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Bromine-enhanced Mercury Emissions Control at Divers Waste Incineration Plants in Germany and France

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The EU-Reference Document for emissions control under the European Union's Directive 2010/75/EU at Large Combustion Plants (LCP – i.e at coal-fired power plants – was finalized in 2017, establishing Prof. Vosteen's Bromine-Enhanced-Mercury-Oxidation (BEMO-technology) as a BAT. In April 2018, the corresponding Waste Incineration BREF has undergone its final revisions by the Technical Working Group, coordinated by the Joint Research Centre (JRC) of the European Commission's Science and Knowledge Service in Seville; for mercury emissions control at Waste Incineration Plants (WIP) the BEMO-technology was established as a BAT, as well. The following paper will report about applications of the technology at divers WIP in Germany (since 2001) and in France (since 2014). A special issue are mercury emission peaks as caused by unforeseen (sometimes criminal) input of *hidden mercury*; also this problem can be handled easily, as will be described again below [1, 3, 7].

In USA, lots of coal-fired power plants are served with high temperature bromide addition – e.g. in the form of pre-combustion bromide addition. In 2018, i.e. today, more than 100 GW_{el} of coal-fired US power plants – which is about one third of the total coal-based US-power generation capacity – are applying $CaBr_2$-solution constantly onto the coal or via high-temperature bromide injection into the fire-box (*boiler bromide addition*), achieving a cost-effective cobenefit compliance with the stringent mercury emissions limits of the Mercury and Air Toxics Standard regulations (US MATS). In principle, mercury emissions control at coal-fired LCP and WIP needs similar tools.

The removal of mercury is still a challenging *process engineering problem*, because the conditions may differ greatly from plant to plant. Applications of the technology must handle very small up to very large volume streams of the raw gas to be treated and very small up to very large Hg-concentrations changing over time. At coal-fired LCP, typical raw gas Hg-concentrations of 10 – 50 – 100 µg/Nm³ are quite small, while at WIP such as Municipal Solid Waste Incinerators (MSWI) or Hazardous Waste Incinerators (HWI) typical raw gas Hg-concentration may vary from about 10 – 100 – 1,000 µg Hg/Nm³ or even more, while the corresponding raw gas volume flow rates may differ by orders of magnitude. Last but not least, the resulting raw gas mercury freights (kg Hg/year) of LCP and WIP may be almost the same – comparing e.g. coal-fired LCP with industrial HWI serving different customers or with e.g. Sewage Sludge Incinerators (SSI) serving a multitude of Waste Water Treatment Plants (WWTP).

One of the most cost-effective tools to handle mercury emissions problems is the Hg-Oxidation as performed by the BEMO-technology. Oxidized mercury is watersoluble, enhancing cobenefit wet mercury capture at wet FGD, and is also readily adsorbable at carbonacious sorbents, enhancing cobenefit dry mercury capture at both LCP and WIP – such as Municipal Solid Waste Incinerators (MSWI), Sewage Sludge Incinerators (SSI), Hazardous Waste Incinerators (HWI) with often rapidly varying Hg-concentrations in the raw gas to be cleaned.

1. Applications at hazardous waste incineration (HWI) plants in Germany

Currenta GmbH & Co OHG operates at its Waste Management Center Leverkusen-Bürrig the four WIP as shown in Figure 1; these are called VA1, VA2, VA3 and VA4 (*Verbrennungsanlagen*) with alltogether a raw gas volume stream of 150,000 Nm³/h (dry basis).

