Mercury Retention in the Catalyst Bed of a Tail-End-SCR Downstream of the Wet Flue Gas Cleaning of a Hazardous Waste Incineration Plant

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Abstract
At the Waste Management Centre of CURRENTA GmbH & Co. OHG in Leverkusen-Buerrig, operational test runs on mercury chlorination and mercury bromination by co-combustion of highly halogenated wastes were performed at two adjacent hazardous waste incineration plants (total capacity 80,000 tpy). The “in-plant research” was aiming at complete mercury oxidation, achieved within the flue gas during its waste heat boiler passage to enable complete wet mercury capture in a multistage wet flue gas cleaning system downstream, mainly in its strong acid quencher stage.

Since 2001, it has been demonstrated that complete mercury oxidation and thus almost complete mercury capture can be achieved indeed by co-combustion of sufficient amounts of halogenated wastes – or, if necessary, by temporary addition of certain halogenated compounds. Even under very high mercury loads (> 10,000 mg/dscm), excellent mercury removal rates (e.g., 99.99 % at the studied plant) were achieved [1], [2], [3], [4].

During the operational tests, some – unknown and at that time still unexpected – side effects were observed: These were the apparent adsorption of elemental (“metallic”) mercury in/at the catalyst bed of a Selective Catalytic NOₓ-Reduction (SCR) unit and the extended elution of oxidized mercury out of the catalyst bed in form of ionic mercury. These side effects shall be reported here in some detail. In June 2000, four mobile mercury-CEMs (continuous emission monitoring systems) were installed around and within the tail-end-SCR to understand and evaluate the behaviors of metallic and ionic mercury. By accumulation of the growing mercury input and output as well, the actual mercury load of the 20 t catalyst (difference between accumulated in- and output) could be evaluated, establishing a dynamic mercury desorption isotherm of the catalyst at its working temperature 305 °C and demonstrating that huge amounts of mercury can be retained in tail-end SCR catalyst beds. Main reaction pathways governing mercury oxidation in/at the catalyst beds and the retarded mercury elution out of it, were identified, applying an advanced experimental method (“oscillating SO₂-freight”).

KEYWORDS: Mercury, Selective Catalytic Reduction (SCR), mercury retention, mercury elution.

¹ former Bayer Industry Services, lately renamed CURRENTA GmbH & Co. OHG on January 1st 2008
**Introduction**

CURRENTA GmbH & Co. OHG operates four rotary kiln units for hazardous waste incineration at its German sites Leverkusen-Buerrig, Dormagen and Uerdingen. The four units have a similar design, see Figure 1. Two of these kilns are located adjacently at the CURRENTA-waste management center in Leverkusen-Bürrig.

![Diagram of hazardous waste incineration plant](image)

**Figure 1:** Hazardous waste incineration plant (KILN A) in Leverkusen-Buerrig with mercury spiking points 13, 14, 15 and mercury measuring points 16,17

The rotary kiln 3 as primary combustion chamber is fired with solid wastes from the bunker 1 via a crane grab 2, with liquid wastes from stationary and mobile storage tanks; waste packages are dropped via a package feeder. The afterburning chamber 4, as a secondary combustion chamber, is also fired with liquid wastes. The flue gas is cooled via the waste-heat boiler 5 and then, as what is termed dirty boiler raw gas, fed to the wet flue gas emission control system. This includes a quencher 6, an acid rotary atomizer scrubber 7, an alkaline rotary atomizer scrubber 8 and a wet electrostatic precipitation system 9 with partial condensation of water vapor by indirect cooling (WESP). Via two ID fans 10 the scrubbed flue gases of both adjacent units are passed into the common downstream “Selective Catalytic NOx Reduction (SCR) Unit”. The NOx reduction of the flue gas mixture is achieved by means of ammonia injection. The SCR-tower comprises a partitioned recuperative heat exchanger with in total 20,000 m² (50 % PTFE, 50 % steel) for heating up/cooling down of the flue gas. There are two catalyst beds in series working at 305 °C, with in total 19,242 kg of catalyst for NH3-based NOx-reduction as well as for oxidative PCDD/F-destruction. The cleaned gas leaving the SCR-tower at 95 °C is emitted via the stack 12.
During many test runs the flue gas was spiked with mercury, either continuously by addition of HgCl₂ via injection lances into the rotary kiln 13 or into the afterburning chamber 14 (continuously up to 20,000 µg/dscm) or discontinuously up to some 200,000 µg/dscm in short time intervals by throwing Hg-bombs into the afterburning chamber 15.

