Energy process engineering and environmental protection

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Study commissioned by the State Environmental Agency of North Rhine-Westphalia

carried out by

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Cologne, December 2003

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The subject of this study is a process for which a patent was filed in July 2002 for bromine-assisted Hg separation from the exhaust gases of combustion plants.

The innovative, highly effective process is cost-effective as it does not require any major retrofitting Investment and only small amounts of bromine-containing additives (injection into the combustion chamber) With optimized application, almost 100 % mercury removal can be achieved can be achieved, both in smaller plants with a flue gas volume flow of only approx. 15,000 m³ dry air/h (e.g. sewage sludge incineration) as in plants with approx. 50,000 m³ dry air/h (e.g. hazardous waste incineration) or approximately 150,000 m³ dry matter/h (e.g. domestic and commercial waste combustion) to large coal-fired power plants with, for example, 2 to 3 million m³ dry matter per hour. Furthermore, occasional Hg concentration peaks can be prevented by rapid control intervention (Er-increase in the supply of “bromine”), provided that the incineration plant the “hidden amounts of mercury” carried are not excessive.

The discussion about a long-term reduction of Hg emissions (limitation of Hg freight) and appropriate and practical control (for example, with the help of continuous or semi-continuous Hg meters) loses in view of the highly effective and at the same time cost-effective procedure, both from the point of view of technical Feasibility as well as cost perspective.

Vosteen Consulting GmbH has received from Bayer Industry Services GmbH, Leverkusen, about a general license of the procedure *) and advises on optimized application and Use.

Prof. Dr.-Ing. Bernhard W. Vosteen Cologne, April 22, 2004
(Vosteen Consulting GmbH)

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*) Vosteen., B., Beyer, J., Bonkhofer, T.-G., Pohontsch, A., Kanefke, R., Nolte, M. et al.: “, German disclosure DE 100233173 A1 (Applicant: BAYER AG, 22. 7. 2002), see http://v3.espacenet.com/textdoc?DB=EPODOC&IDX=CA2435474

The study is reporting on a new mercury abatement process, based on bromine injection into the hot flue gases from waste incineration and power generation plants. The highly effective process for mitigating mercury from incineration flue gases was applied for patent in July 2002.**)

Vosteen Consulting GmbH, Cologne, holds a general license from BAYER Industry Services, Leverkusen, and is ready to solve mercury mitigation problems in cooperation with interested parties customers and to grant sub licenses, based on the pending patent.

Bromine injection for mercury mitigation has been extensively investigated by Bayer Industry Services GmbH in cooperation with Vosteen Consulting GmbH for application in waste incineration and coal combustion, and a number of demonstrations have taken place in hazardous waste incinerators (Bayer Industry Services GmbH, Leverkusen, Germany), as well as in industrial trial PC-fired power station boilers (BAYER AG, Uerdingen, Germany), and in two fluidized bed boilers for communal sewage sludge (Emschergenossenschaft, Essen/Bottrop, Germany), all tests designed and evaluated by Vosteen Consulting GmbH.

Prof. Dr.-Ing. Bernhard W. Vosteen
(Vosteen Consulting GmbH)

Cologne, April 22nd, 2004

**) Vosteen, B., Beyer, J., Bonkhofer, T.-G., Pohontsch, A., Kanefke, R., Nolte, M. et al.: “Process for Removing Mercury from Flue Gases”, US patent application US 2004/001 358 911 A1 (applicant: BAYER AG), Publication info: CA2435474 - 2004-01-22, see: http://v3.espacenet.com/textdoc?DB=EPODOC&IDX=CA2435474

A distinction is made between metallic mercury Hgmet (other names: Hg0 , Hggel) and inorganically or organically bound mercury. Inorganically bound mercury refers to monovalent and divalent mercury Hg+ and Hg++, respectively, i.e., the so-called ionic mercury Hgion = Hg+ + Hg++ in inorganic compounds (other names: Hg0x or Hg2+). Organically bound mercury refers to Hgorg in compounds such as methylmercury (MeHg) and phenylmercuric oleate.

Mercury vapors are highly toxic. This applies to the gaseous chlorinated mercury HgCl2, even more so for the gaseous metallic mercury Hgmet and especially for the organic mechanically bound mercury such as MeHg, cf. Dalton . Due to the thermolysis of the organic mercury compounds (decomposition) and combustion of the organic matter in the combustion chamber, there is practically no organic mercury in the exhaust gases of incineration plants. bound mercury anymore.

After thermolysis and combustion at high temperatures, the mercury is initially present as Hgmet . Inorganic Hg compounds such as the highly water-soluble and also readily adsorbable HgCl2 or HgBr2 only form during flue gas cooling (in the waste heat boiler). by reaction with other flue gas components such as “chlorine” and possibly also “bromine”. The ionic mercury Hg ion = Hg+ + Hg++ is likely to be present after flue gas cooling, i.e. at the boiler end, predominantly as the more stable divalent Hg++ . Usually, in the boiler raw gases (at the boiler end / before flue gas cleaning) – in addition to metallic Mercury Hgmet – from ionic mercury in halogenated form HgX2 (preferably HgCl2) .

With regard to the toxicity of Hgmet on the one hand and Hgion in its halogenated form on the other, the legislator has set a maximum working concentration of cHg, MAK = 100 µg/m^3. For the extremely toxic "organic mercury" such as MeHg, the maximum working concentration is concentration is even limited to the even lower value of only cHg org, MAK = 10 µg/m^3. The total content of gaseous and (ad- or chemisorptive) particle-bound mercury Hgges = Hgmet + Hgion + Hgpart is limited in Germany to 30 µg/Nm^3 tr. (11 vol.% O2 tr.) as the maximum permissible daily mean value in the emitted clean gas, according to 17th BImSchV in the version of 14 August 2003, cf. . The particle-bound Hgpart plays only a minor role in terms of emissions due to the extensive dust separation that is also required. Role.

One could hardly inhale the air near the chimney of an incinerator mercury poisoning (permissible daily average < MAK value). Larger This danger arises from improper, i.e. negligent, handling of liquid mercury

Hgmet or with mercury salts in an unventilated room, because at room temperature of 20 °C, the saturation concentrations of Hgmet or Hgion in the room air are around one to two orders of magnitude above the MAK value, cf. Mercury is less of a Problem of acutely elevated concentrations in the local ambient air as a problem of the total emitted Hg loads, ie the long-term "bioaccumulation in the food chain-te".

The energy from waste incineration plants, coal-fired power plants or other thermal processes The mercury emitted with the (partially) cleaned combustion gases is, due to the total hazardous load (in the USA, for example, about 45 Mg Hg/a), despite low clean gas concentrations become a toxicological problem in the long run, since both the water-water-soluble hydrogen (after its comparatively short path through the near-Earth atmosphere: Leaching in the vicinity of the emission source) as well as the almost water-insoluble Hgmet (after its long journey through the troposphere: oxidation of Hgmet, for example by halogen radicals X available there to form water-soluble HgX2 with subsequent washing in the long range) at some point in the food chain of animals and later also of people reach.

The following three facts are decisive: a) Mercury remains in the cycle between Earth's surface and atmosphere ("lack of an effective Hg sink"); b) in addition to the Hg Ejecta from volcanoes is mobilized by human activities additionally mercury and increases the currently very low Hg concentration in this cycle more and more in the long term; c) the bioaccumulation leads to a Hg concentration by many orders of magnitude in of food such as in freshwater fish and an organic Hg binding (fat binding). Given the toxicity of mercury, this is a long-term concern. In recent years, the emission limit values (concentrations) have been increasing below the MAK values; however, ultimately it is not about concentrations, but about the total emissions. In the USA, where flue gas cleaning has so far been However, less has been done, the aim is to reduce the emissions from coal-fired power plants and other plants with large volume flows – despite mostly low concentrations – can drastically reduce the total emitted loads. When referring to residual Hg emissions from Power plants, it should be noted that in Germany already about half (50 – 60 %), sometimes even the main amount (85 %) of the coal or waste-side Hg input in existing Flue gas cleaning systems. In the case of waste incineration plants, the mercury removal efficiency is generally > 95%.

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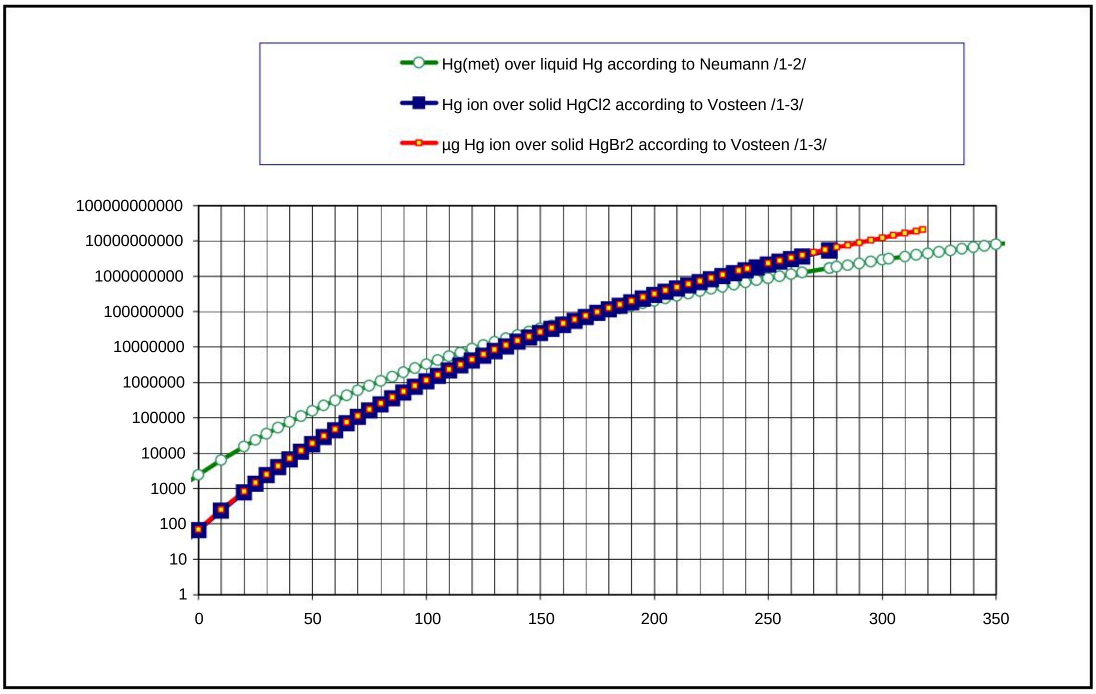
*) Examples: Hg+ like the unstable Hg2Cl2 or Hg++ like the comparatively more stable HgCl2, HgBr2, but also like HgO, HgS, HgSO4, Hg(NO3)2 .



A further improvement of Hg separation is of particular interest in mono- and/or co-incineration of Hg-rich bulk waste such as municipal sewage sludge (SSL) or like the car shredder light fraction (ShLf).

The direct or indirect application of municipal sewage sludge by "agricultural use", "composting" or other mercury-rich waste through "direct landfilling" unless the mercury is in a highly stable form (e.g. as HgS, Hg-TMT-Complex), sooner or later leads to a 100% release of Hg into the environment and is therefore unsustainable in the long term *), if one considers the Hg cycle and the bio-accumulation.

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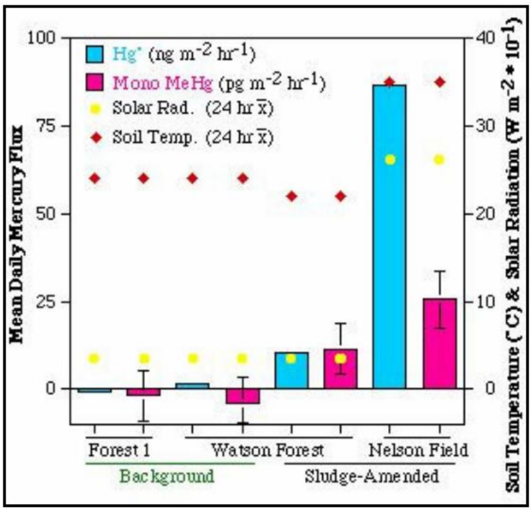
*) Quote from Carpi, :

"We studied the fate and atmospheric emission of mercury (Hg) from soil amended with municipal sewage sludge using a Teflon dynamic flux chamber. A sunlight-mediated, reduction of oxidized Hg to volatile elemental mercury (Hgo) resulted in the atmospheric transport of Hg from land-applied sludge. The reduction of oxidized Hg to Hgo occurred in a shallow, surface layer of soil (<0.5 cm), where light penetration was possible. Sludge application increased soil Hgo emission by 1 - 2 orders of magnitude, to a daily average emissions rate of ~100 ng m-2 hr-1 greater than background. In the United States and Europe, municipal sewage sludge application to land may be responsible for the flux of ~ 5 x 106 g yr-1 of Hgo to the atmosphere. Considering that municipal sewage sludge is used extensively as a soil amendment worldwide, the land application of sewage sludge warrants further study as a global source of atmospheric Hg. This research calls into question the stability of any country application of Hg-contaminated materials; all surface application of Hg waste represents a potential source of atmospheric Hgo .

In an effort to identify the effect of municipal sewage sludge application on mercury (Hg) concentrations in soil, we studied the contamination of sludge-amended soil with inorganic and methyl Hg and the emission of these contaminants to the atmosphere using a Teflon dynamic flux chamber. The routine application of municipal sewage sludge to cropland significantly increased both total and methyl Hg in surface soil from 80 to 6100 µg kg-1 and 0.3 to 8.3 µg kg-1, respectively. Both inorganic and methyl Hg were transported from the sludge/soil matrix to the environment by emission to the atmosphere, however, there was no indication of Hg transport in limited soil water lysimeter experiments. Our data from soil amended with municipal sewage sludge represent the first quantitatively measured terrestrial source of methyl mercury (MeHg) to the atmosphere. Sludge-amended soil emitted an average of 12 to 24 pg m-2 h-1 of monomethyl Hg and ~100 ng m-2 h-1 of elemental mercury (Hgo) to the atmosphere. A simple dispersion model suggests that sludge amended soil may increase regional atmospheric MeHg concentrations by ~5%. These data highlight the need for further research to quantify the transport of Hg from sludge-amended soil and identify the sources of MeHg in the atmosphere."



: Daily average fluxes of Hgo (blue) and MeHg (red) from soil at 2 background forest sites, one sludge-amended forest site, and one sludge-amended open-field site in Oak Ridge, Tennessee, USA. Elevated fluxes over the open-field site were more highly correlated with solar radiation than soil temperature.

	Unit	Daily average (1/2 h average)
Total dust	mg/Nm^3 dry **)	10 (30)
Total carbon Corg.	"	10 (20)
gaseous inorganic chlorine compounds as HCl	"	10 (60)
gaseous inorganic fluorine compounds as HF	"	1 (4)
Sulphur dioxide and trioxide as SO2	"	50 (200)
Nitrogen monoxide and dioxide as NO2	"	200 (400)
Carbon monoxide CO	"	50 (100)
Cd + Tl	"	0.05 *)
Mercury and its compounds as Hg	"	0.03 (0.05)
Sb+As+Pb+Cr+Co+Cu+Mn+Ni+V+Sn	"	0.5 *)
As, Benzo(a)pyrene, Cd, Co, Cr	"	0.05 *)
Dioxins/Furans (TEQ)	ng/Nm^3 dry **)	0.1 *)

*) max. mean value over the respective sampling period

**) The emission limit values refer to a volumetric oxygen content of 11 percent in the exhaust gas (reference oxygen content). For exclusively gaseous substances produced during the pyrolysis or gasification of waste, the reference oxygen content is 3 percent.

Of the 2.5 million Mg/a of sewage sludge dry matter (KS-TS) in the Federal Republic of Germany, in 1998

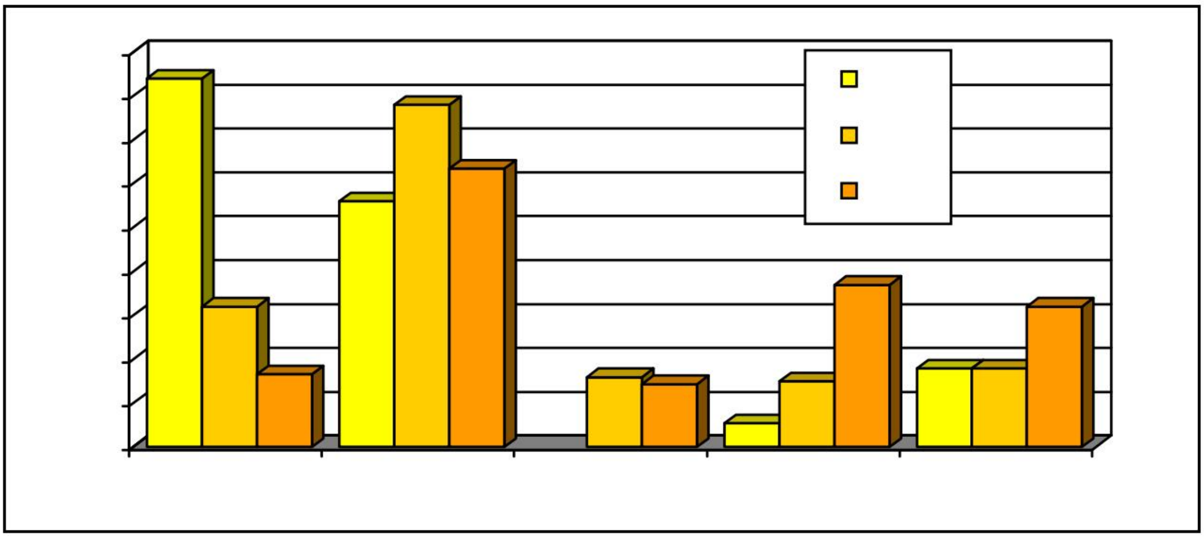
- 31.7% as fertilizer and soil improver in agriculture
- 7.2% as soil improver in landscaping (opencast mining)
- 18.5% goes into composting
- 8.3% in landfills
- 16.0% in sewage sludge incineration

(Rest open)

The distribution has now changed somewhat to the detriment of (direct) landfilling.

A further reduction in landfilling is expected (cf. from), because the Waste Disposal Ordinance of 2001 stipulates in Germany that from 2005 onwards only such Waste whose ignition loss GV < 5% or whose total organic carbon fuel content TOC < 3%. But this does not only apply to sewage sludge.

Since there are fears of pollutant accumulation in the air and soil, the previously rather The increasing agricultural use of digested sewage sludge is under discussion. This is the cheapest recycling option ("shortest disposal route"). However, some federal states are aiming to phase out agricultural use However, the above-described aspect of direct Hg release is not taken into account. However, this has received little attention so far. The discussion must take into account that the agricultural utilisation of sewage sludge by a factor of 10 and (direct) landfilling by at least is and remains at least 5 times more cost-effective than sewage sludge incineration.



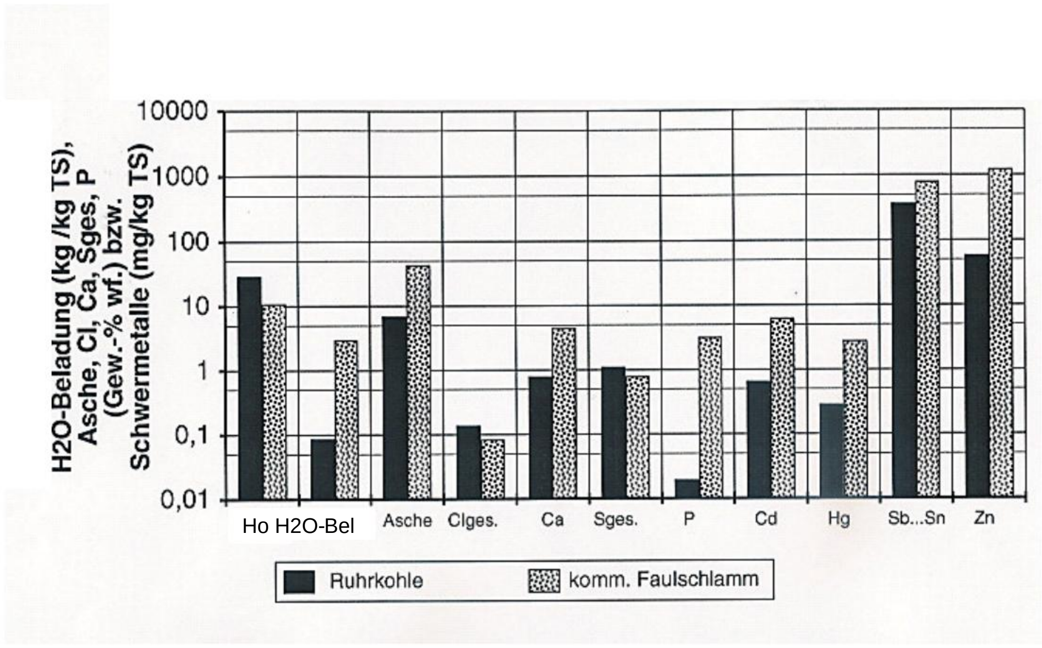
The co-combustion of wet sewage sludge in coal-fired power plants appears to be cost-effective, as only relatively low investments are required; the co-incineration of dry sewage sludge is also not cheap due to the investment required for drying. The same applies to the use of fully dried sewage sludge as a fuel substitute for Coal or heating oil in cement plants, because for the required complete drying of the sewage sludge (TS > 90%), significant investments and later operating costs are incurred. Co-incineration with municipal waste (dispersed filter cake) in existing waste-to-energy plants (MHKW) or in incineration plants for special waste (e.g. co-incineration with the heating valuable car shredder light fraction) is comparatively inexpensive; however, the question of whether larger co-combustion capacities will be available in waste-to-energy plants after 2005. In the near future, the share of mono- and co-combustion will be estimated at 35 - 40%. In the long term, however, it would have to increase significantly, should one politically ban the agricultural use of sewage sludge-wrestle.

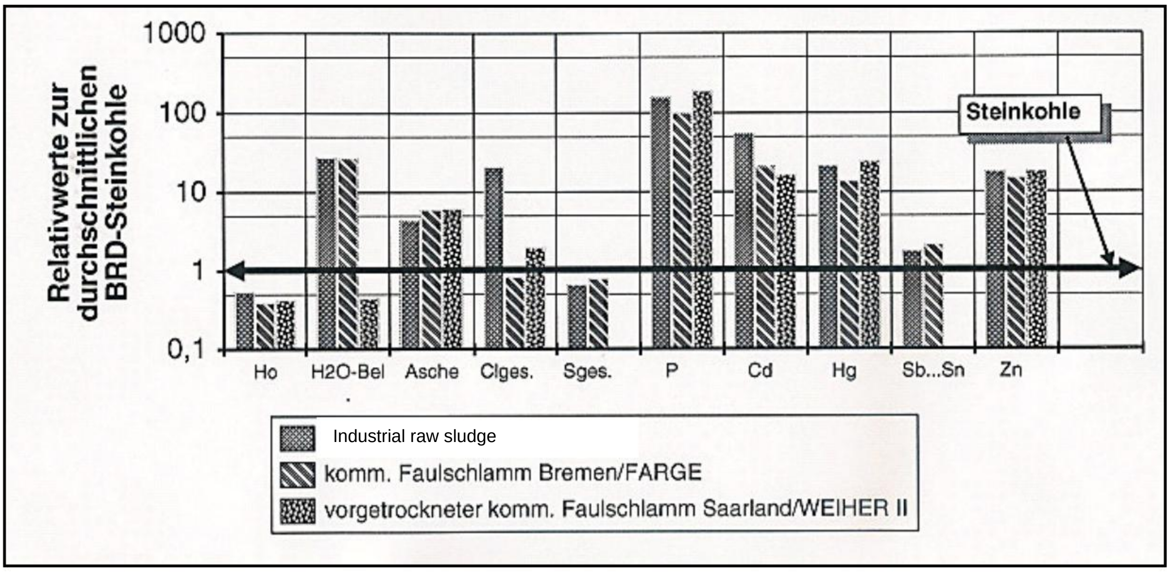
Meanwhile, co-combustion capacities in power plants have been greatly increased nationwide, that mono-incineration plants for sewage sludge and other Hg-rich waste are currently partly still have the problem of utilizing their capacity. In the future, however, the capacity existing mono-combustion plants are far from sufficient.

Some partial problems of co-incineration of sewage sludge in coal-fired power plants as well as in Cement plants can be determined by comparing the sewage sludge contents with a average German hard coal (Ruhr coal) can be seen immediately, cf.

Note the logarithmic division of the ordinate in these figures.

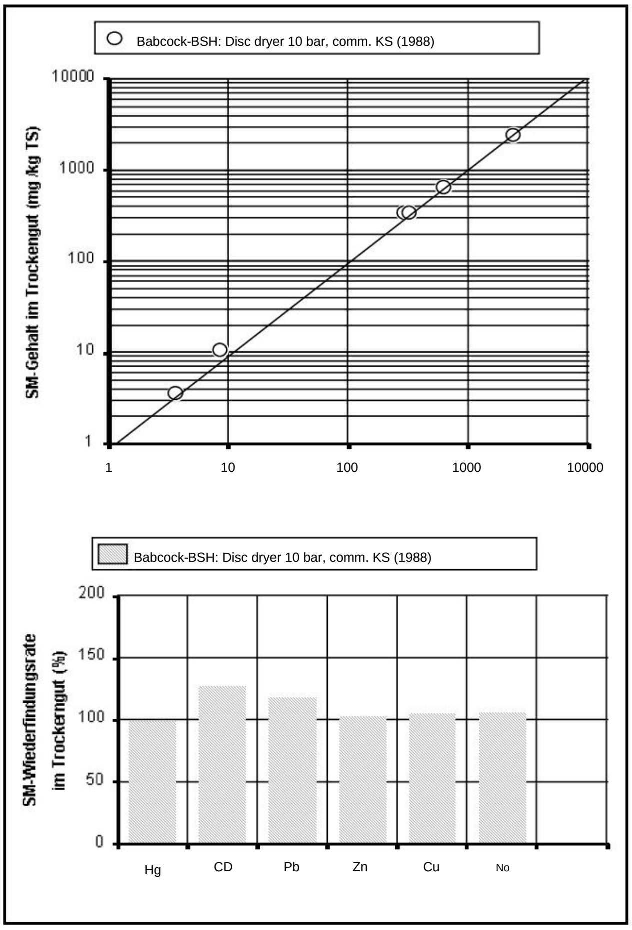
The stated calorific value Ho (calorific value Hu = 0.93 * Ho) refers to the sewage sludge Dry matter (TS = 100%).

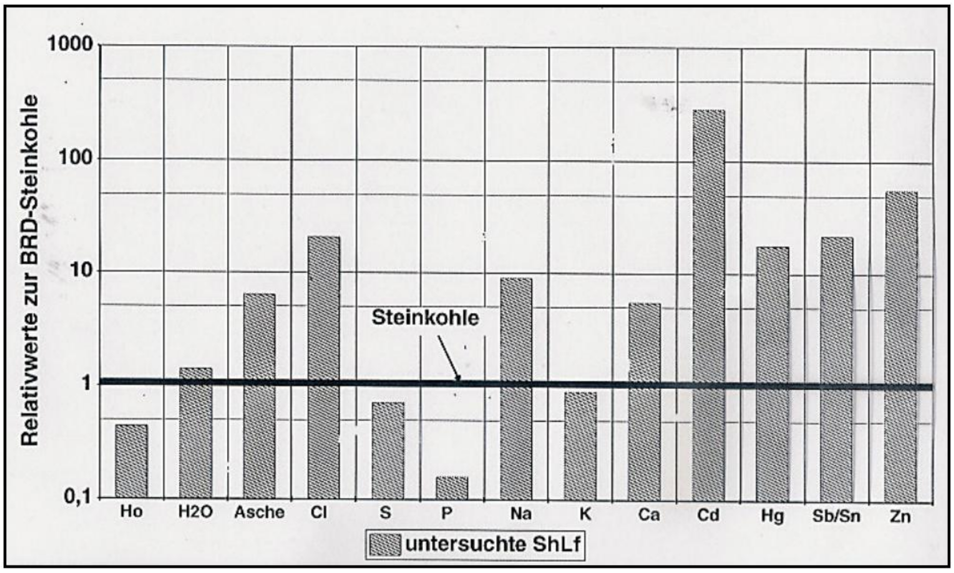




A particular problem is the relatively high mercury content of sewage sludge compared to coal (normally 1 - 2 mg/kg TS, occasionally higher), whether wet or dried, because Hg remains in the dry substance during gentle drying, cf. ; Drying tests by Vosteen on indirectly heated immersion disc and Rotary drum dryers with industrial sewage sludge from BAYER AG led in 1994 to the same result /.

Other mass waste such as car shredders awaiting co-incineration Light fraction (ShLf) have a much higher mercury content (as well as chlorine content) as hard coal, cf. .





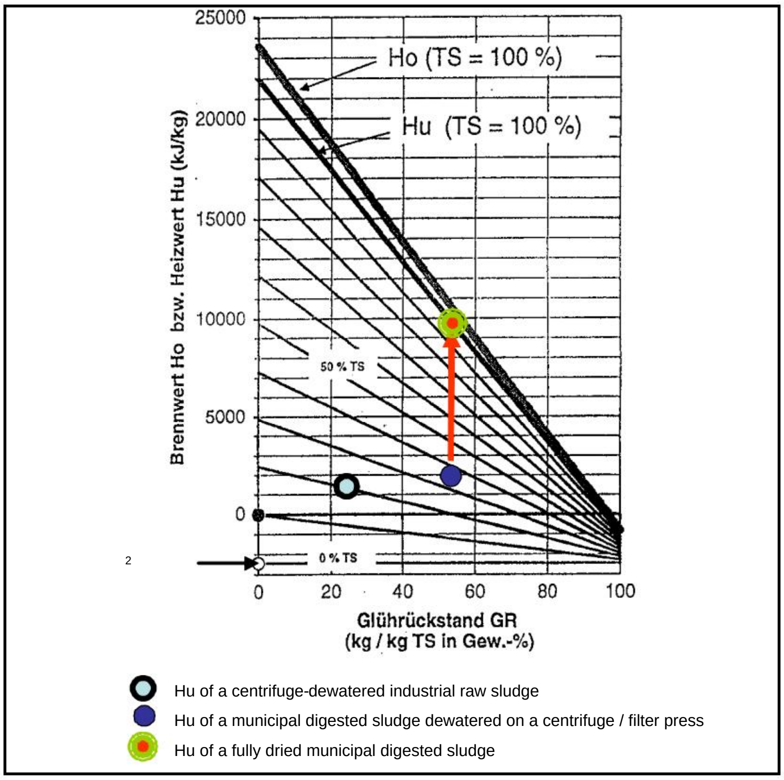
Similar to the flue gas cleaning of waste incineration plants, the flue gas cleaning of a coal-fired power plant due to the increased Hg input in particular to a greater extent. Adequate Hg separation has so far been achieved by the The control rule of the 17th BImSchV is ensured because it lies between the limit values of the 17th BImSchV (waste incineration) and the “zero load values” of the power plant (concentration at chimney with pure coal combustion) according to the proportion of waste in the "combustion thermal output". The zero-load values of the respective power plant were therefore Reference is made because the 13th BImSchV (“Large Combustion Plant Ordinance”) did not previously Hg limit value, especially since the purely coal-related values of mostly only about 10 + 5 µg _ Hg/Nm³ d.c. are generally comparatively low compared to the limit value of the 17th Federal Immission Control Ordinance. From the point of view of logical coordination of waste and coal combustion, However, this approach led to problems such as the specification of an unacceptable bar low Hg limit for the power plant.

The 17th BImSchV in its new version (as of 14 August 2003) still contains the mixing rule; however, this now refers to the new EU limit value for Power plants of (in Germany) 30 µg Hg/Nm³ tr., otherwise even 50 µg Hg/Nm³ tr. (Guideline 2000/76/EC of 4 December 2000). Given the enormous flue gas volume flows of the For large power plants, the increase from the zero-load value to the permitted 30 µg/Nm³ tr. is an enormous relief (“Hg clearance”) for the co-combustion of Hg-rich waste.

From the perspective of the long-term Hg problem described above and not least in the context of view of its current perception in the USA (restriction of the consumption of sweets water fish, administration of selenium tablets as protection against Hg accumulation in the body), however, a critical discussion of the new limit values is unavoidable, so However challenging it may initially be, the requirements of the Waste Ordinance regarding the disposal organic-rich waste through co-incineration in power plants. about the practical coordination of Hg concentrations and Hg loads, including associated practical control options.

Another purely technical problem of cover burning concerns – especially in the case of industrial tritium sewage sludge – the sometimes high chloride content of the waste; the concern is the feared High-temperature underlayer chloride corrosion (pitting due to local release of chlorine by SO2, i.e. sulfation of the chlorides, and removal of the protective iron oxide layer as volatile FeCl2) on the high-temperature superheater heating surfaces of power plant boilers. But also the KS-typical high ash, phosphorus, cadmium and zinc contents etc. of Sewage sludge must be taken into account, e.g. with regard to the later use of the flight ash in the concrete area.

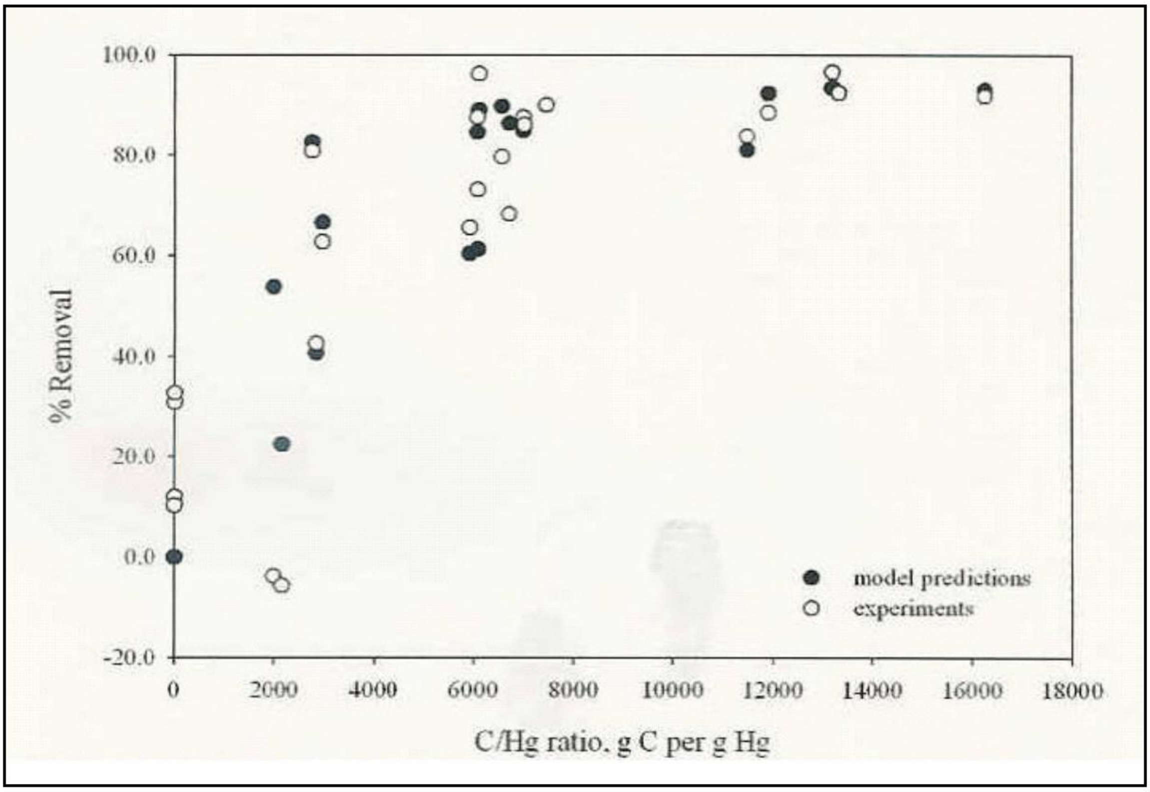
From an energy perspective, fuel substitution in coal-fired power plants as well as in central mentwerk actually only dried sewage sludge is interesting, because only a partially or fully Dried sewage sludge has a higher calorific value, cf. . Raw sludge me (residue on ignition GR approx. 20 … 30 %) as well as the more easily dewaterable digested sludge (Ignition residue GR approx. 45 … 55%) – after conventional mechanical dewatering tion, e.g. by centrifuge and/or filter press – still relatively much filter cake water and therefore have a very low calorific value Hu (relative to the wet filter cake), see the three marked points in this figure.



For various reasons, usually only a small proportion of fuel << 10 % of the thermal output of a power plant (calculated with the calorific value Hu of the dry substance) replaced by wet sewage sludge, although the 17th BImSchV allows up to 25% without the fuel plant as a whole into a waste incineration plant under the licensing law. The focus of co-incineration of wet sewage sludge is therefore less on the aspect of “energy use” than on the aspect of disposal.

The increased Hg input from co-incinerated sewage sludge and other Hg-rich wastes would have to In our opinion, even with low thermal shares, appropriate additional measures during flue gas cleaning of a power plant. Therefore, the reduction of Hg emissions through suitable flue gas cleaning processes continues to be of great importance, see overview of existing processes in the previous study by the State Environment Agency. World Office of North Rhine-Westphalia by Hocquel . The currently available Hg-Reduction techniques often require significant additional investment and are expensive in terms of operating resources, especially when a high Hgges separation efficiency is required.

For an almost complete removal of residual power plant flue gases, it is currently expected that the USA with a requirement of up to 500 mg PAC/Nm³ d. of powdered activated carbon (PAC) as a sorbent additive before electrostatic precipitators or fabric filters, cf. ; with a coal In a 700 MWel power plant , almost complete hydrogen capture (> 95%) by means of PAC injection could result in enormous additional operating costs of approximately EUR 6.5 million. hear. *)



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*) The injection of activated carbon or hearth furnace coke powder in front of the hot electrostatic precipitator or fabric filter as a sorting In addition to safety aspects ("hot spots"), the potential reduction in fly ash quality must also be taken into account. When used as a landfill construction material, the residual carbon content of the fly ash may play a lesser role, but when used in high-quality concrete (pozzolanic aggregate), the risk of

Coal quickly loses its recycling certificate (fly ash quality seal requires a residual C content of < 1 wt.%).

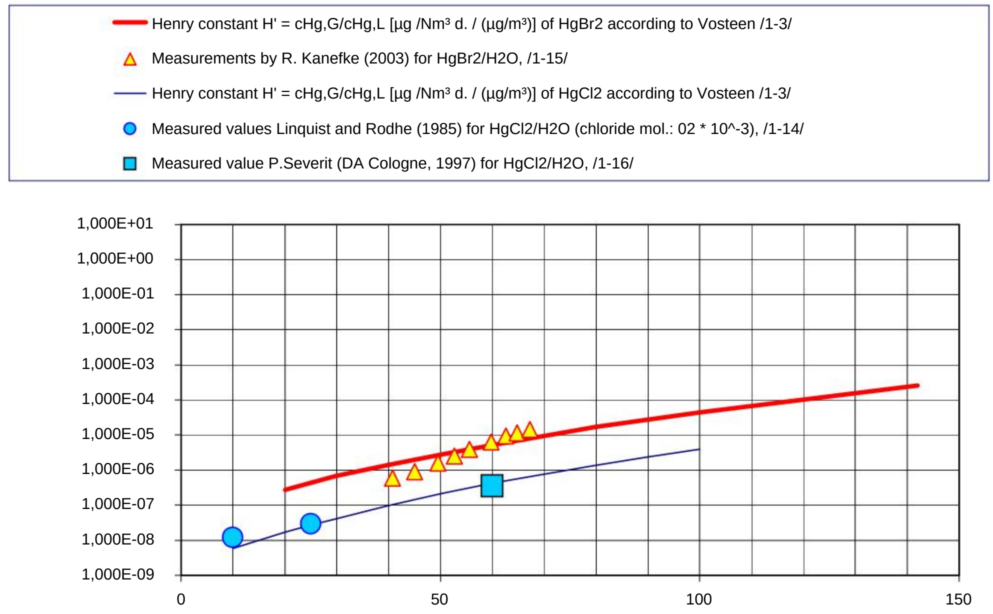
From this perspective, there is still a lack of a highly effective and cost-effective Process for the almost complete removal of mercury from flue gases. This applies both in In the case of almost constant low Hg concentrations (e.g. in the case of pure coal combustion), in the power plant), but also at higher Hg concentrations (e.g. in sewage sludge mono-incineration or sewage sludge co-incineration in the power plant) and possibly also in the case (occasionally) very high Hg concentrations in domestic waste incineration plants (HMVA) or hazardous waste incineration (SVA).

