. Belkin,
Feb. 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

Br vs. Cl

native Br = 1 ... 4 % of native Cl
5000 samples - evaluated by Vosteen Consulting
with courtesy of Prof. Dr. Belkin,
Febr. 20, 2010

- F IN PPM ON DRY, WHOLE-COAL BASIS
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TXU Energy’s Monticello Steam Electric Station (793 MWe)

Unit 3 tested in 2005  (DOE/EPRI Project on BCA)

50 % PRB coal and 50 % Tx-Lignite
Reduction of Baseline Elemental Mercury

Overview over all sites tested by EPRI in 2002 ... 2005 (chlorine) and respectively 2004 ... 2005 (bromine)
Alabama Power’s Plant Miller, 4 x 700 MW

Unit 4 tested 2006 (Phase I) and 2008 (Phase II)
Plant Miller in October 2006

Testing Results
Low Bromine Injection Test

0.5 – 1.0 ppmv HBr Concentration
Miller Average Elemental Mercury Concentrations
Measured During Each Bromide Injection Test (October 2006)
Hg Oxidation at Plant Miller — Modelling Prof. Vosteen:

SCR catalyst lowers the „Stop Temperature of Mercury Bromination“

- no Br added to PRB coal
  - 5.8 ppmw Br native in PRB coal

- 28 ppmw Br added to PRB coal
  + 5.8 ppmw Br native in PRB coal
Plant Miller Unit 4 (710 MWe)
Tests Phase II in 2008 with Pilot-WFGD
Miller Phase II: Testings in March/April 2008 (SCR w/o NH₃) and June/July 2008 (SCR with NH₃)

Wet FGD-pilot (equivalent 2 MW)
Hg_{total} at Pilot-WFGD Inlet and Outlet (mg/Nm^3 dry, at 3 Vol.% O_2)  

Day in March 2008  

25 ppm_w Br in PRB-coal, dry basis
KNX™ Coal Additive – Addition on coal conveyor belt

Coal Conveyor (shown in black)

Injection Spray Header

KNX™ Additive Storage Tank

Metering Pump
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$_{\text{g, total}}$ at stack
< 1 μg/dscm
(both units)
Power Station WE Pleasant Prairie with SCR, ESP, WFGD
25 ppm Br per Coal only, SCR in service with NH₃
- **Further Industrial Demonstration in 2008**
  - PC-fired Wet Bottom Boiler (100 MW\textsubscript{therm}; 140,000 Nm\textsuperscript{3}/h dry)
  - of CURRENTA GmbH & Co OHG in Uerdingen
  - ESP, limestone based wet FGD, tail end DeNOx-SCR

- Spiking with HgCl\textsubscript{2} and NaBr
- CEMs for Hg\textsubscript{total} and Hg\textsubscript{met
- PRAVO
Mercury emissions with CaBr₂ addition to coal only (no PRAVO® added)

50 % German bituminous
50 % Columbian
both 0.8 weight % S

30 % German bituminous
70 % Columbian
both 0.8 weight % S

13.5 t/h coal
90 % load
160 t/h steam
140,000 dscm/h

Hg at stack (µg/Nm³ dry)

ppmw Br per coal

29.4.08 30.4.08 1.5.08 2.5.08 3.5.08 4.5.08 5.5.08
Mercury emissions with CaBr$_2$ addition to coal and PRAVO$^\text{®}$ addition to WFGD

- 50% German bituminous
- 50% Columbian
- both 0.8 weight % S

13.5 t/h coal
90% load
160 t/h steam
140,000 dscm/h

- no CaBr2 and no PRAVO$^\text{®}$ added
- 160 ml/h PRAVO$^\text{®}$ diluted 1:5 continuously

Hg at stack (µg/Nm$^3$ dry)

ppmw Br per coal
**PRAVO®**

is a registered trade mark of Vosteen Consulting, standing for the inorganic precipitation agent containing polysulfide, thiosulfate and bromide

Patents on the combined application of KNX and PRAVO are pending
In co-operation with Evonik Indstry Services GmbH, Essen:

Combination of two established technologies:

„CaBr₂ to Coal” and “PAC to WFGD”,

with subsequent Selective Mercury Precipitation

Large scale demonstrations in 2009 and 2010

at two Evonik power plants of different design

(w/o and with highdust SCR)
Enhanced Mercury Abatement
CaBr$_2$ to Coal and PAC to WFGD
with Selective Mercury Precipitation in WWT
Enhanced Mercury Abatement
CaBr$_2$ to Coal and PAC to WFGD
with Selective Mercury Precipitation in WWT
Tail-End SCR – Plant Marl (375MW)
1. CaBr₂ - IPC with 3 pumps
2. Hg measuring station (Lumex)
3. PAC Dosing
Baseline Results at Marl Unit 5

Flue Gas Outlet

Hg Outlet

- <0.3 Hg^{2+}
- 2.2 Hg\textsuperscript{0}
- <2.5 Hg total

\( \mu g/Nm^3\) dry

Hg capture rate \~ 75%

Flue Gas In

Hg Inlet

- 8.5 Hg^{2+}
- 1.5 Hg\textsuperscript{0}
- 10.0 Hg total

Hg-concentration in absorber solution approx. 300-500 ppb
CaBr$_2$ & PAC Results at Marl Unit 5

Flue Gas Outlet

- Hg Outlet
  - $<0.4$ Hg$^{2+}$
  - $0.1$ Hg$^0$
  - $<0.5$ Hg total

μg/Nm$^3$ dry

Flue Gas In

- CaBr$_2$
  - $9.9$ Hg$^{2+}$
  - $0.1$ Hg$^0$
  - $10.0$ Hg total

- 55 gpm wastewater discharge
- discontinuous dosing of PAC (make-up)

Hg capture rate above 95%

Hg-concentration in absorber solution after initial dosing of PAC approx. 30 ppb
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Former plannings (PAC, tail end bag filter) skipped in favor of the „German technology“

Dr. Larry S. Monroe
Mark S. Berry
(Southern Company)
Halogen Testing at Mercury Research Center

- **Owned by Gulf Power**
  - Plant Crist Unit 5
  - Operated by PCT Inc.

- **5MW Research Facility**
  - Full Environmental Control Technology Suite

- **EPRI - Halogen Injection Program**
  - HCl, xBr, xCl
  - with & w/o SCR
  - 4 different catalyst types
  - Removal across FGD
Evaluating Bromine Fate & Balance-of-Plant (BOP) Impact

BOP

Field Testing

Advisory Committee (EPRI, Utilities, Experts)

Lead Coordinator (URS Corporation)

Literature Survey and update

Sample Acquisition

Laboratory Testing

Simulated Samples

Hg and Br measurements

Ash

Scrubber

Ash Use

Liquid

Solid

Leaching

Corrosion

Mercury Partitioning
Coals vary widely in Inherent Bromine Content

COALQUAL data for Br in US coals

Low Bromine in some coals makes Hg capture difficult
KNX™ Coal Additive - drums and pumps in a full scale test
Bromide solution to coal band feeder
Choose to feed bromide solution to pulverizers F and G.
Three-Dimensional Evaluation (1996)

with courtesy of

Prof. Dr. techn. Reinhard Leithner,
Institute for Thermal and Fuel Technologies,
Technical University Braunschweig (Germany)

Particle trajectories in a Lignite Boiler
(20 m x 20 m x 75 m)

- tangentially fired
- lignite design (pulverizers feed vertical burner row)
- bad internal mixing, i.e. strands of gas and particles

Danger of insufficient bromide pre-distribution
Thanks for Your Attention.

Questions?