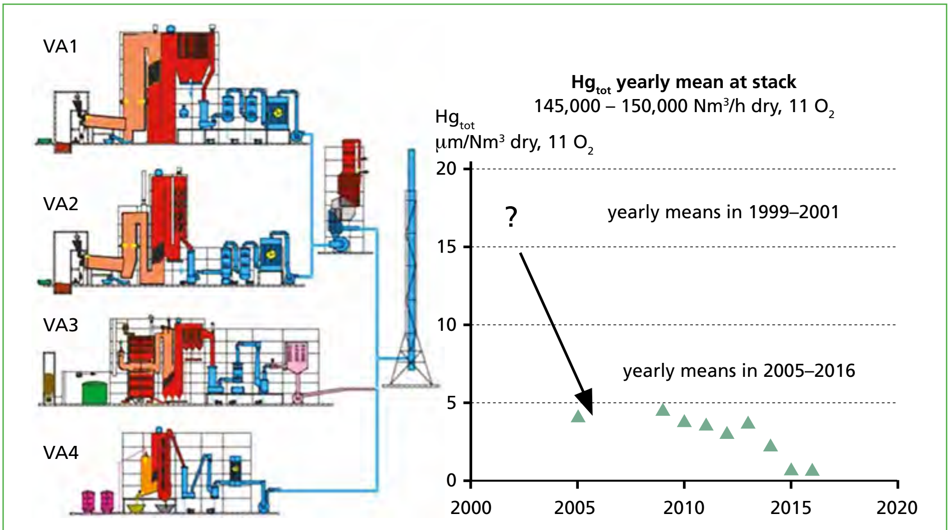

Figure 1: Yearly means 2005 to 2016 of the mercury concentration Hg_{tot} at the stack of the Waste Management Center in Leverkusen-Bürrig

Source: Personal communication on May 19th, 2017, between Dr. Calaminus, managing director Currenta GmbH & Co. OHG, and Prof. Vosteen

At VA1 and VA2 (neighboring rotary kiln furnaces for hazardous wastes) the technology was developed first in 2000 and 2001, and later also at VA3 (multiple hearth furnace for the Bayer industrial sewage sludges). At the small incinerator VA4 for toxic waste water combustion, applying oxigen-enrichment, mercury emissions are no issue.

As Figure 1 shows at its diagramm right hand side, the yearly mean Hg_{tot}-concentration at the common stack was lowered from formerly 20 µg/Nm³ to well below 5 µg/Nm³ (dry basis, corrected to 11 vol.-% O_2).

The SCR denitrification unit behind VA1 and VA2, serving both neighboring plants together, is a *tail-end SCR* with a honeycomb catalyst bed downstream of the multistage wet scrubber system and wet ESP. As described elsewhere, any elemental mercury Hg(0) penetrating the wet APC-stages of VA1 and VA2 is – before entering the stack – effectively retained by adsorption and accumulated at the catalyst bed upstream of the stack [4]. In case of a tail-end SCR, two continuous mercury emissions monitors (CEMs) are necessary to achieve control – one upstream of the tail-end SCR to see what actually happens upstream of the SCR and the other at stack downstream of the SCR [6].

Main elements of a BEMO-technology installation are shown in Figure 2 and Figure 3. All you need is a storage tank for the aqueous bromide-solution, a redundant pumping system with the corresponding tubing up to some injection lances at the post-combustion chamber (or likewise at the rotary kiln‘s front head) – and of course a quick sophisticated control circuit.

A photo of the storage tank (volume: 18 m³) used at VA1 and VA2 is shown in the associated Figure 4. The injection-lances at the post-combustion chamber are watercooled lances with two fluid nozzles, installed just below the tangentially firing liquid waste burners (improved mixing), see Figure 5. In order to start the bromide injection without delay – when needed, the tubing up to the injection lances is kept filled up at any time.

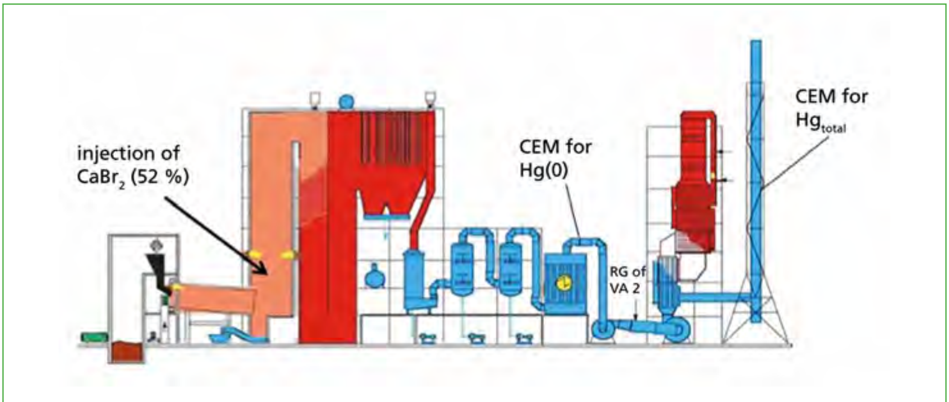

Figure 2: Application of the BEMO-technology at the Currenta HWI plants VA1 and VA2 – Hg-monitoring performed upstream and downstream of the tail-end SCR