The present study will deal with chlorine and especially bromine assisted Hg oxidation, ie the improvement achievable by “targeted addition of chlorine and/or bromine” wet, quasi-dry and dry Hg deposition. In bromine-assisted Hg oxidation is a highly effective and cost-effective process, see recently published patent application DE A 10233173, Vosteen . With suitable process design, the pollution of power plant by-products (fly ash, gypsum) can be be kept low; by adding “bromine” instead of active substances, For example, coal can prevent excessive PAC levels in EGR flue dust.

The innovative process does not require any major retrofitting and requires only small amounts of bromine-containing additives; it leads to a cost-effective, almost 100% mercury removal. separation, both in smaller plants with a flue gas volume flow of only approx. 15,000 (e.g. sewage sludge incineration) as in plants with approx. 50,000 m^3 dry matter/h (e.g. SVA) or approximately 150,000 m^3 i. N. tr./h (e.g. HMVA) up to large power plants with e.g. 2 ... 3 million m^3 i. N. tr./h. Using bromine-assisted Hg separation, excessive Hg concentrations can be peaks that can occur in all plants that process mixed waste with sometimes burn or cover burn significant amounts of “hidden mercury”, provided that the Hg quantities are not too large; however, from the perspective of smaller systems, even a few 1000 g of mercury (= 1000,000,000 µg) can be regarded as a relatively large amount of Hg.

The discussion about the practical limitation of Hg concentrations and in particular of Hg loads and their continuous monitoring (continuous or semi-continuous Hg measurement) loses when using the novel bromine-based method at least From a cost perspective, but also from a technical feasibility perspective, it is becoming increasingly explosive and should therefore be be initiated.

Metallic mercury Hg_{met} is practically insoluble. In contrast, divalent mercury Hg^{++} in the form of mercuric chloride $HgCl_2$ (the most important form of ionic mercury) or mercuric bromide $HgBr_2$ is highly soluble in water. The (dimensionless) Henry coefficient $H' = c_{Hg,G}/c_{Hg,L}$, the ratio of the Hg concentration in the gas phase to the Hg concentration in the liquid, is very small in the case of $HgCl_2$, and also in the case of $HgBr_2$, although by a factor of 10 larger, cf. .



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In wet Hg separation as in a flue gas scrubber typical for waste incineration

with acid and alkaline stage or in a weakly acidic wet flue gas desulphurisation

ation plant (FGD) of a coal-fired power plant, the question arises as to the

The Hg ion/Hg species fraction achieved directly by flue gas scrubbing is desirable. The highest possible leachable

fraction is desired (Hg ion/Hg > 100%). However, even with dry Hg separation
as in filtering dust separators or flow-through packed beds, a high proportion of ionic

chemical mercury is advantageous because of its better sorbability. In the case of quasi-dry

Hg deposition (spray dryers or humidified packed beds) both count, ie both the good water solubility of the Hg ion and its

better sorbability compared to metallic mercury Hgmet. Furthermore, it will be shown that an indirect or direct

The addition of bromine particularly improves Hg sorption on carbon-containing sorbents.

strengthens, cf. Vosteen, Nelson ,

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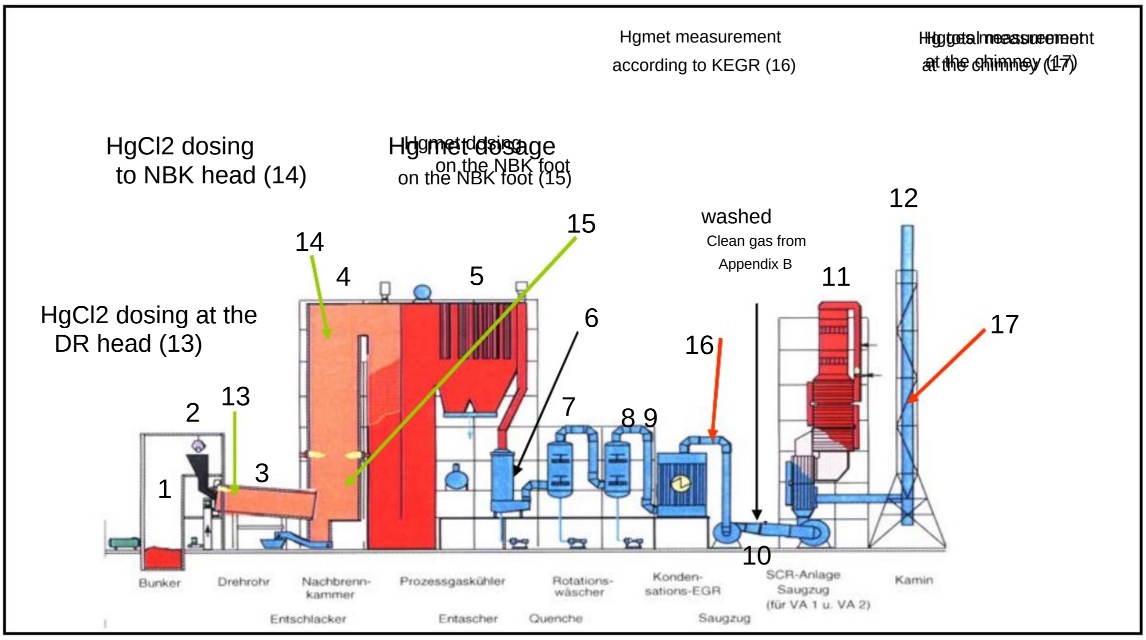
*) The curves in were calculated based on the saturation solubility of HgCl2 or HgBr2 as solids, their vapor pressures and under the assumption of Raoult's behavior, see Vosteen . It will be shown later that the lower solubility of HgBr2 in pure water compared to that of HgCl2 in
pure water is irrelevant as soon as halides are added, since these greatly increase the solubility of HgBr2.
hen.

In this chapter on wet Hg deposition, theoretical preliminary considerations are first given. The effect of “chlorine” and “bromine” in Hg oxidation is said to be “simply” experimentally proven by operational tests and supplementary laboratory tests become.

Bayer Industry Services GmbH operates four rotary plants in Leverkusen, Dormagen and Uerdingen. Tube furnaces for hazardous waste incineration. The four plants have a similar, typical BAYER design, see Two of these systems are located in the BIS-Leverkusen-Bürrig waste disposal centre; they have a common clean gas side SCR (Tail-End-SCR), cf. Vosteen The combustion capacity of the two adjacent The total capacity of rotary kiln SVA A and B is just under 80,000 t/a, corresponding to a clean gas flow (saturated with water vapor at approx. 60 … 70 °C) of a total of approx. 75,000 m³ dry air per hour (full load).



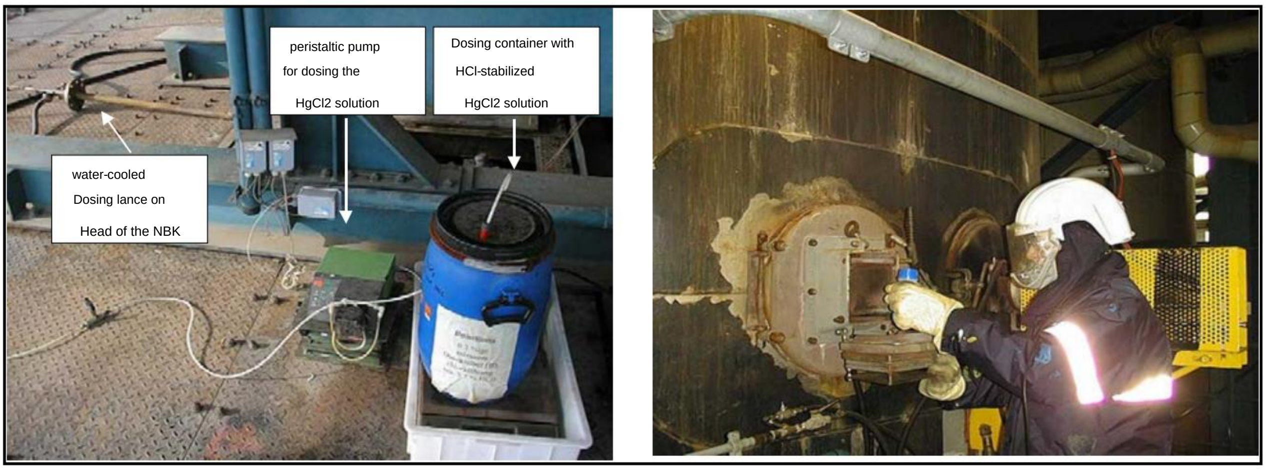
The illustration shows the rotary kiln SVA A with its bunker 1 for solid waste, the crane grab 2 as well as other feed devices for liquid waste and container waste (barrel elevator), the rotary kiln 3, the afterburner chamber 4, the waste heat boiler 5, the strongly acid quench 6, the acidic rotary atomizer washer 7, the weakly alkaline rotary atomizer scrubber 8, the condensation EGR 9 (KEGR), the SVA induced draft fan and the SCR induced draft fan 10, the downstream SCR denitrification plant 11 and the chimney 12. The clean gas from the rotary tube SVA B is mixed with the clean gas from the rotary tube SVA A before the SCR induced draft fan.*)

also shows the results obtained in the approved systematic operational tests used Hg dosing points and Hg measuring points. The two dosing points 13 (rotary tube head) and 14 (NBK ceiling) were used in tests with continuous Hg injection (simulation small to large Hg loads, corresponding to Hg concentrations in the boiler raw gas between 50 and 18,000 µg/m³ i. N. d.) for the injection of $HgCl2$ dosing solution, see also (left). In both cases, ie both when fed at the dosing point 13 (rotary head) and 14 (NBK ceiling), the $HgCl2$ fed in as an aqueous, HCl-stabilized solution in the primary or in the secondary combustion chamber, Hgmet is released and the chlorine released hydrolyzed to HCl. The slight increase in the total Cl load in the µg/Nm³ range caused by the $HgCl2$ feed remains negligible. The mercury is present in the high-temperature flue gas downstream of the NBK/upstream of the boiler largely as Hgmet , see. / in the later chapter 5.

The dosing point 15 in was used in experiments with discontinuous Hg-Feed-in (simulation of small to large individual inputs of hidden mercury) to Insertion of small "Hg bombs." The insertion took place through an inspection hatch at the NBK base, see also (right). The Hg bombs thrown in were small plastic bottles with defined Hgmet quantities. These tests were also conducted under controlled flue gas conditions, ie with a fully Hg load at an appropriate Cltotal or Brtotal load, so that there were hardly any reportable limit value exceedances during the tests.

A specific exception concerns an experiment described below with deliberately induced Hg loading of the downstream tail-end SCR; this concerned the question of Hg retention in/at the SCR catalyst mass, see Vosteen .

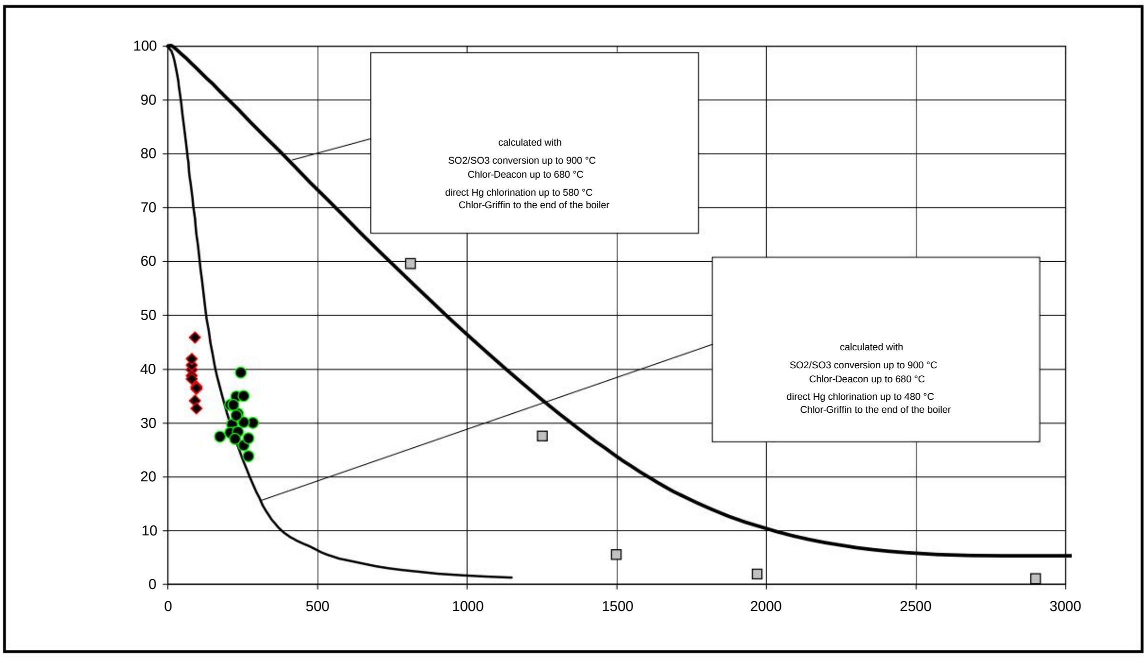
Finally, there are two permanently installed mercury measuring points. Measuring point 17 in the emitted clean gas at the chimney is a gas that was already present in December 1999 permanently installed Hg monitor. The device operates semi-continuously, ie with alternating Hg accumulation by amalgamation on a gold foil and subsequent Hg heating and the associated UV absorption photometer (“Hgmet Monitor”). At the Hg measuring point 16 in the scrubbed clean gas after KEGR (before SCR) is an initially only An additional measuring device used for investigation purposes. This continuously measuring Hgmet measuring device (differentiating UV absorption photometer) has also been permanently installed since spring 2000. In the meantime, measurements were taken over several weeks at measuring point 16 (see) two additional mobile Hg measuring devices simultaneously for the simultaneous continuous measurement of Hgges and Hgmet (Hgion = Hgges - Hgmet) after KEGR/before SCR are used to check whether the water-soluble Hg ion is completely separated in the flue gas scrubber (Hgges = Hgmet, because Hgion = zero).



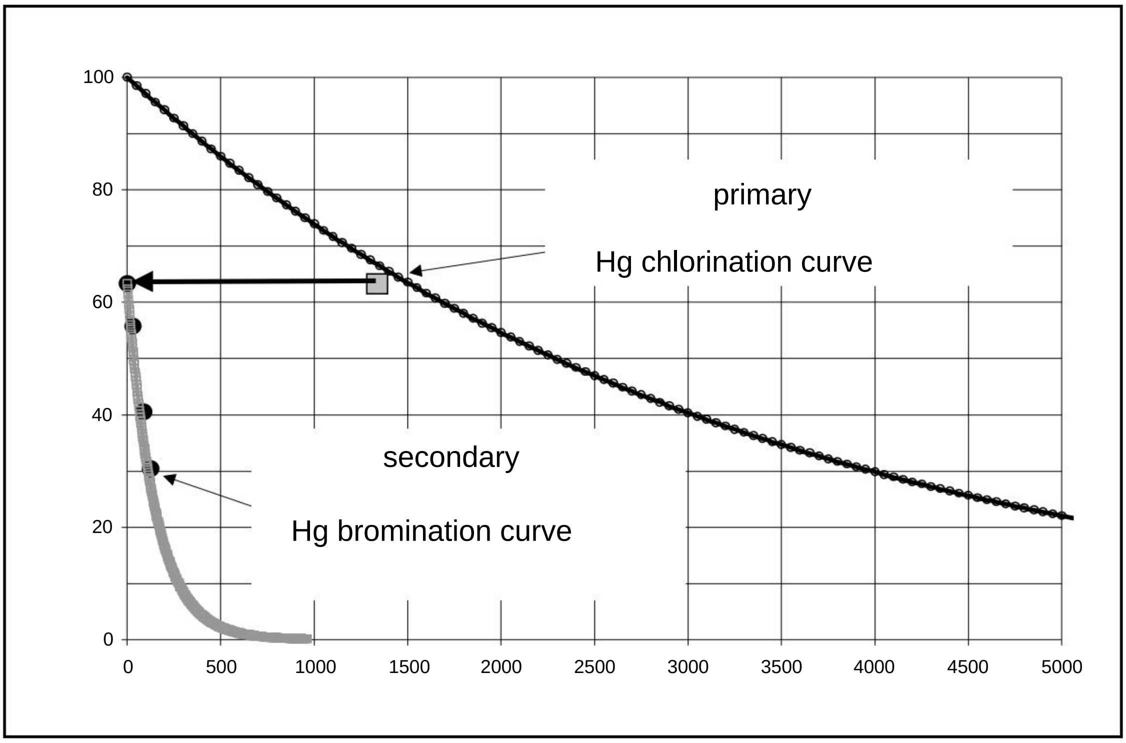
In extensive test series with continuous and discontinuous Hg addition For chlorine- or bromine-assisted Hg separation, in addition to the co-combustion of high-bromine In addition to the liquid waste, the case where bromine-rich waste was not available was also investigated. In this case, small amounts of bromine were added as aqueous HBr or NaBr solution.

Waste disposal facilities contain chlorine-, bromine- and occasionally iodine-rich waste usually ready. In case from power plants that do not regularly incinerate flame-retardant EEE waste or commercial and household textiles as brominated waste, brominated chemicals such as bromine water Hydrogen or bromide salts may be purchased in small quantities.

again concerns the pure "chlorine mode." The upper "Hg chlorination curve" shows the Hgmet/Hgges species fraction (Hgmet/Hgges ratio) achieved in the rotary kiln SVA in the boiler raw gas before quenching as a function of the Cltotal concentration in the boiler flue gas (as the sum of the HCl-related Cl- and the traces of free chlorine Cl2). The measuring points originate from from the SVA large-scale tests with co-incineration of highly chlorinated liquid waste at Raw gas concentrations up to almost 10,000 µg Hg/Nm³ dry; the curve shown was calculated (modeling according to the “stop temperature method”). The lower “Hg-Chlorination curve” refers to large-scale experiments on Hg chlorination discussed below in a coal-fired slag heap boiler power plant at the BAYER plant in Uerdingen.



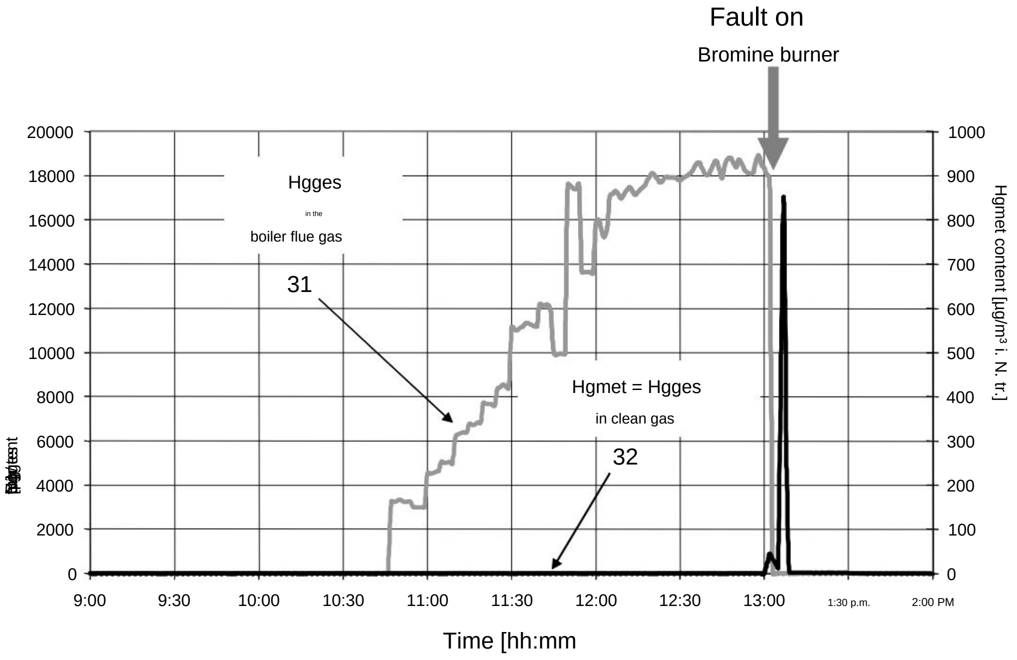
The following now affects both Hg chlorination and Hg Bromination, although both were exclusively based on the rotary kiln wastewater treatment plant. Initially, mercury chlorination was carried out with co-incineration of highly chlorinated liquid waste; this achieved a mercury met/mercury species content of approximately 63% as a starting point for the subsequent mercury bromination. A diluted bromide solution was then added to the NBK; The Hgmet/Hgges species content decreases significantly with increasing bromide addition.



Thus, this figure shows a first comparison of the effects of “chlorine” and “bromine” on the oxidation of elemental mercury Hgmet. The sketched upper “Hg chlorination curve” for the Hgmet species fraction refers to the Cltotal concentration as the abscissa (in the pure "chlorine mode"). The lower "Hg bromination curve" with its corresponding three measuring points concerns the subsequent addition of the bromide solution and refers to the The Br concentration achieved by adding bromide is shown as the abscissa. , that Note that the (secondary) Hg bromination curve is shifted far to the left compared to the (primary) Hg chlorination curve. This considerable "shift to the left" at comparatively low Br contents demonstrates the disproportionately higher effectiveness of "bromine": Even small additions of bromide are sufficient to significantly reduce the Hgmet/Hgtotal species content. If "bromine" - similar to "chlorine" - were only involved to a small percentage in the Hg oxidation, the Hg bromination curve, taking into account the higher molecular mass of Br (79.90 g/mol) compared to that of Cl (35.45 g/mol), compared to the chlorination curve far to the right. But this is not the case; on the contrary, it shifts strongly to the left, apparently because “bromine” – in contrast to “chlorine” – is involved in the Hg oxidation not only to about 4 wt.% but to almost 100 wt.% (factor 100% / 4% = 25)!

To experimentally demonstrate the oxidative effect of “bromine” using another example, An SVA experiment involving co-incineration of highly brominated liquid waste is described. The test was carried out at a bromine content of 9000 mg Brtot/Nm³ dry matter and at an SO_2 content of 4000 mg SO_2/Nm³ dry matter in the boiler flue gas. Over a period of approximately 2.5 hours, An aqueous HCl-stabilized HgCl2 solution was injected in increasing amounts into the NBK head ; the concentration was increased to 18,000 µg Hgges/Nm³ tr. (Curve 31 in

); the Hg concentration achieved in the boiler flue gas is calculated from the added HgCl2 mass flow and the operationally measured flue gas volume flow. The Hg concentration in the scrubbed flue gas, ie after the condensation electrostatic precipitator (CEGR), remained consistently < 5 µg/Nm³ tr despite the relatively high increase in Hg content in the boiler flue gas. (Curve 32). Since in the multi-stage flue gas scrubber of this plant all Hgion is scrubbed (monitored by the two mercury monitors at measuring point 16), the Hg content in the scrubbed flue gas is almost zero, which is equal to the Hg content determined in this test. Thus, almost 100% Hg removal was achieved.



Boiler flue gas with 9,000 mg Brges/Nm³ dry, 4,000 mg SO2 /Nm³ dry.

*)

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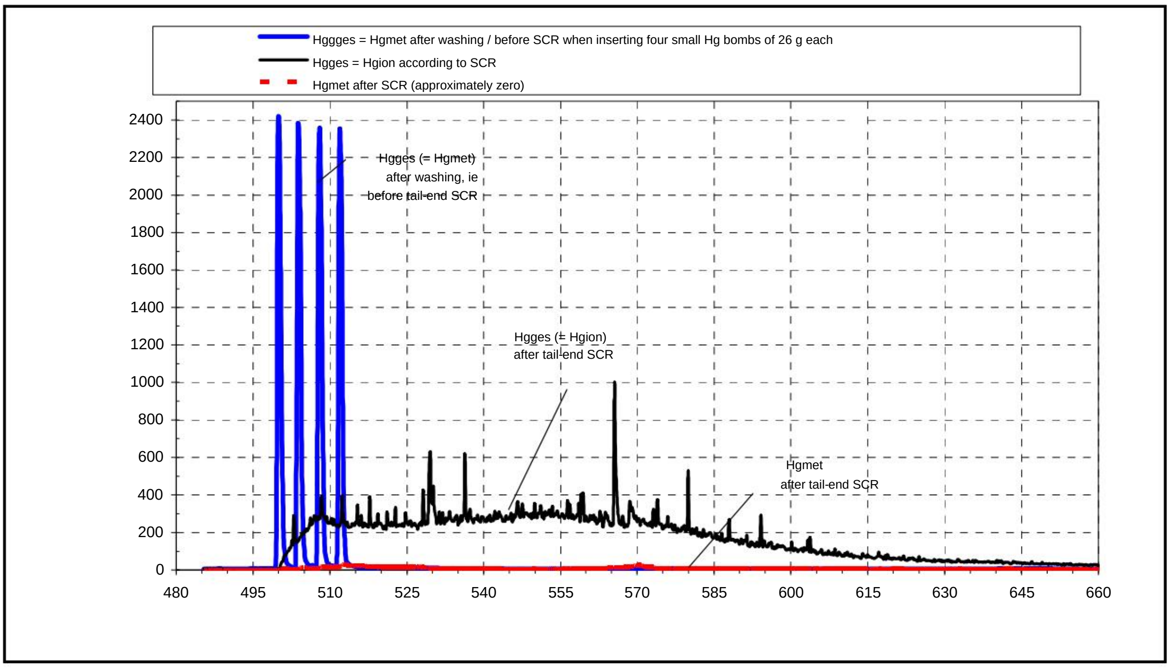
*) Around 13:05 there was a malfunction in the “bromine burner”; as a result, the Hgmet concentration in the scrubbed clean gas rose sharply, but returned to its low initial value of less than 5 µg/Nm³ d., because the burner malfunction, the HgCl2 injection into the NBK was immediately stopped.

concerns the chlorine procedure again. This earlier experiment with discontinuous

The Hg addition was carried out under a – from the SVA point of view – only medium-high Cltotal concentration in the boiler flue gas of approx. 10,000 mg/Nm³ d. and a residual SO2 content in the Boiler raw gas (at the boiler end) of approx. 2,200 mg/Nm³ tr. At intervals of approx. 4 min, At the foot of the NBK four vials, each containing 26 g of liquid mercury (Hgmet), were thrown in (Hg-Total amount: 104 g). The four vials resulted in four Hgmet peaks ("Hg bomb comb") with values of just under 2400 µg Hgmet/Nm³ tr. in the scrubbed clean gas behind KEGR. From the figure, the Hg concentration in the scrubbed clean gas (after scrubbing / before SCR) a temporal peak width of approximately 3 min can be read.*)



In contrast to the insertion of the four small "Hg bombs" (a total of 104 g in 16 min) in we now come to the introduction of a "series of much larger Hg bombs" (in Total 3,400 g in 116 min), cf. or .

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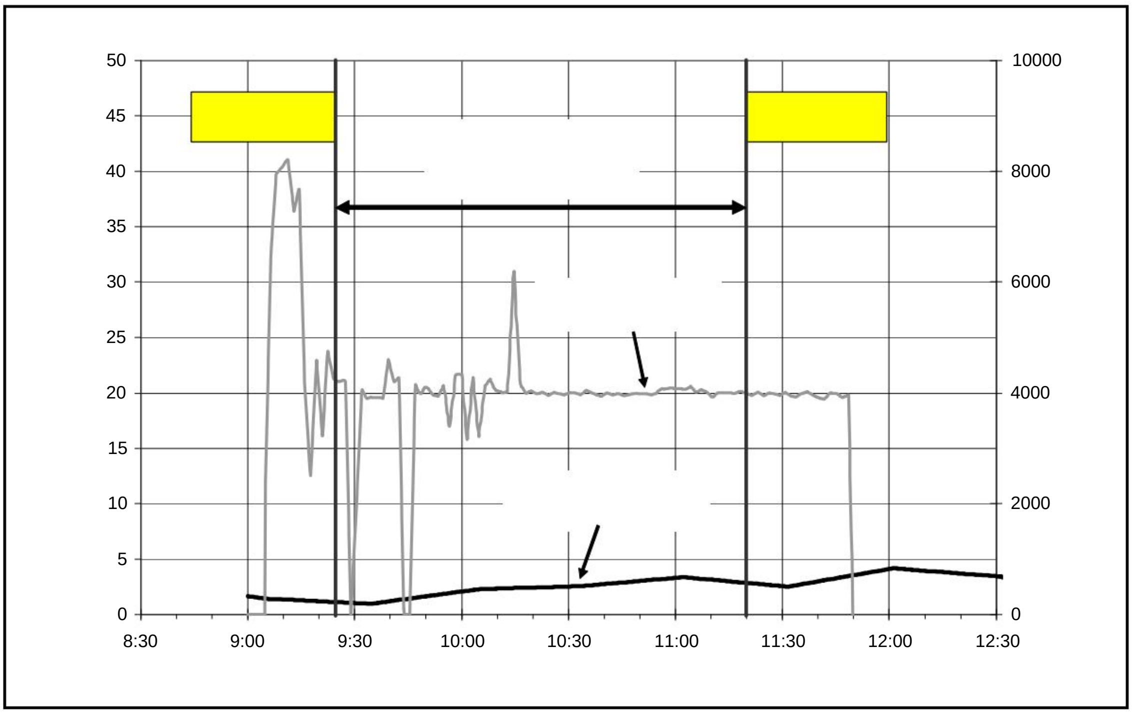
*) The temporal (and thus spatial) peak width in the boiler flue gas further upstream must have been considerably smaller (broadening of the Hgmet peaks during scrubber passage due to axial mixing).

Amounts of Hg bombs dropped during the experiment on October 26, 2001			
time	Hg amount [G]	time	Hg amount [G]
9:24	5	10:32	180
9:32	10	10:37	200
9:38	15	10:43	220
9:49	20	10:48	240
9:54	40	10:53	260
9:59	60	10:58	280
10:04	80	11:03	300
10:09	100	11:08	310
10:15	120	11:13	320
10:20	140	11:20	340
10:26	160		
		Sum of Hg amounts [G]	
116		3,400	



This exceptional experiment with discontinuous Hg addition was carried out under a (from the SVA perspective) only medium bromine load, namely a Brges content in the boiler flue gas of approximately 4,000 mg/Nm³ d., and a residual SO2 content at the boiler end of 5,000 – 6,500

mg/Nm³ tr. The series began with the introduction of only 5 g Hgmet. Over the course of 116 minutes, the introduction quantity ("bomb size") was increased in steps and at short intervals.

the (approx. 5 minutes) continuously increased up to 340 g/throw, see .

When throwing the increasingly larger bombs into the approximately 1100 °C hot "Schlag-ckesee" in the NBK base assumes rapid Hg evaporation and thus an approximate Hg peak width of 3 min, it follows for this experiment that Hg peaks with a final concentration of > 130,000 µg/Nm³ tr. must have been present in the boiler flue gas.

And yet, under the maintained average Brges load, a practically 100% Hgmet removal was achieved throughout, because the Hgmet (= Hgges) concentrations in the scrubbed clean gas at measuring point 16 after KEGR remained consistently < 5 µg /Nm³ tr.

shows the coal-fired power plant N230 at the BAYER plant in Uerdingen, where in 1993

Large-scale experiments on chlorine-assisted Hg oxidation and later in 2002 also on bromine-assisted Hg oxidation has taken place. The power plant comprises two slag heap boilers (SKK) of 100 MWtherm each, two electrostatic precipitators, a common flue gas treatment plant with limestone powder

Desulphurisation plant (REA, pH = 5.3) for 2 x 120,000 Nm³ tr./h and two parallel tail-

Final SCR afterwards.

In 1993, a test lasting several weeks was carried out on one of the boilers for the co-incineration of BAYER's own sewage sludge with (due to the neutralization of acidic plant wastewater)

before biological wastewater treatment) comparatively high chloride content. In preliminary tests

The KS cover combustion was initially only simulated. For this purpose, the coal belt in front of the mill

dry rock salt (NaCl) and aqueous HCl-stabilized HgCl2 solution were added in small quantities. The main aim was to improve the expected chloride load by increasing the

of Hg deposition in the weak acid FGD. In these preliminary tests with and without

experimental TMT addition to the REA (Trimercapto–S-triazine for the purpose of hydrogen precipitation already in the FGD), manual Hg measurements were carried out in the dedusted raw gas after EGR/before FGD and in the denitrified clean gas after SCR. In addition to the Hg content (wet-chemical), the contents of the Hg species Hgmet (dry on DOWEX resin) and Hgion (dry on

iodine-doped activated carbon) with pure coal combustion ("zero load") and with simulated KS-

Cover burning. *)

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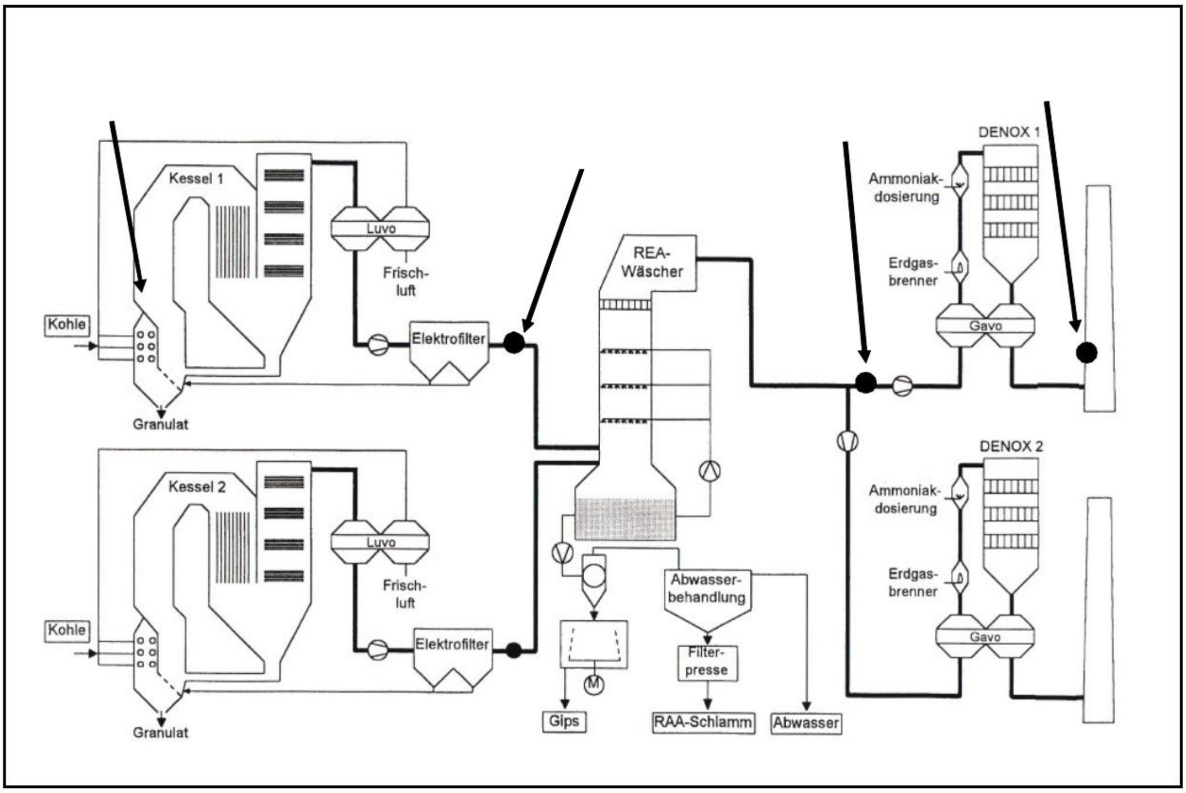
*) For the measurement technology of that time, see Gutberlet, Tembrink et al. directly involved. Dipl.-Ing. Tembrink was involved in the measurements in 1993

The Hg chlorination curve of the Uerdingen SKK power plant achieved in 1993 was already presented; it is fortunately , as can be seen there, compared to the rotary kiln SVA shifted to relatively low Cltotal contents in the boiler flue gas.

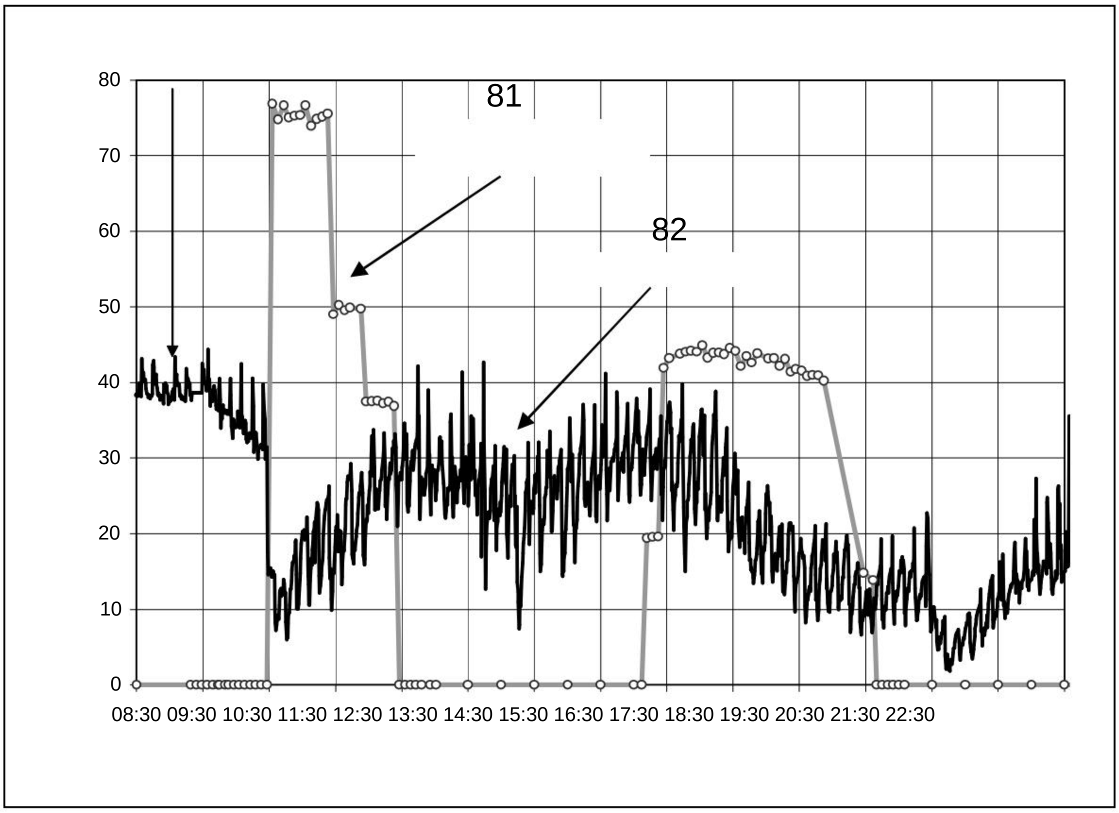


As can be seen, the position of each Hg chlorination curve depends on the plant design (temperature-residence time profile) and their operating conditions (contents of O_2, H_2O, SO_2, Metal oxide content and spectrum as well as residual C content in the flue dust) depends

Compared to the Hg chlorination curve of a rotary kiln wastewater treatment plant, the Hg chlorination curve of the power plant shifted to comparatively low Cltotal contents, as just mentioned. In analogy to the comparison to of the Hg chlorination curve and the Hg Bromination curve of the rotary kiln SVA one would now also expect that in the case of the power plant also shifts its (secondary) Hg bromination curve even further to the left compared to its primary Hg chlorination curve “strongly to the left”, i.e. towards very low Brges contents.

