Cost-effective mercury abatement at hard coal-fired boilers by small amounts of bromide and PRAVO®

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At hard-coal fired Power Plants you do need very little...
1000 liter IBC-container for the tested CaBr$_2$-solution (52%), membrane dosing pumps with plastic tubings and injection lances at each coal-feeder
Small Containers for the tested precipitation agent PRAVO®, membrane dosing pump with plastic tubing and injection lance at wet FGD
The precipitation agents of PAN Chemie Dr. Fülöp and Vosteen Consulting are

Precipan, PRAVO®100, PRAVO®200

These are inorganic liquid agents containing polysulfides and thiosulfate.

The highest content of active sulfur has PRAVO®200.

For mercury precipitation at wet FGD, only small injection rates are needed (e.g. < 1 liter /hour PRAVO® at 120.000 Nm³/h flue gas)

An important initial step in such applications is the

Formation of highly reactive polysulfanes as $\text{H-S-S-S-S-H}$
by PRAVO® addition directly to the acidic milieu
as performed since 2008 at 3 MSWI lines of ENTEGA/HSE in Darmstadt

PRAVO® does work effectively also in the neutral or basical scrubber stage as performed since 2007/8 at 2 Fluidized Bed Incinerator lines for sewage sludge combustion at WWTP Karlsruhe –Neureuth
Background of Bromine-Enhanced-Mercury-Oxidation (BEMO-Technology)
Bromine far more effective than chlorine

Mercury-Related Chemistry in Waste Incineration and Thermal Process Flue Gases

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Richard Ullrich, WastePro Engineering Inc., Kennett Square, PA

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

(BAYER patent applications pending worldwide)

Spiking the boiler raw gas with 9600 μg Hg/Nm³ dry

Mass ratio Br/Hg = 100 ... 500 needed ("without high dust SCR")
Industrial Tests by US EPRI and US DOE-NETL with Chlorides as Oxidizer starting in 2002 and with Bromides as Oxidizer in 2004

Internal US EPRI Report, March 2006
Chapter 3: "Boiler Chemical Additives"

<table>
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<tr>
<th>Unit</th>
<th>Test Period</th>
<th>Reagents Tested</th>
<th>Addition Method</th>
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<tr>
<td>Laramie 2</td>
<td>May 2002*</td>
<td>NaCl, CaCl₂, Fe/NaCl</td>
<td>Solid addition to coal feed</td>
</tr>
<tr>
<td></td>
<td>Sept. 2005*</td>
<td>MgCl₂, HCl</td>
<td>Liquid addition to boiler</td>
</tr>
<tr>
<td></td>
<td>Aug. 2005*</td>
<td>CaCl₂, CaBr₂</td>
<td>Solid addition to coal feed</td>
</tr>
<tr>
<td>Meramec 2</td>
<td>Sept. 2004**</td>
<td>KNX, SEA2</td>
<td>Liquid addition to coal feed</td>
</tr>
<tr>
<td>Baldwin 1</td>
<td>Aug. 2005*</td>
<td>CaCl₂, CaBr₂</td>
<td>Liquid addition to boiler</td>
</tr>
<tr>
<td>Limestone 1</td>
<td>Sept.-Oct. 2004*</td>
<td>CaCl₂, CaBr₂</td>
<td>Liquid addition to boiler</td>
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<tr>
<td>Monticello 1</td>
<td>Oct.-Dec. 2005**</td>
<td>CaCl₂, CaBr₂</td>
<td>Liquid addition to coal feed</td>
</tr>
<tr>
<td>Milton River</td>
<td>April 2005**</td>
<td>CaCl₂, MgCl₂, SEA²</td>
<td>Liquid addition to coal feed</td>
</tr>
<tr>
<td>Young 2</td>
<td>April 2002*</td>
<td>NaCl, MgCl₂, FeCl₂</td>
<td>Liquid addition to boiler</td>
</tr>
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</table>

* - EPRI-conducted tests
** - Tests conducted as part of DOE-NETL Cooperative Agreement Programs
Large Scale Tests in Germany
Figure 1:
Flow sheet of the neighboring industrial Slag-tap Boilers N230 with 100 MW_{therm} each with twin APC system N266 at the Bayer site Uerdingen