Source: Vosteen, B. W.; Chaucherie, X.; Berg, P.; Kanefke, R.: Vermeidung von Quecksilber-Emissionsspitzen in der Abfallverbrennung. In: Thomé-Kozmiensky, K. J.; Löschau, M. (Eds.): Immissionsschutz, Band 5 – Recht – Umsetzung – Messung – Emissionsminderung. Neuruppin: TK Verlag Karl Thomé-Kozmiensky, 2015, pp. 207-227

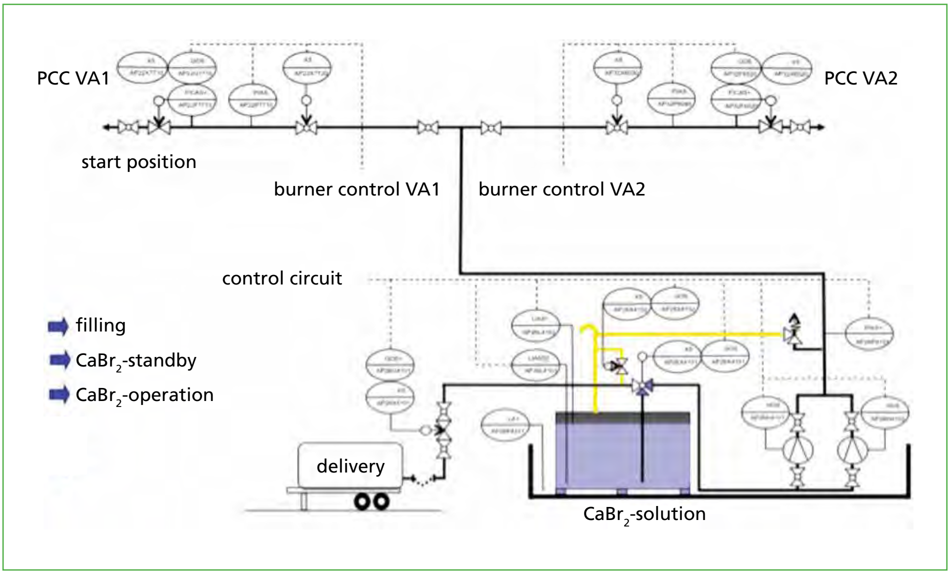

Figure 3: Bromide feeding system for both neighboring VA1 and VA2

Source: Vosteen, B. W.; Chaucherie, X.; Berg, P.; Kanefke, R.: Vermeidung von Quecksilber-Emissionsspitzen in der Abfallverbrennung. In: Thomé-Kozmiensky, K. J.; Löschau, M. (Eds.): Immissionsschutz, Band 5 – Recht – Umsetzung – Messung – Emissionsminderung. Neuruppin: TK Verlag Karl Thomé-Kozmiensky, 2015, pp. 207-227

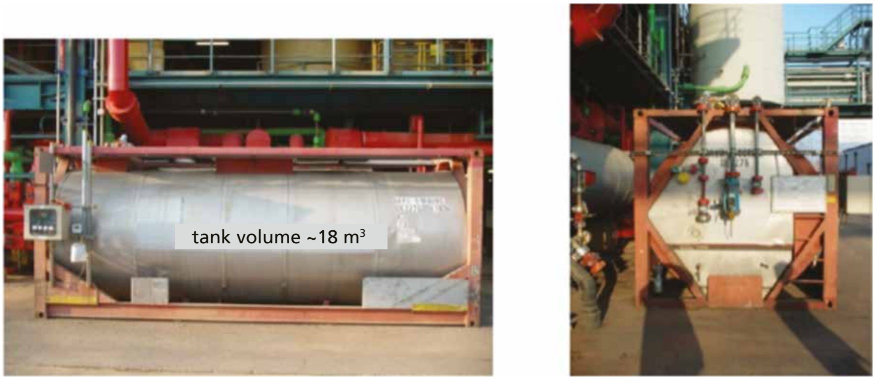

Figure 4: Storage tank für the $CaBr_2$-solution

Source: Vosteen, B. W.; Chaucherie, X.; Berg, P.; Kanefke, R.: Vermeidung von Quecksilber-Emissionsspitzen in der Abfallverbrennung. In: Thomé-Kozmiensky, K. J.; Löschau, M. (Eds.): Immissionsschutz, Band 5 – Recht – Umsetzung – Messung – Emissionsminderung. Neuruppin: TK Verlag Karl Thomé-Kozmiensky, 2015, pp. 207-227