In order to examine this question, further attempts were made in 2002 (cf. Nolte /34/), now but more with the addition of aqueous NaBr solution and, at the same time, aqueous HCl-stabilized $HgCl_2$ solution into the SKK combustion chamber. The Hg measurement after the electrostatic precipitator/before the FGD as well as after REA and after SCR were carried out continuously in 2002; a total of four measuring devices of the type HM 1400 from DURAG/Verewa. These are certified according to the 17th BImSchV approved measuring devices, it is a special version with a Dr. Klein (formerly L. & C. Steinmüller) further developed wet chemical sample gas preparation under Use of sodium borohydride as a reducing agent.*)

In two large-scale (due to practical problems with the dosing only relatively short-term) trials in April and August 2002 were carried out with coal combustion alone (zero load driving style). This resulted in – similar to the earlier tests in 1993 (cf. previous) – a Hgmet/Hgges species content of approximately 40 wt.% in the dedusted gas after the electrostatic precipitator, see the following and in the time before 9:20 a.m.



With the start of the addition of bromine into the SKK combustion chamber (in the form of aqueous NaBr-solution) at 10:30 a.m., the Hgmet/Hgges species content drops abruptly below 10 wt.%. A similar, albeit delayed, occurs again after 4:00 p.m. with renewed bromine Encore.

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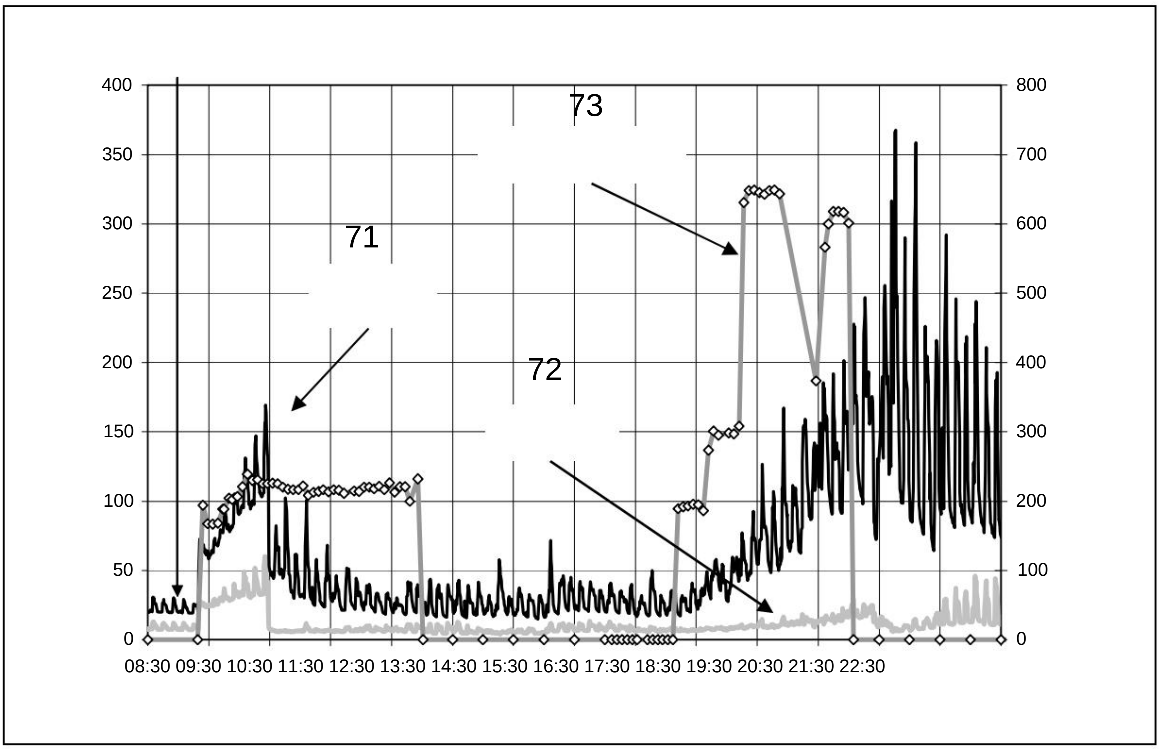
*) The four continuous measuring instruments used in 2002 are now owned by the research group "Hg Separation from Combustion and Process Exhaust Gases" at the Institute of Environmental Protection Technology at Martin Luther University Halle-Wittenberg in Merseburg (Head: Prof. Dr.-Ing. habil. H. Köser). The establishment and part of the ongoing research work of this research group has been funded by Bayer Industry Services GmbH since March 2002.

From 9:20 a.m., as can be seen from the following can be read, the Hg-Load in the boiler flue gas by adding aqueous HCl-stabilized HgCl2 solution in the SKK combustion chamber was drastically increased, initially calculated to approximately 200 µg Hgges/Nm³ tr. and, after an interruption, later gradually to values above 600 µg Hgges/Nm³ tr.; these calculated Hgges contents are "minimum values".



As will be explained in more detail in Chapter 3 on Hg dry sorption, under the Bromine influence leads to a significantly increased Hg sorption on the EGR fly ash. Since the fly ash is 100% returned to the melting chamber, builds up with increasing Hg-Dosing until a steady operating state is reached, a steadily increasing Hg circuit between melting chamber and electrostatic precipitator, ie the unmeasured (since HgCl2 concentrations in the boiler flue gas upstream of the electrostatic precipitator (which are hardly measurable without major effort) are likely to be significantly higher than the calculated minimum values imposed by the HgCl2 addition. The achievement of a steady-state operating condition with full breakthrough of the The high minimum mercury concentrations were never waited for; rather, the the addition of “bromine” has begun in order to lower the Hgmet concentration after EGR / before REA. As expected, the Hg concentration after FGD corresponded to the low Hg concentration before FGD (almost complete separation of the Hg ion in the FGD).

How to As can be seen very clearly from curve 72, the Hgmet-Content in the dedusted clean gas after electrostatic precipitator / raw gas before FGD due to bromine addition – despite the drastic increase in Hgges content in the boiler flue gas – in the lowest measuring range; the Hgmet content even decreased below the Hgmet content at initial no-load.

As expected, the test result is: With small, but still not minimized additions of “bromine” in the SKK combustion chamber, the Hgmet concentration in the dedusted clean gas after electrostatic precipitator / raw gas before FGD almost to zero, even if (here simulated by simultaneous $HgCl_2$ addition) an approximately 30-fold higher Hg concentration should occur in the boiler flue gas.

The Emschergenossenschaft operates two stationary fluidized bed combustion plants in Bottrop for Combustion of municipal sewage sludge (flue gas volume flow approx. 15,000 Nm³ each tr./h). Each of the lines includes a waste heat boiler, an EGR, and a two-stage wet flue gas cleaning system (of different designs). Initial tests were carried out in December 2003 (Vosteen) for complete Hg oxidation using “bromine”, instead of the previously used expensive chlorine dioxide ($NaClO_2$). In the experiments, highly diluted hydrobromic acid was used for use. shows the storage/dilution tank used for this purpose and a spray lance for injecting the aqueous HBr solution into the vortex layer firebox (freeboard area).

The Hgges content in the boiler flue gas was reduced due to the disturbing high dust and SO_2 Loads were not measured directly, but were determined based on the Hg discharge with the EGR fly ash and the scrubber wastewater; it was over 200 µg /Nm³ tr.. Favoured by the relatively high chloride content of the sewage sludge of 0.36 wt.% wf. (measured value: 147 mg Cltotal/Nm³ d. in the dedusted raw gas after electrostatic precipitator), the mercury in the boiler flue gas is chlorinated to approximately 85%; however, this is not quite sufficient, since the dedusted raw gas after EGR still contains approximately 30 ... 35 µg Hgmet/Nm³ d. of non-leachable metallic mercury. One reason for this is the unusually high sulphur content of the pyrite-rich fine coal le preconditioned sewage sludge (4.4 wt.% wf.), cf. Chlor-Griffin reaction Eq. (5-2).

The descending “Hgmet step curve” in shows the starting point of the first HBr The drop in Hgmet content in the dedusted raw gas (after EGR/before suction) that occurs after injection laundry) again.

covers several test days and shows the influence of bromide addition on the Hgmet content according to EGR. The fluctuations at the beginning of the experiment clearly show the interaction between the two. The corresponding figure shows how the Hg-Loading of the sewage sludge fly ash separated in the electrostatic precipitator with renewed bromide

Addition (into the upper fluidized bed combustion chamber) significantly increases the Hg adsorption on the fly ash improved, as the Hg loading of the fly ash (residual C content < 1%) increased from 0.3 … 0.4 mg/kg to about 1.1 mg/kg (factor 2.5, see also the following chapter 3 on Hg-dry sorption).

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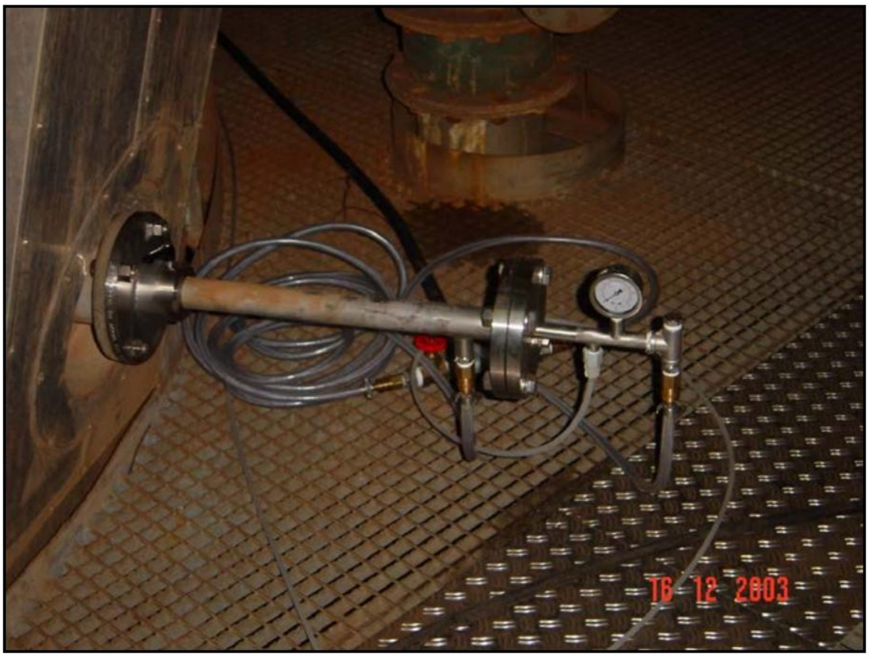
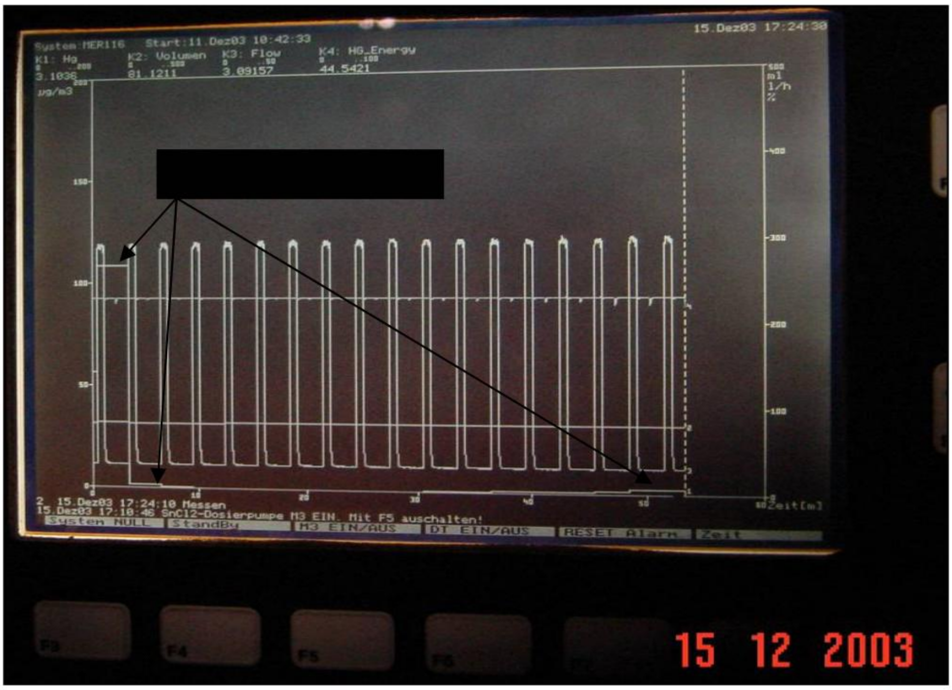




[redacted]

System:MER116 Start:11.Dez03 10:42:33

K1: Hg 3.1036

K2: Volumen 81.1211

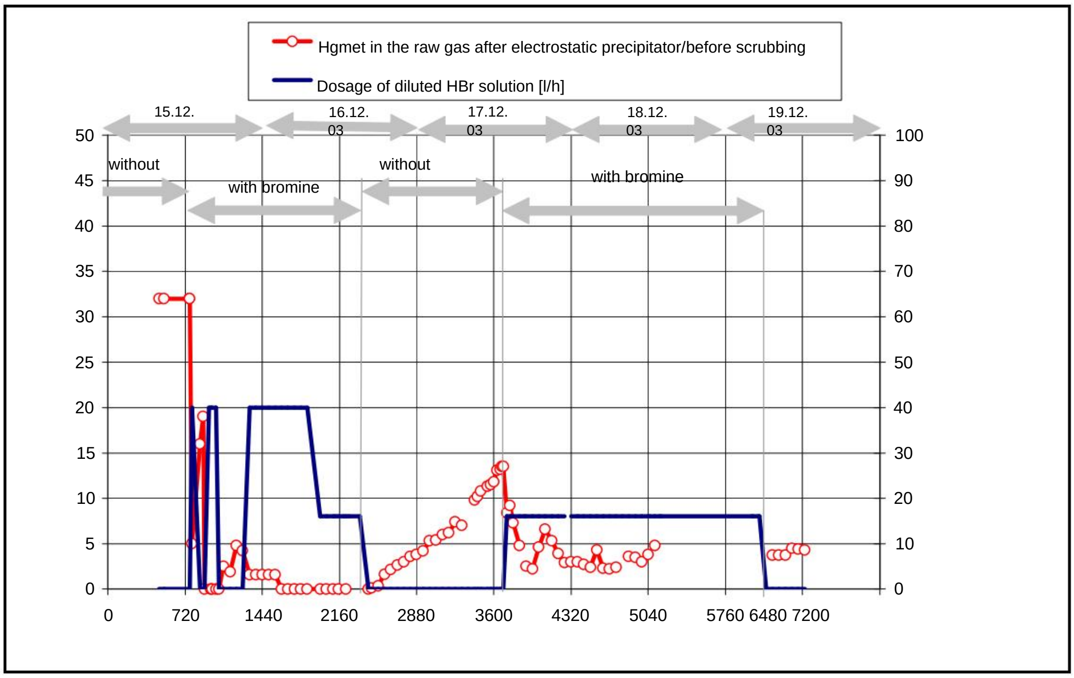
K3: Flow 3.09157

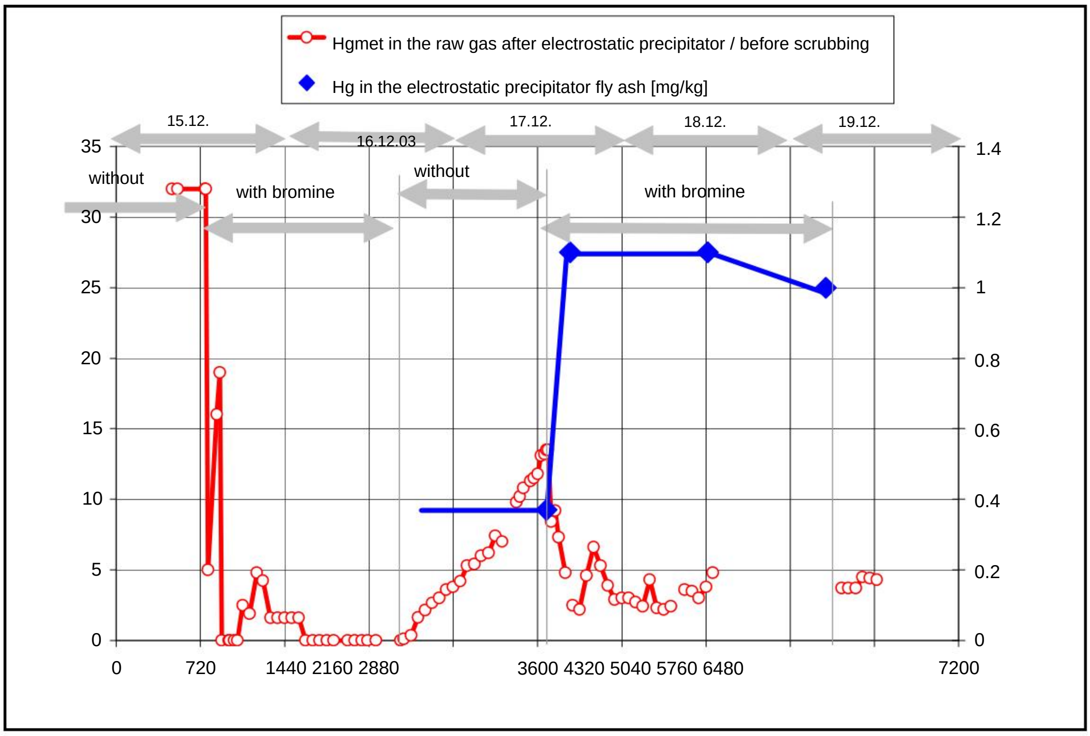
K4: HG_Energy 44.5421

15.Dez03 17:24:30

2 15.Dez03 17:24:10 Messen

15.Dez03 17:10:46 SnCl2-Dosierpumpe M3 EIN. Mit F5 auschalten!

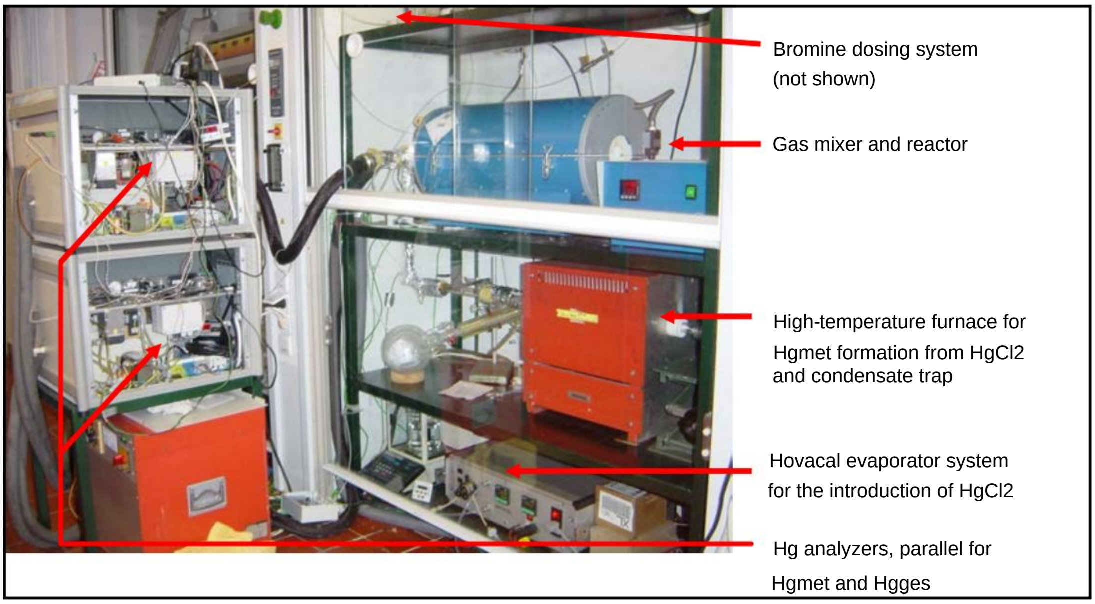



Hgmet in the raw gas after electrostatic precipitator / before scrubbing
Hg in the electrostatic precipitator fly ash [mg/kg]
15.12.
16.12.03
17.12.
18.12.
19.12.
without
with bromine
without
with bromine
35
30
25
20
15
10
5
0
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
720
1440 2160 2880
3600 4320 5040 5760 6480
7200

Within the framework of the newly established research project with the support of Bayer Industry Services GmbH, research focus “Hg separation from combustion and process exhaust gases” at the MLU Institute for Environmental Protection Technology (Head: Prof. Dr.-Ing. habil. Heinz Köser) in Merseburg, several laboratory test benches were set up, see Kanefke .

shows the test rig for flue gas-side Hg halogenation, cf. Ziegler

The heart of the test rig is a glass-made, electrically heated annular gap furnace as reactor



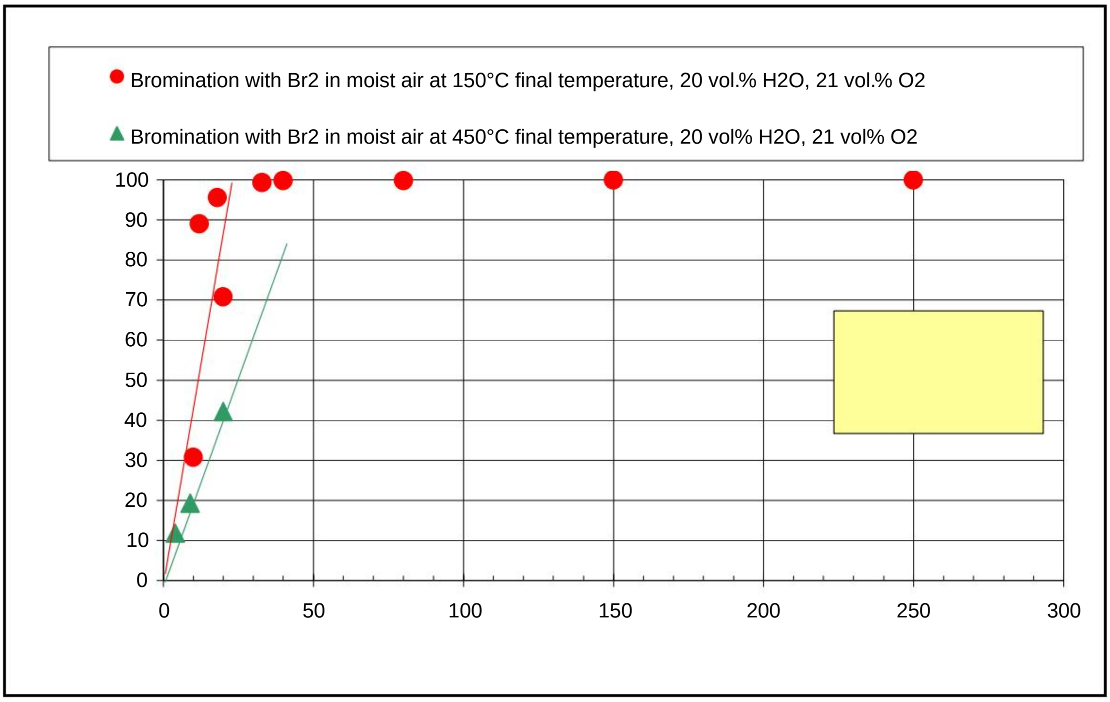
As a first example from the supplementary laboratory tests carried out in 2002/2003, a measurement result for the direct bromination of elemental mercury by free bromine Br_2 in SO_2-free humid air, cf. Ziegler Apparently, at 150 °C as well as at 450 °C (residence times < 2 seconds) a 100% halogenation is easily achieved; The molar ratio of Br_2 to Hgmet required in the laboratory apparatus is around 40 relatively “tight” above the stoichiometrically required ratio of 1:1, ie only approx. 40-A molar excess of Br_2 is sufficient. However, if the raw gas contains SO_2, the Hg bromination on the flue gas side is significantly reduced at the temperatures mentioned. low SO_2 levels of only 50 to 100 mg/Nm³ d. a strong decline is observed

Hg bromination, cf. According to this figure, the molar excess of free hydrogen required for complete Hg bromination in the low SO_2-containing exhaust gas would have to be em bromine can be increased considerably, namely to a molar Br_2/Hg_{met} ratio >> 1500.*)

If a bromine compound such as hydrogen bromide is used in the presence of SO_2 instead of the free bromine Br_2 , only weak Hg bromination is observed, as with Br_2 .

Finally, it highlights the extremely important influence of temperature (Influence on the kinetics): From this figure you can see first of all how the Hg-Bromination in SO_2-containing exhaust gas improved with an increase in temperature to 650 °C; however, in SO_2-containing humid air, even at molar Br_2/Hg ratios up to 3500, 100 % Hg bromination was still not achieved. In contrast, the large-scale operational tests on the rotary kiln SVA of Bayer Industry Services GmbH in Lever-Kusen-Bürrig has shown that even under molar Br_2/Hg_{ges} ratios of only about 400 – 600 and even under very high SO_2 contents of e.g. 2000 – 6000 mg/Nm^3 d. with bromine Dosing into the high-temperature combustion chamber achieves 100 % Hg bromination (see thick circle point in). With the two following

and Finally, we will refer again to an SVA operational test. A 100 % Hg bromination was achieved operationally with both HBr and NaBr (as in the furnace aqueous bromine compounds dosed into the room) as well as with corresponding co-combustion highly brominated waste. For the sulfation of NaBr (bromine release with subsequent Bromine hydrolysis in the moist flue gas as HBr/Br_2) as well as for the direct Hg bromination, the introduction of the “bromine” at high temperature, preferably in the high-temperature ten combustion chamber, beneficial.



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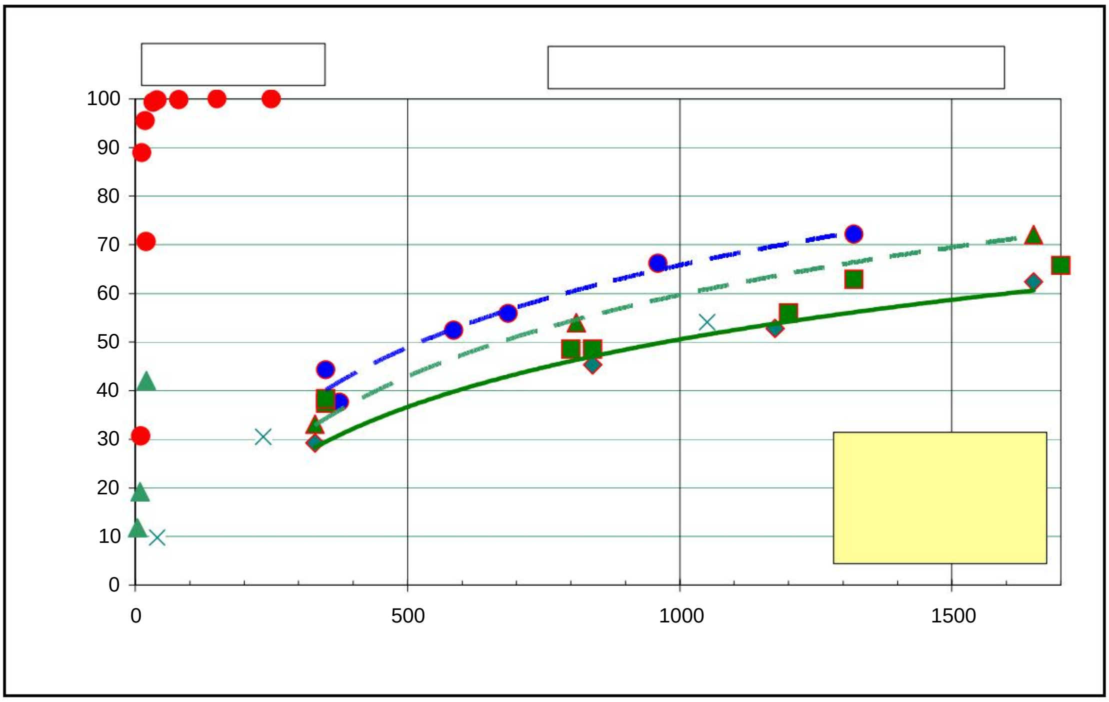
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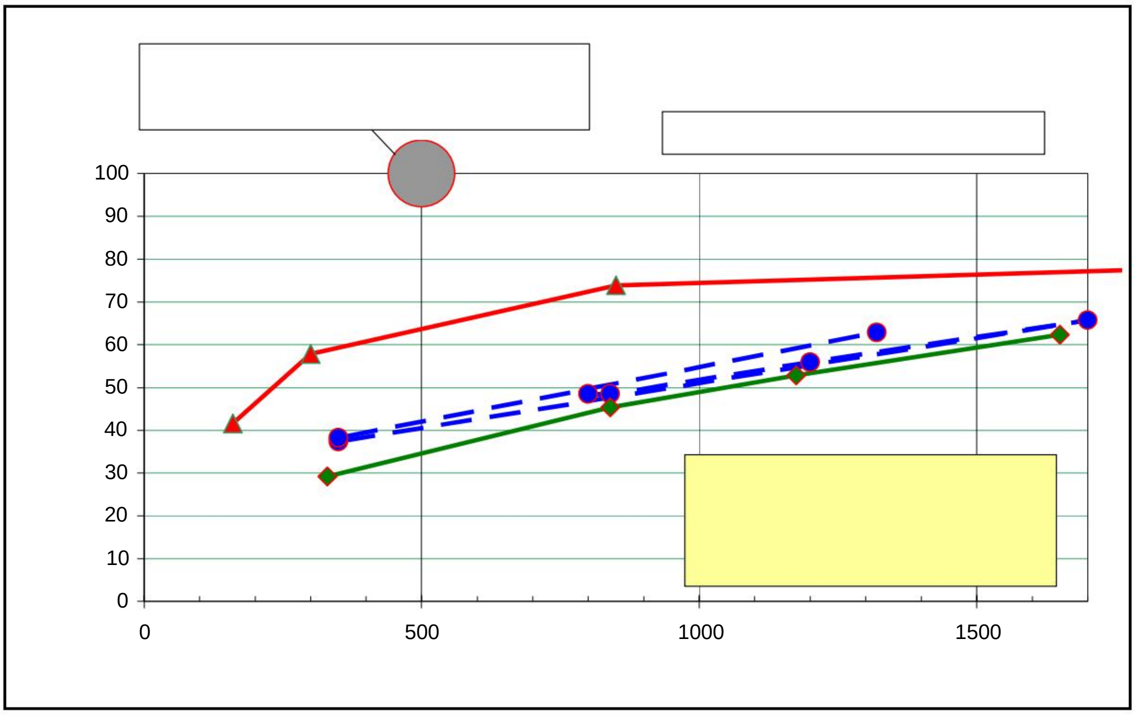
1500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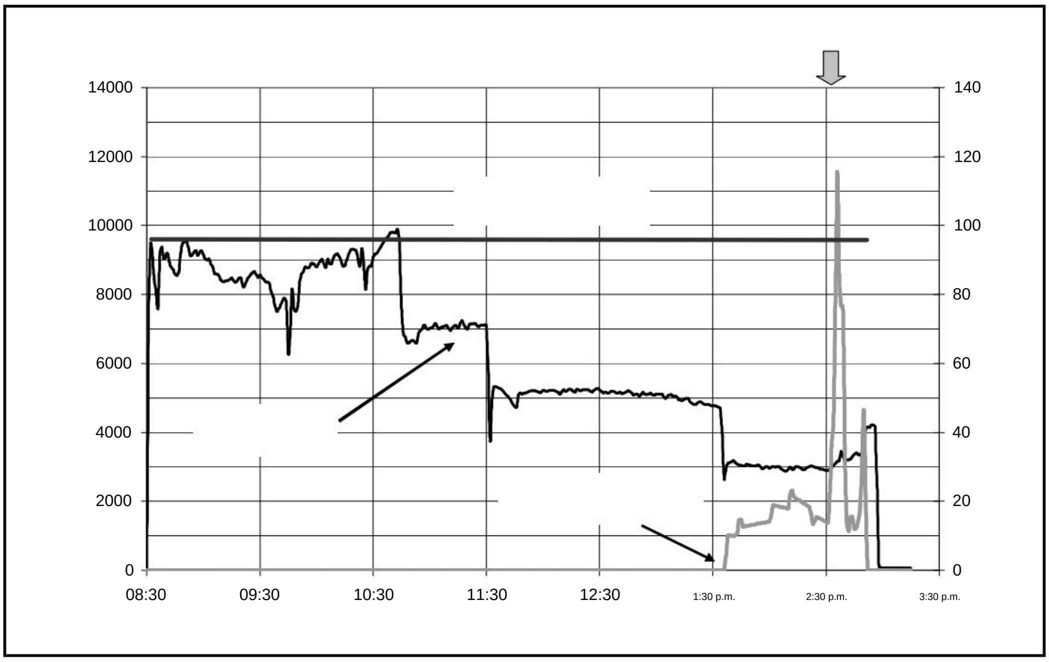
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12000
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8000
6000
4000
2000
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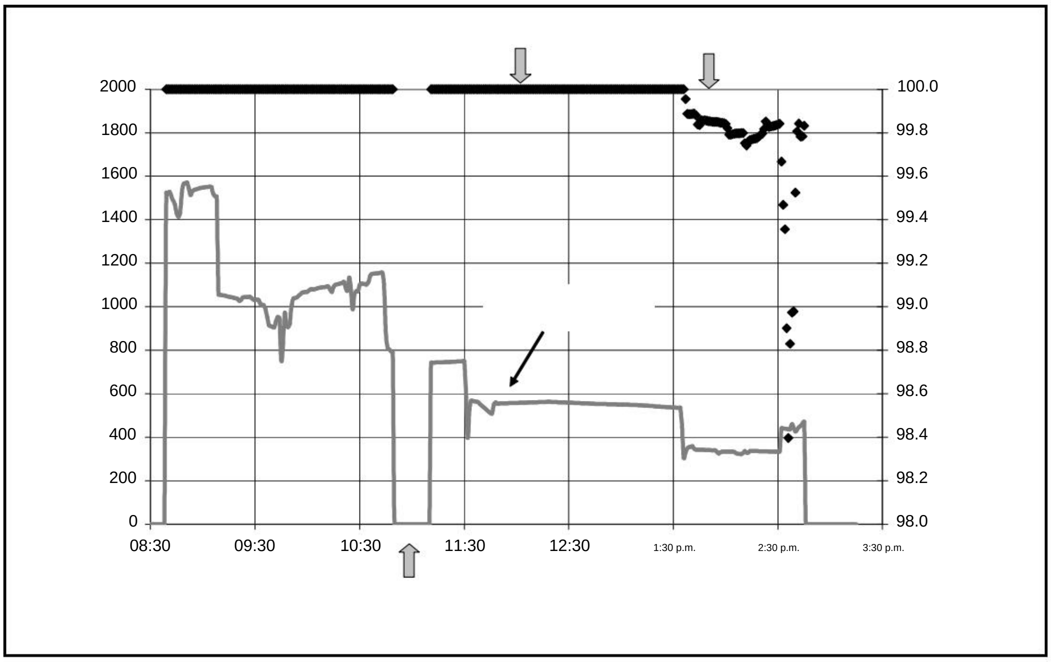
140
120
100
80
60
40
20
0
08:30
09:30
10:30
11:30
12:30
1:30 p.m.
2:30 p.m.
3:30 p.m.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In flue gas cleaning, a distinction is made between wet, quasi-dry
and dry separation. In all cases, a
The highest possible Hgion/Hgges species content in the raw gas to be cleaned, since the oxidized mercury Hgion (= Hgges – Hgmet) – in contrast to Hgmet – is water-soluble and is generally much better adsorbed on coal/lime-based sorbents than Hgmet.

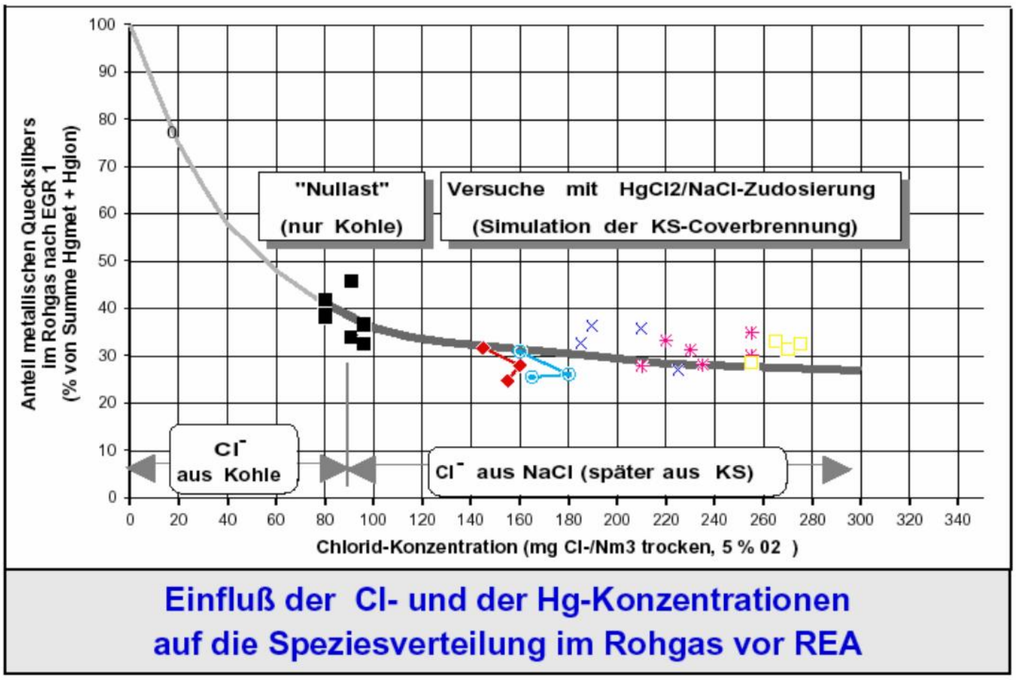
In the large-scale tests on the melting chamber boiler described in the previous chapter, sel power plant at the BAYER Uerdingen plant, the main focus in 2002 was on the Hg-Bromination as a basis for wet Hg separation in the weak acid power plant FGD. However, these large-
cf. Nolte scale tests in 2002 also showed – as a side result – a
previously largely unknown phenomenon, namely the bromine-induced intensification of the Hg Adsorption on coke-containing EGR filter dust.

Additional laboratory tests on Hg dry sorption will demonstrate how the addition of "Bromine" the adsorption of ionic and elemental mercury on residual C-containing airborne particles ash (below the low EGR temperature of 170 °C) increased noticeably, see Tippelt ,
Vosteen et al. . As was recently announced, the same applies to advance, i.e. external Brominated sorbents containing activated carbon or carbon black, see US patent application Nelson
for the external bromination of coal/lime-based sorbents. "Bromine" apparently favors the Hg dry sorption not only by a preceding Hg bromination in the boiler flue gas, but also directly "on the carbon-containing adsorbent on site", see also the earlier japanic patent application Shoichi et al. .

The Hg sorption on C-containing EGR filter dusts supports the Hg separation from the Raw gas and relieved (but only in "dry ash-removed boiler plants without fly ash recirculation) management) the subsequent further flue gas cleaning of mercury and thus the gypsum produced in a wet flue gas desulfurization plant (FGD). Apparently, the adsorbed te (presumably "chemisorbed") HgBr2 bound to the C-containing sorbents in an elution-resistant manner
; Chapter 5 below also provides information on this. In power plants with smelting chamber boilers sel and flue dust recirculation into the high-temperature furnace plays the interim Hg load of the EGR filter dust is not important at all, because the high-temperature SKK melt granulate flowing directly from the melting chamber is due to the high furnace temperature always (almost) Hg-free.

In the following, operational experience with chlorine- and bromine-based dry Hg deposition on the EGR filter dust from the investigated melt chamber boilers with high residual C contents typical of SKK. This is followed by a study carried out at the Institute for environmental technology, the laboratory test bench for “Hg dry sorption” is described and on laboratory results for chlorine- and bromine-assisted dry Hg deposition at two coke-containing EGR filter dusts (zero-load samples) from the large-scale tests in the SKK power plant and on a coke-free $CaCO_3$-rich cement raw meal, see Tippelt . Concluding The operational results for Hg sorption are then compared with the corresponding laboratory results. results on the EGR filter dust.*)

In the large-scale tests in 1993 with the addition of $HgCl_2$ and NaCl to the coal belt, about chlorine-assisted wet Hg deposition, see Chapter 2. A first interesting The research result concerned Hg chlorination, cf. .



