Bromine-enhanced Mercury Abatement from Combustion Flue Gases – Recent Industrial Applications and Laboratory Research

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**Kurzfassung**

Bromgestützte Quecksilberabscheidung aus Verbrennungsabgasen – Neuere industrielle Anwendungen und Laborforschung


The new process of bromine enhanced mercury abatement [1] was discovered by Vosteen and Pohontsch in 2000 [2] and studied in more detail by Kanefke and Nolte in 2001/2002 [3, 4] and since then constantly applied industrially at the Hazardous Waste Combustors (HWC) of BIS, Figure 1. Since August 2004 the new process is constantly applied, too, at two Stationary Fluidised Bed Combustors (SFBC) for the mono- and co-combustion of municipal sewage sludge of Emscherogenossenschaft, Essen/Bottrop (Germany) [5]. The two SFBC plants in Bottrop, each equipped with heat recovery boiler, ESP and two-staged scrubber (acidic and neutral), primarily used the expensive NaClO$_2$ as oxidising agent injected at the scrubber entrance, but did now change over to aqueous sodium bromide injected into the hot SFBC free board. Changing over to this comparatively cheap and easy-to-handle oxidising agent has cut down the operating costs of both plants considerably.

**In-plant Research**

BAYER Industry Services GmbH & Co oHG operates at its German sites Leverkusen, Dormagen and Uerdingen four rotary kiln units for hazardous waste incineration. Two of them are located at the BAYER waste management centre in Leverkusen-Bürrig. The four units have a similar, BAYER-typical design as shown in Figure 1. Since 2000 extensive mercury-related in-plant research [2 to 4] has been carried out at the Leverkusen HWC kilns. Results on adsorption and oxidation (elution) of mercury at the tail-end SCR-DENOX-catalyst bed have already been published in detail [6]. During almost all test runs the flue gas was spiked more or less with mercury, either continuously (up to 20,000 µg/Nm$^3$, dry) or discontinuously (up to some 200,000 µg/Nm$^3$, dry): Mercury in form of an aqueous HgCl$_2$ solution was injected continuously at the head of the rotary kiln or at the top of the post-combustion chamber; at the high combustion temperatures, all HgCl$_2$ added is directly converted into Hg$_{met}$. On the other hand, metallic mercury as such was injected “discontinuously” via the oven inspection port near to the bottom of the post-combustion chamber; this was achieved by throwing in small plastic bottles filled with mercury (“Hg bombs” of 5 g to 340 g Hg$_{met}$ every 5 minutes), Figure 2.

Gaseous mercury was continuously measured by different CEMs (continuously measuring emission control monitors) installed at different places (details see [6], there Figure 2, showing four measuring points in front of and behind the tail-end SCR as well as in front of and behind the catalyst beds inside), e.g. a) in the scrubbed flue gas behind the Condensation Electrostatic Precipitator (CESP) and b) in front of the tail-end SCR-DENOX catalyst-bed, c) behind the tail-end SCR-DENOX catalyst-bed and d) in the clean gas behind the tail-end SCR-DENOX.

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![Figure 1. Hazardous Waste Combustor KILN A of BAYER Industry Services GmbH & Co. oHG in Leverkusen, Germany.](image-url)
At these measuring points from time to time CEMS were measuring simultaneously for mercury speciation, i.e. they were working in parallel either without reductive gas pre-treatment (no reduction of Hg$^{2+}$ for measurement of Hg$_{\text{total}}$ only) or with reductive gas pre-treatment (reduction of all Hg$^{2+}$ to Hg$_{\text{met}}$ for measurement of Hg$_{\text{total}}$), followed by a Hg$_{\text{met}}$-monitor (based on cold vapour AAS), see Figure 3. The official Hg$_{\text{total}}$ emission control at the stack was equipped with a SCEM (semi-continuous measuring emission control monitor) working with reductive gas pre-treatment by SnCl$_2$ and applying gold amalgamation. As described in [1], bromine was added by co-combustion of bromine-rich (and chlorine-rich) wastes (normal HWC working conditions) or by injection of diluted HBr or aqueous NaBr (exceptional HWC working conditions). During co-combustion of highly halogenated wastes controlled sulphur-addition in the form of granulated sulphur was applied as described in [9] (see also [2], [7] and [8]).

Applying Br/Hg mass ratios $>$ 300 complete mercury oxidation was achieved, i.e. all mercury in the boiler exit flue gas was converted in its watersoluble ionic form Hg$^{2+}$ (100 % Hg$_{\text{ion}}$, 0 % Hg$_{\text{met}}$), mainly as HgBr$_2$ and some HgCl$_2$; therefore in the existing multistage scrubbing system excellent mercury removal (abatement efficiency $\eta > 99.8 %$) was realised, Figure 4.