The injection rate of the $CaBr_2$-solution (52 % by weight) depends on the steepness and height of the observed Hg(0) rise at the beginning of a peak. Figure 6 illustrates the typical control action during ongoing suppression of a long lasting peak. The question is whether the bromide is still needed or not, because the Hgtot-peak is all over. To clarify this and to minimize the bromide consumption, the injection should be interrupted intermediately (Figure 6); if the Hg(0)- concentration upstream of the tail-end SCR rapidly increases again – due to missing bromination – the bromide feed is immediately ramped up again (Figure 6). During further operations, when there is no longer a need for bromide, the bromide injection is finally omitted completely until a next incidental Hg_{tot}-peak will occure – possibly after many days or within the next minutes. The automated procedure has proven itself practicable and effective over several years.

injection lance for $CaBr_2$-solution afterburning chamber

number of injection lances at the ABC varies between 1 and 3 (depending on the mixing situation)

Figure 5: Bromide injection lances at the afterburning chamber

Source: Vosteen, B. W.; Chaucherie, X.; Berg, P.; Kanefke, R.: Vermeidung von Quecksilber-Emissionsspitzen in der Abfallverbrennung. In: Thomé-Kozmiensky, K. J.; Löschau, M. (Eds.): Immissionsschutz, Band 5 – Recht – Umsetzung – Messung – Emissionsminderung. Neuruppin: TK Verlag Karl Thomé-Kozmiensky, 2015, pp. 207-227

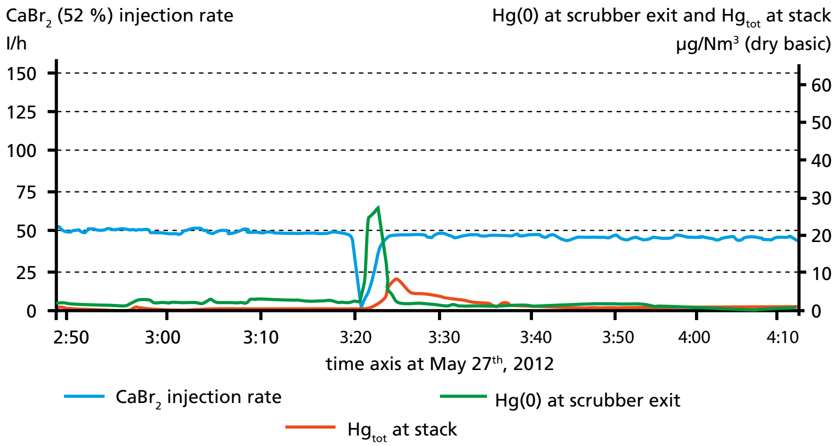

Figure 6: Control of the bromide need on May 27, 2012 at 3:22 a.m. by intermediate interruption of the bromide injection feed

2. Applications at hazardous waste incineration plants of different design in France

Sarpi-Veolia operates in Europe 14 HWI lines (all with rotary kiln) – distributed over 10 sites (Figure 7). Since 2014 the BEMO-technology has been tested at most of the French sites. The testings are ongoing step by step.

Figure 7: Sarpi-Veolia sites with one up to three HWI kiln lines in Europe

At Sedibex en Normandie, three neighboring rotary kiln lines are operated, each with wet Air Pollution Control systems (wet APCs), showing in principle a similar design as the HWI plants in Figure 2 – in principle, but of course there are some important differences: the three kiln-lines all have dry ESPs, but do not have tail-end SCRs; therefore, only one mercury CEM is needed per kiln-line at stack. The technology was installed at Sedibex in 2016 and is since then successfully applied at the three lines (Figure 8).

Figure 8:

Three neighboring HWI-plants with wet APCs at Sedibex

Most other French HWI plants of Sarpi-Veolia have dry or semi-dry APCs. A typical HWI plant with dry APC only (applying slaked lime and activated carbon) is shown in Figure 9 and Figure 10.