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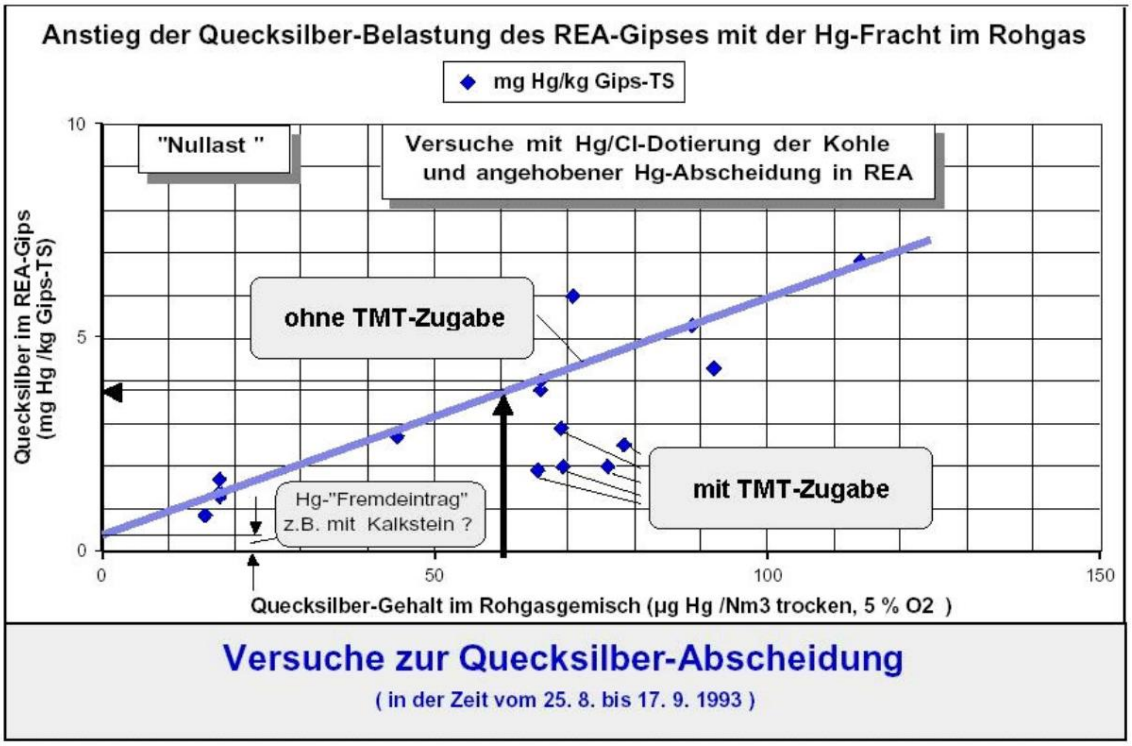
from coal-fired provide an overview of recent, primarily US-based research on the reduction of mercury emissions power plants. A large number of the papers cited therein deal with dry mercury sorption on coal fly ash and activated carbon, or on coal/lime-based sorbent mixtures.
Therefore, some of the observations presented below – based on our own operational and laboratory tests – have already been addressed in various cited works. However, studies on bromine-based mercury deposition are lacking in entirely.

In fly ash from dry-ash boilers (“dry firing”) with residual C contents < 1 wt.% (according to the quality seal for use as pozzolanic aggregate in concrete), the (essentially coke-related)
Adsorption phenomena are similar, but due to the low residual C content they are much less pronounced.

Another interesting test result concerned the Hg load of the REA gypsum and the Possible prevention of an increased Hg load in the plaster by adding TMT 15 (Tri-mercapto-S-triazine) into the REA scrubber circuit, cf.



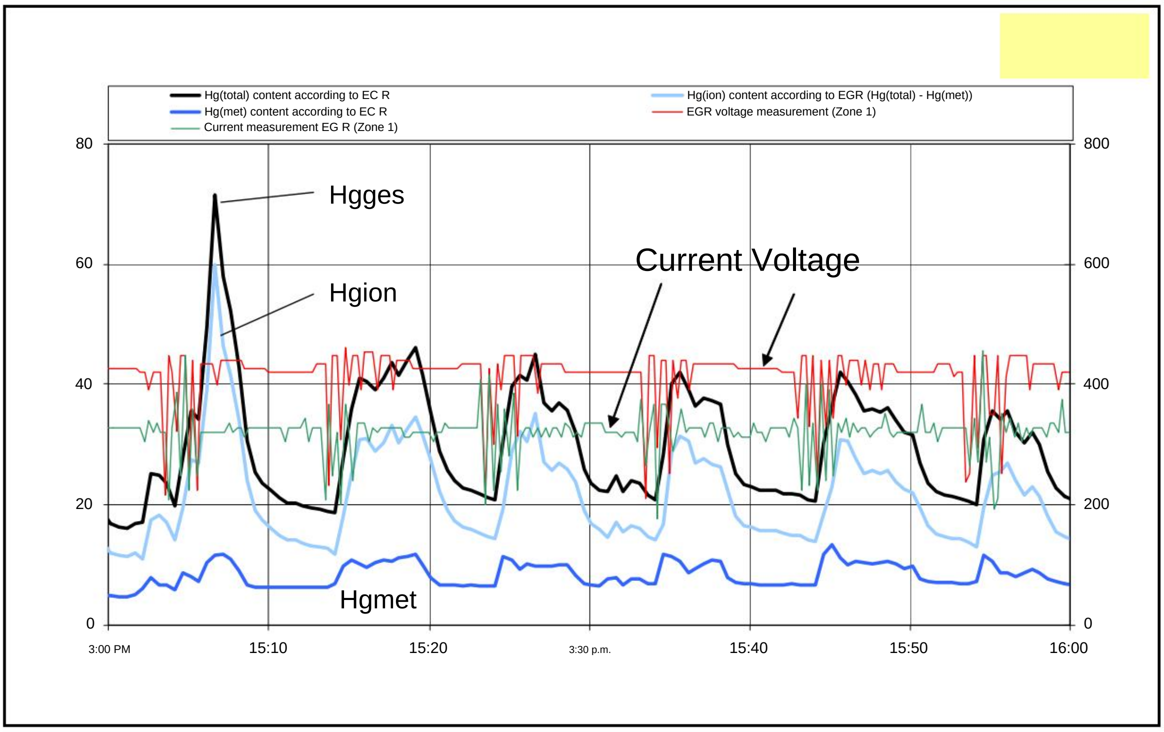
After the previous tests on chlorine-assisted wet Hg separation with dosing of HgCl2 and NaCl into the SKK combustion chamber (simulation of the co-combustion of sewage sludge-men) new experiments were carried out in 2002, now for bromine-supported wet Hg separation by adding HgCl2 and NaBr to the SKK combustion chamber, see Chapter 2. The species measurements behind the electrostatic precipitator (EGR) provided almost "microscopic" insights into the dry Hg deposition by adsorption on the EGR filter dust. The close connection The connection between cleaning of the EGR plate electrodes and Hg adsorption on the filter dust was visible.

Especially in the US literature, semi-continuous Hg measurement (SCEM) in power plants is currently often reported, cf. . In the USA, people often (supposedly) avoid unrealistic operating conditions and prefers to limit itself to pure coal combustion (zero-load driving) as a realistic operating condition, ie one usually dispenses with to "artificially" increase the Hg concentrations in the boiler flue gas, as we have done. Furthermore, many US coals are comparatively low in Hg. The Hg concentrations in the clean gas range (e.g., 7 to 1 µg/ Nm³ dry) are limited for measurement reasons.

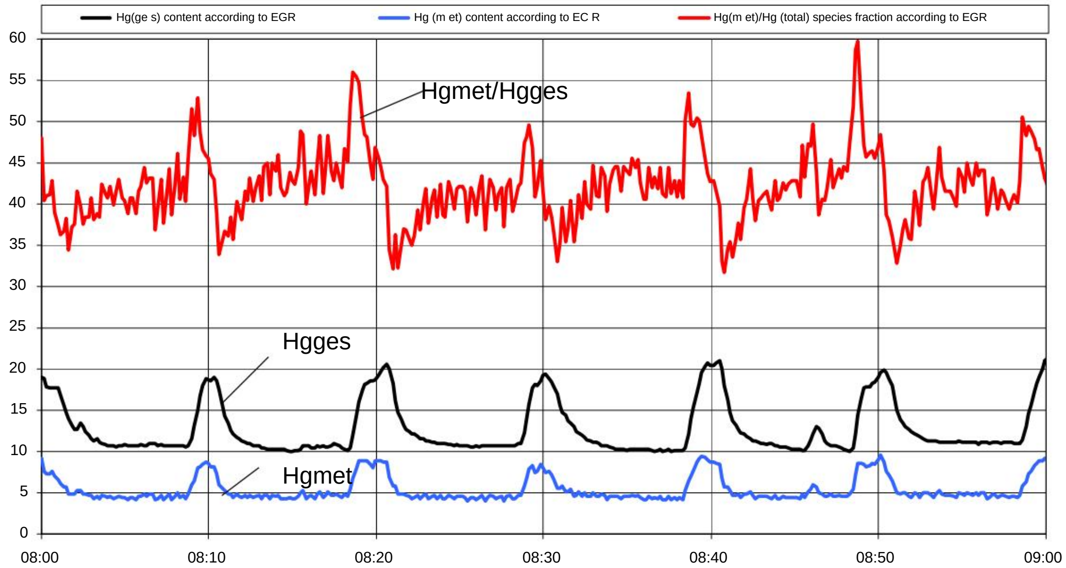
The semi-continuous Hg measurement, which is preferable for accuracy, works with an intermediate Hg collection on a gold trap ("amalgamation") and consequently low time resolution

CEM measurements with high time resolution, such as the continuous measurement described by us behind EGR / before REA, have not been published to our knowledge so far.

shows a species measurement after EGR with pure coal operation (hereinafter "zero load") in April 2002. This alone (unspectacular from the point of view of Hg concentrations) re) Example of a zero-load driving style provides an insight into the connection between EGR cleaning and Hg adsorption and thus demonstrates the influence of the pulsed electrode Knocking on the Hg adsorption on the EGR filter dust and thus on the Hg content in the corresponding dusty clean gas after EGR / raw gas before REA. The Hg peaks after EGR are synchronous to the current and voltage peaks of the cleaning process (cycle time: 10 min). *)



Another example concerns a zero-load driving style from August 2002. Here In addition to the HgMet and HgMet content, the HgMet/HgMet species fraction after EGR is also plotted. This HgMet/HgMet species fraction fluctuates between 35% (cleaned plates) and approximately 50% (covered plates) as a result of the cleaning process. The physical cause of the "link" between cleaning and dry Hg deposition visible in both figures is likely due to the changing dust coverage of the plate electrodes. For example, the Hg content in the dedusted raw gas decreases immediately after the start of the cleaning (dropping off the dust deposits) increases sharply, since – due to the lack of a "dust deposit on the EGR plate electrodes" – less mercury is adsorbed and therefore more passes through the electrostatic precipitator. The Hg content and thus the Hg ion content (as the difference between the two continuously measured Hg and Hg ions) increase particularly sharply .



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It is possible that there will be an increase in the dedusted clean gas up to the higher concentration level before EGR, which is likely to be above the coal-related base level (approx. 25 µg Hgges/Nm³ tr. in April 2002, approx. 12 µg Hgges/Nm³ tr. in August 2002) due to the dust recirculation (circulation between the SKK combustion chamber and EGR).

Oxidized mercury such as $HgCl_2$ is known to be adsorbed more strongly than metallic mercury, ie the current lack of flue dust as a “sorbent on the plate electrodes” should are particularly noticeable in the Hgion ; this is exactly what the two previous illustrations showed. clearly and distinctly: With each new build-up of dust on the EGR

Plate electrodes allow mercury to be adsorbed more intensively. Thus, the Hg Contents in the raw gas after EGR decrease again during the plate loading, especially here with the better adsorbable Hg ion. *)

Another important insight into the sorption processes in the EGR was already provided by . Starting from “zero load”, the two previous and

You can see there that with the start of the Hg addition the Hg content in the dedusted clean gas after EGR / raw gas before REA, but only gradually. The reason for the surprisingly slow Increase is the Hg sorption on the EGR filter dust and its return to the SKK combustion: The Hgion and Hgmet cycle between EGR and SKK leads to increasing Hgion and Hgmet levels in the raw gas before EGR (not measured). Due to the increase in levels in Raw gas before EGR makes use of the connection between clocked EGR Cleaning (removal and reconstruction of the adsorbing dust coating on the plate electrodes) and the Hg content in the dedusted clean gas after EGR are increasingly more noticeable (increase in the periodic fluctuation amplitude, especially in the better adsorbable Hg ion).

One would assume that already in the pipe section from the air preheater (LUVO) to the EGR an adsorption/desorption equilibrium between the Hg ion-rich raw gas and the entrained This is apparently true – at least in part – because otherwise it would have been each cleaning of the EGR plate electrodes to a full hydrogen breakdown up to the level the minimum Hg content (imposed by $HgCl_2$ addition) must be reached.

From the recirculated EGR filter dust (mixture of the extracted from all EGR fields Fly ash) were taken at regular intervals and used for selected test sections for their contents of Hg, Br, Cl, S, residual C and Ca wet chemical examined, cf. further down.

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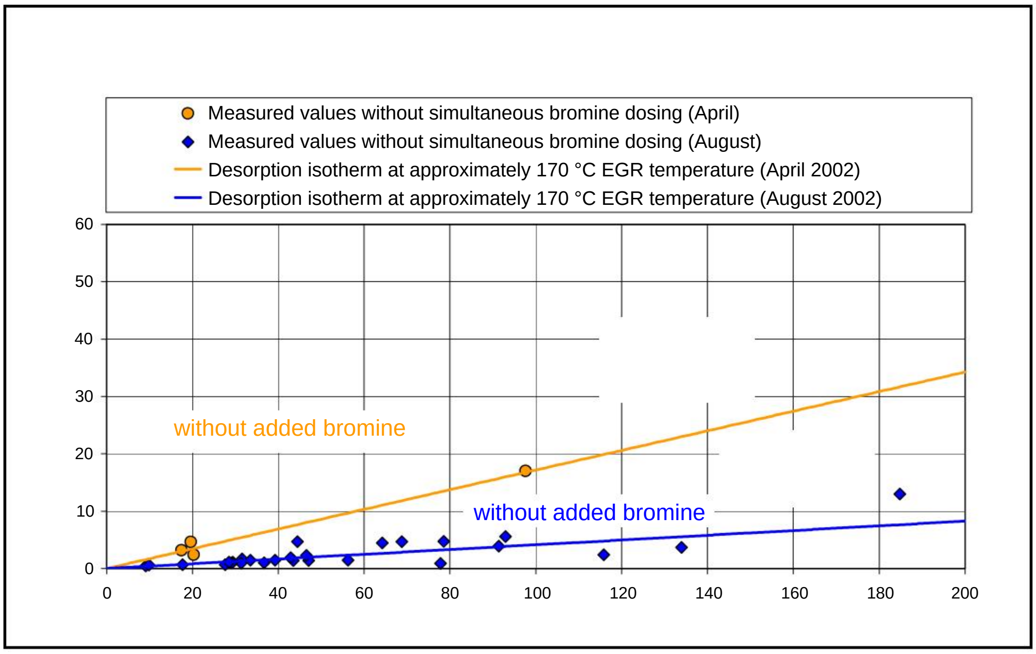
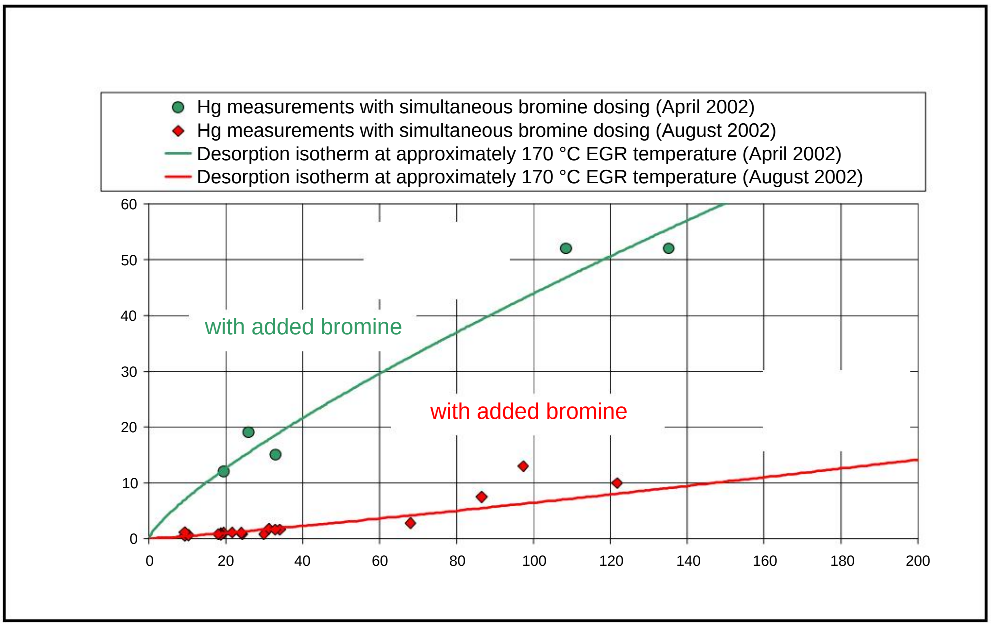
*) A differentiating (non-simultaneous) plate cleaning within the EGR fields appears due to the Hg-Measurement results make sense

concerns the chlorine-induced Hg sorption and then the brombeding-

Hg sorption.





As expected, in both cases the Hg content after EGR increases with increasing Hg loading of the EGR filter dust. As can be seen further, it is obvious

The residual carbon content of the fly ash is decisive for the dry Hg sorption.

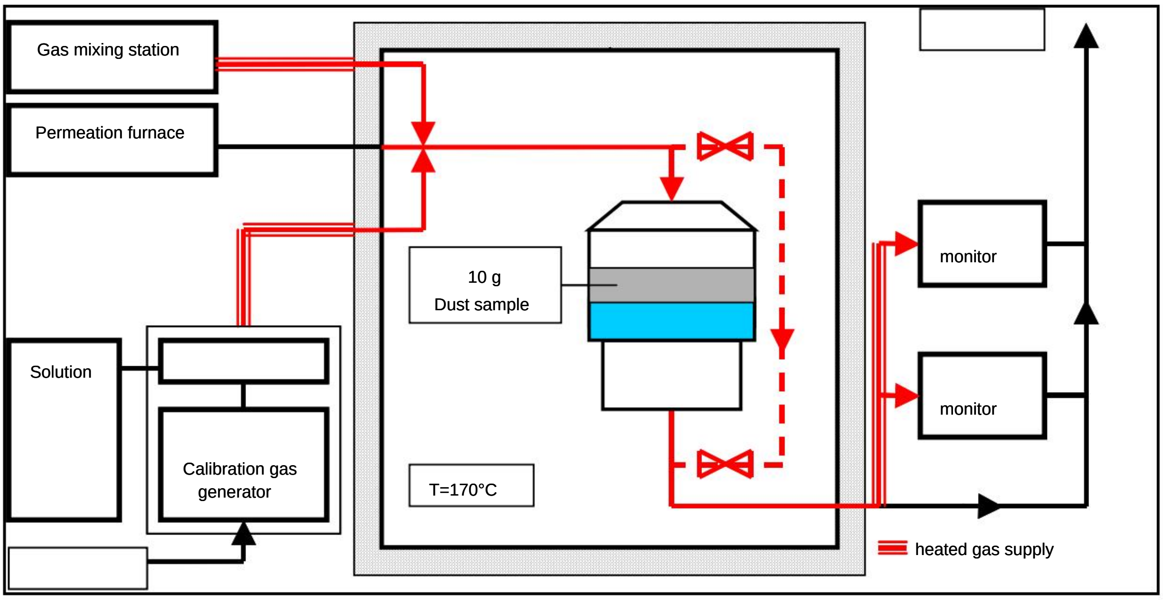
equal to the two figures it follows that “bromine” increases the Hg adsorption on the filter dust significantly intensified, especially in the filter dust with higher residual C content.

The phenomenon of bromine-induced intensification of Hg sorption was known to us from the specialist literature. ture (except for the recently published US patent applications Nelson) not before known and therefore seemed worthy of closer investigation. At the same time, the observations suggested that the bromine-induced intensification of Hg sorption to be used for other purposes, whether in connection with activated carbon or HOK-containing sorbents mixtures with a larger internal surface or integrated into thermal processes such as Cement burning (dry Hg deposition on the freshly fed CaCO3-rich cement raw meal in the head area of a raw meal suspended gas heat exchanger or in the area of the raw flour mills).

Therefore, the MLU Institute of Environmental Technology was involved in the “Research Focus point mercury” a laboratory test bench for dry Hg separation was also set up. In 2003, additional tests were carried out on this test bench for chlorine- and bromine-supported ten Hg sorption, see Tippelt .

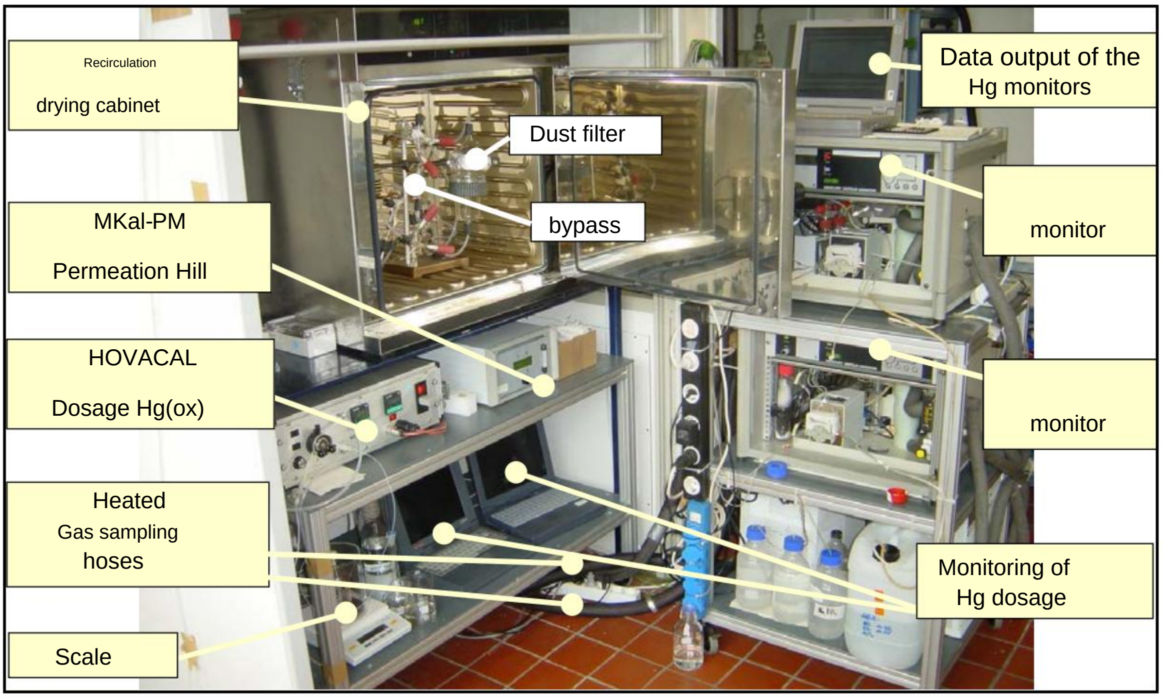
Initially, two of the EGR flue dusts (zero load samples) from the The two fly ash samples had different residual carbon contents of 22.3 and 7.4 wt.%, respectively; both residual C contents are well above the value of 1% (fly ash with quality seal), which in the case of dry-ash boilers is usually to be observed, in this case a SKK furnace with 100% dust recirculation In addition, a coke-free CaCO3-rich cement raw meal was examined.

The two and show the test rig. The actual test section (thin-film dust filter) is located in a temperature-controlled air circulation cabinet (drying cabinet), cf. The thin-film dust filter consists of two parts (both made of glass). Between the upper and lower parts is the flow-through “filter element”, whose Structure from The thickness of the dust layer corresponds to the height of the Sealing ring (previously: 3 mm, with a weight of 10 g EGR filter dust).



To generate defined Hg model gas concentrations and Hg species fractions, a Hovacal liquid evaporator ($HgCl_2$ as primary Hg ion) and an MKal-Permeation evaporator (Hgmet). Acidic components (such as HCl and HBr) and water vapor are also supplied as aqueous solutions via the Hovacal evaporator. Additional model gas components (e.g., SO_2) are provided via a gas mixing station.

The model gas thus generated can be either passed through the dust layer or via a bypass around This ensures that the raw gas (before entering the dust layer) can be measured with the same continuous mercury measuring instruments that are also used to measure the clean gas. Therefore, the test bench “Hg dry sorption” – only two continuous mercury measuring devices (for Hgges and for Hgmet) are connected.



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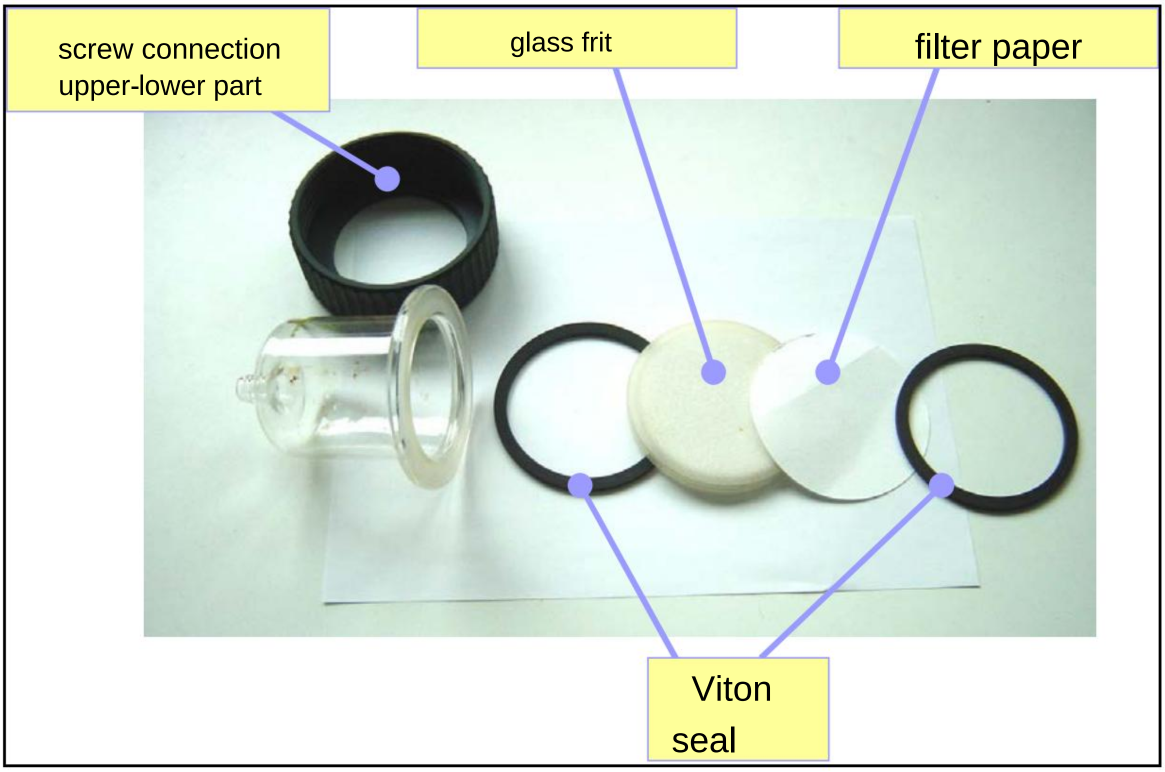

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*) In the pictures and diagrams of the laboratory experiments, metallic mercury Hgmet is referred to as Hgel and divalent ionic mercury Hgion is referred to as Hgox .

The samples examined with different residual C contents had a certain Hg-Pre-loading, see. The EGR filter dust from August 2002 was primarily charged with 7.4 % residual C and a Hg preload of 0.49 mg Hg/kg dust; this low The filter dust accumulated at the beginning of the large-scale test was in pure coal operation (“zero load”, without Hg and also without bromine addition). For the comparison of operational results and Laboratory results were supplemented by laboratory tests on the carbon-rich EGR Filter dust from April 2002, which with 22.3% residual C is three times the amount of carbon fuel and with 2.4 mg Hg/kg dust had five times the Hg pre-load; this higher-loaded EGR filter dust also occurred during coal-fired operation (“zero load”, without Hg and also without bromine additive). Before each laboratory test, the original dust samples were at least Pre-tempered for 30 minutes at 170°C in a circulating air drying cabinet; no reduction the Hg preload can be determined.

parameter	EGR fly ash from August 2002	EGR fly ash from April 2002	Unit
mercury	0.49	2.4	mg/kg
chlorine	30	46	mg/kg
bromine	1.4	14	mg/kg
Calcium	30000	12500	mg/kg
Residual carbon	7.4	22.3	% by weight
sulfur	0.21	0.25	% by weight

The water vapor content of the model exhaust gases investigated was set to 20 vol.%. During the test period of 2 - 12 hours, the temperature remained constant in all previous search constant at 170°C.

Depending on the experimental configuration, the model gas was loaded with 200 µg Hgges/Nm³ in the form of Hgmet or $HgCl_2$. At the beginning of the experiment, this Hg input concentration (“Hg content in the raw gas”) in bypass operation. After the Hg inlet concentration had remained constant over a period of half an hour, the switch to Reactor operation (flow through the thin filter dust layer). The flow velocity was 1 Nm3 /(m2 min). At the end of the test, the reactor was switched back to bypass operation in order to to check the Hg raw gas concentration again.

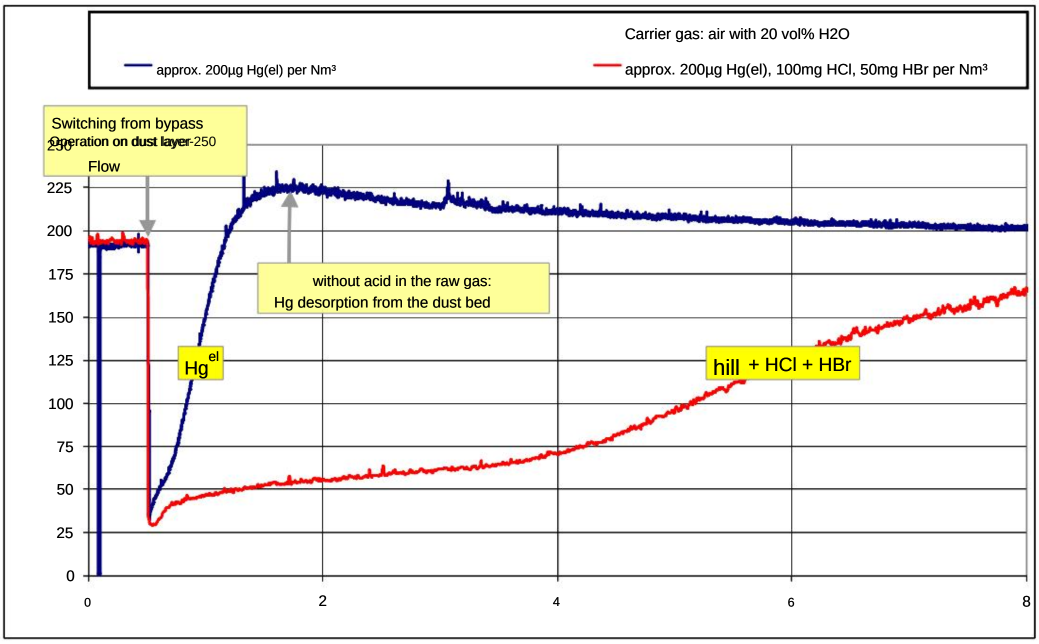
shows two examples of Hgges concentration curves in the raw and clean gas. Initially, the model gas (humid air) contained only Hgmet, later HCl and HBr were added in addition to Hgmet . The Hgmet content in the raw gas was recorded for the first half hour . Afterwards, the flow is switched to the thin fly ash layer and the Hgges concentration in the “dedusted clean gas” is measured.

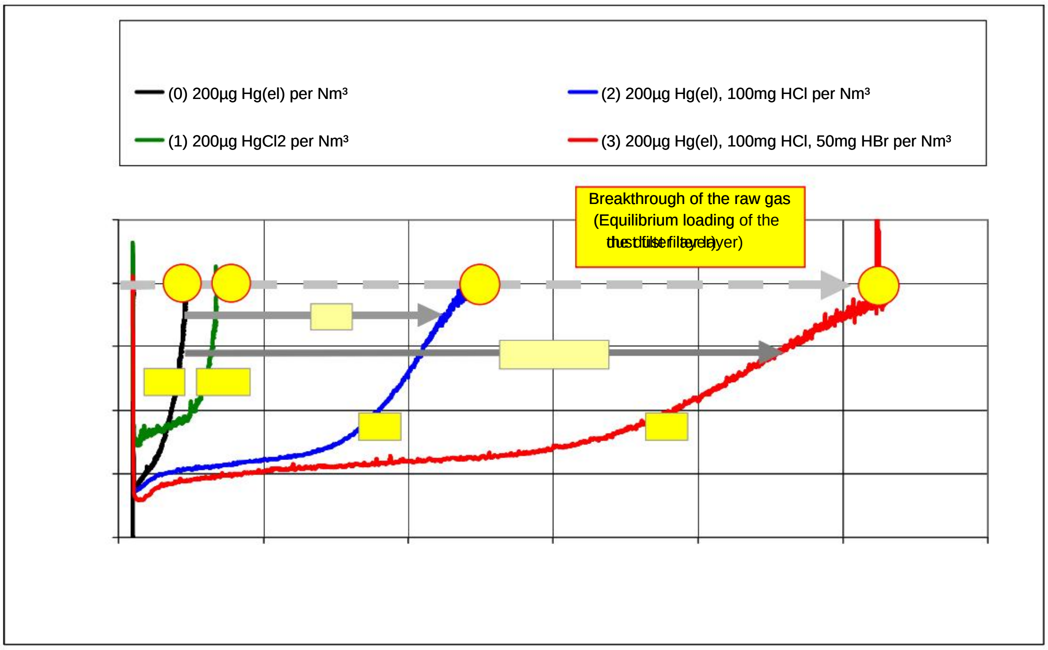
Without HCl and HBr in the model gas, Hgmet is only slightly adsorbed on the investigated flue dust. so that the raw gas concentration is reduced after only half an hour by the dust Interestingly, the clean gas concentration is then (approximately five hours) above the raw gas concentration; presumably the desorbed gas in the first half After an hour, Hg partially adsorbed during the further course of the experiment.

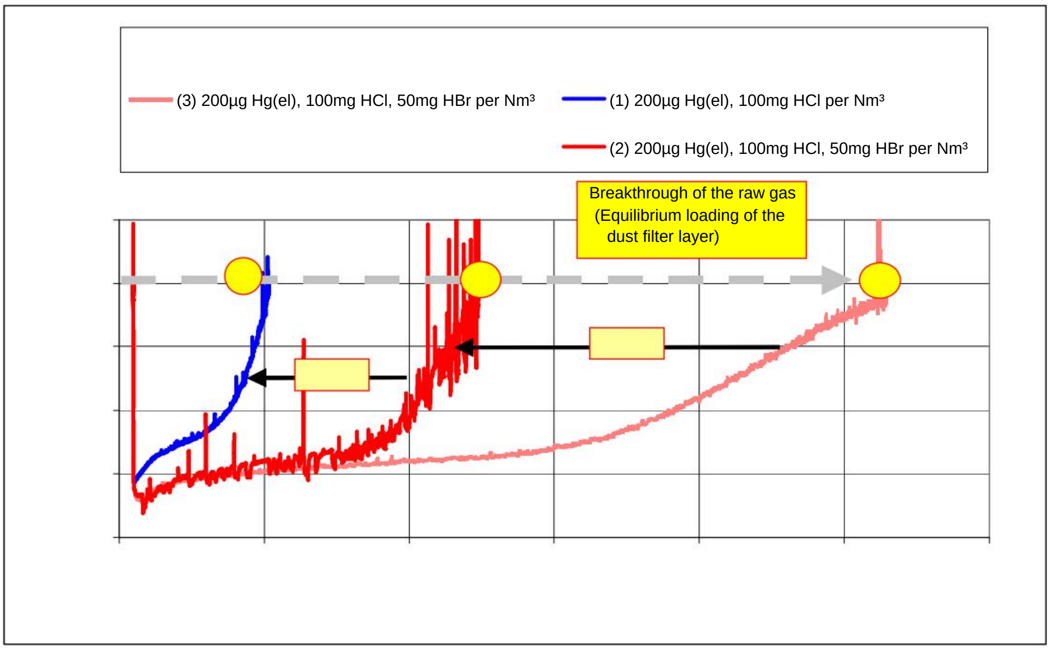
In the presence of HCl and HBr, however, the Hg adsorption increases considerably. Even after After 7 h of test time, the equilibrium loading (breakthrough) under the test conditions not yet reached, ie Hg was still absorbed by the dust from the model gas. taken.

In the following and the test results are in other Here the Hg concentration in the clean gas is plotted against the specific Hg The loading of the dust sample (calculated from the difference between the Hg contents in the raw and clean gas and the volume flow) is plotted. As can be seen, the Hg Sorption on the investigated hard coal fly ash in the following order:

Raw gas with Hgmet
Raw gas with $HgCl_2$
Raw gas with Hgmet and HCl
Raw gas with Hgmet, HCl and HBr.


Carrier gas: air with 20 vol% H2O
approx. 200µg Hg(el) per Nm³
approx. 200µg Hg(el), 100mg HCl, 50mg HBr per Nm³
Switching from bypass
Operation on dust layer
Flow
250
225
200
175
150
125
100
75
50
25
0
without acid in the raw gas:
Hg desorption from the dust bed
Hg el
hill + HCl + HBr
0
2
4
6
8


(0) 200µg Hg(el) per Nm³
(1) 200µg HgCl2 per Nm³
(2) 200µg Hg(el), 100mg HCl per Nm³
(3) 200µg Hg(el), 100mg HCl, 50mg HBr per Nm³
Breakthrough of the raw gas
(Equilibrium loading of the
the dust filter layer)



first shows the course of the Hgmet loading without SO_2 (curve (3), right) and then under comparable conditions also the course in the presence of 2000 mg SO_2/Nm³ with HCl and HBr addition (curve (2)) and with HCl addition alone (curve 1). SO_2 The Hgmet adsorption is clearly reduced. The measurement results indicate an interaction interaction of the components HCl and HBr with SO_2 ; presumably these are reactions with the adsorbed mercury on the flue dust and with the flue dust itself.