The metallic mercury content (Hgₘₑₙ) and if appropriate the total mercury content (Hgₜₒₜₜₜ) at measuring point 16, i.e. in the scrubbed gas downstream of the WESP, was determined continuously by a mercury-CEM (continuous emission monitoring system) using AAS photometers, in case of Hgₜₒₜₜ at the CEM with wet gas pretreatment by NaBH₄ for mercury reduction.

The total mercury content (Hgₜₒₜₜ) at the measuring point 17 in the emitted clean gas at the stack was determined semi-continuously, by amalgamation on a gold film heated at intervals (MERCEM of Sick MAIHAK with SnCl₂ based mercury reduction).

In June 2000 up to four mercury-CEMs were installed in parallel for some weeks at and within the Tail-End-SCR to evaluate the behaviors of metallic and ionic mercury in more detail, see Figure 3.
Figure 3: Mercury-CEMs around and within the tail-end SCR in June 2000 – after WESP (16), after heat up in heat exchangers (18), after catalyst beds (19), after cool down in heat exchangers (20), at stack (17)

The CEM mercury measurements at points 16, 18, 19, and 20 were taken in summer 2000. It was verified that no Hg\textsubscript{met} sorption occurred at the recuperative heat exchanger surfaces, neither on the cold side PTFE tubes nor on the hot side steel tubes. Thus it was shown, that the Hg\textsubscript{met} adsorption occurs on the V\textsubscript{2}O\textsubscript{5}-rich honeycomb catalyst mass in the SCR-tower.

**In-plant Research Applying Sulphur Granulat Injection**

Beginning in 1997, extensive operational tests had been performed at the two adjacent kilns in Leverkusen-Buerrig to promote emission-free combustion of highly chlorinated liquid wastes

When combusting high loads of halogenated wastes, the SO$_2$ concentrations in the boiler flue gas should be held high enough to prevent free halogen emissions [2], [5]. The impact of SO$_2$ on the molecular halogens is different for Cl$_2$ and Br$_2$ or I$_2$. SO$_2$ in the flue gas will reduce molecular chlorine already during boiler passage (Chlorine Griffin Reaction: Cl$_2$ + SO$_2$ + H$_2$O $\rightarrow$ 2 HCl + SO$_3$) and prevent de-novo-synthesis of polychlorinated dioxins/furans. Any residual Cl$_2$ (being almost insoluble in acid water) will pass the acid scrubber to be chemisorbed in the alkaline scrubber, forming there 50%/50% NaCl and NaOCl. The fairly unstable NaOCl (with a considerable Cl$_2$ vapor pressure) can be reduced there to the stable NaCl also. The reduction of NaOCl to NaCl is achieved by SO$_2$ chemisorbed in the alkaline scrubber, as well. In contrast to molecular chlorine, molecular bromine or molecular iodine will not be reduced by SO$_2$ already during boiler passage; further – once again in contrast to Cl$_2$ – both are well soluble in acid water and reduced by SO$_2$ already in the quencher. A sufficient sulphur supply precludes brown plumes (molecular bromine) or purple plumes (molecular iodine) at the stack. The necessary sulphur supply can be achieved by controlled feed of sulphur granulates into the rotary kiln, see Figure 4a; the patented control circuit of the sulphur feeding system as applied successfully since 1997 is shown in Figure 4b.

Figure 4a: Screw feeder for sulphur granulate addition into the rotary kiln
Additionally, beginning in January 2000, extensive operational tests had been conducted in parallel to promote mercury capture when combusting mercury rich wastes by co-combustion of chlorinated wastes and/or brominated wastes. The general knowledge about SO₂-related gas phase reactions as attained in the preceding operational tests on combustion of halogenated liquid wastes only (boiler flue gas chemistry), was very helpful to understand the incidentally discovered – at first sight astonishing – advantages of mercury bromination in contrast to mercury chlorination, in the boiler flue gas as well as in/at the catalyst of the tail-end SCR.