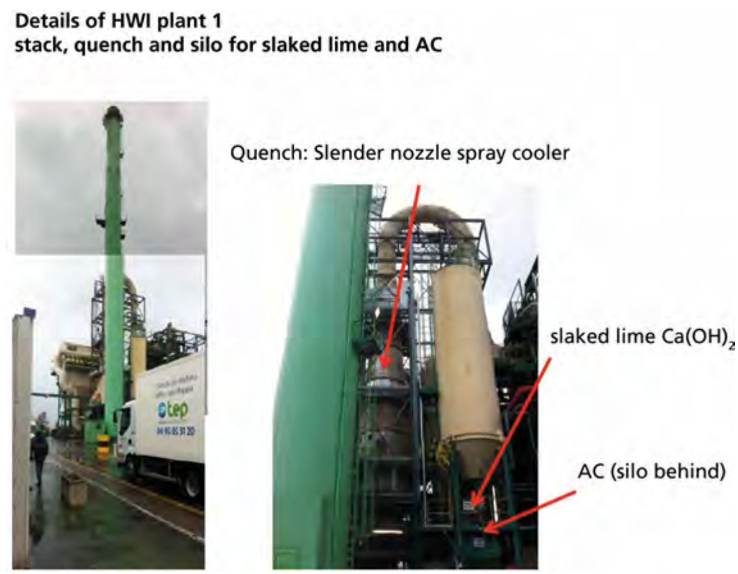

Figure 9: HWI plant 1 with dry APC only

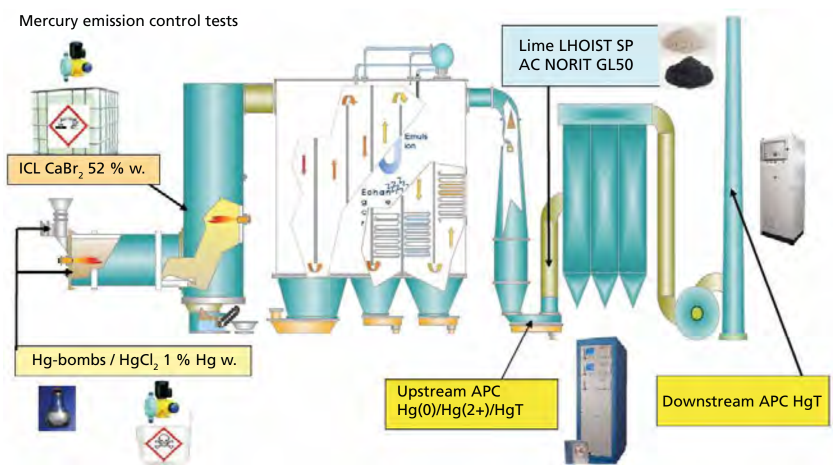

Figure 10: BEMO-technology as tested at HWI plant 1

Test runs at HWI plant 1 were performed in 2014 and have already been described. [1] Therefore, only some interesting results are represented again, (Figure 11, 12 and 13).

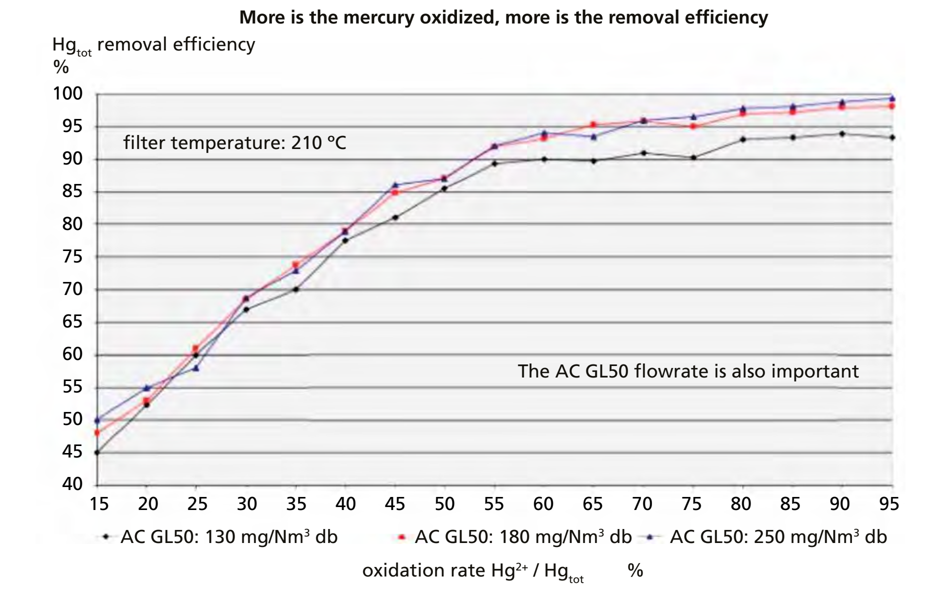

Figure 11: Higher mercury oxidation rates improve dry mercury removal towards 99 % by adsorption at pulverized activated carbon (PAC GL50 of Cabot Norrit)