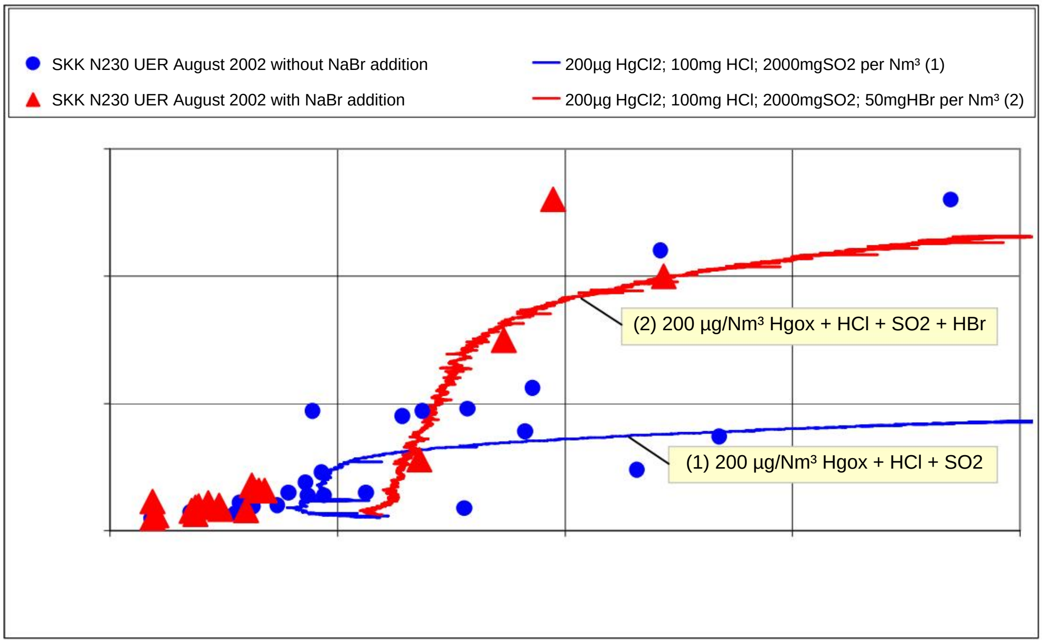
What happens in detail during adsorptive Hgmet sorption on the airborne dust and what causes the positive influence of HCl and/or HBr is partially cancelled out by SO_2, remains provisionally open, see also Chapter 5. Taking into account the recently published patent specification of Nelson It is probably a matter of chemisorptive processes.

The adsorption of $HgCl_2$ on the fly ash appears only slightly better than that of Hgmet.

In the presence of HCl, significantly higher Hgmet loadings are achieved. By adding of HBr, the Hgmet loading is even doubled compared to the gas containing HCl alone. That and why on carbon-containing sorbents in the presence of “bromine” the Hgmet in is adsorbed to a considerable extent, initially surprised us, corresponds but also the recently published results of Nelson In any case, the bromine-supported Hgmet sorption on carbon surfaces involves processes that are not yet fully understood.

Based on Results of laboratory tests are compared with those of In the form of a “Hg sorption isotherm” (at 170 °C) the respective Hg loading of the fly ash above the corresponding clean gas concentration carried; in the operational tests this means the Hgges concentration in the dedusted clean gas behind the EGR, in the laboratory test the Hgges concentration in the clean gas behind the dust layer.

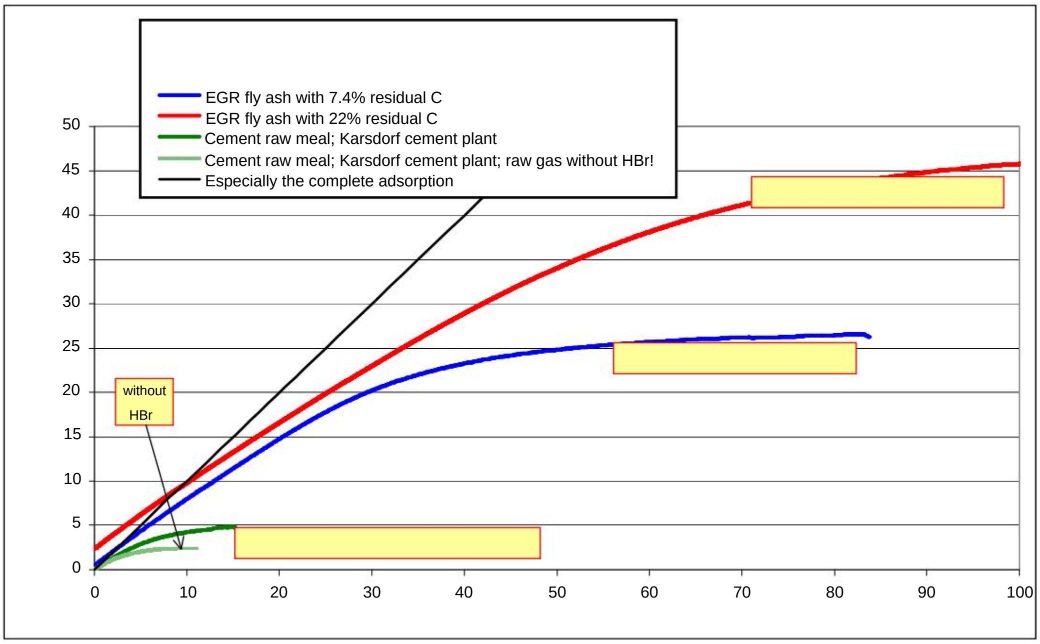
The Hg raw gas concentration in the laboratory tests was 200 µg Hg/Nm³; in the power plant the Hg raw gas concentration before the EGR filter was not determined, see previous section 2.4. Laboratory and operational tests refer to a fly ash with 7.4% residual C from the Au- August 2002. The laboratory results are shown as a curve, the present operating results Results from Nolte as points.



The Hg loadings obtained in the laboratory test correspond in size to the loadings, which were achieved under comparable conditions in a large-scale test at the BAYER power plant in Uerdingen – with and without NaBr addition to the SKK combustion chamber.

Some laboratory tests should provide information on whether a bromine-induced improvement in Hg deposition can also be observed on coke-free, essentially “inert” sorbents.

The Hgmet sorption on the two coke-rich hard coal fly ashes different residual coal nutrient content is measured in For example, Hgmet sorption on coke-free cement raw flour. A positive effect of “bromine” can also be seen here.
However, under identical test conditions, Hgmet sorption on CaCO3-rich cement raw material flour, as expected, significantly lower than the higher residual C-
salary.



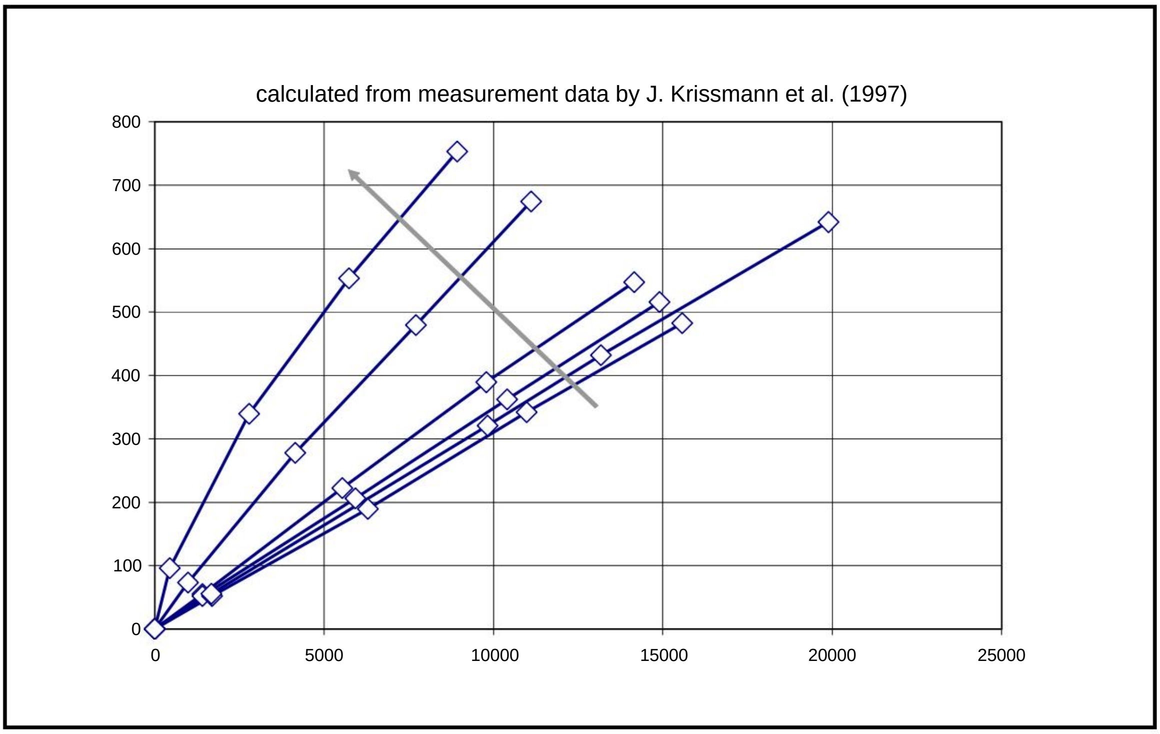
The cement raw meal examined from the Karsdorf cement plant is a thermally unstressed, residual C-free raw meal with 76.8 wt.% calcium carbonate (CaCO3) as Main component. The raw meal had an average grain size of 88 µm, cf. .

parameter	Cement raw meal Karsdorf cement plant
$CaCO_3$	76.8%
SiO_2	13.6%
Al_2O_3	3.3%
Fe_2O_3	1.8%
Average grain diameter	88 µm

Two large-scale tests on a smelting chamber boiler (100 MWtherm) at the BAYER plant in Uerdin-Based on continuous measurements of Hgges and Hgmet in the dedusted clean gas after EGR / raw gas before FGD, they provided a “microscopic insight” into the connection between EGR and Cleaning and Hg adsorption on the EGR filter dust on the plate electrodes. The Hg content in the dedusted clean gas fluctuate periodically during the cleaning cycle of the EGR. The higher the Hg- The higher the concentrations in the raw gas before EGR, the higher the Hg ion peak values (and thus the Hg values) are shortly after cleaning the EGR plate electrodes (lack of fly ash coating as a sorbent). The Hg ion concentrations in the dedusted clean gas follow the Hg ion Fluctuations in the EGR cleaning cycle also occur, but with a much lower The differences prove that oxidized mercury Hgion on the filter dust deposit is adsorbed considerably more strongly than elemental Hgmet. The Hg adsorption increases considerably when bromine is added to the SKK combustion chamber. This is confirmed by additional wet chemical analyses the Hg loading of the EGR filter dust returned to the melting chamber. The Hg loading of the EGR filter dust was plotted against the Hg content in the outgoing dedusted clean gas (“Hg sorption isotherm of the EGR filter dust at 170 °C”). The isotherms for bromine additive in the combustion chamber are significantly higher than the purely chlorine-related isotherms with pure Coal combustion (“zero load”), especially in the case of higher residual carbon contents of the filter dust.

The laboratory experiments showed that in the case of bromine-assisted operation, Hgmet is also adsorbed in an increased manner. As Nelson suspects, we also assume that active Carbon surfaces certain, but not yet fully understood, reactions between carbon lenstoff, “bromine” and Hgmet , ie the bromine-supported Hgmet sorption on carbon surfaces is a chemisorptive process that is not yet known in detail, cf. Notes in Chapter 5.

This Chapter 4 again focuses on wet Hg deposition. It deals with However, it only deals with the physical absorption of HgX2 and therefore – in contrast to to related studies (cf. Keller /44/ on the case of “iodine”) – without the concept of “Redox potential” of the washing solutions.*) The washing out of the highly water-soluble HgX2 from the raw gas is only in principle “easy and simple”, ie the leaching often takes place not without problems, see Neumann /1/, page 12 ff. The main problems are an incomplete absorption of gaseous HgX2 in the scrubber water or the desorption of dissolved HgX2 from the scrubber water back into the scrubbed clean gas, but possibly also a reduction from dissolved HgX2 to the almost water-insoluble, which evaporates from the scrubber water For the reduction of dissolved Hg ion it can be used – in weakly acidic (e.g. power plant REA), neutral or alkaline solutions – if, in addition to the HgX2 , reducing substances forming solvents such as SO2 go into solution, cf. to SO2 Solubility in the lower pH range. From the dissolved SO2, in case of insufficient Oxidation by the residual oxygen in the flue gas produces the reducing agent HSO3 - (hydrogen sulfite).



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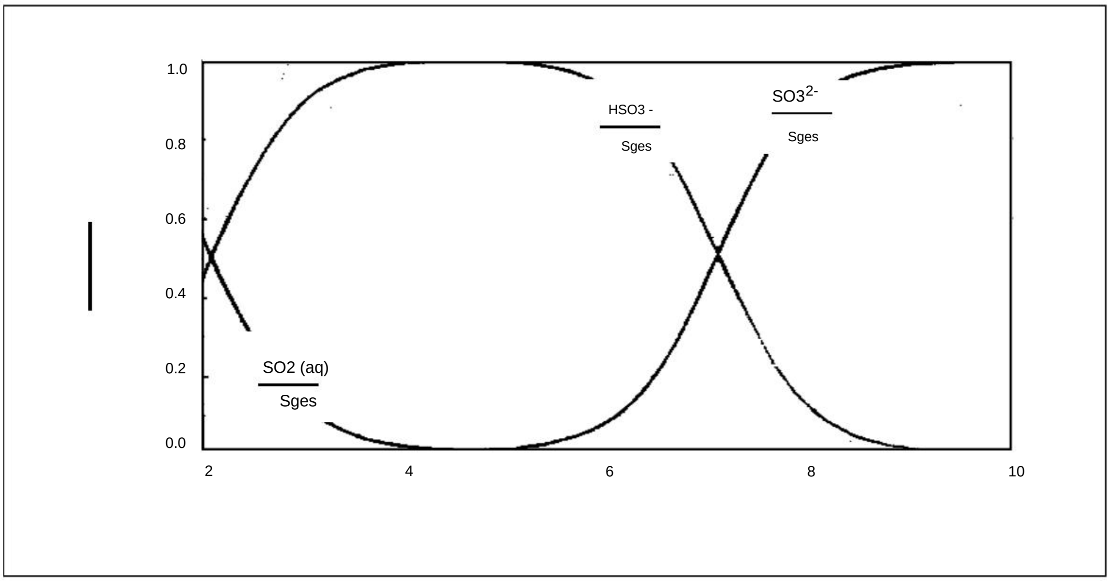
*) The redox potential plays a role when considering the reduction of HgX2 with release of Hgmet in weakly acidic to slightly alkaline washing solutions.

Higher pH values also promote the formation of hydrogen sulfite (HSO_3^-), cf.
, which in the alkaline scrubber area for the stable binding of free halogens such as Cl_2 is definitely desirable (avoiding residual emissions of Cl_2 by reducing the unstable hypohalide NaOCl to the stable halide NaCl), but on the other hand contributes to the unwanted hydrogen ion reduction. In the case of multi-stage flue gas scrubbing, this reduction Danger of HgX_2 carryover by droplets from the strongly acidic scrubber stage to the weakly alkaline scrubber stage (installation of a droplet separator).



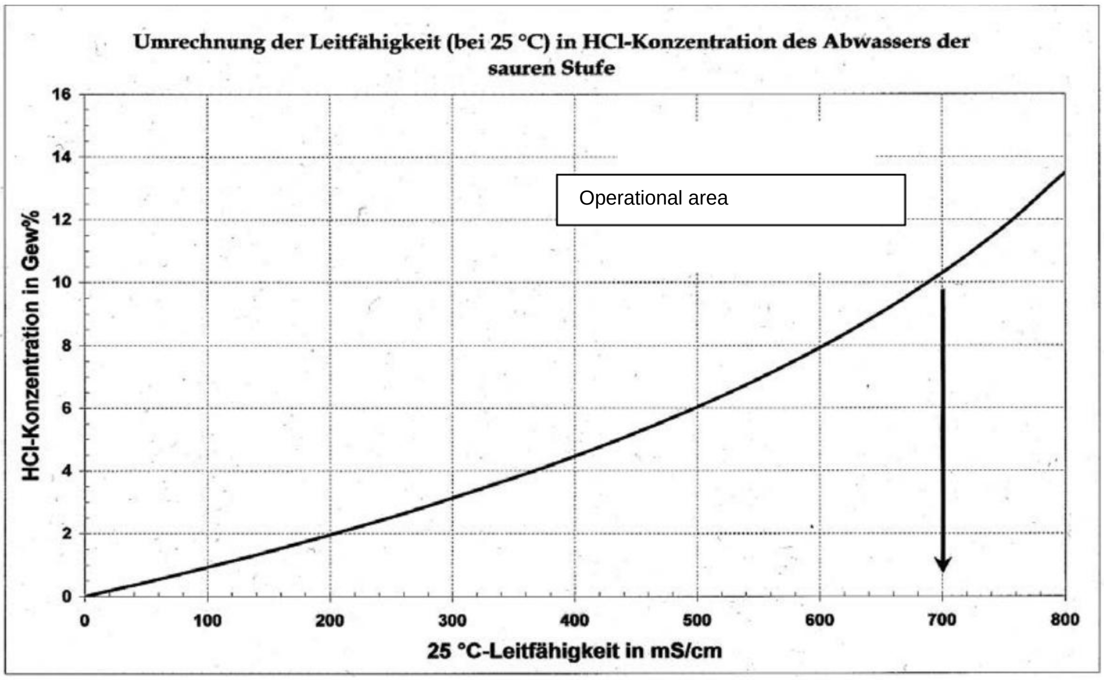
The HgX_2 vapor pressure in the clean gas can be kept low by removing the dissolved HgX_2 by Complexation (e.g. HgXX2ÿ2ÿ]HgX$_2$[$_4^{2ÿ}$) escapes the absorption/desorption equilibrium or by precipitating it in the scrubber as a poorly soluble Hg compound (ie solid), e.g. using TMT 15. Both measures simultaneously reduce the risk of a reduction from dissolved HgX_2 to volatile Hgmet.*)

From extensive studies on the example of “chlorine” (cf. Neumann) we know that Dissolved $HgCl_2$ reacts reversibly with chloride ions Cl^- available in the scrubber water to form complex ions. The so-called trichloro and tetrachloro complexes ($HgCl_3^-$, $HgCl_4^{2-}$ etc.), which dissociate ionically and then have no vapor pressure as ions. With increasing gender halide concentration in the wash water (e.g. due to increased combustion of highly halogenated waste), the proportion of uncomplexed $HgCl_2$ in the scrubber water decreases as a result of this complexation and thus the concentration of the $HgCl_2$ in the scrubber water.

The statements on physical absorption also affect Hg sorption on “dry sorbents” as soon as whose pores contain water condensate (due to Thompson's capillary condensation).

this molecularly available $HgCl_2$ and consequently also the corresponding $HgCl_2$ Equilibrium concentration or the corresponding $HgCl_2$ partial pressure in the scrubbed clean gas . As is already qualitatively known from the described operational tests, something similar should also apply in the case of "bromine", ie for the complexation of dissolved $HgBr_2$ by means of bromide ions Br^- , apply.

Often, as part of a "combustion menu" of a hazardous waste Incineration is carried out alongside highly brominated and highly chlorinated waste. Therefore one would like to know whether dissolved $HgCl_2$ can also be complexed by means of bromide ions Br^- or whether dissolved $HgBr_2$ can also be complexed by means of chloride ions Cl^- and thus avoid undesired desorption For example, when changing the operating mode from chlorine- on brominated waste (already a lot of chloride in the scrubber), whether this The chloride introduced also directly complexes the $HgBr_2$ that is now added. However, the question of "mutual complexation" is not only of interest in the combustion highly brominated hazardous waste, which usually contains chlorine in addition to bromine, but also of coal combustion (e.g. in the case that chloride and bromide are added to the coal's own ized bromide is added). For mutual HgX_2 complexation by means of dissimilar halides (formed by dissociation of the corresponding dissolved hydrogen halides or their alkali halides) is, to our knowledge, not yet known in the literature.



Note: In case of chloride introduction by HCl into the acid quench as first scrubber stage, the pH value is = - lg10 [cH^+/(mol/l)] with the so-called pCl^- value = - lg10 [cCl^-/(mol/l)] identical. Where c_{H}^{+} - the hydrogen or chloride ion concentration in or c_{Cl} scrubber water. The same applies to the input of HBr, see Chapter 5 below.

Chloride and bromide concentrations in total are often determined using the (at 25 °C calculated) electrical conductivity of the scrubber water was measured, cf. . In the works of Hübner and Wieland is the connection between Chloride or bromide content and conductivity are shown in detail.

HgX2 is dissolved in the scrubber water physically as such (molecularly), ie the absorbed HgX2 is initially present largely in the form of undissociated HgX2 molecules. Therefore, HgX2 via a vapor pressure and can desorb as such. In the washed clean gas after scrubber is (with a large exchange area and sufficient residence time) between the clean gas and the scrubber water, a temperature-dependent /desorption equilibrium. It is expected that on the clean gas side the equilibrium concentration of c''HgX2 or the mathematically corresponding concentration c''Hgion_gas (with Hgion_gas as the mercury of the gaseous HgX2) increases with increasing HgX2 concentration cHgX2 in the scrubber water or its corresponding concentration cHgion_liquid (with Hgion_liquid as the mercury of the total dissolved HgX2) .

According to the ideal gas law (with R as the general gas constant, MHgX2 as the molar mass of HgX2 and T as the absolute temperature), an equilibrium concentration c''HgX2 in the gas phase corresponds to an equilibrium vapor pressure p“Hgion_gas of

$$p''_{gas\_Hgion} \;\text{ÿÿ==}\; p''_{2HgX} \quad c''_{2HgX} \frac{R}{M_{2HgX}} T \qquad (4\text{-}1)$$

For the equilibrium vapor pressure p'' of pure substances (as in the case of the vaporization equation, weight of water/water vapor) is known to be

$$\frac{dp''}{dT} = \frac{\text{ÿ}\, h_V}{V\text{ÿ}T_V}$$

with ÿhV as the temperature-dependent molar enthalpy of vaporization of the pure substance and ÿVV as the difference between its molar volumes in the vapor phase and liquid phase.

neglecting the molar volume in the liquid phase against that in the vapor phase (V'') and assuming ideal behavior for the vapor phase (V'' = RT/p''), one arrives at the Slope of the vapor pressure curve to

$$\frac{dp''}{dT} = \frac{\text{ÿ}\, h_V}{p/RT''^2}$$

and with dp''/p'' = d ln p'' and with dT/T2 = - d(1/T) one obtains

$$\frac{\text{plnd}''}{\text{T/1(d)}} \ \text{ÿ=} \ \frac{\text{ÿ}\, h_V}{R} \qquad (4\text{-}2)$$

The same applies in the case of binary or ternary ideal solutions for the vapor pressure of the dissolved components such as HgX2; but then ÿhV denotes the (weakly) tempera- temperature and concentration-dependent partial molar “desorption enthalpy” of the considered component. Neglecting the temperature dependence of ÿhV, the following results from Integration of Eq. (4-2):

$$'' \quad - \quad = \text{ÿ} \quad ''_{0} \quad \frac{\text{ÿ}}{\text{ÿ}} \quad \frac{\text{ÿ}}{0} \quad \frac{\text{ÿ}}{\text{ÿ}} \qquad (4\text{-}3)$$

Here, ÿhV is now the mean partial molar desorption enthalpy of HgX2 during desorption tion from the dilute solution of the concentration cHgion_liquid. Furthermore, in Eq. (4-3) p''_0 is the equilibrium vapor pressure at a reference temperature To.

From equations (4-1) and (4-3) it follows that the equilibrium concentration c''Hgion_gas of HgX2 in the scrubbed clean gas should increase exponentially with temperature. We will This can be demonstrated using the example of a HgBr2/water solution, see below.

In the range of high dilution, here at low concentrations cHgion_liquid --> 0, the equilibrium concentration c''Hgion_gas in the gas phase is known to be directly proportional to the concentration of the molecularly dissolved HgX2 , ie

$$c''_{gas\_Hgion} \ \text{ÿ=}\ c'H_{mol\_liquid\_Hgion} \qquad (4\text{-}4)$$

The temperature-dependent proportionality factor H' is called (dimensionless) “Henry coefficients”, see in the introductory chapter. With cHgion_liquid_mol the Concentration of the remaining molecularly dissolved HgX2 in the water after complexation shear water is meant.

For the case of high dilution in flue gas scrubbing, it is expected that this Henry coefficient H' in the considered low concentration range concentration-independent We will illustrate this using the example of dilute aqueous $HgBr_2$ solutions at 60 °C exemplified, see below. The temperature dependence H'(T) will also be investigated later, using the example of an aqueous $HgBr_2$ solution of constant Hg concentration.

The proportion of the still molecularly available, ie the uncomplexed $HgXl_2$ in the water total HgX_2 added is:

$$=\text{ÿ}\ c\ \frac{c_{mol\_liquid\_Hgion}}{liquid\_Hgion\ \_\ total} \qquad (4\text{-}5)$$

From equations (4) and (5) we then get – with cHgion_liquid_total as the total Hg concentration in the scrubber water:

$$c''_{gas\_Hgion}\ \text{ÿÿÿ}= c'H_{\_liquid\_Hgion\ total}\ . \qquad (4\text{-}6)$$

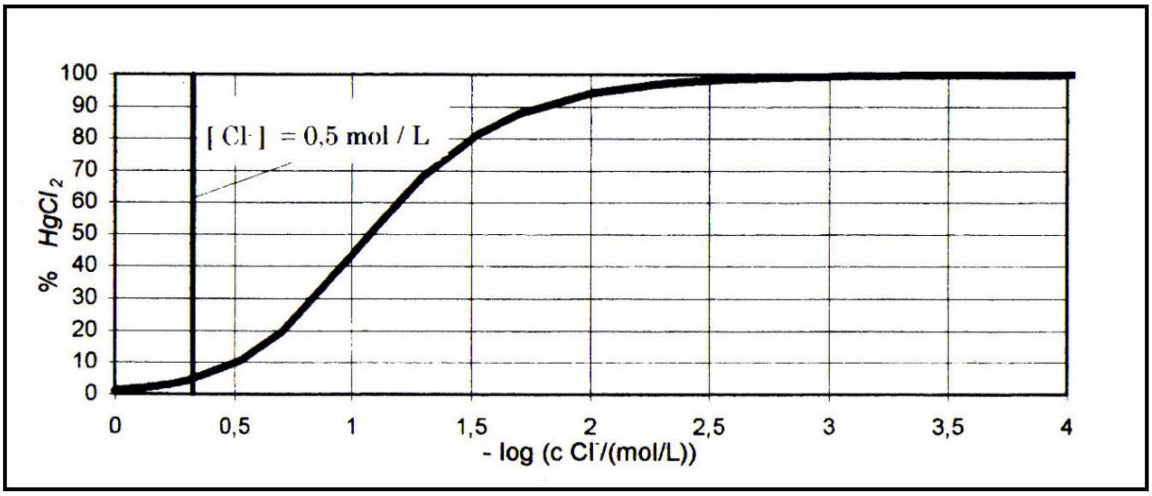
The proportion of uncomplexed $HgXl_2$ in the total amount of $HgXl_2$ released into the scrubber water, as defined by Eq. (4-5), including the HgX_2 deposited depends on the halide content available in the scrubber water. Concentration c_{X^-} and probably also on its type (chloride or bromide). It serves to describe the influence of complexation on the equilibrium concentration c''Hgion_gas or on the corresponding vapor pressure ("vapor pressure reduction due to complexation").
and depends essentially on the halide concentration in the scrubber water and thus from its easily measured electrical conductivity (calculated at e.g. 25 °C).
It is unclear whether chloride and bromide ions contribute equally to complexation; we This question is addressed using the example of the complexation of $HgBr_2$ using bromides and Chlorides will be examined in more detail later, see below.

The halide concentration c_{X^-}, ie c_{Cl^-} and/or c_{Br^-} or the corresponding sum value in In the case of strongly dissociated hydrogen halide acids, scrubber water can be Describe the pH value (pX^- = pH), see introductory notes on pH value and the corresponding corresponding pCl^- or pBr^- values:

$$pX^- = -\lg 10\ [(c_{Cl^-} + c_{Br^-})/(mol/l)] \qquad (4\text{-}7)$$

The proportion of uncomplexed and thus still available HgCl2 in the concentration $c_{mol\_liquid\_HgOx}$ on the total dissolved Hg of the concentration c _liquid_Hgox total

In the case of "chlorine" according to Braun predict, cf. :



According to Neumann, at chloride concentrations > 0.5 mol/l (ie pCl values < 0.3) to all mercuric chloride complexes; at chloride concentrations less than 0.01 mol/l (pCl- - Values > 2), however, the dissolved mercury is predominantly uncomplexed, ie molecularly solved, before.

Starting from Eq. (4-5) above and with

15,273/)15,2ÿ3/1(/1 (4-8)

as a rough approximation (with the low Celsius temperatures ÿ the washing solution) and a Summary of the constant quantities from the ideal gas law, Henry's law and Clausius-Clapeyron's law for the adjustment coefficient A) results in a semi-empirical Calculation equation for the equilibrium concentration in the scrubbed clean gas:

ÿÿ= ÿÿ ÿÿ)15,ÿ273/1( )ÿ15,273((4-9)

with	as	
c_{gas_Hgion}	Clean gas concentration of oxidized Hg	[µg/Nm³]
$c_{\_liquid\_hydrogen\ total}$	Total concentration of Hgion in the scrubber	[mg/l]
$c_{ÿ X}$	Halide concentration in the scrubber	[mg/l]
ÿ	Washer temperature	[°C]

and with the adjustment coefficients:

A	Adjustment coefficient 1 (gas equation, temperature, vapor pressure)
B	Adjustment coefficient 2 (vapor pressure)
C	Adjustment coefficient 3 (complexing function)
D	Adjustment coefficient 4 (complexing function)

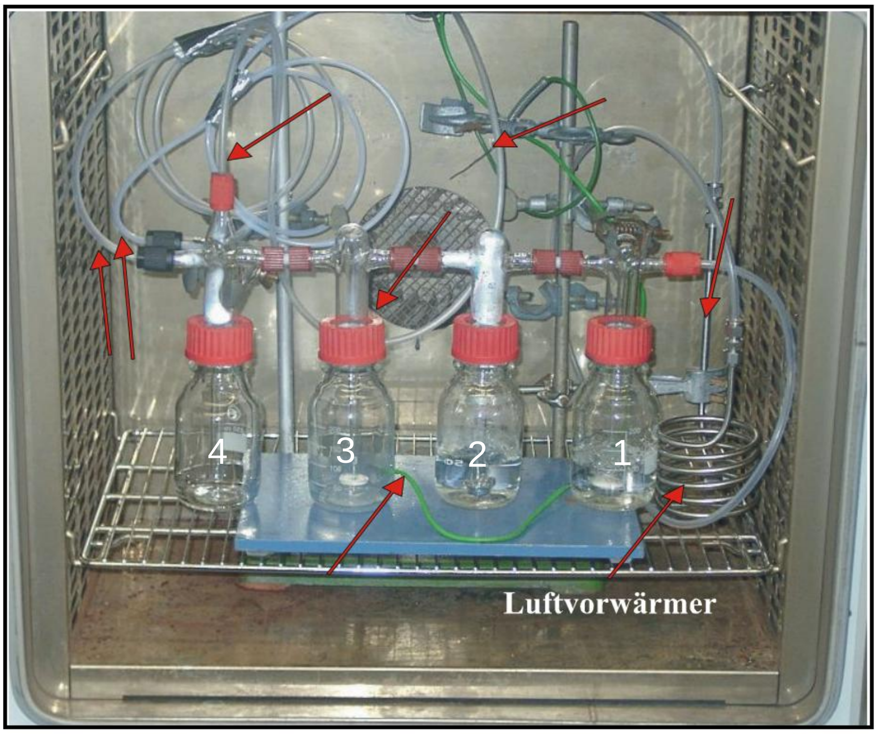
These adjustment coefficients will be shown below using the example of HgBr2 from our own measurements determined and finally in Table 4-1 for similar and dissimilar halide additives be specified.

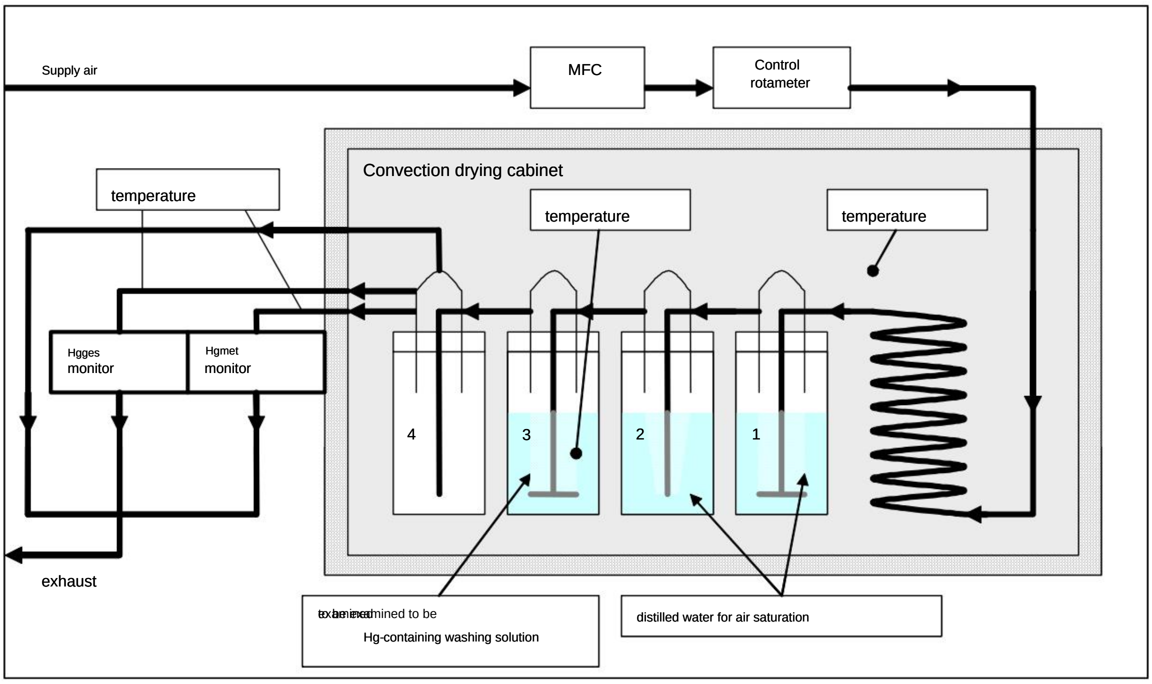
Inspired by the earlier operational tests at Bayer Industry Services GmbH (see Ka-), additional nefke and Nolte laboratory tests were carried out to investigate the desorption of HgBr2 from aqueous solutions. The experimental setup and its step-by-step Improvement and tests were carried out in the Bergmann and Stolle works .

To investigate the desorption equilibria between a Hg-containing washing solution and A glass "laboratory scrubber" was used for the carrier gas. It consists of four wash bottles through which a carrier gas (air) flows in series, see figure. or . The core is the wash bottle 3 with the Hg-containing wash solution to be examined. The two pre-switched wash bottles 1 and 2 are filled with distilled water and are only used for saturation of the carrier gas. The fourth cylinder serves to protect the downstream system against any drops/aerosols that may be entrained from the wash bottle 3.

The glass apparatus is located in an electrically heated circulating air cabinet (drying cabinet). By controlling the temperature of the chamber, the temperature of the Washing solution in wash bottle 3 is adjusted to specified values and kept constant.

In the experiments described below, air was chosen as the carrier gas. gas volume flow (approx. 180 Nl/h) is controlled by an upstream mass flow controller (MFC). Before the air enters the solution to be examined (wash bottle 3), They are heated to cabinet temperature in a preheater coil. This air is then As mentioned above, in the first two wash bottles, completely saturated with water vapor. The reason for this is that in this way a direct evaporation/recondensation of the mercury-containing washing solution itself (in washing bottle 3) to be examined. is avoided.



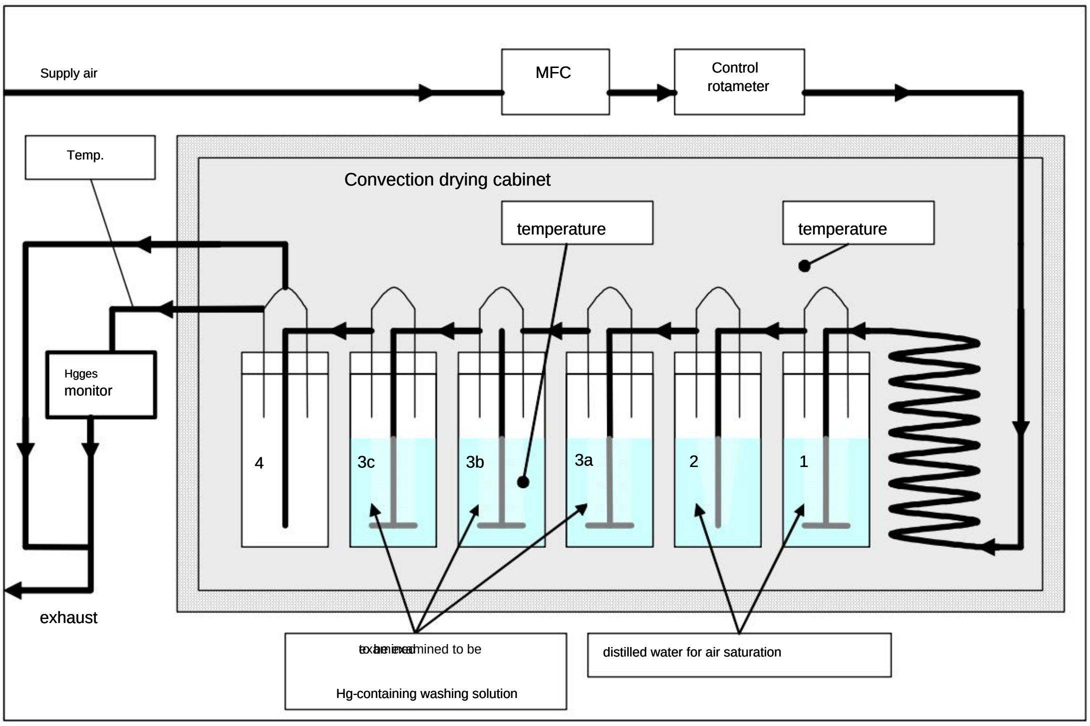


The cabinet heating therefore serves several purposes, namely the preheating of the carrier gas in a preheater coil and the compensation of the evaporative cooling in the washing bottles 1 and 2 (due to saturation of the carrier gas with water vapor) and at the same time the

Avoidance of subcooling (condensation) on the inner wash bottle and Hose walls.

To demonstrate by way of example that there is actually a

Gas/liquid equilibrium is established, has meanwhile been compared with three equal properly filled wash bottles 3a, 3b and 3c, cf. . The results confirmed that with this tripling of the exchange area and the residence time, no different results are achieved.



The temperature of the mercury-containing washing solution is continuously monitored by Temperature measurement on the glass wall of the wash bottle 3. Since comparative temperature measurements within the solution in wash bottle 3 or on its wall – due to the minimized evaporation/recondensation and good temperature compensation – identical values, direct temperature measurement in the liquid was not necessary.
den.*) The laboratory washer therefore leaves a water vapor saturated mercury-containing Exhaust gas stream (washed clean gas in desorption equilibrium with the Hg-containing wash solution This exhaust gas flow is continuously measured in two parallel Hg measuring devices analyzed to determine the “Hg species distribution after scrubber”, see section 3.3. The The necessary measuring gas flows of approx. 2 x 80 Nl/h are taken from the withdrawing carrier

To avoid adsorption and absorption effects on the sample gas lines before entering

To keep the wet chemical gas processing of the Hg measuring devices as low as possible,

The hoses used are electrically heated to 180 °C and have a PFA core.