Industrial Tests in Germany by BAYER AG with Chlorides and TMT15 starting far earlier in 1993
Figure 2:
Influence of the Cl⁻-content on the mercury speciation in the raw gas at the FGD-inlet
Figure 6:
Increasing mercury content in the FGD-scrubber sump – 655 m³ containing up to 1400 g Hg
Coal: Comparing ESP fly ash with Granulate

Coal-fired Bayer Slag Tap Boiler N 230 in UER (baseline test on Sept. 14, 1993)

Figure 3:
Comparison of the heavy metal contents in the ESP fly ash and in the bottom slag granulate at the Industrial Power Plant N230 of CURRENTA GmbH & Co OHG in Uerdingen
Industrial Tests in Germany by BAYER AG with Bromides and TMT15 starting already in 2001

Figure 4:
Pre-combustion bromide addition onto the fired coal respectively in the hot fire-box in 2002 at the Industrial Power Plant N230 of CURRENTA GmbH & Co OHG in Uerdingen
Industrial Tests in Germany by BAYER AG with CaBr₂ and PRAVO® in 2008

Figure 7:
Large Scale Tests with CaBr₂ and PRAVO®100 in April and September 2008
Start of the test on April 29th, 2008,
with 19 mg Hg/Nm³ in raw gas (FGD Inlet, base-line)
respectively 8 mg Hg/Nm³ at the FGD outlet – followed by bromide-addition
(heightened from 45 to 150 ppmw Br per coal)
Ongoing tests under bromide-addition of 150 ppmw Br per coal, followed by reduced bromide addition of 45 ppmw Br per coal and addition of only 160 ml/h of our scrubber additive PRAVO®100
Figure 10b:
Ongoing tests under reduced bromide-addition of 45 ppmw Br per coal
and addition of only 160 ml/h of our scrubber additive PRAVO®100
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

Figure 11:
Study of dry mercury capture at the ESP fly ash UBC
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)

Figure 12:
Pre-combustion bromide addition improves dry mercury capture at ESP fly ash with 22,3 % UBC
Figure 13:

Mainly ionic mercury is adsorbed at ESP fly ash, preferably at the fly ash covering the plate electrodes.

Cleaning of the plate electrodes by periodic rattling influences mainly the UBC-bound capture of ionic mercury Hg$^{2+}$.
Large Scale Tests in USA
Calcium Bromide 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

Figure 14:
Alabama Power’s J.H. Miller Station
Units 1, 2, 3 and 4
Figure 15:

Hg(0) concentrations at the SCR Inlet and SCR Outlet as well as at the ESP Inlet and ESP Outlet.
Figure 16:

Hg-concentrations at stack
during final long-time test (72 days @ 24 h/d) under 20 ppmw Br per dry coal
License granted in 2008 to WE Pleasant Prairie Unit 1 and Unit 2 (2 x 600 MWe with SCR, ESP, WFGD) - In commercial operation since January 1, 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

Hg$_{\text{total}}$ at stack
< 1 μg/dscm
(both units)
Figure 18b:
Very first test results applying the BEMO-technology at WE Peasant Prairie in March and April 2008
Figure 19:
Mercury removal efficiency achieved at WE Pleasant Prairie during tests with small CaBr₂-addition rates in 2008
Figure 20:
Boiler load and PRAVO addition during the tests at WE Pleasant Prairie in March 2010
Figure 21:
Influence of boiler load on $\text{Hg}_{\text{tot}}$ at stack
Test on CaBr2 + PRAVO at We Energy Pleasant Prairie
Reported Period: March 14, 00:00, 2010 until March 23, 24:00, 2010

The Hg(0)-shift at stack - without and with PRAVO addition to WFGD - stays very limited: There is no PRAVO-need.

The fired PRB coal is a low sulfur coal.

Figure 22:
Influence of PRAVO addition on Hg(0) at stack
Figure 23:
Influence of PRAVO addition on $\text{Hg}_{\text{ox}}$ at stack

PRAVO®100 lowers the $\text{Hg}_{\text{ox}}$-concentration at stack by 0.2 $\mu$g/Nm$^3$ dry
Experiences with PRAVO®
Testings in 2008 (Dipl.-Ing. Ulrich Mielke)

Experiments on Mercury Deposition at MHKW Darmstadt

Scheme MHKW Darmstadt

Flue gas cleaning consists of spray dryer, E-Filter, wet scrubber and SCR Denox- and Dioxin reduction stage.