Source: Chaucherie, X., Berg, P., Vosteen, B.W.: Mercury emissions control in two hazardous waste incineration plants with dry and semi-dry gas cleaning. In: VDI Wissensforum – 15th Conference on Mercury Measurement and Control, April 15, 2015, Meliá Hotel, Dusseldorf

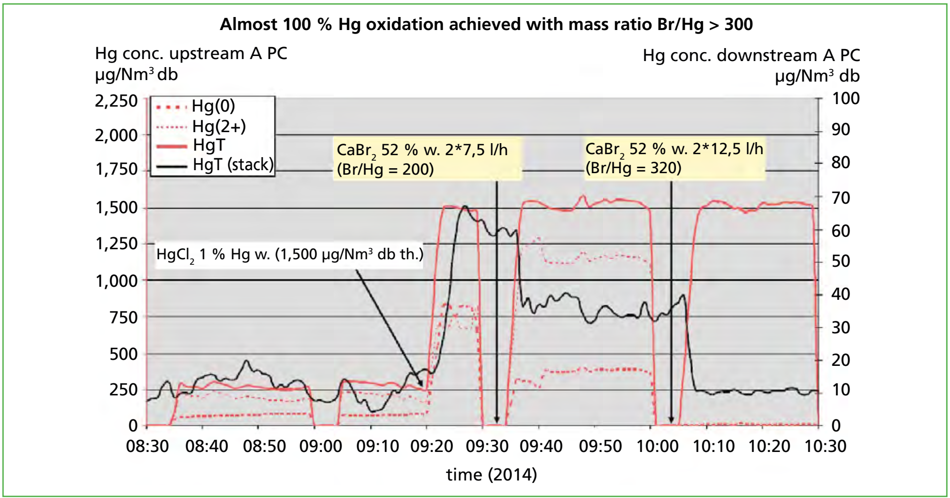

Figure 12: Tests demonstrate that 100 % mercury oxidation can be attained at HWI plant 1 by applying a mass ratio Br/Hg > 300

Source: Chaucherie, X., Berg, P., Vosteen, B.W.: Mercury emissions control in two hazardous waste incineration plants with dry and semi-dry gas cleaning. In: VDI Wissensforum – 15th Conference on Mercury Measurement and Control, April 15, 2015, Meliá Hotel, Dusseldorf

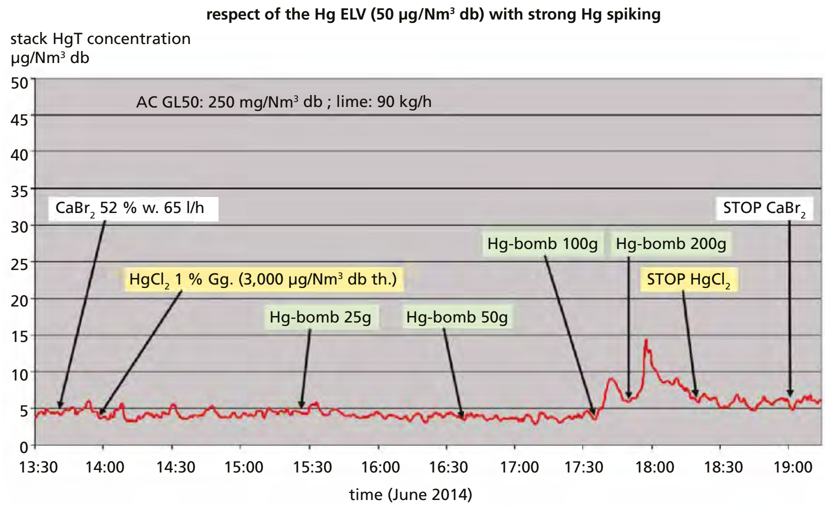

Figure 13: Injection of Hg-bombs into the afterburning chamber to simulate *hidden mercury*