The sulphur feed device installed for combustion of halogenated wastes, did allow for highly interesting test runs too in case of co-combustion of mercury rich wastes, e.g. when studying mercury chlorination: “Sharpening” the sulphur feeding control circuit more and more, it was possible to achieve harmoniously oscillating SO₂ concentrations in the boiler raw gas, see Figure 5. The term Cl_total is understood to be the sum of the chloride Cl⁻ (hydrogen chloride HCl) and free chlorine Cl₂. In spite of a high chlorine load (Cl_total concentration of ca. 20,000 mg/dscm), the induced oscillations of the SO₂ concentration were inducing themselves – without any delay – concurrent oscillations of the Hg_{net} concentration in the flue gas at the boiler exit / behind the scrubber system and also in the diluted flue gas behind the SCR heat exchangers, before entering the first catalyst bed. This demonstrates that mercury
chlorination in the boiler raw gas is apparently proceeding via a reaction with Cl₂ or related radicals, but not via the reaction with HCl itself, and further that Cl₂, intermediately formed in the boiler flue gas in small quantities (via the Chlorine Deacon Reaction: 4 HCl + O₂ -> 2 Cl₂ + 2 H₂O), is reconsumed by reaction with SO₂ (Chlorine Griffin Reaction: Cl₂ + SO₂ + H₂O -> 2 HCl + SO₃).

Figure 5: Artificially induced oscillations of the SO₂ concentration are inducing – without any delay – concurrent oscillations of the Hgₘₖₑₜ concentrations

Figure 6 is showing the corresponding oscillations of the (mainly ionic) mercury in the cleaned gas directly behind the catalyst beds and also further downstream at the SCR-DeNOx-tower exit (behind the heat exchangers). These Hg离子-oscillations are no longer concurrent, but quite astonishingly countercurrent to the artificially induced oscillations of the SO₂ concentration in the boiler raw gas.

The different behaviours of mercury as demonstrated in these Figures 5 and 6 is not at all contradictive, but can be explained and understood with help of a simplifying working hypothesis. This hypothesis assumes that the main reactions governing mercury oxidation in the boiler raw gas are also governing mercury oxidation in/at the catalyst. There is only one – at first sight missing – puzzle piece to be added: As the SO₂ concentration in the boiler raw gas is dropping, there is less Cl₂ consumed, i.e. more Cl₂ is left for mercury oxidation in the boiler raw gas (Hgₘₖₑₜ in the boiler raw gas dropping concurrently, see Figure 5), and there is more residual Cl₂, which passes through the acid scrubber zone and then gets chemisorbed in the alkaline scrubber, forming more unstable sodium hypochlorite NaOCl. But the unstable sodium hypochlorite NaOCl is inducing a Cl₂-vapour pressure (Henry behavior) in the off gas, i.e. there will be some more Cl₂ leaving with the scrubbed flue gas towards the SCR when SO₂ in the boiler raw gas is dropping, as assumed. If, on the other hand, the SO₂
concentration in the boiler raw gas is increasing, the Cl\textsubscript{2} concentration will drop (Chlorine Griffin Reaction), but not only in the boiler raw gas, in the scrubbed flue gas, as well. This means: The artificially induced oscillations of the SO\textsubscript{2} concentration in the boiler raw gas induce countercurrent oscillations of very small Cl\textsubscript{2} concentrations in the scrubbed flue gas entering the SCR DeNOx catalyst tower, inhibiting (if not present) or promoting (if present) the mercury oxidation in/at the catalyst and therewith the elution as Hg\textsubscript{ion}.

As an indication of the CEMs’ time resolution, even the short time delay between the two Hg\textsubscript{ion}-curves of the cleaned flue gas before and after the heat exchangers (residence time of the flue gas on its way back through the heat exchangers) is visible in Figure 6.