Test runs at the HWC plants of BIS in Leverkusen-Bürig and later at a PC-fired wet bottom boiler of BAYER AG in Uerdingen (as shown in Figure 13) have been demonstrating that bromine is much more effective in Hg-oxidation than chlorine - under high Cl$_{\text{total}}$-loads as in waste incineration at least $> 25$ times more and up to $> 100$ times more under low Cl$_{\text{total}}$-loads as in coal combustion [1], [10], Figure 5.
Thermodynamics and Kinetics

Chlorine-based mercury oxidation is governed by four simultaneous global reactions, Figure 6. For kinetical reasons only the direct mercury oxidation by Cl₂ has to be considered (Hg + Cl₂ -> HgCl₂), while the so-called indirect mercury oxidation (Hg + 2 HCl + 0.5 O₂ -> HgCl₂ + H₂O) is staying irrelevant. This important fact has been demonstrated by a fascinating “in-plant experiment”, Figure 7 and Figure 8. The boiler raw gas was containing about 20,000 mg HCl/Nm³ dry, while the artificial oscillations of the SO₂ concentration were induced by corresponding oscillations of sulphur addition to the rotary kiln [2], [10]. Figure 7 is showing the resulting concurrent oscillations of the Hg₂⁺-concentrations in the scrubbed flue gas behind the CESP as well as in front of the tail-end SCR-DENOX – after dilution with the scrubbed flue gases of the neighbouring HWC plant. In Figure 7 it becomes (indirectly) visible that SO₂ is consuming Cl₂ with the consequence that Cl₂ is lacking for mercury chlorination: Hg₂⁺ is going up or down when SO₂ is going up or down respectively.

Figure 8 is showing the resulting countercurrent oscillations of the Hgtotal (mainly oxidised) concentration behind the SCR-DENOX catalyst bed as well as behind the heat exchanger at the SCR-DENOX exit. This - at first sight astonishing - behaviour is (indirectly) showing the fact that those four global reactions, governing already the mercury oxidation in the boiler raw gas (containing e.g. a certain fly ash metal oxide inventory as catalysts), are also governing the mercury oxidation in a SCR-DENOX catalyst bed, see remarks further down.

For modelling of mercury oxidation in waste incineration boilers as well as in power station boilers, it is necessary to combine equilibrium thermodynamics (Gibbs free enthalpy minimisation) of those four homogeneous (uncatalysed) or heterogeneously catalysed global reactions with an adequate modelling of the corresponding chemical kinetics. This has been achieved for mercury chlorination following the so-called “stop temperature method of Vosteen”, which for in-plant experiments is giving way to realistic results [5]. Above its individual stop temperature, any reaction is running in its equilibrium, below its stop temperature the reaction is not going anymore (“frozen”). Thus, the simplifying modelling (“only global reactions considered”) is still fairly realistic (“halogenides and SO₂ sufficiently considered”) and complex; not only linearly independent reactions as e.g. the chlorine Deacon reaction and the chlorine Griffin reaction are taken into account, but linearly dependent reactions, too (as the direct SO₂/SO₃ conversion).

Free chlorine is needed for direct mercury chlorination, Figure 6. At high temperatures the equilibrium of the chlorine Deacon reaction is lying mainly on the left side (much HCl, little Cl₂). With decreasing flue gas temperature during boiler passage, this reaction should produce more and more Cl₂ until its stop temperature is reached, which was evaluated to be 680 °C, [5].

Below this temperature until the boiler exit, the chlorine Griffin reaction is consuming more and more of the intermediately formed Cl₂, depending on the SO₂ concentration, which itself is influenced by the direct SO₂/SO₃ conversion, having been kinetically stopped already at a considerably higher stop temperature of 900 °C.

The stop temperature of the direct mercury chlorination itself was evaluated to be 580 °C in the studied HWC plants and 480 °C respectively in the studied PC-fired wet bottom boiler.