Source: Chaucherie, X., Berg, P., Vosteen, B.W.: Mercury emissions control in two hazardous waste incineration plants with dry and semi-dry gas cleaning. In: VDI Wissensforum – 15th Conference on Mercury Measurement and Control, April 15, 2015, Meliá Hotel, Dusseldorf

In 2014 some tests were performed to simulate also at the HWI plant 1 unforeseen input of hidden mercury during a whole day, see Figure 13. Any mercury emission peaks at stack were hold well below 50 µg/Nm³ (actual French emission limit in 2014) under a constant injetion rate of 65 liters/h $CaBr_2$-solution to the afterburning-chamber.

3. Applications at sewage sludge incineration plants in Germany

The application of the BEMO-technology at the industrieal sewage sludge incineration plant VA3 (multiple hearth incinerator) at the Waste Management Center in Leverkusen-Bürrig was already mentioned, see SSI plant VA3 in Figure 1.

Further applications of the technology at two communal sewage sludge incinerators in the Central Sludge Treatment Plant of Emscher-Genossenschaft / Lippe-Verband (EGLV) in Bottrop go back to 2004, see Figure 14. In the past 14 years until today, this SSI plant with two neighboring fluidized bed combustors (FBC) is operated injecting a NaBr-solution (45 % of weight) just above the stationary fluidized bed surface into the 850 °C freeboard.

In 2008, also another, but quite similar SSI-applications of the technology at the two neighboring fluidized bed incinerators for communal sewage sludge at the WWT plant Karslruhe-Neureut were performed, see Figure 15, Figure 16 and Figure 17. Details were already described elsewhere. [8, 9]

Figure 14:

Central sludge treatment plant of EGLV in Bottrop with two stationary FBC

Figure 15:

Waste water treatment plant in Karlsruhe-Neureut with two stationary fluidized bed combustors (FBC) for sewage sludge

Source: Vosteen, B. W.; Maurer, M.; Milz, R.; Lehrmann, F.; Schwabe, G.: KNX and PRAVO – a Perfect Duo for Mercury Capture – Recent Industrial Applications in Waste Incineration. In: VDI Wissensforum Seminar Nr. 431806: Messung und Minderung von Quecksilberemissionen, 26.-27. Februar 2008, see https://www.vosteen-consulting.de

Figure 16:

FBC-Unit 2 in the WWT plant Karlsruhe-Neureut

Source: Vosteen, B. W.; Maurer, M.; Milz, R.; Lehrmann, F.; Schwabe, G.: KNX and PRAVO – a Perfect Duo for Mercury Capture – Recent Industrial Applications in Waste Incineration. In: VDI Wissensforum Seminar Nr. 431806: Messung und Minderung von Quecksilberemissionen, 26.-27. Februar 2008, see https://www.vosteen-consulting.de

Figure 17: Bromide-storage tank (NaBr-solution, 45 %) at WWT plant Karlsruhe-Neureut

Source: Vosteen, B. W.; Maurer, M.; Milz, R.; Lehrmann, F.; Schwabe, G.: KNX and PRAVO – a Perfect Duo for Mercury Capture – Recent Industrial Applications in Waste Incineration. In: VDI Wissensforum Seminar Nr. 431806: Messung und Minderung von Quecksilberemissionen, 26.-27. Februar 2008, see https://www.vosteen-consulting.de

4. Applications at other waste incineration or thermal treatment plants

There are some more applications of the technology at other WI plants (e.g. MSWI, thermal soil treatment), not only including bromide addition for enhanced mercury oxidation, but also applying the inorganic scrubber additive PRAVO (Precipitation Agent Vosteen), which is a polysulfide – thiosulfate mixture of our partner PANChemie Dr. Fülöp, Kerpen. The PRAVO is produced in different qualities – heightened content of active sulfur to get waterinsoluble HgS –, improving mercury retention in wet scrubbers and in downstream WWT plants. [9]. Three neighboring lines of ENTEGA's Müllheizkraftwerk Darmstadt are applying PRAVO 100 since 2008, i.e. since about ten years.

5. Corrosion, dioxins and furans

Up to now, serious corrosion problems were not observed when applying the Technology commercially at Waste-to-Energy plants – neither in Germany (commercially since 2001), nor in France (commercially since 2014).