The saturation of the air stream supplied as carrier gas in the wash bottles (1) and (2)

leads to a cooling, ie the temperature in these wash bottles as well as in the

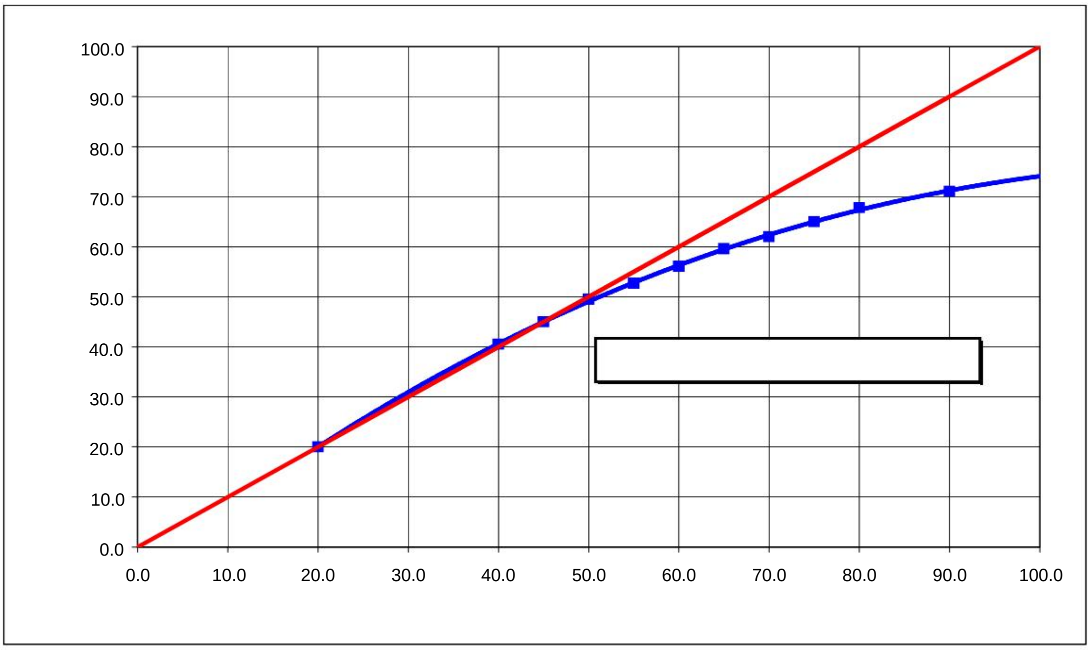
of the actual “scrubber solution” in wash bottle 3 drops due to evaporation.

cooling below the thermostatted temperature in the interior of the heated recirculation

cabinet (“cabinet temperature”). For this reason, the interior temperature – when washing

shear temperatures > 50 °C – slightly above the desired temperature for the respective investigations

Scrubber temperature must be maintained, cf. :



Two parallel connected devices were used for the analysis

for the continuous measurement of the clean gas concentrations of Hgges

and Hgmet (or from Hgion = Hgges – Hgmet).

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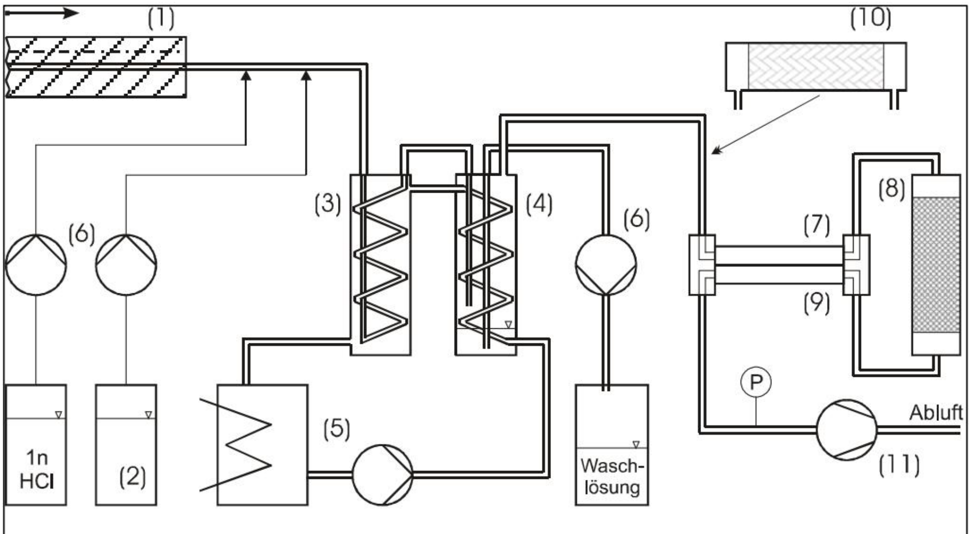
*) Direct temperature measurements in the solution using an immersed, bare Ni-Cr-Ni thermocouple lead to

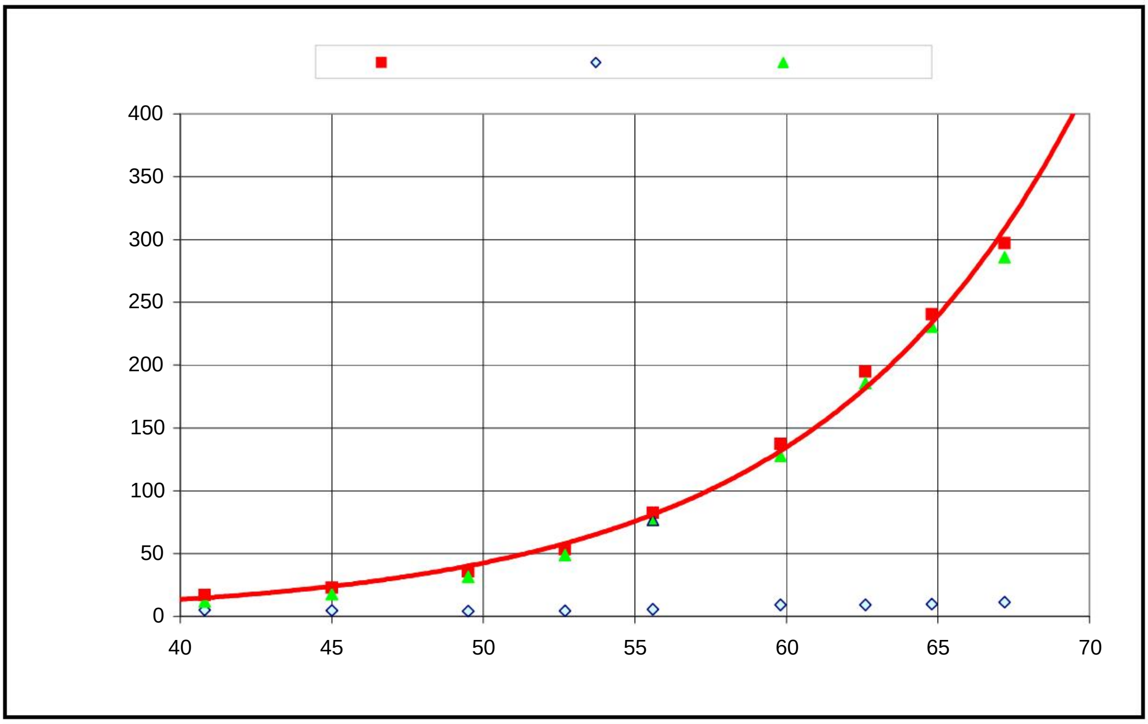
As has been shown, this leads to a shift in the species distribution in the outgoing “clean gas” towards the Hgmet (catalytic effects).

The core of the previously described devices is a Hgmet monitor (based on the comparative atomic absorption of the Hgmet band radiation) with upstream wet-chemical chemical sample gas preparation (using sodium borohydride NaBH4 to reduce of oxidized mercury to Hgmet). The “normal installation” of these measuring devices at the search status is in schematically sketched.



(1) Heizschlauch (ϑ ca. 180°C)
(2) Vorratsbehälter für
1n HCl bei Hg^0- bzw. 0,2n NaOH
+ 5 $g{\cdot}l^{-1}$ $NaBH_4$ bei Hg^{2+}-Bestimmung
(3) Absorptions- und Reaktionsspirale
(4) Kondensatfalle (Abscheidung von Hg^{ion})
(5) Kühler (Wasser/Isopropanol, ϑ_{soll}= 0°C)
(6) Schlauchpumpe
(7) Meßküvette (UV, λ=253,7nm)
(8) jodierte Aktivkohle
(9) Referenzküvette
(10) SO_2-Falle (50 Vol% Raschigringe
+ 50 Vol% NaOH-Pellets)
(11) Gaspumpe (Absaugvolumenstrom)

This concerns an experiment on the influence of scrubber temperature. Here, deionized HgBr2 was added to deionized water (pH = 7) . The solution was perfused with air as a carrier gas. bubbles (180 Nl/h). During the short test duration, the Hg concentration of the solution remained approximately constant at 20 mg Hg^{2+} /l (as dissolved $HgBr_2$) . One can see how the Hg vapor pressure and the corresponding Hg concentration in the withdrawn clean gas increased exponentially. increases with the scrubber temperature. In the clean gas, as can also be seen, hardly any Hgmet was find, since in this experiment (without SO_2 loading of the carrier gas) hardly any reducing influences exist, ie it essentially desorbs only oxidized mercury Hgion (as $HgBr_2$).



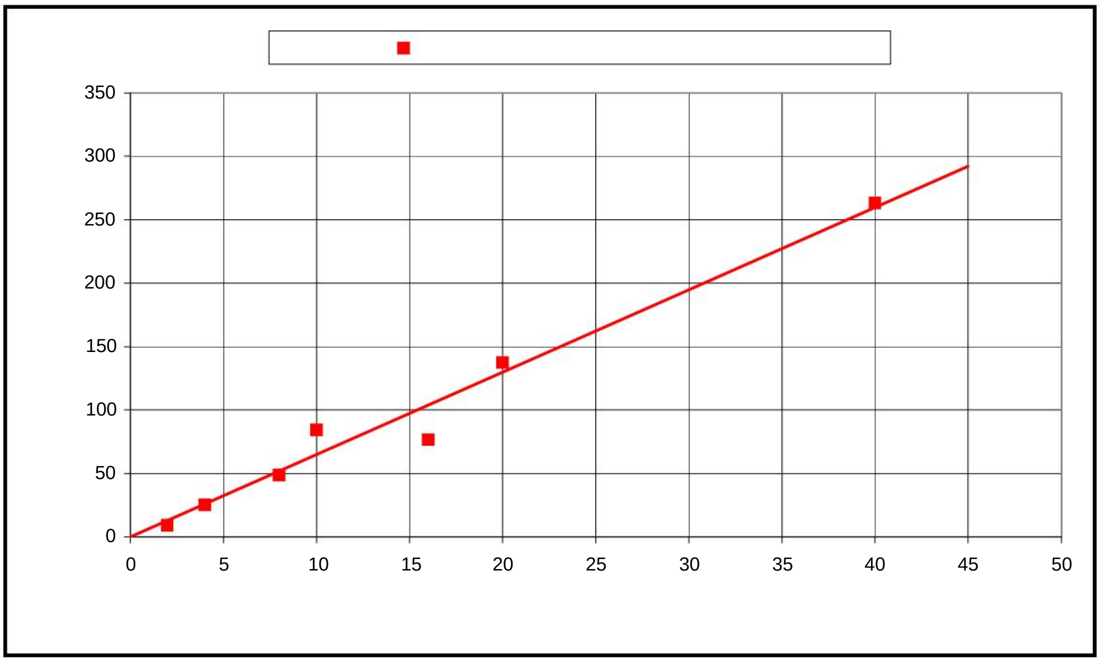
also refers to a neutral aqueous solution of $HgBr_2$ (without separate halide additives). Different Hg concentrations between 0 and 20 mg Hg^{2+}/l were added to the washing solution (deionized water) .

A constant scrubber temperature of 60 °C was chosen. The figure shows an example the dependence of the Hg concentration in the scrubbed clean gas on the Hg content of the scrubbing solutions As expected, the Hg ion concentration in the clean gas increases with increasing Hg Concentration in the washing solution increased linearly (“Henry's behavior”); however, the concentrations of Hgmet in the clean gas increased slightly (not shown here).

The determined Henry coefficient (slope of the Henry line) is

$$H' (60\ °C) = 6.4929\ (\mu g/Nm^3)/(mg/l) = 0.0000064929,$$

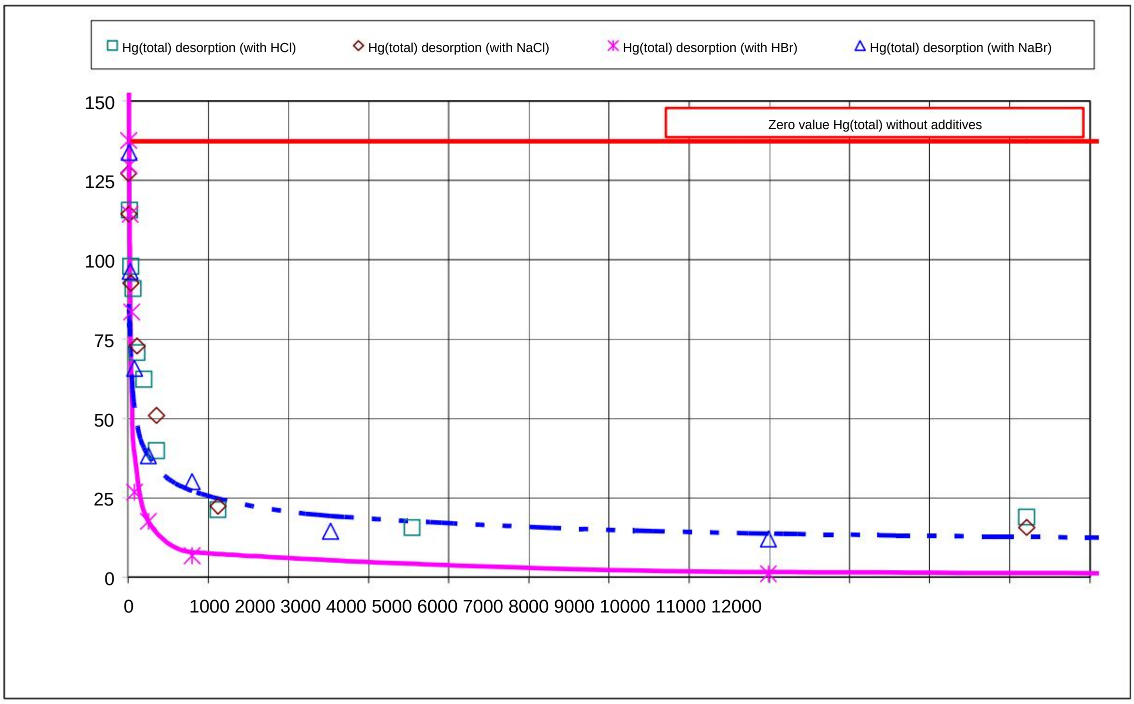
(cf. previous). This Henry coefficient H' applies only to the lower investigated case of an aqueous solution of $HgBr_2$ (without other halide additives) at 60 °C scrubber temperature.



The reduction of vapor pressure or concentration in the clean gas by “complexation” using

The formation of further X^- ions has long been known and studied in detail for $HgCl_2$, as explained in the introduction. Therefore, the task was to investigate the Hg complexation for the first time also for the case of "bromine". The corresponding test series again used an aqueous $HgBr_2$-solution of constant Hg content (20 mg Hg^{2+}/l) and constant temperature (60 °C). The halide additives used were HCl, NaCl, HBr, NaBr, and later also $CaCl_2$. shows a summary of the results of four series of measurements of the respective Hgges clean gas concentration versus the halide concentration in the scrubber in direct, i.e. non-logarithmic representation.

Please note that this is the complexation of $HgBr_2$ by chloride or by Bromide. With increasing halide concentration, the vapor pressure above the wash solution the same applies to the Henry coefficient H'. As shown in the figure, noticeable, the strong reduction already occurs with the first halide addition, ie in the range low halide concentrations (decrease in values near the ordinate). The strong decrease kung makes it clear that the aforementioned 10-fold lower solubility of $HgBr_2$ in pure water becomes practically irrelevant compared to that of $HgCl_2$ in pure water, ie in real scrubber solutions with low or high halide contents.



It was thus shown, as already well known from the complexation of $HgCl_2$ by chloride, that by increasing the halide concentration (and thus the conductivity in the scrubber) a almost complete retention of the oxidized mercury in the acidic wash solution

2 can be reached. For the complexation of HgX_2 (e.g. as ÿÿÿ+ 2][ ) 4 2ÿ

It is apparently not important whether the halide is made from a hydrohalic acid of the same or a different type or from a – much cheaper – halide salt of the same or a different kind.

The halide concentrations and conductivities in the acidic scrubber area of special Waste incineration plants are usually considerably larger (cf.) than in the above- test series (because the maximum value of 12000 mg X- /l chosen in the laboratory corresponds only about 1.2% by weight).

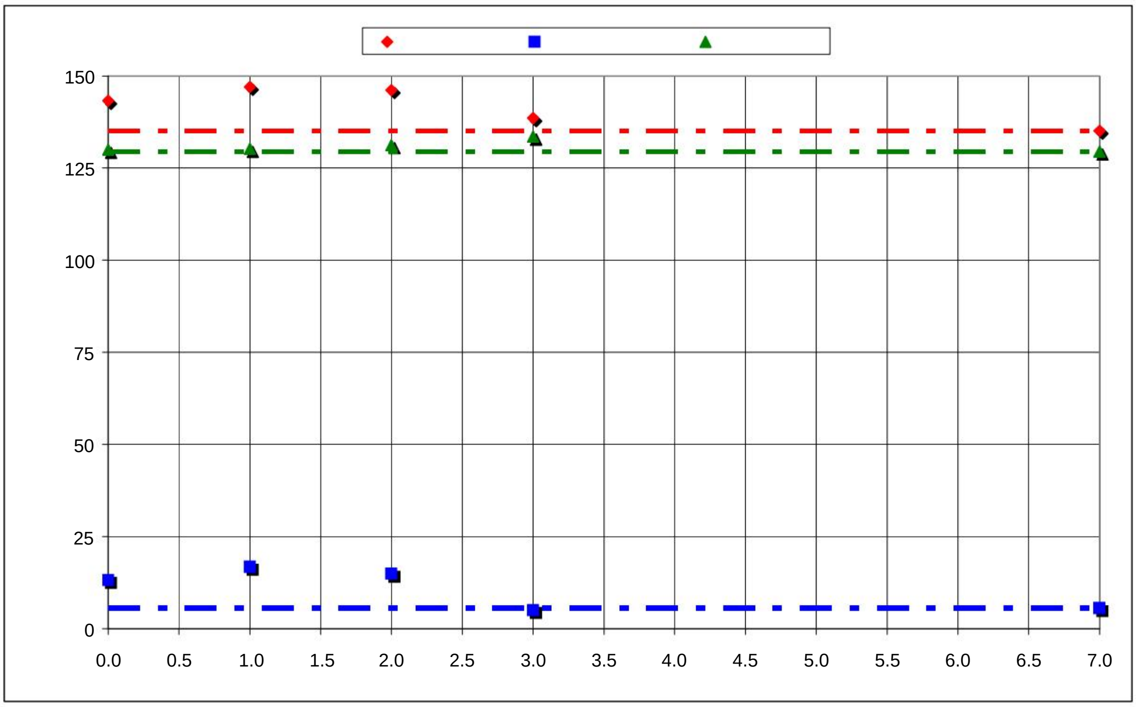
At this point it should be remembered that the addition of a hydrohalic acid HX is not not only reduces the pX- value, but also lowers the pH value to the same extent, thus SO_2 solubility (cf.) as well as the formation of the reducing sulfite and thus reduces the reduction of dissolved mercury.

Already S. Neumann (BAYER AG Leverkusen, 1995, see also) had by adding saltpetersäure demonstrates that – as explained above – with regard to the hydrogen vapor pressure in In the case of "chlorine", it is not the pH value but the pX- , ie the chloride content in the scrubber It was now our aim to do this for the case of "bromine", ie using the example of dissolved tem $HgBr_2$. For this reason, comparative tests were carried out with the addition of Nitric acid or sulfuric acid.

In the experiments with the addition of HNO_3 to the diluted and initially purely aqueous $HgBr_2$-Solution was – as expected – no reduction of the Hgges clean gas concentration from the pH to determine value.

Even when acidified with H_2SO_4 (cf.) as expected, no complexation of the dissolved $HgBr_2$, but in the lower pH range an increased reductive release composition of Hgmet (from $HgBr_2$); this can be recognized by the fact that the Hgmet-Clean gas concentrations in the lower pH range over the Hgmet clean gas concentrations without H_2SO_4 addition (pH = 7). This increase is due to a partial reduction of $HgBr_2$ to volatile Hgmet ("stripping" of Hgmet).

Similar effects are observed in all reducing scrubber stages, e.g. in weakly acidic wet flue gas desulphurisation plants (power plant FGD) and even more so in SO_2 alkaline scrubbers. In multi-stage scrubbers with strongly acidic first This danger is less present in the third stage, since the SO_2 is hardly in solution in a strongly acidic stage but only in the subsequent alkaline stage. If, due to a lack of sufficient HgX_2 deposition in the strongly acidic stage (e.g. defective spray nozzles) or by droplet flight (e.g. defective droplet separation) leads to HgX_2 carryover from the acidic to the alkaline stage, where the SO_2 is chemisorbed, then dissolved HgX_2 should be removed by adding Precipitants such as TMT 15 quickly remove the formed reducing agent from its reach.



As explained in more detail above, the washing solution is complexed

Molecularly dissolved HgBr2, ie, "desorbable Hg ion," is removed. Regarding complexation, there are evidently certain differences between similar and dissimilar halides.

The adjustment coefficients A, B, C and D in the semi-empirical equation (4-9) depend on the type of mercury halide and also the type of halide additive.

In the case of the investigated HgBr2, the complexation by the “similar” bromide Br- is somewhat stronger than by the “dissimilar” chloride Cl- , see previous or subsequent

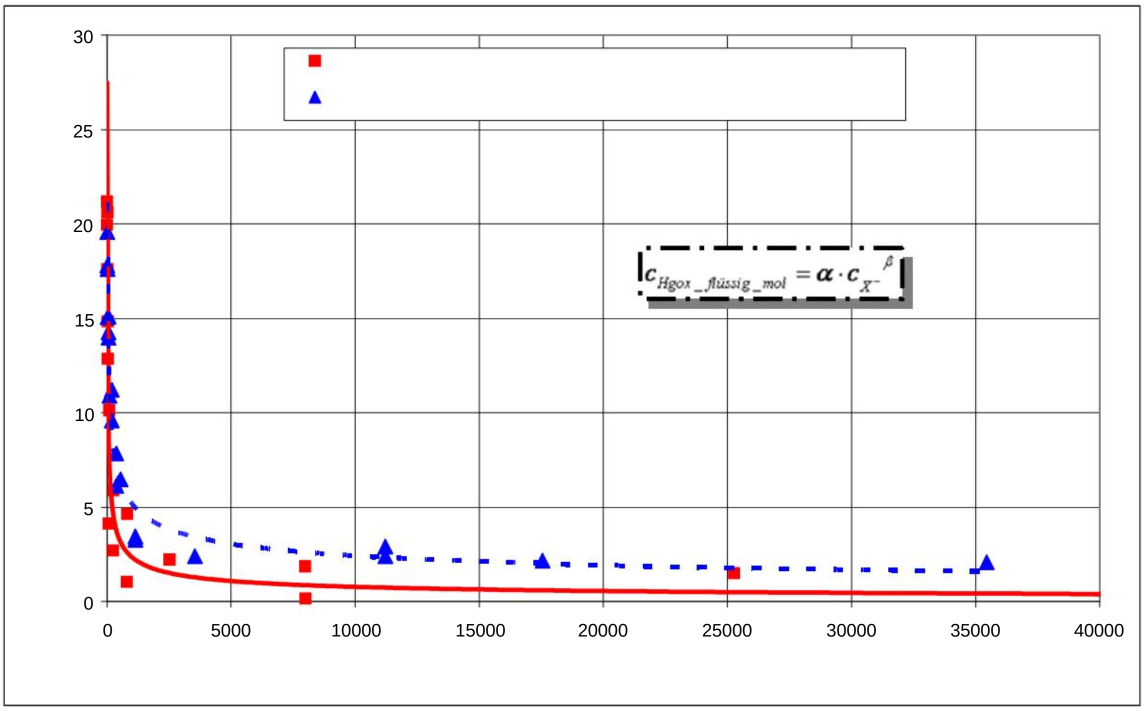
de .

The complexation of HgBr2 by bromide or chloride according to can be found in

Form of a simple power function. Taking this power function into account, the values of the adjustment coefficients A, B, C and D given in

for the evaluation of the semi-empirical equations (4-9).

	A	B	C	D
dissimilar halide additive (Chloride)	3.59649E+18	-1.35137E+04	1.44927E+00	-2.44703E-01
similar halide additive (Bromide)	3.59649E+18	-1.35137E+04	1.97058E+00	-3.26862E-01



With the Using the adjustment coefficients given for Eq. (4-9), it is possible to In the case of bromine-assisted wet Hg deposition, the minimum Hg ion concentration achievable in the pure gas after an acid scrubber (in equilibrium state).

The semi-empirical equation (4-9) for the “vapor pressure reduction by complexation” was probably Note that this is not formulated as a magnitude equation, but as a numerical value equation. The quantities in Equation (4-9) as well as the numerical values of the corresponding adjustment coefficients in are therefore bound to the units mentioned.

Where the desired Hg oxidation (halogenation) takes place, whether in the boiler or, for example, only at the scrubber inlet or in the scrubber itself or, for example, at the water vapor-saturated dry sorbent on site (Thompson capillary condensation in the sorbent spores), open for now and doesn't matter at first.

In 2002, see Vosteen , has already been extensively discussed about chlorine-assisted Hg oxidation in Combustion flue gases were reported.

a) the global reactions involved in the Hg chlorination in the flue gas,
b) the corresponding equilibrium thermodynamics and
c) their chemical kinetics and in particular d) the
modelling of the simultaneous reaction process using the novel
“Stop temperature method according to Vosteen”,

which links the equilibrium thermodynamics and kinetics of global reactions.
The complex modeling cannot be discussed in detail here; we limit ourselves to experimentally supported models.
Rather, we will focus on introductory information. According to the
According to current ideas, Hg chlorination involves the following four equilibrium reactions:

a) Chlor-Deacon reaction (5-1)
(Cl2 replication from HCl)

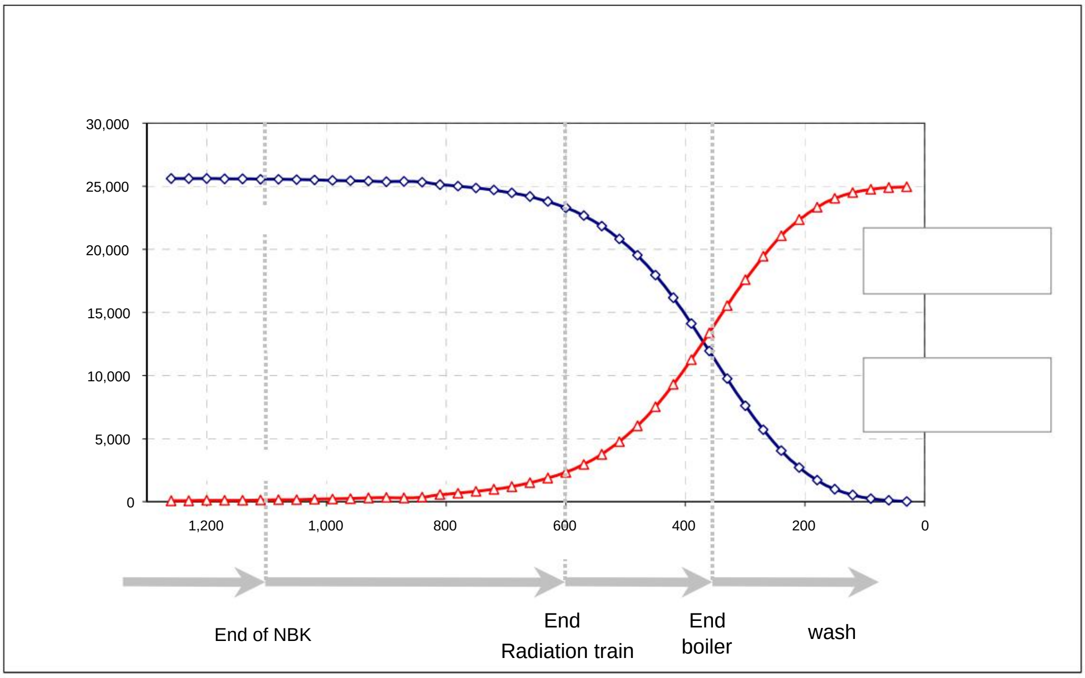
b) Chloro-Griffin reaction (5-2)
(Cl2 consumption by SO2 with formation of SO3)

c) oxidative SO2/SO3 conversion (5-3)
(direct oxidation of SO2 to SO3)

d) direct Hg chlorination (5-4)

Whether the “global reactions” mentioned, each of which can proceed via many intermediate reactions, are homogeneous gas phase reactions or (e.g. at the Metall oxides in the flue dust) heterogeneously catalyzed reactions, remains open.

The actual reaction partner of metallic mercury Hg_{met} is, from the perspective of global reaction tions the so-called free chlorine Cl_2. In the high-temperature combustion chamber, the introduced “Chlorine” initially occurs predominantly as HCl; however, with progressive flue gas cooling According to the Chlor-Deacon reaction Eq. (5-1), more and more Cl_2 is formed from HCl. This reaction (5-1), which is catalysed by metal oxides in the dust-containing flue gas, freezes after Our operational tests on the flue gas path through the boiler at about 680 °C therefore, ultimately only a limited Cl_2 replication of a few pro- percent of the total freight, cf. . *)



In the high-temperature combustion chamber, “sulfur” is predominantly present as SO_2; with progressive According to equation (5-3), more and more SO_3 should be formed from SO_2 during flue gas cooling. This oxidative SO_2/SO_3 conversion is also known to be kinetically strongly inhibited (from the point of view of sulfuric acid corrosion: thank goodness); according to our Investigations (cf. sulfur balance in below) in the SVA flue gas already at approx. 900 °C, cf. .

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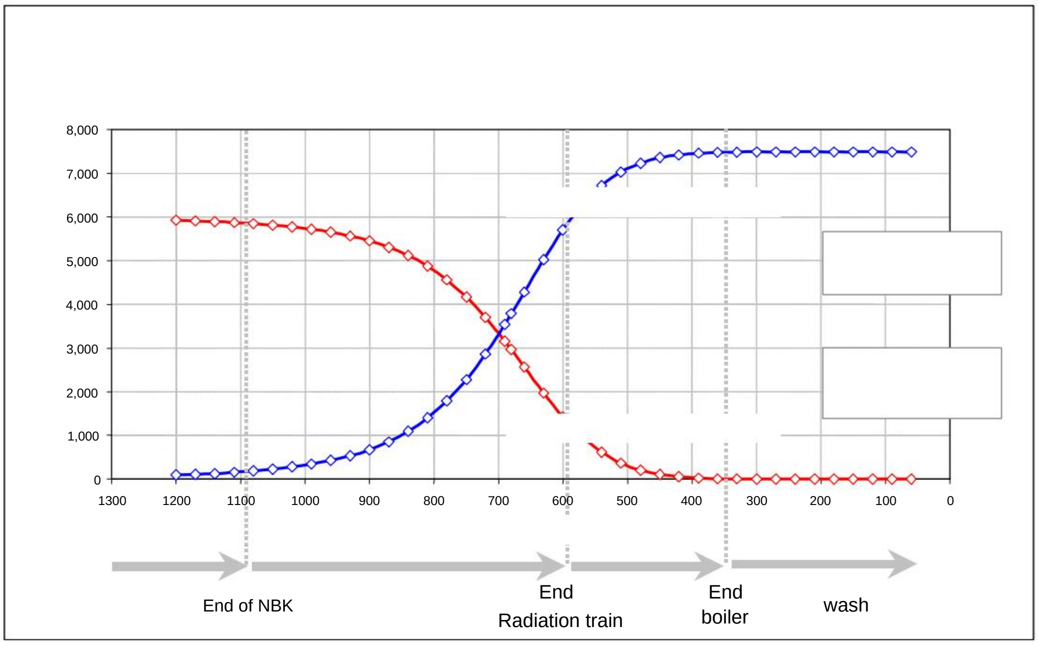
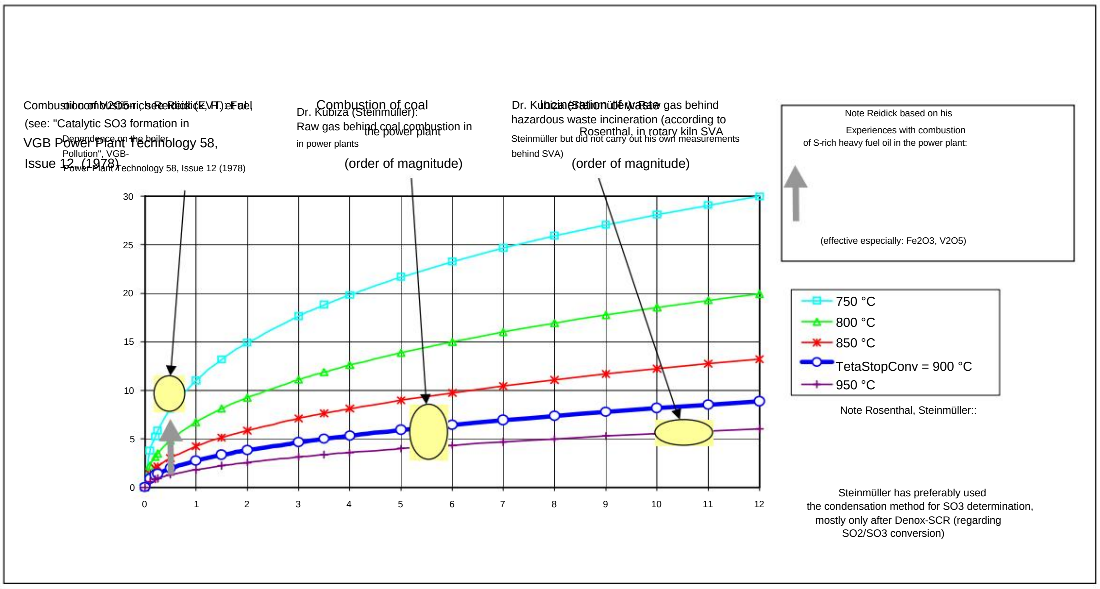
*) Total chlorine (Cl_{total}) is defined as the sum of HCl-induced chloride Cl^- and free chlorine Cl_2. Considering the generally low HCl concentrations of, for example, 10 to 50 µg/Nm³ tr. in the boiler flue gas of coal-fired power plants, low Cl_2 concentrations of, for example, only 1 to 5 mg/Nm³ tr. are still comparatively high (by a factor of 1000).



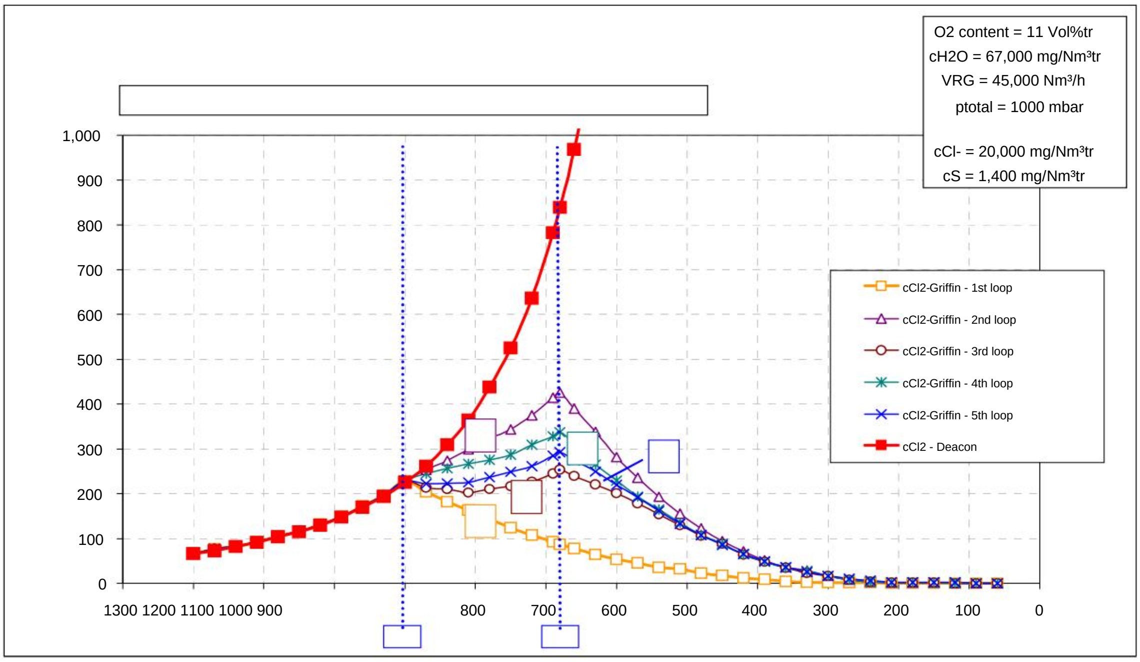


The SO2/SO3 conversion by the flue gas oxygen is possibly catalytically mobilized by metal oxides in the flue dust such as iron oxide and vanadium pentoxide down to lower temperatures.

an interesting operational example of this was provided by power plant investigations into Combustion of vanadium-rich heating oil, see Reidick .

If the direct oxidation were uninhibited, the interaction of the three simultaneous reactions would result in tions (5-1), (5-2) and (5-3) mathematically (Gibbs Free Energy Minimization) nothing else than already in calculated using the Chlor-Deacon reaction alone as an example. den, ie the Chlor-Griffin reaction according to Eq. (5-2) is virtually not effective at all, because the SO3 production according to Eq. (5-3) suppresses the Cl2 consumption according to Eq. (5-2).*)

However, if only the direct oxidation of SO2 to SO3 is frozen below 900 °C, at temperatures < 900 °C due to the still ongoing Chlor-Griffin reaction mathematically (and realistically) to “Cl2 consumption under consumption of SO2”, cf. According to our investigations, the Chlor-Griffin reaction probably even up to the SVA boiler end (approx. 380 °C), see “closed sulfur balances” further below. ten.



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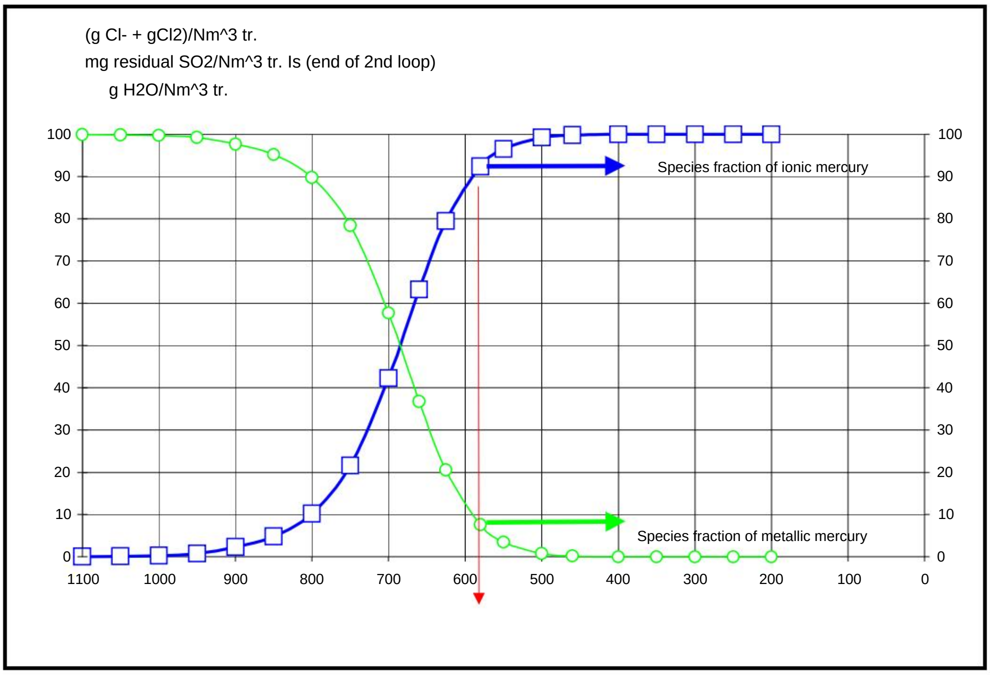
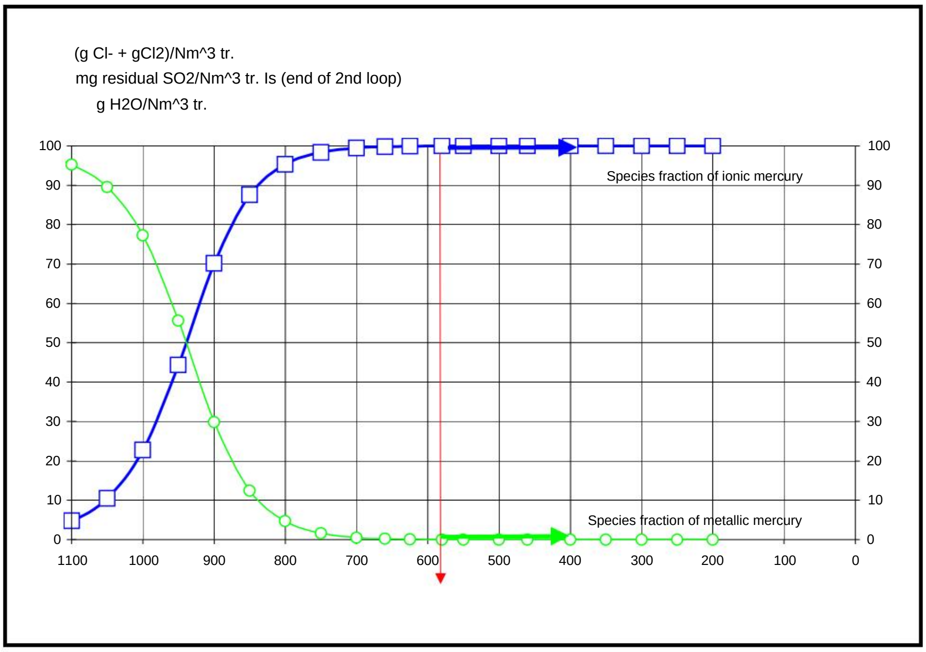
*) The reaction equations (5-1), (5-2) and (5-3) are linearly dependent on each other; for example, Eq. (5-2) from the two equations (5-1) and (5-2). From the perspective of equilibrium thermodynamics alone (Gibbs Free Energy Minimization) would therefore make one of the three equations superfluous.