Bromine-based mercury oxidation is governed by a similar, but not exactly corresponding set of global reactions, Figure 9. Even at higher temperatures the bromine Deacon reaction is lying far more at the side of free bromine, i.e. the bromine Deacon reaction is producing comparatively much more free halogens (Br₂) than the chlorine Deacon reaction is producing Cl₂. The next completely different step is the Griffin reaction. In contrast to chlorine, the bromine Griffin reaction is thermodynamically not favoured, at least at temperatures > 100 °C, because the Gibbs free reaction enthalpy of the bromine Griffin reaction is strongly positive, within the whole boiler temperature range. Therefore, SO₂ is not consuming Br₂ during boiler passage or during passage of a high dust SCR-DENOX catalyst bed. There is a further difference to be considered: While Cl₂ is almost insoluble in water and its solubility is even decreasing with growing content of halogenides, Br₂ is easily soluble in water, especially in the presence of halogenides. At temperatures below 100 °C the so-called bromine Bunsen reaction will be going on (consumption of free bromine by SO₂ under formation of 2 HBr and H₂SO₄), Figure 9.

In the stationary estate of a SCR-DENOX both Hg₂⁺-adsorption and chemically enhanced Hg₂⁺-desorption are in a dynamic equilibrium.

Instationary mercury oxidation in a SCR-DENOX was already studied in [2] and published in [6]: Hg₂⁺-peaks entering the SCR-catalyst bed are not “answered” by corresponding peaks at the SCR-exit: Mercury is leaving the SCR catalyst bed as oxidised mercury HgO, only and at low, exponentially decreasing concentrations. Thus, mercury oxidation in any SCR-DENOX catalyst bed has to be interpreted as a superposition of Hg₂⁺-adsorption and of chemically enhanced Hg₂⁺-desorption (eluation). The mercury fluxes as well as the momentary mercury load of the catalyst bed will be permanently adjusted corresponding to the chang-
ing flue gas concentrations of mercury species and of reactive compounds as SO₂, Cl₂ or Br₂.

Since our in-plant research started in 2000, it soon became known – under high chlorine loads in the raw gas – that SO₂ peaks are inhibiting mercury elution out of a tail-end SCR-DENOX, while Cl₂ peaks are enhancing mercury elution [2]. This fact becomes also (indirectly) visible in Figure 8, showing those artificially induced oscillations of the SO₂ concentration in the boiler raw gas inducing countercurrent oscillations of the Hgtotal concentration (mainly oxidised mercury) in the effluent flue gas behind the SCR: Higher SO₂ concentrations in the boiler raw gas are inducing better Cl₂ chemisorption in the alkaline scrubber (reducing residual hypochlorides), thus diminishing traces of Cl₂ in the scrubbed flue gas and therefore diminishing also the mercury eluation out of the SCR catalyst bed.

**Low-cost Technology**

The bromine enhanced mercury abatement is a low-cost technology, with respect to the amount of bromine necessary for complete mercury oxidation (Br/Hg > some 300 kg/kg) as well with respect to low installation costs. This may be illustrated by Figures 10 and 11 from those test runs at the two SCCB-plants of Emschergenossenschaft in Bottrop. Figure 10 is showing two (alternatively used) plastic tanks (1000 /H5129/ and three small membrane pumps to pump the solution to three dual fluid spaying nozzles, installed in the lower SFBC freeboard region as shown in Figure 11.

**Achievable Mercury Removal Efficiencies**

Even in flue gases of very high SO₂ concentration a complete mercury bromination is easily attained by adding small amounts of bromine into the combustion chamber. Thus, the achievable mercury removal efficiency can be > 90 %, provided that the wet or dry gas cleaning system downstream is well designed and well operated, Figure 12.

To minimise the bromine need, good distribution and mixing of the bromine compound with the flue gas is necessary.

**Polychlorinated and Polybrominated Dibenzo-dioxins and – furans**

Denovo-synthesis of polychlorinated and polybrominated dioxins and furans (PCDD/F and PBDD/F) were investigated at both SFBC plants in Bottrop and shown to be irrelevant. The measurements were done during bromide addition. The PCDD/F were lying with 0.001 to 0.003 ng TEQ (Nato/CCMS)/Nm³ dry well below 0.1 ng TEQ/Nm³ dry as limiting value of the 17. BlmSchV (German emission control act). The corresponding values of PBDD/F were lying with 0.0003 ng TEQ/Nm³ dry near to the detection limit.

**Dry Mercury Adsorption on Carbonaceous and Non-carbonaceous Sorbents**

It has been demonstrated by in plant experiments [3], [4] (Figure 14) and by laboratory tests [11], that bromine addition into the combustion chamber increases mercury adsorption at carbonaceous sorbents. The adsorption is enhanced by “internal bromination” of unburned fly ash carbon (UBC) or of injected normal powdered activated carbon (PAC), and specific non-carbonaceous sorbents of high porosity, too.