Another issue of interest might be the denovo-synthesis of dioxins and furans, as also addressed by the Technical Working Group in Seville. It is known, that toxicity equivalents for a set of chlorine-based PCDD/F are well established, but not for their corresponding bromine-based PBDD/F or even of PCBDD/F. Therefore, the established chlorine-based TEQ are used also for the corresponding bromine-based isomeres.

As described earlier, both chlorinated dioxins and furans (PCDD/F) and brominated dioxins and furans (PBCC/F) as well as a limited set of PCBDD/F, for which standards are available, were analysed in the emitted stack effluents in 2004 at the EGLV sewage sludge combustors in Bottrop. [5, 8]

Similar PCDD/F and PBDD/F measurements at stack were recently performed by Sarpi-Veolia at the three neighboring HWI-plants with wet APCs, operated by Sarpi-Veolia in Sedibex: Also here no critical concentrations were detected. This corresponds to the well documented results of a German large scale tests on *co-combustion of wastes containing chlorine and bromine* in the late 1990s [2, 5].

6. Summary

The BEMO-technology is a low-cost technology with respect to investment and running O+M-costs. It has been successfully applied in Germany since 2001 and in France since 2014 at in total about twenty kiln-lines. Therefore, this technology has recently been established as a BAT for mercury emissions control also at Waste Incineration Plants (WIP).

7. References

[1] Chaucherie, X.; Berg, P.; Vosteen, B.W.: Mercury emissions control in two hazardous waste incineration plants with dry and semi-dry gas cleaning. In: VDI Wissensforum – 15th Conference on Mercury Measurement and Control, April 15, 2015, Meliá Hotel, Dusseldorf

[2] Funcke, W.; Hemminghaus, H.-J.; Mark, F. E.; Vehlow, J.: PXDF/D in flue gas from an incinerator charging wastes containing Cl an Br and a statistical description of the resulting PXDF/D combustion profiles. In: Organohalogen Compounds 31, 93 – 98 (1997)

[3] Vosteen, B.W. et al.: Process for Removing Mercury from Flue Gas. In: German Patent Application DE 102 33 173 of July 22, 2002, and European Patent Application EP 1 386 655 of July 15, 2003

[4] Vosteen, B.W. et al.: Hg-Rückhaltung im reingasseitigen SCR-Katalysatorbett hinter der Rauchgaswäsche einer Sonderabfall-Verbrennungsanlage. In: VGB PowerTech 4/2003, 82-91

[5] Vosteen, B.W.; Funcke, W.; Vehlow, J.: The Influence of Fuel Chlorine & Bromine on Dioxins and Furans at Waste Incinerators and Coal-Fired Power Plants – as related to Bromine Enhanced Mercury Abatement. In: Poster at the International Conference on Mercury as a Global Pollutant (ICMGP), July 28 to August 2 (2013)

[6] Vosteen, B. W.; Chaucherie, X.; Berg, P.; Kanefke, R.: Vermeidung von Quecksilber-Emissionsspitzen in der Abfallverbrennung. In: Thomé-Kozmiensky, K. J.; Löschau, M. (Eds.): Immissionsschutz, Band 5 – Recht – Umsetzung – Messung – Emissionsminderung. Neuruppin: TK Verlag Karl Thomé-Kozmiensky, 2015, pp. 207-227, ISBN 978-3-944310-23-7

[7] Vosteen, B.; Kanefke, R.: Bromgestützte Quecksilber-Abscheidung aus den Abgasen von Verbrennungsanlagen. In: Study for the State Environmental Agency of North Rhine-Westphalia (2003), see https://www.vosteen-consulting.de

[8] Vosteen, B.W.; Kanefke, R.; Köser, H.: Bromine-enhanced Mercury Abatement from Combustion Flue Gases – Recent Industrial Applications and Laboratory Research. In: VGB PowerTech 3/2006, 70-75

[9] Vosteen, B. W.; Maurer, M.; Milz, R.; Lehrmann, F.; Schwabe, G.: KNX and PRAVO – a Perfect Duo for Mercury Capture – Recent Industrial Applications in Waste Incineration. In: VDI Wissensforum Seminar Nr. 431806: Messung und Minderung von Quecksilberemissionen, 26.-27. Februar 2008, see https://www.vosteen-consulting.de

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