**Figure 6:** Artificially induced oscillations of the SO\textsubscript{2} concentration in boiler raw gas are inducing countercurrent oscillations of the Hg\textsubscript{ion} concentrations behind SCR

**In-plant Research Applying Continuous Mercury Spiking under High Chlorine Load**

Systematic operational tests were performed spiking the flue gas continuously with HgCl\textsubscript{2} under co-combustion of highly chlorinated liquid wastes as shown in Figure 7. These tests demonstrated that a high enough Cl\textsubscript{total} supply leads to nearly 100% Hg\textsubscript{met} Chlorination during boiler passage and thereby to nearly 100% mercury removal by absorption in the acid scrubber zone (strong acid quench and acid rotary spray scrubber). Figure 7 is based on many
tests of different (total) chlorine load at different total mercury concentrations in the boiler raw gas ranging from 10 µg/dscm up to 10,000 µg/dscm.

Figure 7: Hg_{met} / Hg_{total} species fraction in the crude gas at boiler exit

The Hg_{met} oxidation by chlorination during boiler passage, i.e. the Hg_{met} species fraction achieved at the boiler end of this hazardous waste incineration plant (ca. 350 °C) depends not only on the Cl_{total} concentration, but also on the SO_{2} concentration, as just discussed. Under sufficient Cl_{total} supply > 5000 mg/dscm, all Hg_{met} is oxidized at the boiler exit, i.e. all mercury entering the strong acid scrubber zone with pCl⁻ < 1 in the quench will be water-soluble Hg_{ion} only. There the watersoluble Hg_{ion} is scrubbed out almost completely. Normally, no Hg_{ion} and no Hg_{met} should be leaving with the scrubbed gas before SCR (ca. 99.99 % Hg_{total} removal in the scrubber system). Only in case of limited Cl_{total} supply << 5000 mg/dscm and at the same time very high SO_{2} load, will noticeable Hg_{met} concentrations be present.

Therefore, in the CURRENTA units, Hg_{met} passage from the boiler through the scrubber system to the SCR is normally strictly prevented by means of sufficient halogen supply, i.e. by co-combustion of highly halogenated liquid wastes, under minimized sulphur supply.
In-plant Research Applying Discontinuous Mercury Spiking under High Chlorine Load

During in-plant research on mercury chlorination as described, defined H$_{\text{met}}$ penetration was intentionally induced because this was the only way to get more insight into the – at that time to us still unknown – adsorption and desorption behavior of mercury in/at the SCR catalyst beds. Any H$_{\text{met}}$ passing through the scrubber system is adsorbed by the SCR catalyst beds and later released again, but then as oxidized mercury, the so called H$_{\text{ion}}$. This happened, as was expected following Figure 7, under a Cl$_{\text{total}}$ load of 3000 … 4000 mg Cl$_{\text{total}}$/dscm and a SO$_2$ load of 500 … 1200 mg/dscm, which is still adequate for nearly emissions-free combustion of the low Cl$_{\text{total}}$ load.

The complex adsorption and desorption behavior of mercury in/at the SCR catalyst bed could be demonstrated best throwing Hg-bombs into the afterburning chamber, i.e. by discontinuous Hg feeding. The applied sequential insertion of four small Hg bombs under well chosen operating conditions, being low enough in chlorine to allow for incomplete mercury chlorination and thus leading to an intended H$_{\text{met}}$-breakthrough at the scrubber, which is shown in Figure 8: Four H$_{\text{met}}$ peaks are entering the SCR tower with the scrubbed flue gas and one can see how these peaks do virtually disappear during passage through the SCR catalyst beds, for the mercury discharge out of the SCR catalyst beds does not contain H$_{\text{met}}$ at all, but H$_{\text{ion}}$ only. Obviously, the mercury discharge from the SCR (desorption) – despite purely H$_{\text{met}}$ being inserted – occurs essentially as H$_{\text{ion}}$ elution, at a comparatively low level of exponentially decreasing concentrations. Complete elution was attained in this experiment at 750 min (end outside of Figure 8).