The adsorption of brominated mercury at ESP fly ashes with relatively high UBC contents was especially studied in 2002 during...
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the test runs at a 100 MWth coal-fired wet bottom boiler of BAYER AG in Uerdingen, Figure 13. It was demonstrated [4] that the injection of only small amounts of bromine into the combustion chamber (as e.g. hydrogen bromide or as sodium bromide) was sufficient for complete mercury bromination and intensifying the mercury adsorption at the ESP fly ash by the factor 2.5 to 3 in case of high loss on ignition (LOI), Figure 14.

Similar effects on mercury adsorption at the ESP fly ash were observed in December 2003 during the afore mentioned test runs at the SFBC plants of Emschergenossenschaft in Bottrop.

Mercury Oxidation in SCR-DENOX Plants

During those test runs in 2002 at the PC-fired boiler shown in Figure 13, continuous mercury measurements were carried out in front of and behind the wet flue gas desulphurisation (FGD) as well as behind one of the tail-end DENOX SCR, i.e. at the stack. These measurements revealed – for the first time, as far as we know – that already tiny amounts of HBr/Br2 (well below some 1 mg/Nm3 dry) are drastically accelerating mercury oxidation in a SCR catalyst bed, as visible by accelerated mercury elution out of the tail-end SCR-DENOX under high boiler bromide load, Figure 15.

The chlorine Deacon equilibrium under low Cltotal concentration as in tail-end SCR-DENOXs is lying at the side of HCl, see “HCl excursions behind tail-end SCR-DENOX” as observed and explained in [7]. In contrast to chlorine, the bromine Deacon equilibrium is under these conditions lying at the side of Br2, even in case of very low Brtotal concentrations, as already shown by Wieland [8]. Thus, from HBr in the SCR free bromine is formed oxidising the adsorbed metallic mercury and promoting the elution of adsorbed HgBr2.

Laboratory Research on Bromine-Enhanced Mercury Abatement

In early 2002 mercury-related research work was started at the Institute for Environmental Engineering at the Martin-Luther-University Halle-Wittenberg (Campus Merseburg) by Professor Köser. The start-up of this research work was possible with financial support of BAYER Industry Services GmbH & Co. oHG. The post-graduate work coached by Professor Köser and Professor Vosteen is mainly centred around bromine-enhanced mercury abatement and all its aspects in wet and dry flue gas cleaning.
In 2004 other companies such as E.ON Engineering (Professor Guther) were joining in.

Since 2002 the mercury research group has built quite a lot of test rigs as listed below:

— flue gas chemistry (test rig with high temperature reactor),
— wet flue gas cleaning: mercury complexation by halogenides (test rig),
— wet flue gas cleaning: red-ox-potential and pH, pCl or pBr (test rig),
— dry flue gas cleaning: adsorption at different sorbents (test rig),
— mercury retention and mercury oxidation in tail-end SCR-DENOX (test rig),
— mercury oxidation in high temperature SCR-DENOX (test rig),
— CEM and SCEM artefacts caused by free halogens (test rig); development of a dry mercury converter working at low temperature.

Of considerable interest are new insights into mercury complexation in FGD scrubbers by bromides and their inherent protection against mercury reduction.

Some of the running laboratory research on wet and/or dry mercury abatement was concerned with artifacts in the continuous measuring of total mercury by CEMs or SCEMs or caused by free halogens was developed and established.

**Demonstration Test Runs in the USA**

Vosteen Consulting GmbH has been granting an exclusive license to ALSTOM ECS (Environmental Control Systems), Knoxville/TN, for joint exploitation and commercialisation of this technology in North America. ADFA-ES in co-operation with Alstom ECS and others have conducted demonstration test runs under the US-DOE contract No. DE-FC26-03FT41991 (“Large-scale Mercury Control Technology Testing for Lignite-fired Utilities – Oxidation Systems for Wet FGD”) applying bromide addition to the coal feed at a 800 MWel unit (TXU’s Monticello Steam Electric Station Unit 3) has been run successfully [14]; the evaluation of this test run is still in progress.

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**References**


3. **Kanefke, R.:** Durch Hg-Bromierung verbesserte Hg-Abscheidung aus den Kesselrauchgasen von Abfallverbrennungsanlagen und Kohlekraftwerken, nicht publizierte Diplomarbeit, BAYER AG Leverkusen (Betreuer: Vosteen), Martin-Luther-Universität Halle-Wittenberg, 2002.

4. **Nolte, M.:** Untersuchungen zur Hg-Abscheidung mittels Brom aus den Rauchgasen von Abfallverbrennungsanlagen und Kohlekraftwerken, nicht publizierte Diplomarbeit, BAYER AG Leverkusen (Betreuer: Vosteen), Technische Universität Clausthal, 2002.