Mercury deposition at MHKW Darmstadt takes place in the wet scrubber with acidic quenching stage and packed bed and neutral ring-jet-stage.

The washer fluid is neutralized externally and evaporated in the spray dryer.
PRAVO container (diluted 1:10) for continuous addition to upper WFGD-stage

PRAVO (diluted 1:10) for discontinuous addition to upper WFGD-stage

Figure 27:
Testing PRAVO®100 in 2007 at the 3-staged scrubbers (design von Roll) of the three Municipal Solid Waste Incinerators of ENTEGA AG (formerly HSE) in Darmstadt - addition to the highly acidic upper scrubber stage (pH = 2)
Dosing curve of PRAVO®100
as measured at MSWI line
to suppress mercury reemissions

Hg$_{tot}$ in clean gas behind scrubber

PRAVO®100 flow rate

0,00 g/h  200,00 g/h  400,00 g/h  600,00 g/h  800,00 g/h  1000,00 g/h  1200,00 g/h  1400,00 g/h  1600,00 g/h  1800,00 g/h

0 µg/m³  5 µg/m³  10 µg/m³  15 µg/m³  20 µg/m³  25 µg/m³  30 µg/m³  35 µg/m³  40 µg/m³  45 µg/m³  50 µg/m³  55 µg/m³

Testings in 2008 (Dipl.-Ing. Ulrich Mielke)
Figure 24:
Unit 2 of Stadtwerke München (SWM) in Munich-North (Unterföhring)
Testing PRAVO®200 at SWM in 2014

Figure 25:
1000 liter IBC-container for the tested PRAVO®200 solution and its 2 membrane dosing pumps to serve the wet FGD-sumps
Figure 26 a (left) and Figure 26 b (right):

$\text{Hg}_{\text{tot}}$-concentrations at both FGD outlets of SWM Unit 2
- dropping reproducibly from about 3 $\mu$g/Nm$^3$ to < 1 $\mu$g/Nm$^3$ (dry basis)
  under PRAVO®200 addition
References for successful industrial applications of PRAVO®100 and PRAVO®200 at wet FGD:

- HWI, 3 lines (Germany, since 2001)
- Industrial SSI, 1 line (Germany, since 2001)
- Communal SSI, 2 lines (Germany, since 2004)
- MSWI, 3 lines (Germany, since 2008)
- Communal SSI, 2 lines (Germany, since 2008)
- HWI, 10 lines (France, since 2014)
- Thermal Soil Treatment (NL, since 2016)

- Hard coal-fired Power Plant 360 MW\(_e\) (Germany, since 2016)
- Lignite-fired Power Plant 900 MW\(_e\) (Germany, since 2018)
Figure 28:
Advanced FGD-residuals discharge of ANDRITZ AG
Hydrocyclone Development
General background

- Addition of washwater without causing turbulence
- Flow direction of suspension and water are parallel
- Flushing water does not pass through the suspension but covers it
- Coarse particles can pass through the sedimentation layer,
- Fines are caught within flushing water and carried towards overflow

Figure 29:
Mercury split between gypsum (underflow) and waste water (overflow)
Figure 30:
Mercury transfer from the FGD-suspension (hydrocyclone inlet) to the wastewater (hydrocyclone overflow)
Special thanks for cooperation since 2003 to

Dr. Alfred Grissinger,
Luc Zonnenberg

Merquel™ (CaBr₂)

ICL-IP Largest Producer of Bromine and Bromine Compounds Worldwide
Conclusions

The cost-effective mercury abatement by small amounts of bromide as coal additive and PRAVO® as scrubber additive is a well established and highly successful technology for hard coal-fired power plants – the BEMO-Technology of Prof. Vosteen.

For applications at coal-fired power plants, Andritz AG (Austria) holds an exclusive license since 2017 as based on the European Patent EP 1 386 655.

The BEMO-Technology is tested at lignite-fired power plants, as well. In case of very high mercury content in the coal, the combination of pre-combustion halide-addition with PAC injection or other technologies might become necessary.