![Figure 8: Hg bomb peaks for verification of the H$_{\text{met}}$ retention in the tail-end SCR](image-url)
**Hg Sorption Isotherm of the Tail-End SCR catalyst at 305°C Operating Temperature**

Of special interest was a second test run with staged continuous mercury spiking at the after burning chamber of plant A on June 15th, 2000, Figure 9. During this test, the SCR was charged with the scrubbed gas of plant A only (SCR partial load). Again, parallel CEM measurements of \( \text{Hg}_{\text{total}} \) and \( \text{Hg}_{\text{met}} \) were performed at the measurement point 16. This showed again that only \( \text{Hg}_{\text{met}} \) passes through the scrubber, i.e., \( \text{Hg}_{\text{total}} = \text{Hg}_{\text{met}} \) and \( \text{Hg}_{\text{ion}} = 0 \) after WESP. In Figure 9 the zero point of that \( \text{Hg}_{\text{met}} \) measurement was shifted for better visibility in order to hold the two almost identical test data curves (because \( \text{Hg}_{\text{total}} = \text{Hg}_{\text{met}} \) in this case) apart.

The calculated \( \text{Hg}_{\text{total}} \) concentrations in the boiler raw gas, established by controlled spiking, equalled 1240 \( \mu \text{g/dscm} \) during the first Hg short-term input (June 15, 2000, \( t = 780 \ldots 810 \) min), and also during the following Hg long-term input (June 15, 2000, \( t = 930 \ldots 1010 \) min) and then 2300 \( \mu \text{g/dscm} \) during the increased third addition step (June 15, 2000, \( t = 1010 \ldots 1060 \) min).

![Test in plant A](image)

**Fig. 9:** Second test at plant A on June 15th, 2000 (plant B not in operation) – \( \text{Hg}_{\text{total}} \) and \( \text{Hg}_{\text{met}} \) before and after SCR during the test on June 15, 2000

In order to be able to learn from this test, the \( \text{Cl}_{\text{total}} \) load was intentionally held low again (co-combustion of low amounts of chlorinated liquid wastes) and simultaneously the \( \text{SO}_2 \) load was increased by means of sulphur granulate injection, consuming free chlorine and thus reducing the Hg halogenation in the boiler crude gas. This led to the targeted \( \text{Hg}_{\text{met}} \) passage
through the wet scrubber visible in Figure 9, corresponding to an $\text{Hg}_{\text{met}}$ breakthrough in the range of nearly 20% of the $\text{Hg}_{\text{total}}$ load in the boiler crude gas. As already shown in Figure 8, the $\text{Hg}_{\text{met}}$ retention in the SCR catalyst beds can also be clearly recognized, see Figure 9. Also here, only $\text{Hg}_{\text{ion}}$ is eluted from the SCR catalyst beds ($\text{Hg}_{\text{met}} = \text{zero}$).

By data evaluation it becomes possible to accumulate the mercury input, entering the SCR catalyst beds as metallic mercury $\text{Hg}_{\text{met}}$, and also the mercury output, leaving the SCR catalyst beds as oxidized mercury $\text{Hg}_{\text{ion}}$. The accumulation of both leads to its difference, which is the instantaneous Hg amount stored at any time in the SCR (ordinate values, [g Hg]). This load can be converted into a corresponding mean specific Hg load of the catalyst, by dividing the stored mass of mercury by the total mass of the catalyst beds. One can see in Figure 10, e.g., that a maximum load of only ca. 2 g $\text{Hg}_{\text{met}}$ (corresponding to a mean specific mercury load of ca. 0.1 mg/kg only) might be tolerated in order not to exceed $\text{Hg}_{\text{total}}$ concentrations of 50 µg/dscm in the cleaned gas after the SCR / at the stack ($\text{Hg}_{\text{total}} = \text{Hg}_{\text{ion}}$, because $\text{Hg}_{\text{met}}$ after SCR equals zero).