When referring to the Gibbs free energy of reaction, the reaction is always referred to from left to right.

In the combustion chamber, the “mercury” lies according to equilibrium thermodynamics (Pohontsch) predominantly as Hgmet ; with progressive flue gas cooling, according to Eq. (5-4) but more and more of the desired Hg ion (as $HgCl_2$) is formed as soon as below 900 °C According to Equation (5-1), the reaction partner Cl_2 is provided in sufficient quantity and as long as it has not yet been completely consumed. But this reaction, Equation (5-4), is also openbar kinetically inhibited. If equation (5-4) is added to the model, the which in (Co-incineration of Hg-containing waste with low-chlorinated liquid waste) calculated as examples for the two species Hgmet and Hgion. From the comparison with our measurement results, we determined for direct Hg chlorination according to Eq. (5-4) a stop temperature of the “direct Hg chlorination” of 580 °C in the rotary kiln SVA or of 480 °C in the SKK power plant.



If the rotary kiln SVA is operated at much higher temperatures, as is common in the chemical industry, Chlorine loads, there will be no metallic mercury at all at the end of the boiler. find, cf. as a calculation example for the case of co-combustion of Hg-containing waste with highly chlorinated liquid waste; the Hgion/Hgges species content rises to 100 wt.% long before the boiler end, ie all mercury is in the desired according to ionic form and is – in an optimal multi-stage flue gas scrubber – almost completely washed out.

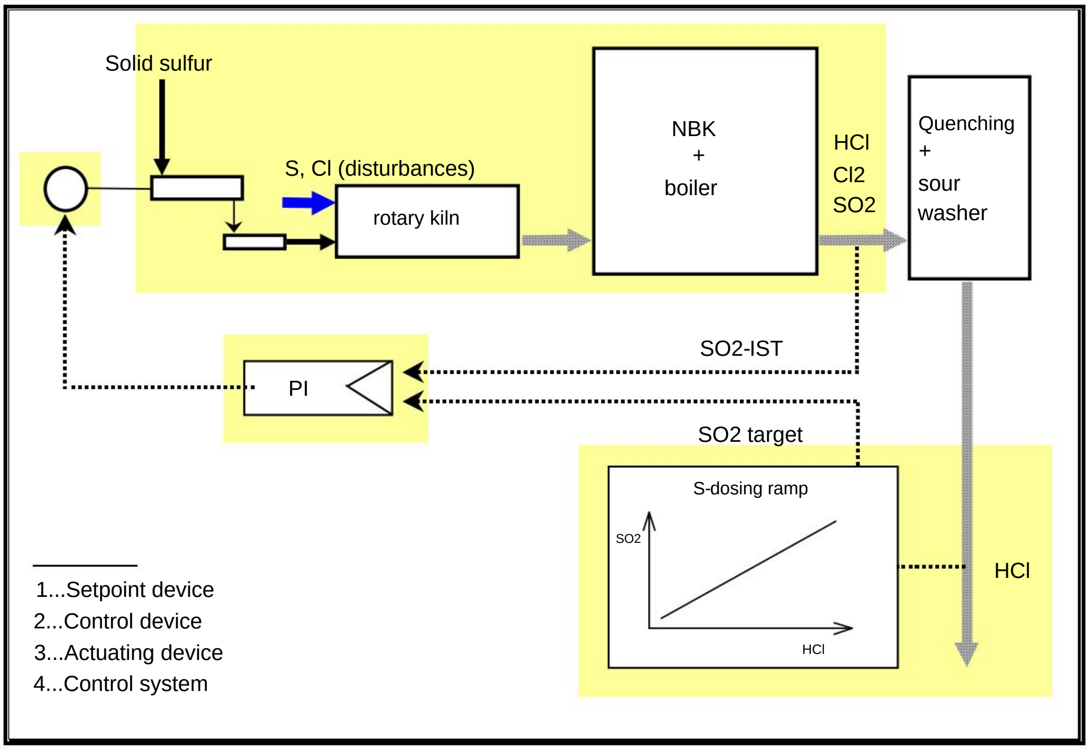


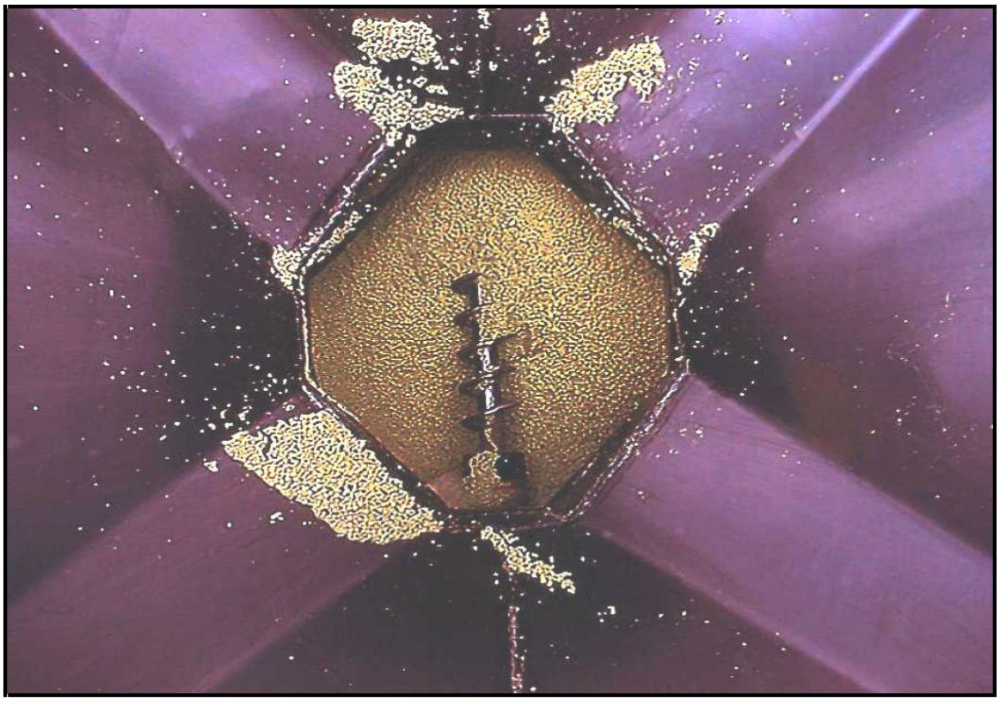
The chlorine-specific set of equations (5-1) to (5-4) contains, it should be noted, only the so-called "di-direct Hg chlorination", but not the "indirect Hg chlorination"

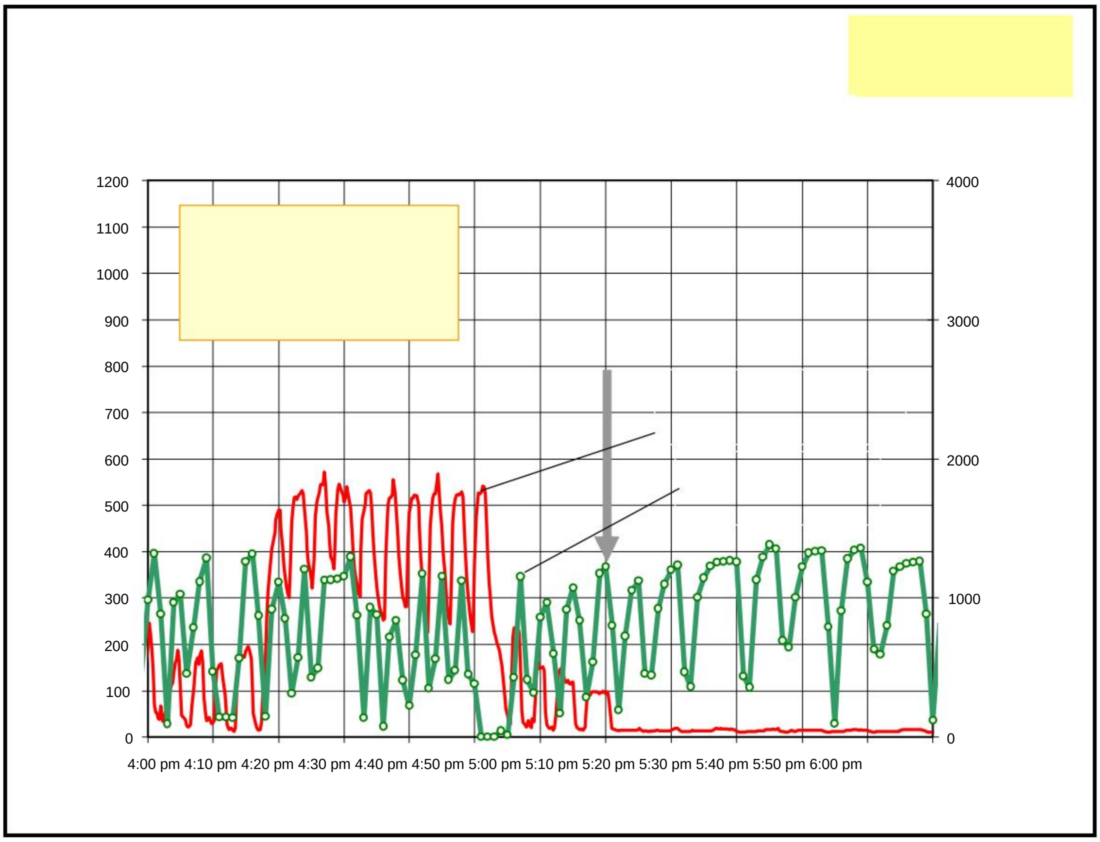
(5-5)

which is often assumed. This Hg chlorination using HCl and oxygen with the formation of water vapor is also thermodynamically permissible as a global reaction (negative Gibbs free energy of reaction), but according to our investigations, it seems that kinetic reasons hardly play a role in the boiler flue gas.

This was demonstrated, among other things, by the SVA operational tests described in more detail with deliberately induced led to (harmonically oscillating) fluctuations in the SO_2 content under high Cltotal load (approx. 20,000 mg HCl/Nm³ dry matter). At the rotary kiln SVA of Bayer Industry Services in Leverkusen-Bürrig works with a controlled sulfur dosage, cf. or patent application Vosteen . The tightening of the regulator intervention by means of the Sulphur granulate dosing screw (cf.) induced (harmonically oscillating fluctuations in the boiler flue gas had the same direction fluctuations in the Hgmet content in the boiler flue gas, cf. . With higher SO_2 content the boiler-internal Cl_2 reduction is strengthened according to Eq. (5-2) and thus reduced – despite high HCl load – the Hg chlorination according to Eq. (5-4), ie with increasing residual SO_2- At the same time, the Hgmet content in the boiler raw gas must also increase and vice versa.


Solid sulfur
S, Cl (disturbances)
rotary kiln
NBK
+
boiler
HCl
Cl2
SO2
Quenching
+
sour
washer
SO2-IST
PI
SO2 target
S-dosing ramp
SO2
HCl
HCl
1...Setpoint device
2...Control device
3...Actuating device
4...Control system





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In a sense, elemental mercury in the boiler flue gas could be found in a sea of clouds of gaseous hydrogen chloride HCl (here approx. 20,000 mg/Nm³ tr.) and it would still hardly anything, unless the gaseous free chlorine Cl_2, formed from HCl, is present as an intermediate. However, how much of the reproduced and quickly consumed (intermediate) free chlorine serves as a reactant for the direct chlorination of the gaseous metallic The amount of mercury available depends on the SO_2 content. This applies at least in the boiler flue gas before the SCR-DeNOx catalyst.

During the subsequent flow through an SCR (not present in the rotary kiln SVA) DeNOx catalysts in raw gas circuit (before flue gas scrubbing), on the other hand, would very likely apparently catalytically accelerates all of the above-mentioned reactions, not least the Chlorine-Deacon reaction according to Eq. (5-1) and direct Hg chlorination according to Eq. (5-4), cf. Vosteen . Furthermore, a V_2O_5-rich SCR DeNOx catalyst would probably also an indirect Hg oxidation according to Eq. (5-5) can take place (without the requirement of a “three-erstoßes”), mediated by the V_2O_5 as a self-regenerating oxygen donor for the components reacting with each other in the adsorbed state on the catalyst surface. components Hgmet and HCl, cf. Bierögel . *)

In /20/ there was talk of “closed sulfur and chlorine balances” in SVA combustion. chlorinated liquid waste has been reported, cf. The sulfur Inputs via the added sulfur granulate (and the waste) compared to the sulfur discharges with the flue gas (SO2) or with the waste water (SO4 2-)); based on such sulfur balances, a rising chlorine load in the boiler flue gas was determined according to the chlorine Griffin reaction increasing SO2 consumption or a corresponding Cl2 consumption of Boiler flue gas approx. 3% of the total Cl load.

Based on such balance sheets, shown that the boiler flue gas always contains only small amounts of intermediate free chlorine are involved.**)

Increased SO2 loads, which are specifically used to suppress free chlorine and if necessary from other free halogens and thus to the desirable suppression of dioxin /furan denovosynthesis are used in practice (see for example Vosteen), remove the reaction partner Cl2 from this undesirable reaction, but limit but at the same time the desired direct Hg chlorination occurs.

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*) The fact that Hgmet adsorbs on a V2O5-rich SCR DeNOx catalyst, but is chlorinated by HCl/Cl2 to the more volatile HgCl2 and then desorbed as Hg ion with the denitrified clean gas, was already observed and investigated in detail in the work /22/ in 2000, see also /23/, /24/. In this context, note the earlier ; there it was seen how four Hgmet peaks in the tail-end SCR of the rotary kiln SVA "disappear", each if they do not reappear in the denitrified clean gas; instead, a slightly increased, long-term discharge to Hgion.

**) In the Leverkusen-Bürrig waste disposal center of Bayer Industry Services GmbH, in addition to the “closed Sulphur and chlorine balances” also “closed sulphur and bromine balances” and finally “closed Sulphur and iodine balances”, cf. Wieland /26/, Standau /28/.

From the ordinate sections at 0 mg Cl- /Nm³ d. (chlorine-free operation) an SO2 for the case of “chlorine” consumption of 8 wt.% caused solely by direct SO2/SO3 conversion is obtained , corresponding to a stop temperature of 900 °C (at the rotary kiln SVA investigated, in the investigated operating condition).

However, at high Cl loads, not only 3 wt.%, but a total of approximately 4 wt.% of the Cl load is present as free chlorine Cl2. The 3 wt.% (= 75% of the intermediate free chlorine) is found as HCl in the acidic scrubber wastewater, as evident from the SO2 consumption (balance up to and including the acidic scrubber zone). An additional 1 wt.% (= 25% of the intermediate free chlorine) is found as NaCl in the alkaline wastewater, based on the balance up to and including the alkaline scrubber zone; see Wieland.

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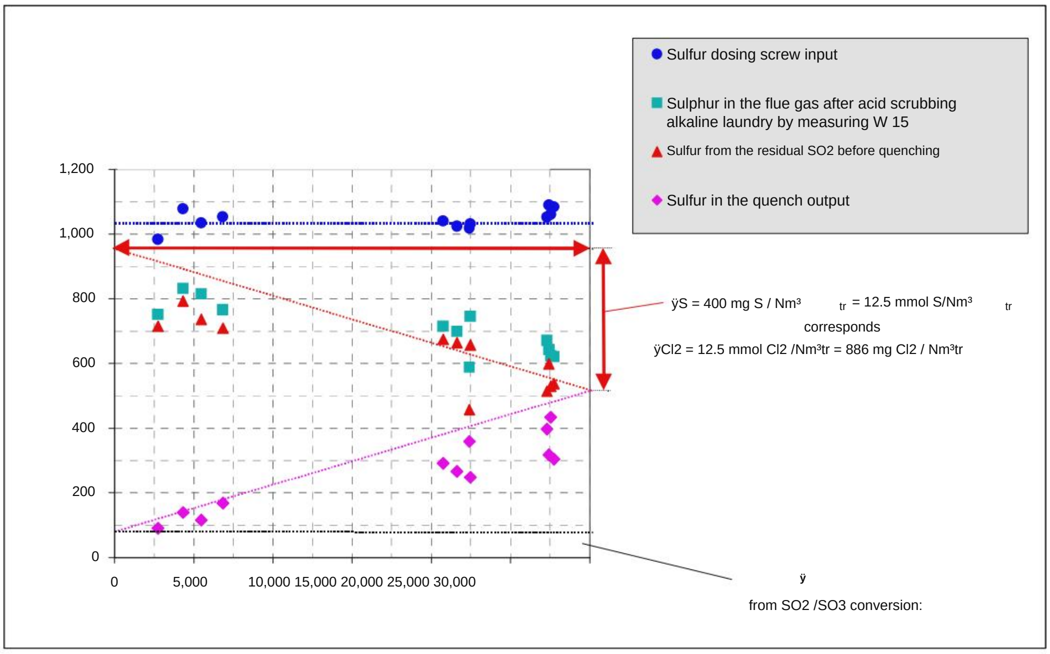
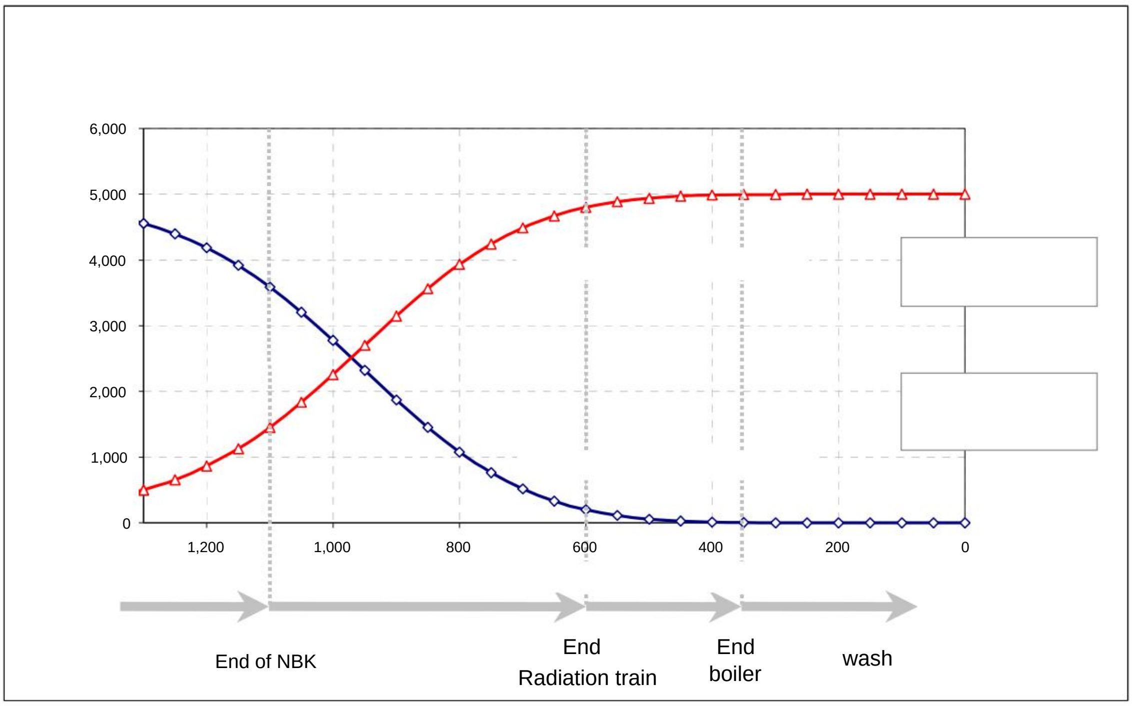
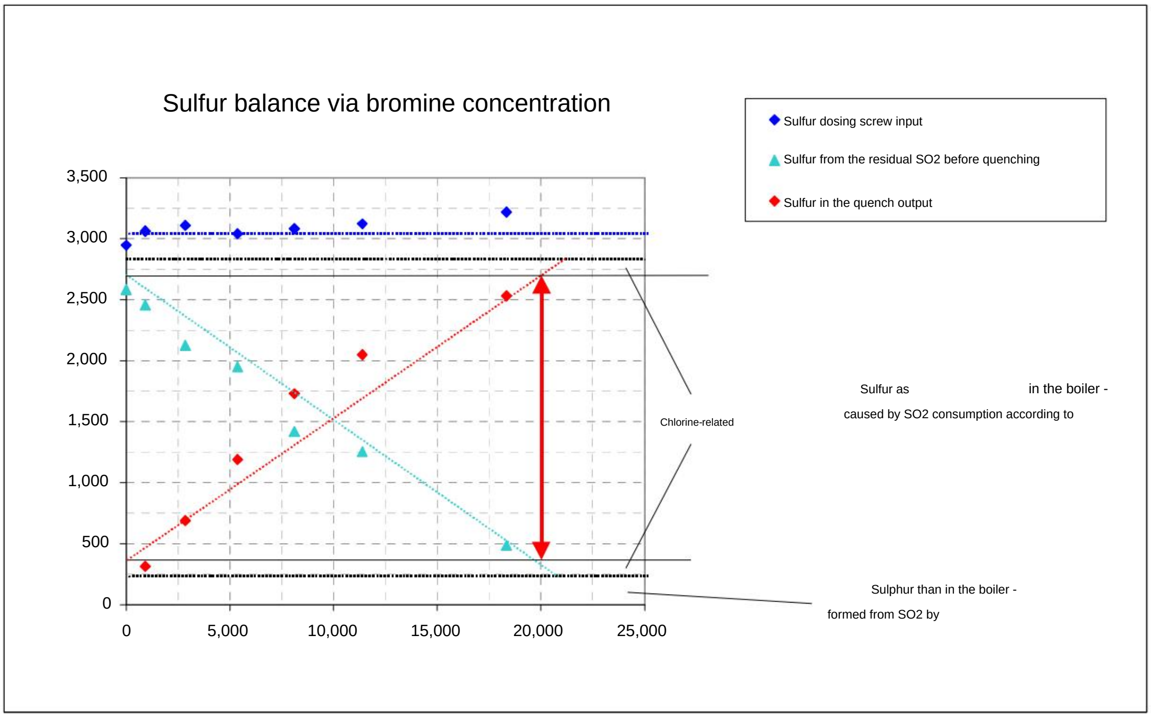
At low Cltotal loads, as in the case of pure coal combustion, the proportion of intermediate free chlorine increases to considerably lower proportions far below 1 wt.%, cf. Pohontsch Wieland This essentially follows from the concentration dependence of the chlorine-Deacon equilibrium.



Between the chlorine- or bromine-assisted Hg oxidation in combustion flue gases – such as in Boiler flue gas from a hazardous waste incineration plant (SVA) or a coal-fired Although there are considerable similarities at first glance, such as a slag-chamber boiler power plant or a fluidized-bed incinerator for sewage sludge, as examples discussed below, these only concern parts of the reaction process. hens, but there are also considerable differences (“analogy deficits”), which have not yet been are enlightened.

Probably in the case of “bromine” only direct Hg-halogenation is possible, ie a Hg-Bromination analogous to Eq. (5-4) and not an indirect Hg bromination analogous to Eq. (5-5), bend; therefore, it seems favorable that the equilibrium of the Brom-Deacon reaction, as As shown by a calculation example, lies much more strongly on the side of the free halogen (here, Br2) than in the case of "chlorine". Note the concentration dependence here too (shift of the "intersection" of both curves to the right with decreasing Br concentration and vice versa). If the previously unknown stop temperature of the bromine deacon-reaction as high as the stop temperature of the Chlor-Deacon reaction (namely at 680°C), the “bromine” in the rear part of the kettle would largely be present as the highly reactive Br2. The same applies to the iodine-Deacon reaction, cf. Standau .





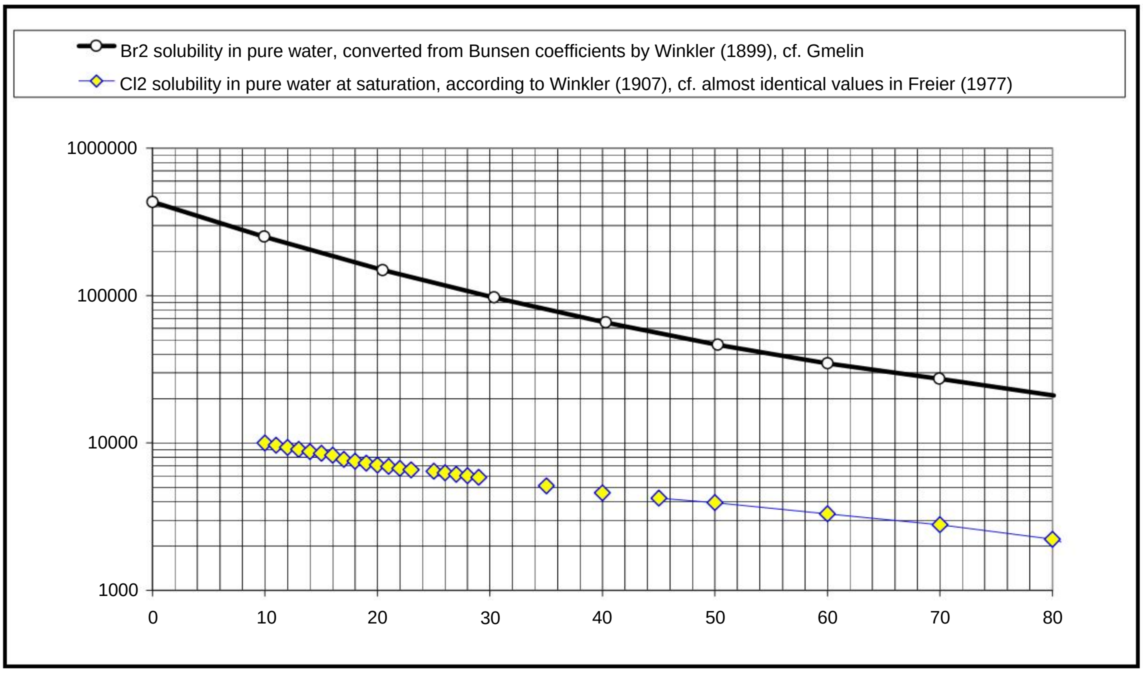
The sulfur balance in the case of “bromine”, cf. , very similar to the Schwe-

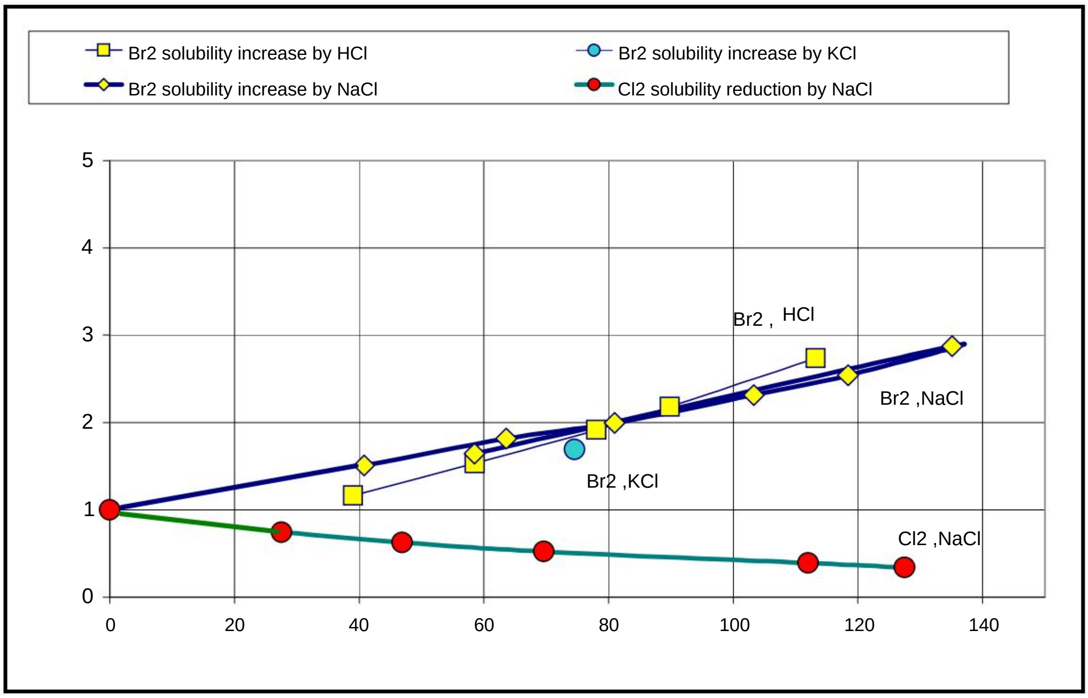
field balance in the case of “chlorine”, see previous .

The visible (supposed) SO_2 consumption is based – in contrast for the case of “chlorine” – not on a “bromine-Griffin reaction” analogous to Eq. (5-2). Because in the In contrast to the Chloro-Griffin reaction according to Eq. (5-2) (Gibbs free reaction enthalpy < 0) is The bromine-Griffin reaction is not thermodynamically favored (Gibbs free energy of reaction > 0), see Wieland. The same applies to the iodine-Griffin reaction, see Standau .

Vosteen had initially tried to use alleged To solve the “bromine puzzle” by considering other possible gas phase reactions between Br_2 and SO_2 be included, such as chloro-sulfurylation ( ) or the bromine Sulfurylation ( ), see Standau While the chlorosulfurylation remains uninteresting from a thermodynamic point of view, since thermodynamically it is not favored (Gibbs free reaction energy > 0) , bromo-sulfurylation is quite conceivable, because it is thermodynamically favored (Gibbs free reaction enthalpy < 0), and chen are the subsequent reactions between sulfuryl bromide and Hgmet, cf. Standau In contrast to sulfuryl chloride (not of interest here) as a well-studied Intermediate product in chlorine chemistry, little is known about sulfuryl bromide. Therefore It remains open until further notice whether the conceivable reaction of Br_2 and SO_2 to Br_2SO_2 with subsequent following gas phase oxidation of metallic mercury by the hypothetical Br_2SO_2 at all. Doubts about this were expressed by Ziegler, among others. The question of possible Gas phase reactions are currently being investigated in more detail by Kanefke using laser mass spectroscopy. seeks.

The at first glance extremely similar sulphur balance in can, as we today know, can also be interpreted quite differently. The first thing to consider is the following: The extremely low water solubility of Cl_2 is offset by a considerably better water solubility ity of the Br_2 , cf. ; the solubility of Br_2 is evident in the scrubber temperature range of interest from 55 °C to 75 °C, even in halide-free (pure) water, is more than 10 times greater than that of Cl_2. In addition, the sub- difference in the solubilities of Br_2 and Cl_2 increased even further when halides were added, by increasing the Br_2 solubility with the addition of halide, while the Cl_2 solubility continues decreases, cf. .





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Next, it should be noted that SO_2 and Br_2 with the other flue gas components (especially with H_2O and O_2) other reactions – not yet considered here – can occur.

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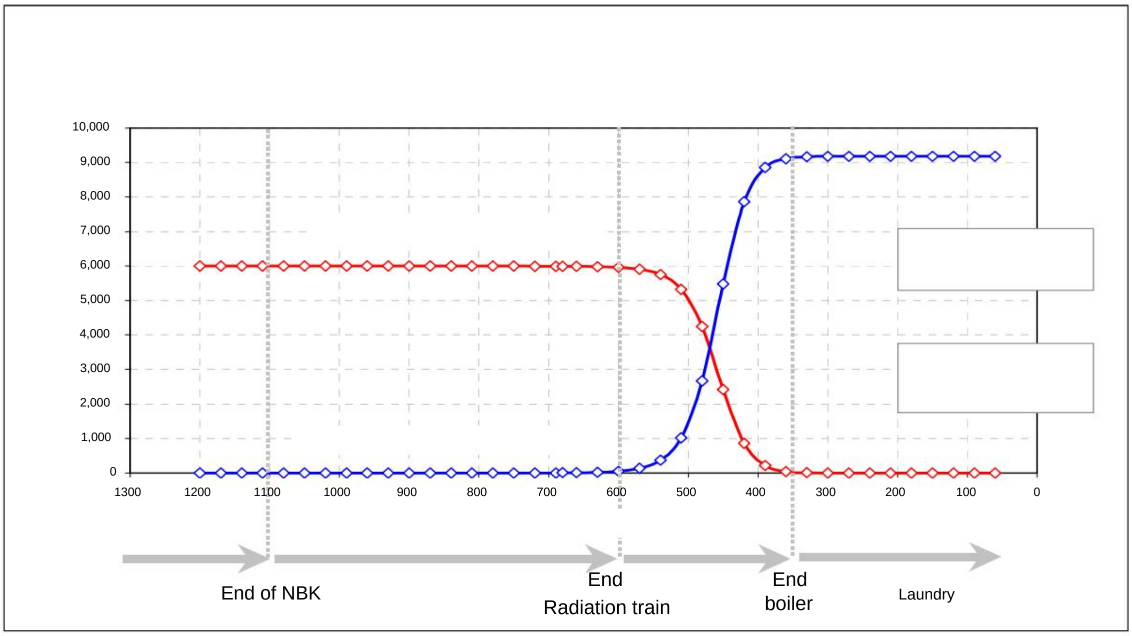
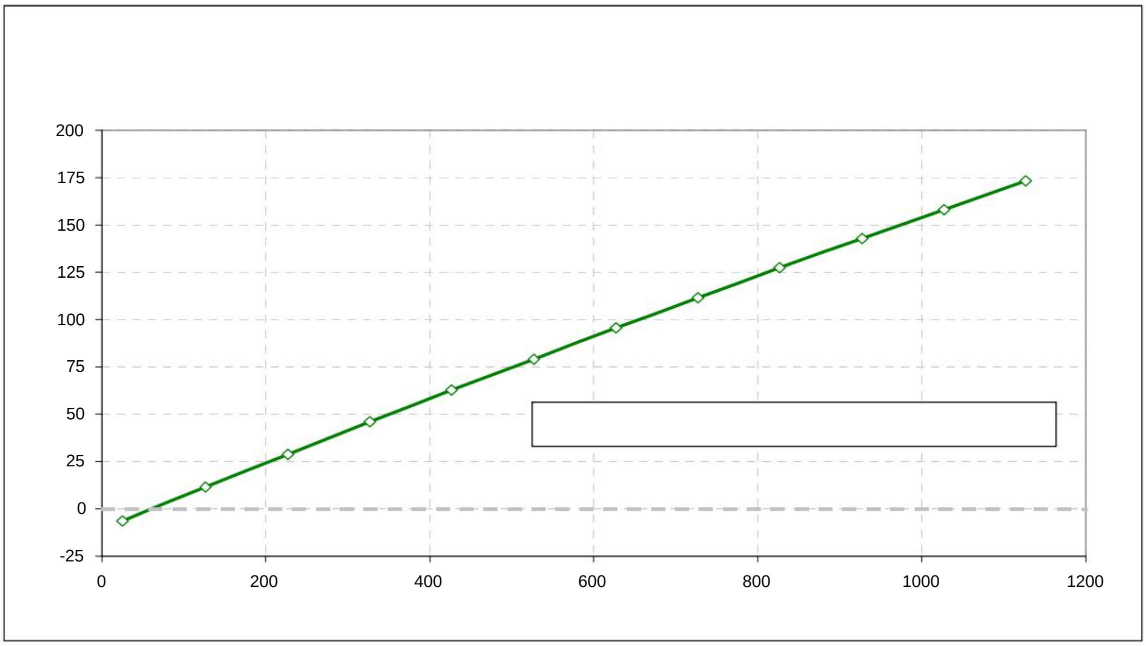
*) Br_2 measurement data at 25 °C (and 20.8 °C) from Seidell (1919) and Linke (1958), Cl_2 measurement data at 20.1 °C according to Oliveri-Mandala (1920), Gmelin, Vol. Cl, p. 45. In the case of Cl_2, a similar reduction is observed upon addition of HCl or Metal chlorides, see Gmelin, Volume Cl, p.46.

This shows an example calculation for the SO_2/H_2SO_4 conversion. This This reaction could contribute to the SO_2 consumption. However, it is assumed that this reaction tion in the boiler flue gas is kinetically strongly inhibited, otherwise every rotary kiln SVA would have enormous me problems from sulfuric acid aerosols, which thankfully is not the case.





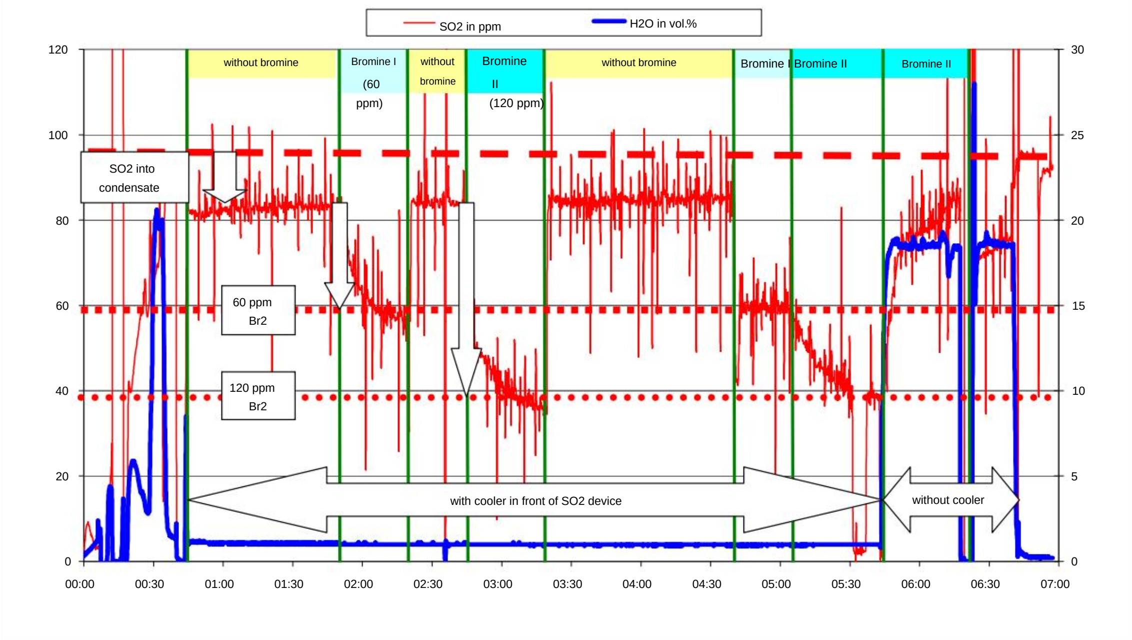
The (thermodynamically unfavored) Bromo-Griffin reaction results in a sense by summation of the Brom-Deacon reaction and the direct SO2/SO3 conversion. there is the so-called bromine-Bunsen reaction as a summation of the bromine-Deacon reaction and the SO2/H2SO4 conversion. The bromine-Bunsen Reaction is thermodynamically favored only in the lowest temperature range, namely in the shear range, cf. ·

The bromine-Bunsen reaction is thermodynamically not possible at the higher flue gas temperatures temperatures in the boiler, but in the range of low scrubber temperatures, when even weakly, cf. The observed SO2 consumption could therefore be in the acidic scrubber area as the first scrubber stage, either in the gas phase or at/in the bromine-containing important washing water drops.