![Figure 10: Hg desorption isotherm of the tail-end SCR at 305°C (19,242 kg catalyst mass) during test on June 15, 2000, early afternoon](image)

This established isotherm in Figure 10 is a desorption isotherm (triangular points). The additional square points refer to adsorption and desorption tests performed earlier in February to May 2000.
In-plant Research Applying Continuous Mercury Spiking under High Bromine Load

In 2001, more extensive operational tests were performed under co-combustion of some low-chlorine wastes and much high-bromine wastes. In these tests somewhat larger and even extremely large \( H_{\text{g,total}} \) concentrations were induced, at first by continuous and later by discontinuous spiking. In case of continuous spiking (controlled injection of a watery \( \text{HgCl}_2 \)-solution), \( H_{\text{g,total}} \) concentrations up to 18,000 µg/dscm were induced for extended time. In case of discontinuous mercury spiking (injection of “\( \text{Hg}_\text{met} \)-bombs" of up to 330 g each, every 5 … 10 minutes), mercury rich flue gas “clouds” of 3 … 5 min length with \( H_{\text{g,total}} \) concentrations > 130,000 µg/dscm were achieved, passing through the boiler and then entering the scrubber system.

Figure 11 illustrates a basic experiment demonstrating the influence of chlorine and of bromine on the oxidation of mercury in the boiler flue gas. In this test, the \( H_{\text{g,total}} \) content achieved by injection of \( \text{HgCl}_2 \) was 150 µg/dscm, available at a relatively low chlorine content (\( C_{\text{l,total}} \)), set by co-combustion of low-chlorine waste at 1,350 mg \( C_{\text{l,total}}/\text{dscm} \) in the boiler raw gas and at a residual sulphur dioxide content in the boiler raw gas set by adding sulphur granules of 1,500 mg \( \text{SO}_2/\text{dscm} \). Measurement point 63 shows the “baseline proportion” of \( \text{Hg}_\text{met} \) species of approximately 63% by weight in the boiler raw gas upstream of the wet scrubber as achieved by chlorine only. The plant-specific chlorination curve which is based on approximately 20 operational experiments with incineration of highly chlorinated liquid waste only (see again Figure 7) shows how the proportion of \( \text{Hg}_\text{met}/H_{\text{g,total}} \) decreases further with increasing chlorine content \( C_{\text{l,total}} \) in the boiler flue gas.

Figure 11: Mercury oxidation above baseline by chlorine and by bromine
Starting from a “baseline-proportion” $Hg_{met}/Hg_{total}$ of approximately 63% by weight in the boiler raw gas upstream of the wet scrubber (measurement point 63 with $Cl_{total}$ content as x axis and then measurement point 63’ with $Br_{total}$ content as x axis), an increasing amount of a bromine compound was added (see arrow 64 which marks the transition from the plot of the proportion of $Hg_{met}$ species as a function of $Cl_{total}$ content to the plot as a function of $Br_{total}$ content). The bromine content in the boiler flue gas can be increased from initially 0 mg/dscm (measurement point 63’ with $Br_{total}$ content as x axis) by adding aqueous hydrogen bromide solution (injection to the afterburning chamber 14, cf. again Figure 1) and increasing the $Br_{total}$ content in three steps to 50, 100 and 120 mg/dscm (measurement points 62 with $Br_{total}$ content as x axis). In this experiment the proportion of $Hg_{met}$ species ($Hg_{met}/Hg_{total}$) in the boiler raw gas upstream of the wet scrubber (starting from approximately 63% by weight) decreased to 30% by weight. 

The comparison is evidence for the markedly more effective oxidation of mercury by bromine compounds than by chlorine compounds. To achieve a proportion of $Hg_{met}$ species of only 30% using chlorine alone, the $Cl_{total}$ content, according to the chlorination curve 61, would have to be increased to 4,000 mg/dscm. Instead, this was achieved adding only 120 mg/dscm of bromine. Bromine therefore appears to be far more active than chlorine. The same applies to the developing case of power station flue gases where the plant-specific Hg chlorination curve and Hg bromination curve are shifted to substantially lower total halogen contents.

**Figure 12:** Mass ratio $Br/Hg$ and achieved Hg removal rate in a test run spiking the boiler raw gas with 9,600 µg Hg/Nm³ dry
Figure 12 shows the equally interesting results of a related test run (under continuous spiking with 9,600 µg Hg\textsubscript{total}/dscm) to define the necessary mass ratio Br/Hg $\geq$ 500, necessary to achieve complete mercury capture in this plant without hotside, but tail-end SCR DeNO\textsubscript{x} catalyst bed.

**In-plant Research Applying Discontinuous Mercury Spiking under High Bromine Load**

Another example shall illustrate how well bromine promotes mercury capture in an even more impressive way. This was a test run with discontinuous spiking, throwing larger and larger “Hg-bombs” into the afterburning chamber, see Table 1. Over a period of 116 minutes, a series of metallic mercury samples in plastic capsules (in total 3400 g) were fed to the afterburning chamber 4 via the inspection port 15, cf. again Figure 1. The injection of these mercury bombs was performed at intervals of approximately 5 … 10 minutes with increasing amounts of mercury. The mercury introduced into the afterburning chamber vaporizes within 2 … 4 minutes; thus, the instantaneous peak mercury concentrations occurring in the boiler flue gas at a volume flow rate of 45,000 dscm/h could be estimated. Towards the end of the experiment, the huge bombs induced peak mercury concentrations of 130,000 … 200,000 µg/dscm (evaluated, not measured).

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**Table 1:** Injection of Hg bombs [g]

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During the experimental period co-combusting a highly brominated liquid waste (addition to the rotary kiln head), a bromine content of approximately 4,000 mg Br\(_{\text{total}}\)/dscm was maintained in the boiler raw gas, as shown by curve 22 (right y axis) in Figure 13 (determined on the basis of throughput and bromine content of the highly brominated liquid waste). The residual SO\(_2\) content in the boiler raw gas upstream of the quench was set unusually high to 5,500 mg/dscm by adding sulphur granulate to the rotary kiln head (direct SO\(_2\) measurement in the dirty boiler gas upstream of the quench). The other combustibles in the feed menu consisted of solid wastes and low-chlorine solvents.

Before, during and after the addition of mercury, the concentration of mercury in the flue gas was measured at measurement point 16 behind WESP. As the lower curve of the mercury concentration after WESP, i.e. in the scrubbed flue gas (left y axis) in Figure 13 shows, the concentration of metallic mercury passing through the scrubber did not increase, despite the addition of considerable amounts of mercury.

**Figure 13:** Injection of larger and larger Hg-bombs (see Table 1) under sufficient bromine supply [6], [7]
In-plant Research on Dioxin Denovo-Synthesis

The controlled injection of sulphur granulate into the kiln is suppressing Cl\textsubscript{2} already in the gas phase via the Chlorine Griffin Reaction (Cl\textsubscript{2} + SO\textsubscript{2} + H\textsubscript{2}O → 2 HCl + SO\textsubscript{3}), and thereby suppressing the “denovo synthesis” of polychlorinated dioxins and furans, as well. In the test runs combusting highly brominated wastes, Br\textsubscript{2} seemed to be “consumed” by SO\textsubscript{2} in a similar way, see Figure 14:

Figure 14: SO\textsubscript{2} at boiler entrance as achieved by injection of sulphur granulate, and SO\textsubscript{2} at boiler exit / behind quencher under increasing bromine freight as achieved by co-combustion of highly brominated wastes

But, an explanation of this observation via the similar Bromine Griffin Reaction (Br\textsubscript{2} + SO\textsubscript{2} + H\textsubscript{2}O → 2 HBr + SO\textsubscript{3}) is not correct in the boiler temperature range: While equilibrium thermodynamics show that the Chlorine Griffin Reaction may well proceed in the boiler flue gas, the at first sight similar Bromine Griffin Reaction may not proceed at elevated temperatures (Gibbs Free Enthalpy of Reaction > 0). As was lately shown by laboratory experiments of Kanefke /8/, the apparent “consumption” of Br\textsubscript{2} by SO\textsubscript{2} under formation of HBr and SO\textsubscript{3} is not proceeding in the hot boiler flue gas, but a) in the condenser-cooler of a cold SO\textsubscript{2} measuring system and likewise b) in the first (acid) scrubber stage at temperatures < 100 °C (Gibbs Free Enthalpy of Reaction < 0).
This indicates that molecular bromine, formed in the boiler flue gas via the Bromine Deacon Reaction will not be suppressed by SO$_2$ in the boiler range and exit the boiler. Therefore, the question of denovo synthesis of polybrominated dioxins and furans does arise. As reported in Ref. [2], extensive PCDD/PCDF and PBDD/PBDF measurements were done at a fluidized bed incineration plant with waste heat boiler, ESP and WFGD combusting municipal sewage sludge and applying sodium bromide injection into the kiln’s freeboard for enhanced mercury capture in presence of high SO$_2$ concentrations. In the baseline case (no bromide injected), the PCDD/PCDF concentrations were $<< 0.1$ ng TEQ/dscm. But also with bromide injection for enhanced mercury oxidation, the PCDD/PCDF and PBDD/PBDF concentrations were both $<< 0.1$ ng TEQ/dscm, as well [2].

**Practical Relevance**

The observed side effects are of high operational importance in a variety of plants, because they may mask both mercury feed incidents (“hidden mercury”), and scrubbing impacts, in hazardous waste combustion as well as in municipal solid waste combustion. As an example, Figure 15 shows a recent case from December 2006 which occurred in a municipal solid waste incineration plant with multistage wet scrubbing system (von Roll scrubber) and tail-end SCR.

![Figure 15](image)

*Figure 15:* Example of a typical long time mercury elution peak from a tail-End SCR behind the wet scrubbing system of a municipal solid waste incinerator [9]
In 2001 another municipal solid waste incineration plant with WFGD and tail-end SCR near Cologne experienced a much more drastic and perhaps unique mercury event due to a "huge hidden Hg spike", which not only contaminated the plant’s scrubber system with mercury, but also contaminated the tail-end SCR catalyst beds. Extensive cleaning measures were performed after this “accident” on almost the entire plant, especially on the scrubber stages; but in spite high mercury emission concentrations were going on. Finally, it became apparent that a considerable amount of mercury had been retained in the tail-end SCR catalyst bed, eluting from there with exponentially decreasing concentrations over a long period of time.

Conclusions

Observations and testing at a CURRENTA waste incineration plant has derived the following aspects of mercury behavior in the plant’s waste heat boiler and its gas cleaning train:

- $\text{Hg}_{\text{met}}$ is oxidized to $\text{Hg}_{\text{ion}}$ most readily by bromine, and also by chlorine,
- sulfur ($\text{SO}_2$) can inhibit $\text{Hg}_{\text{met}}$ chlorination, less $\text{Hg}_{\text{met}}$ bromination,
- $\text{Hg}_{\text{met}}$ passes through scrubbers and is adsorbed onto the catalyst bed of a tail-end SCR, slowly oxidized and finally elutes off as $\text{Hg}_{\text{ion}}$,
- sulfur ($\text{SO}_2$) impacts the reduction of molecular halogens in different ways; $\text{SO}_2$ reduces $\text{Cl}_2$ at elevated temperatures (boiler range), but reduces $\text{Br}_2$ only at low temperatures (scrubber range)

The operational tests and studies performed in the spring and summer of 2000 at this plant led to some specific knowledge about $\text{Hg}_{\text{met}}$ adsorption and also $\text{Hg}_{\text{ion}}$ desorption at the catalyst bed of a tail-end SCR. This knowledge, which was at that time in many respects novel, has provided more insight into the mercury oxidation behaviour.

Today, process options derived from this knowledge could be implemented in hazardous waste incineration plants and also municipal solid waste incineration plants, to achieve complete mercury halogenation in the boiler flue gas, ahead of the scrubber system, at any time. This might prevent penetration of metallic mercury to the tail-end SCR and avoid the corresponding long time mercury elution.

For effective prevention to be achieved in practice, it is strongly recommended to also install a continuously measuring (possibly uncalibrated) AAS mercury monitor for immediate detection of any unexpected $\text{Hg}_{\text{met}}$ breakthrough, for example caused by "hidden mercury” in the waste feed, and to initiate the rapid (preferably automatized) injection of some bromine compound before even more mercury is transferred into the tail-end SCR, stored there as $\text{Hg}_{\text{met}}$, oxidized and eluted on the long run as $\text{Hg}_{\text{ion}}$, i.e., finally led via the stack into the environment.
The addition of halogenides has a positive impact on mercury capture in a WFGD via mercury complexation; this phenomenon has been described elsewhere [10].

References