The bromine-Bunsen reaction is the basis of a patent filed in 1984 for a process for flue gas desulfurization using Br2, which is produced by electrolysis from aqueous HBr solution. will be won, cf. Langenkamp and van Velzen According to the patent, SO2 and Br2 react in the scrubber according to the bromine-Bunsen reaction. The HBr- and H2SO4-rich scrubber wastewater is separated into two separate stages for the purpose of a) recovery of concentrated HBr solution, b) Evaporated to obtain concentrated sulfuric acid.

Finally, let us take a recent laboratory experiment by Kanefke with Conventional operational SO2 measuring devices - such as the one at the end of the boiler of the rotary kiln wastewater treatment plant in Leverkusen-Bürrig - are designed to protect against contamination and acidic flue gas components with an upstream cooler. Instead, the Laboratory a so-called hot gas measuring device (initially without upstream cooler) from the company Leybold-Heraeus, now Emerson Process, (model BINOS HT 5). Internally, SO2 is measured using UV absorption and vaporous H2O is measured. by means of IR absorption. This device is rarely manufactured today because of the corrosive on-resistant expensive interior design (acid gases) is hardly used in incineration plants The entire test section was heated to >110°C to ensure that no acid condenses out under the test conditions. The model gas was slightly humid air and humidified air with 18 .. 19 vol-% H2O were used (200 °C, 200 Nl/h). Furthermore, the normally dry operating hot gas measuring device has been given a Flue gas cooler from Gröger and Obst (model: G0-PKK) is installed upstream, which cools the Br2 and SO2-containing model gas cools below 5°C and thus its water vapor is almost completely condensed.

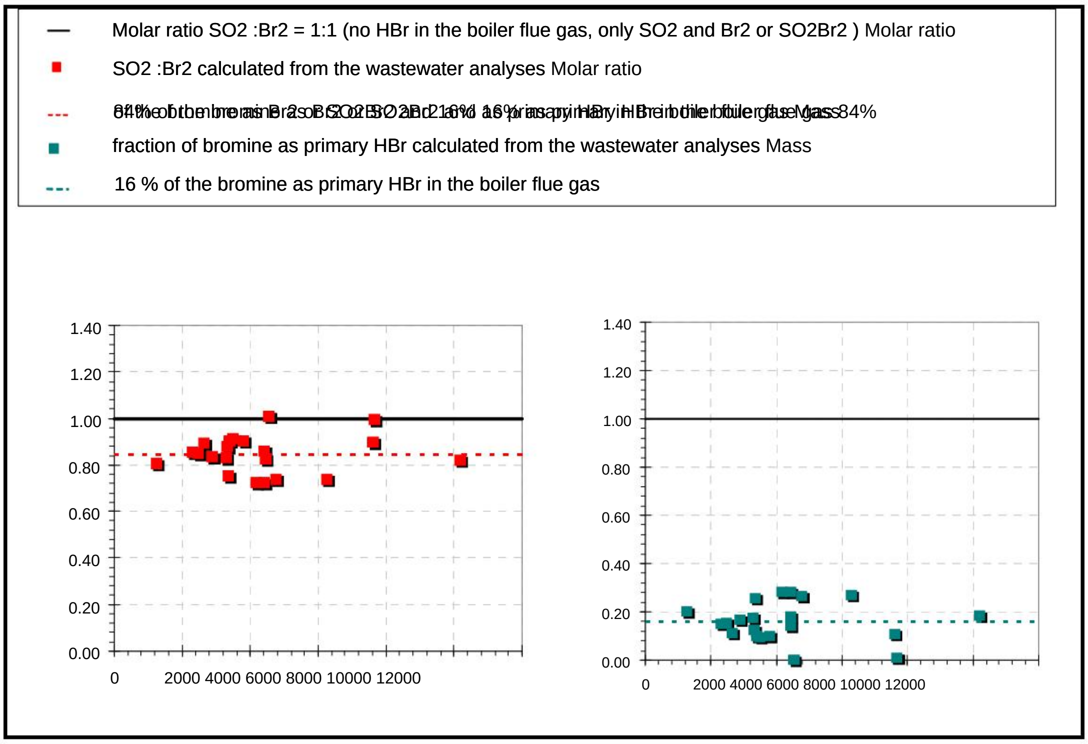
The comparison measurements without upstream cooler (hot gas measurement) and with upstream cooler (simulated operation of today's common SO2 measuring devices) in order to detect possible "bromoto uncover the “side effects” of today’s standard SO2 measurements. The highly in-interesting result shows the following The SO2 concentration in the The raw gas was set to approximately 95 mg SO2/Nm³ f. When the cooler is in operation, Apparently, a small amount of SO2 is in the condensate. If 60 ppmv (“Bromine I”) or If 120 ppmv of Br2 (“Bromine II”) is added, the SO2 level drops (still during cooler operation). measurement signal (delayed Br2 injection due to Br2/carrier gas mixing vessel). sudden shutdown of the Br2 feed (bypassing the Br2/carrier gas mixing vessel) the SO2 measurement signal increases abruptly. The further course of the experiment showed that if the cooler is not in operation, the Br2 addition of 60 ppmv (“Bromine I”) or 120 ppmv (“Bromine II") did not lead to a reduction in the SO2 measurement signal. The fact that (towards the end of the test) the 95 mg SO2/Nm³ f. was achieved is due to the increased addition of water vapor.



The experiment described proves two things: The previously observed sulphur balances The SO2 consumption by “bromine” is still due to free bromine, but it is not necessarily be attributed to a gas phase reaction in the boiler flue gas. Boiler flue gas no SO2 consumption and therefore no corresponding Cl2 consumption; but this is not certain either, because a (preceding) gas phase reaction in the high-temperature rated boiler flue gas (< 200 °C) cannot yet be ruled out.

The SO2 concentration observed in the operational SO2 measurement (presumably in the boiler flue gas) The following SO2 and Cl2 consumption is at least partly a result of the bromine-Bunsen reaction in the sample gas cooler. From the point of view of exact SO2 measurement, this SO2 consumption in the cooler causes This is an SO2 measurement error. However, from a process engineering point of view, the “artifact” is by no means disturbing, quite the opposite. Exactly what happens in the cooler in the presence of condensate, namely the bromine-Bunsen reaction, also takes place in the first acid scrubber stage and has The result is that in the acidic scrubber wastewater almost all “bromine” is recovered as dissolved HBr. Wieland. Of this HBr dissolved in the acidic scrubber wastewater, as

shows, for example, only about 16% as primary, ie as already in the boiler flue gas HBr present, while 84% is to be regarded as secondary, ie as only in the scrubber according to HBr formed from Cl2 in the Bunsen reaction . The latter is determined from the corresponding SO4 2- concentration in the acidic scrubber wastewater.



The example of bromine-assisted wet Hg deposition on a comparatively small mono-incineration plant for waste, namely a fluidized bed combustion plant for municipal sewage sludge, had shown that the The costs associated with the process, both in terms of investment and operating resource requirements are low, so that the process leads to significant annual savings tion leads.

In addition, a comparative cost estimate for the application of bromine-based Hg capture on coal combustion or the co-combustion of waste in coal power plants.

The combustion of a German hard coal with 0.2 mg Hg/kg coal wf. *) and 0.1 wt.% Cl is assumed. In the USA, for example, such a hard coal would be equivalent to a comparable to “eastern bituminous coal”.

It is a power plant of 700 MWel (= 700,000 kWh/h), corresponding to approximately 1750 MWtherm, with a volume flow of approximately 2.1 million Nm³ dry matter/h (at approximately 5 vol.% O2 dry matter). The Hg concentration in the boiler flue gas is (due to 10 Nm³ dry matter/kg hard coal dry matter) approximately 20 µg Hg/Nm³ dry matter in the boiler flue gas (= 42 g Hg/h = 344.4 kg Hg/a at 8,200 h/a in the case of high availability). Examples with significantly different flue gas cleaning systems are considered. (RGR):

This power plant only uses primary RGR measures, ie it has no further downstream flue gas cleaning, but only a fabric or electrostatic precipitator (EGR). This is the case in Germany, for example, when burning lignite in circulating In the USA, there are still many dust-fired Power plant boilers only with dust filter, ie without additional primary or secondary RGR Measures.

This power plant with dry ash boiler also works with fabric filter or EGR (no flue dust recirculation into the furnace), but then has a wet flue gas desulfurization plant (weak acid REA).

This power plant with wet ash smelter boiler also works with fabric filter or EGR (but now with flue dust recirculation into the slag heap boiler furnace) and then again has a wet flue gas desulphurisation plant (weak acid REA).

This power plant with fabric filter or EGR has a dry or wet ash boiler (without/with flue dust recirculation into the furnace) and also have a wet flue gas desulfurization plant (weak acid REA), but now with an upstream SCR DeNOx catalyst.

The residual C-containing coal dust in the fabric or electrostatic precipitator is, as we have shown, 33.3% of the Hg is adsorbed and – in power plant examples A and B without dust recirculation into the furnace – removed with the flue dust, ie the Hg-Concentration in the dedusted raw gas is reduced by one third to approx. 13.33 µg/Nm³ tr. In Power plant example A, ie without downstream wet FGD, this would also correspond to the con-concentration at the chimney. The mercury discharge with the filter dust would therefore be 14 g Hg/h (= 114.8 kg Hg/a at 8,200 h/a in case of high availability).

In power plant example C, a further wet Hg separation (Hgion-Absorption in the subsequent wet FGD). The Hgion/Hgges species fraction and thus the Hgges separation efficiency of the FGD is around 60%, given the coal-related only approx. 100 mg Clges/Nm³ dry matter. The Hg concentration in the scrubbed clean gas after REA and thus at the stack decreases therefore to approximately 5.33 µg Hg/Nm³ tr. The additional Hg-Discharge with the REA fine sludge and the REA gypsum (REA wastewater almost Hg-free) thus carries 16.8 g Hg/h (= approx. 137.8 kg Hg/a at 8,200 h/a in case of high availability).

If, apart from other problems (hot spots, fly ash quality seal), one wanted to achieve If PAC injection before the dust filter achieves approximately 95% Hg separation, then approximately 18,000 kg PAC/kg Hg is required, see Figure 1-8 in the introductory chapter. This would correspond to 18 x 20 mg PAC/Nm³ tr. = 360 mg PAC/Nm³ tr. This figure corresponds to a US guideline size of < 500 mg PAC/Nm³ tr. (Babcock Power Environment). This corresponds to an activated coal requirement of 18000 kg PAC/kg Hg x 95% x 344.4 kg Hg/a = 5889 t PAC/a. In

In the USA, activated carbon currently costs approximately \$0.50/lb, equivalent to \$1110/t, for large quantities. This results in PAC costs of \$6.54 million per year, or approximately \$5.30 million. *)

In the USA, work is currently being done on Hg reduction by injection of sodium tetrasulfide as a more cost-effective "emerging technology", see Gale . The former L. & C. Steinmüller GmbH, Gummersbach, is used in Germany, for example, in the waste Kassel combined heat and power plant has been successfully used for a long time. According to Babcock Power Environment According to the latest pilot plant experiments at the Southern Research The Soil Science Institute (SRI) estimates that approximately 100 mg Na_2S_4/Nm^3 dry matter is sufficient for 95% Hg removal. Sodium tetrasulfide currently costs \$800/t of 35% solution in the USA, which corresponds to \$2286/t of pure Na_2S_4 . The annual requirement is calculated at 1722 t Na_2S_4/a, corresponding to corresponding Na_2S_4 costs of \$3.89 million/year = approx. 3.15 million

In the power plant example A considered, a 95% Hg separation can only be achieved with dust filters. and injection of bromine alone is unlikely to achieve this. However, 95% Hg removal could be achieved by combining the bromine injection with a limited PAC injection. To further validate this variant of the bromine-supported Hg dry sorption was recently tested in cooperation with Vosteen Consulting GmbH by SRI at the (DOE) a corresponding three-year research project applied for, see Gale . Although we do not want to compromise the further research results anticipate, but based on the experiences described in this study justifies that a bromine addition of just under 20 mg Br_{ges}/Nm^3 tr. will be sufficient (Br/Hg mass ratio >> 500) and that the PAC injection can be reduced to approx. 100 mg/Nm^3 tr. due to the bromine addition, ie to only one fifth of the previously required The amount of PAC required has been reduced. This results in PAC costs of only approximately 1.06 million. Fifth of the previous 5.3 million

Bromine costs would be added. Bromine can be supplied in various forms, e.g., as an aqueous solution of 48 wt. % HBr, as dry NaBr salt, or as aqueous NaBr-Solution.

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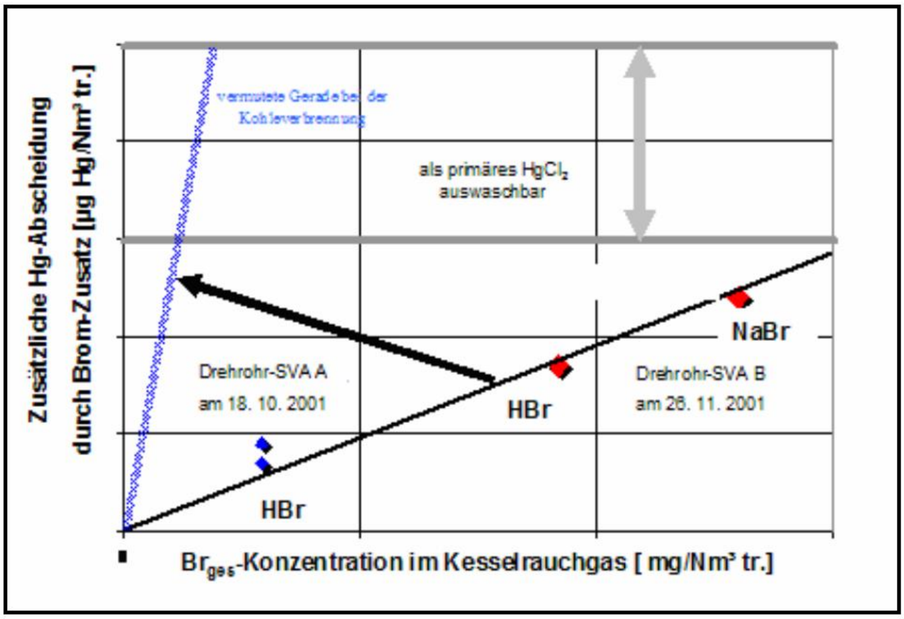
*) The American literature so far assumes PAC injection as the basic technology and currently estimates the Costs for additional Hg separation at \$22,000 … \$33,000/lbs Hg = approx. \$48,888 … \$73,333/kg Hg, cf. Pavllish /. In the above case study A1 (only fabric or electrostatic precipitator, only PAC injection, 95% total Hg removal) According to the example calculation, we arrived at PAC costs of \$6.54 million/year and an additional Hg removal of approximately 217.9 kg/year (66.6% of the raw gas load, less 5%), resulting in approximately \$30,000/kg of additional Hg removed. However, this does not include the investment for PAC provision and injection. In any case, our Estimate for this comparison case by no means too high.

The guide price for (high-purity) products is currently around 750 HBr 48 for bulk deliveries % equivalent to 1582 /t bromine (pure), or 1100 -salt, equivalent to 1417 t bromine (pure), on average about 1500 In the case of small deliveries, the price may by almost double; for example, 1350 HBr 48% was paid for small deliveries for operational trials in 2003. Since high-purity products are not required,

However, the bromine price will still be significantly lower. The bromine requirement is calculated at estimated 20 mg “bromine”/Nm³ d. to approximately 340 t bromine (pure)/a, corresponding to an average of 1500 Bromine (pure) the annual bromine costs amounted to 340 t/ax 1500 total operating 1 million . In costs would therefore be 1.57 million /a for bromine and PAC in total.

This is significantly cheaper than in the two previously considered cases A1 (5.3 million). and A2 (3.15 million . Another advantage (with regard to the quality seal for the fly ash Recycling in concrete) would be the noticeable relief of the EGR filter dust from PAC-related Residual carbon.



This power plant with dry ash-cleaned boiler (without fly ash recirculation into the furnace), or with wet ash-removed boiler (with fly ash recirculation into the SKK furnace) works with fabric filter or electrostatic precipitator and then has a wet flue gas desulfurization plant (weak acid REA). Therefore, PAC addition does not appear necessary at all. If bromine is added (as before), this would be fed into the FGD with the dedusted raw gas The mercury introduced, probably almost completely oxidized (approx. 13.33 µg Hg/Nm³ dry matter) is washed out there to approximately 0.7 µg Hg/Nm³ dry matter (at the stack) (Hg removal efficiency of the FGD > 90%). Therefore, no PAC costs would be incurred here. The bromine costs and the associated with the additional operating costs totaling 340 t/ax as before

1500 0.51 million When co-incinerating sewage sludge containing Hg, for example, the bromine requirement may increase slightly.

Thus, the additional operating costs would be 5.30 million per year compared to the pure PAC-Injection in power plant example A1 previously (only fabric or electrostatic precipitator) to 0.51 million $/a for the pure bromine injection (fabric or electrostatic precipitator + wet FGD), ie by about a factor 10 reduce.

These example cases differ from the previously considered example cases B and C only by the fact that the wet REA is preceded by an SCR-DeNOx catalyst, whether before or The question of whether the dust filter is suitable remains to be seen. The SCR catalyst is known to have a further de Hg oxidation, simply due to the “chlorine” caused by the coal. Since the catalyst bed all reactions involved and thus also the Hg bromination are “accelerated” it can be assumed that the bromine demand will decrease even further.

Overall, the bromine-based process presented in this study offers Hg oxidation thus supported both the technical possibility for a significant improvement wet or dry Hg separation and at the same time a considerable savings potential, especially in the power plant sector.

The process of bromine-assisted Hg deposition has been used very successfully since autumn 2000 at two hazardous waste incineration plants of Bayer Industry Services GmbH (rotary kiln furnaces with multi-stage wet RGR, wet EGR, and tail-end SCR). From autumn In 2004, another industrial application of the process was carried out at two municipal sewage treatment plants. sludge incineration plants (fluidized bed combustion with NSCR denitrification, EGR and two-stage wet RGR). Operational trials for coal combustion itself as well as for the co-combustion of Hg-containing waste in coal-fired power plants were carried out in 2002 at a Industrial power plant with slag heap firing (SKK firing with EGR, wet FGD, tail-End-SCR). Further tests on dry- and wet-ash de-ashed large power plants with wet RGR are planned in the Ruhr area. In April 2004, the Southern Research Institute submitted a three-year research project to the US Department of Energy on bromine-supported Hg Deposition has been applied for; extensive test series are planned on the dust-fired SRI pilot plant with different cleaning variants (dry or wet RGR).

At the MLU Institute for Environmental Protection Technology (Head: Prof. Dr.-Ing. habil. H. Köser) in spring 2002, in cooperation with Prof. Vosteen and Prof. Köser with support from the Bavarian er Industry Services GmbH has established a new “research focus on mercury.” Four Test benches have been created since then . In cooperation with industry (Bayer Industry Services GmbH, E-ON Engineering GmbH, Lhoist Research & Development, Vosteen Consulting GmbH) laboratory tests on Hg deposition are carried out, including further leading work specifically on flue gas-side Hg halogenation (without and with SCR) and on bromine-assisted wet and dry Hg deposition.

The following overall picture has emerged for bromine-assisted wet Hg deposition to date:

a) Due to the Brom-Deacon reaction, the boiler flue gas – even at higher Temperature – a comparatively high proportion of the “bromine” as the reactive Br_2 is available. placed.

b) Since the Bromine-Griffin reaction is not thermodynamically favored, there is possibly hardly any sulfur-related Br_2 consumption in the boiler flue gas, ie the Br_2 would be for the desired Hg bromination in the entire boiler.

c) If sulfuryl bromide is formed from Br_2 and SO_2 in the boiler flue gas (detection is missing so far) as a further reaction partner for Hg bromination, would be - despite the due to conditional Br_2 consumption in the boiler flue gas – a flue gas-side Hg-Bromination is also possible in this (previously hypothetical) way.

d) The Br_2 separation in the subsequent wet flue gas cleaning is in the presence of sufficient SO_2 is not a problem at all (due to the bromine-Bunsen reaction).

e) HBr deposition is also not a problem due to its good water solubility.

For the bromine-assisted dry Hg deposition, in addition to the above-mentioned ten points – furthermore:

f) flue gas components such as hydrogen halides and free halogens, SO_2/SO_3/H_2SO_4 as well as of course H_2O and O_2 play a role in the chemisorptive processes on the C-containing or C-free adsorbent on site, ie on/in the highly porous sorbent grain. a big role. *)

g) The increased "production" of various substances in the case of bromine addition probably leads to diluted sulfuric acid on/in the sorbent grain to its immediate "self-doping" and thus promotes the dry Hg separation to a particularly high degree, since Hgmet in Sulphuric acid dissolves very well and is present there as the relatively stable, insoluble mercury sulfate $HgSO_4$ precipitates, see earlier German literature on self-doping of activated carbon**) as well as Schofield //.

There are still some questions open here, although Schofield // recently said: "Mercury combustion resolved chemistry". *)

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*) Consider, for example, the condensation of diluted sulfur compounds, which is also possible at elevated temperatures. acid in the micropores of activated carbon (Thompson capillary condensation, acid dew point undershoot).

**) The Hgmet deposition on activated carbon (not pre-doped with sulfur or iodine) or corresponding hearth furnace coke (HOK) requires "self-doping", see Vosteen . This is based on bromine-free moist Flue gases on the SO_2/SO_3 conversion at the active centers of the carbon surfaces and the local formation production of sulfuric acid.

Dalton, LW: “”, C & EN, January 19, 2004, pp. 70-
71

Neumann, S.: "

“, Inaugural dissertation, University of Cologne (1997)

Vosteen, B., Kanefke, R., Bierögel, S.: "

“, previously unpublished

light internal study (December 2003), Vosteen Consulting GmbH, Cologne

Carpi, A., Lindberg, SE "

"Environmental Science & Technology 31(7)

(1997), pp. 2085-2091)

Carpi, A., Lindberg, SE, Prestbo, EM, Bloom, NS: "

"

Journal of Environmental Quality 26(6) (1997), pp.1650-1655.)

Dräger, R., Vosteen, B.: "

“, VDI Knowledge Forum, Seminar 433625 on sewage sludge,

Animal meal, waste wood, biogenic waste, 12-13 February 2004, Munich

Waste Disposal Ordinance, "

“, BR

596/00,31.01.01

Vosteen, B.: "

“, GVC technical committee meeting

“High Temperature Technology”, Leverkusen, 26 – 27 January 1995, see also:

Vosteen, B.: " “, lecture at

of the TU Clausthal (1995 … 2003) and “Thermal treatment of waste in the

chemical industry”, lecture at the Martin Luther University Halle-Wittenberg (1999 … 2003)

Hocquel, M.: “ ”, study

on behalf of the State Environment Agency of North Rhine-Westphalia, Essen, ISSN: Technical

reports LUA NRW 2/2003, see also:

Hocquel, M.: “

“, April 2001, Funding project PEF 398002 of the state of Baden-Württemberg, see: http://www.xfaweb.baden-wuerttemberg.de/fofawPEF 398002,eb/print/PEF398002SBer.pdf

Flora, JRV et al.: “

”, Proceedings of the Air Quality (III) Conference ence (2002), see:
http://www.netl.doe.gov/publications/proceedings/02/air_q3/Hargis%20Poster.pdf

Vosteen., B., Beyer, J., Bonkhofer, T.-G., Pohontsch, A., Kanefke, R., Nolte, M. et al.: “”, German disclosure
document DE 100233173 A1 (filed: 22. 7. 2002), see:
http://v3.espacenet.com/textdoc?DB=EPODOC&IDX=CA2435474

Lindquist, O., Rodhe, H.: “”, Tellus (1985), 37 b., pp.
136 - 159

Kanefke, R., Vosteen, B., Köser, H.: "

“, VDI Knowledge Forum Seminar No. 431802: “Mercury – Emissions, Measurement and Mitigation Techniques”, 29-30 September 2003, Dusseldorf

Severit, P.: "

“, Diploma thesis University of Cologne (1997)

Vosteen, B., Nolte, M., Tippelt, P., Kanefke, R.: “Eds

“, VDI Knowledge forum Seminar No. 431802: “Mercury – Emissions, Measurement and Reduction Techniques ken”, September 29-30, 2003, Düsseldorf

Nelson, SG, Jr.: "Sor

”, published patent application WO 03/093518 A1

Nelson, SG, Jr.: "

”, published application US 2004/0003716 A1

Vosteen, B.; Beyer, J.; Bonkhofer, T.-G.: "

“, VDI Knowledge Forum Seminar No. 431801: “Mercury – Emissions, Measurement and Mitigation Techniques”, 26-27 September 2002, Düsseldorf

Bierögel, S., Köser, H., Vosteen, B.: "
“, VDI Knowledge Forum Seminar No. 431802: “Mercury – Emissions, Measurement and Mitigation Techniques”, 29 - 30 September December 2003, Düsseldorf

Pohontsch, A.: "
“, Diploma thesis, BAYER AG, Leverkusen (Supervisor: Vosteen), Zittau/Görlitz University of Applied Sciences – Department of Mechanical Engineering, 2000

Vosteen, B., Beyer, J. and Bonkhofer, T.-G.: "
“, VDI Knowledge Forum Seminar No. 431801: “Mercury – Emissions, Measurement and Minimization techniques”, 26-27 September 2002, Düsseldorf

Vosteen, B., Beyer, J. and Bonkhofer, T.-G.: "
VGB PowerTech 4/2003, pp. 76 – 91, see: http://v3.espacenet.com/textdoc?DB=EPODOC&IDX=CA2435474

Hübner, S.: "
“, Diploma thesis, BAYER AG Leverkusen (Supervisor: Vosteen) Zittau/Görlitz University of Applied Sciences, Department Mechanical Engineering, 1999

Wieland, A.: "
“, Diploma thesis, BAYER AG Leverkusen (Supervisor: Vosteen), Montanuniversität Leoben, 2001

Hazen, C.A, Vosteen, B. et al.: “ ”, Patent application US2003166988 (03/14/2001)

Standau, E.: "
“, Diploma thesis, BAYER AG Leverkusen (Supervisor: Vosteen), Martin-Luther University Halle-Wittenberg, 2002

Vosteen, B., Beyer, J. et al.: "
“, patent application Application DE 10131464 A1 of BAYER AG, 2001, see: http://v3.espacenet.com/origdoc?DB=EPODOC&IDX=JP2003065522&RPN=DE10131464&DOC=cb973ee59d540cc67e39f6b17931d8a84f

Vosteen, B., Kanefke, R., Beyer, J. et al.: " “, Air Quality (IV) Conference, Poster Session, Arlington / Washington DC, September 22 - 24, 2003

Scherer, V., Greczmiel, M.:“ “, Disclosure document DE 44 22 661 of 4 January. 1996

Keller, J.: " “, VDI Knowledge Forum Seminar No. 431801: “Mercury ber – Emissions, Measurement and Reduction Techniques”, 26-27 September 2002, Düsseldorf-village

Kanefke, R.: " “, Diploma thesis, BAYER AG Leverkusen (Supervisor: Vosteen), Martin Luther University Halle-Wittenberg, 2002

Nolte, M.: " “, Diploma thesis, BAYER AG Leverkusen (supervisor: Vosteen), Clausthal University of Technology, 2002

Vosteen, B., Kanefke, R.: " “, internal report, Vosteen Consulting GmbH, Cologne

Kanefke, R.: " “, see: http://ust.iw.uni-halle.de/deutsch/hg-minderung.html

Ziegler, M.: " “, Diploma thesis (supervisors: Vosteen, Köser, Baltin), Martin-Luther University Halle-Wittenberg, 2003

Gutberlet, H., Spiesberger, A., Kastner, F., Tembrink, J.: " “, VGB Power Plant Technology 72 (1992), Issue 7, pp. 636 – 641

Tippelt, P.: " “, Diploma thesis (Be-faithful: Köser, Vosteen, Kanefke), Martin Luther University Halle-Wittenberg, 2003

Pavlish JH, Sondreal EA, Mann MD, Olson ES, Galbreath KC, Laudal D. L., Benson, SA: "", Fuel Processing Technology 82 (2003), pp. 89 - 165

Shoichi, T.; Motoso, I.; Kazuto, M.: " ", patent application JP 2000 197811 (2000)

Vosteen. B.: " ", GVC High Temperature Technology Committee, Leverkusen, January 26-27, 1995

Vosteen. B., Kanefke, R., Nolte, M., Ziegler, M.: " ", VDI Knowledge Forum Seminar No. 431802: "Mercury – Emissions, Measurement and Mitigation Techniques", 29-30 September December 2003, Düsseldorf

Keller, J.: "Hg- ", VDI Knowledge Forum Seminar No. 431801: "Mercury ber – Emissions, Measurement and Reduction Techniques", 26-27 September 2002, Düsseldorf-village

Braun, H., Metzger, M. and Vogg, H.: " ", Chem.-Ing.Techn. MS 1654/88

Bergmann, F.: " ", student work (supervisor: Kanefke), Martin-Luther University Halle-Wittenberg, 2002/03

Stolle, R.: " ", Student work (supervisor: Kanefke), Martin Luther University Halle-Wittenberg, 2002/03

Reidick, H., Reifenhäuser, R.: " ", VGB Power Plant Technology 58 , Issue 12 (1978)

Vosteen, B., Beyer, J., Krippner P.: " ", German pa-Patent application DE10131464 A1 (filed 19 June 2001)

Langenkamp, HW, van Welzen, D.: " ", European Patent O 171 570 B1 (pending July 2, 1985)

Kanefke, R.: "

", 2003 / 2004

Vosteen, B.: "

", contribution to

Industry seminar: "State of the art – flue gas cleaning in combustion plants and Thermal Processes", Stuttgart, 1998

Licata, T.: Personal Communication, Babcock Power Environmental, November 2003

Gale, TK and Merritt, RL: "C

, International Conference on Air Quality IV, Mercury, Trace Elements, and Particulate Matter, Arlington, VA, September 22-24, 2003.

Gale, T.K., "",

Quarterly Report – DE-PS26-02NT41183 for period Oct. 1st through Dec. 31st, 2002.

Gale, TK: "

", research proposal to the US Department of Energy, Southern Research Institute - Environment, Energy, and Engineering Division, Birmingham / AL, in cooperation with Vosteen Consulting GmbH, Cologne, April 2, 2004

Schofield, K.: "y ",

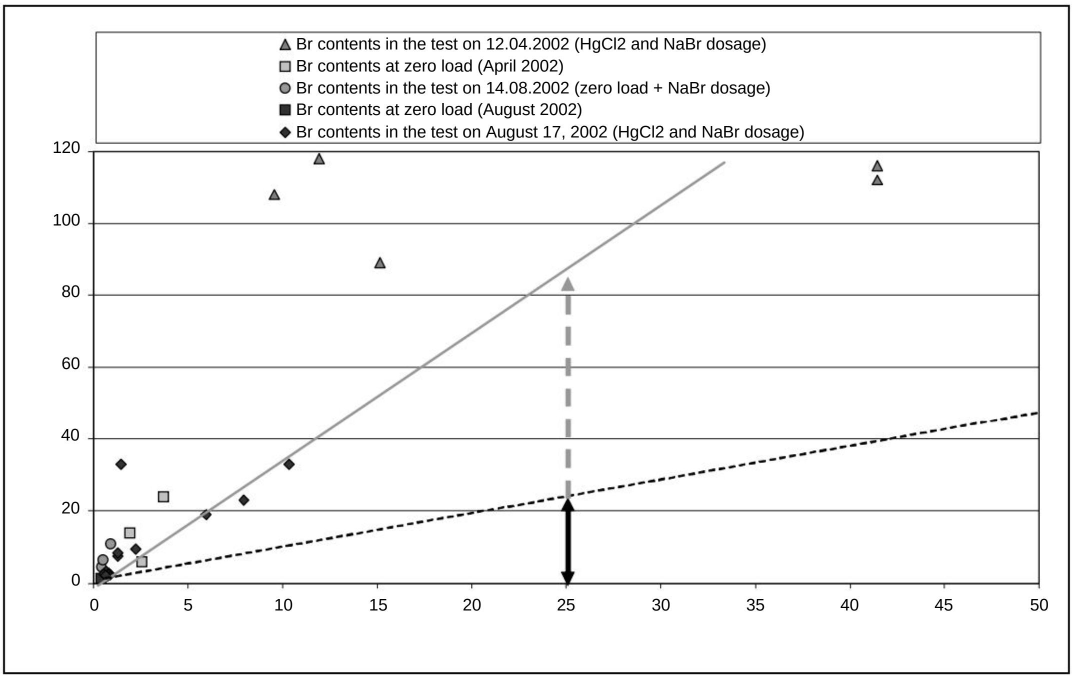
American Chemical Society, Division of Chemistry (2003) 48(2), pp. 777-778

Schulle, M., Ham, R., Neumann, S., Vosteen, B.:

BAYER-

Internal test report for the Leverkusen-Bürrig waste disposal center, 27.03.1996

as well as the other following figures refer to some airborne dust proben, where in addition to the Hg content, the bromine content was also determined.



The abscissa and thus also the dashed diagonal of the image describe the calculated Bromine content corresponding to the Hg content (bromine as adsorbed HgBr2); assuming Adsorption of bromine only in the form of mercury bromide (HgBr2) should reduce the Hg and Bromine contents are in a stoichiometric ratio (dashed diagonal).
HgBr2-related bromine input into the flue dust (and here preferably into the flue coke) makes apparently accounts for less than about 25% of the total bromine input. This shows that in There is far more bromine in the airborne dust than corresponds to a loading of HgBr2 alone. Bromine must therefore also be present in other chemical bonds.
bond could be calcium bromide (CaBr2), for example . As is the case at medium and low temperatures, in the presence of hydrogen chloride (or free chlorine) to form calcium chloride (CaCl2) , hydrogen bromide could lead to the formation of CaBr2 (direct

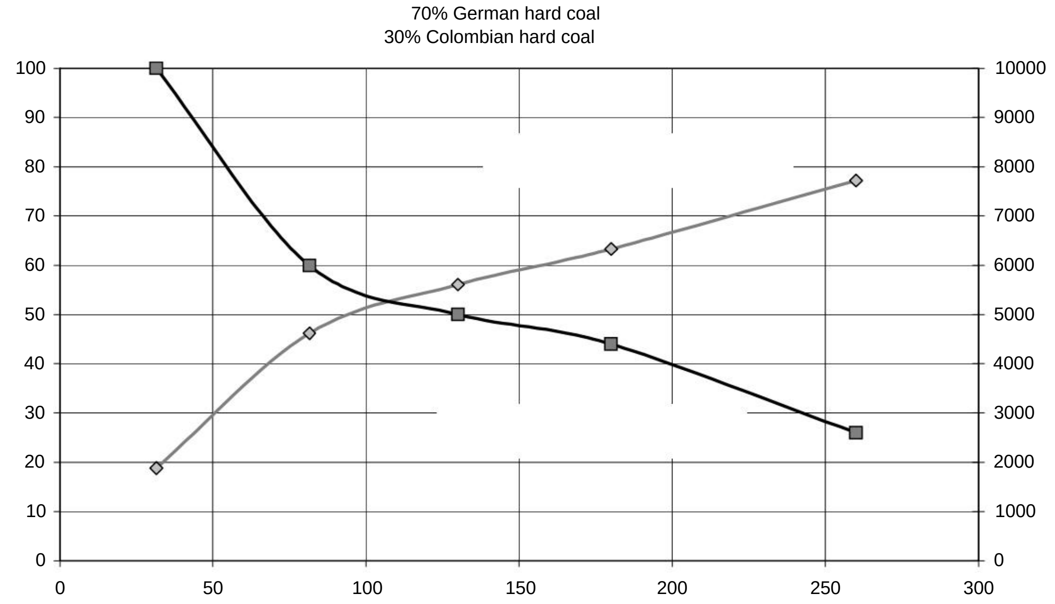
evidence is missing), see previous statements on the bromine-induced SO2/H2SO4 conversion (Bromine-Bunsen reaction with formation of H2SO4 and HBr). However, in the case considered here In the case of a SKK furnace with combustion chamber temperatures of approximately 1450 °C, it can be assumed that the lime produced there from the fly ash carbonates is “burned to death”, ie it is hardly reactive.

In the experiment on 12 April 2002, as a result of the (deliberately excessive) HgCl2 addition in the SKK combustion achieves unusually high Hg contents in the flue dust, cf. . The The zero-load value (pure coal combustion) before the start of bromine addition was already relatively high at 2.4 mg/kg, which was due to the unusually high residual carbon content of the filter dust. was located.

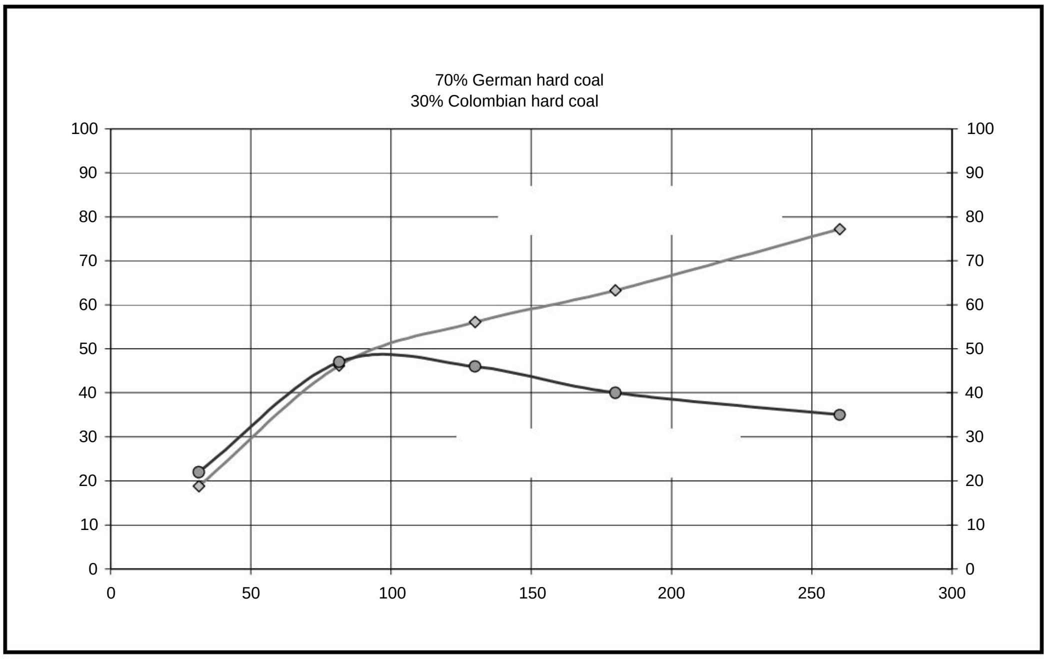
Time [hh:mm]	Hg [mg/kg]	Br [mg/kg	Cl [mg/kg]	S [%]	Rest-C [%]	Ca [mg/kg]
08:40	2.4 (no load)					
10:09	12					
11:20	19					
12:25	17					
17:40	15					
19:35	52					
8:00 PM	52					

Further investigations were carried out on the highly contaminated airborne dust sample from 12.04.2004, 19:35. regarding the distribution of adsorbed mercury. The sample was sieved divided into several sieve fractions; the analysis results show . One be- Make sure that the Ca content is below 1 wt.% (10000 mg Ca/kg = 1 wt.%), while the residual C content is much higher, see also The fact that in the It seems plausible that more and more fly coke is found in the coarser sieve fractions, because is probably due to the incomplete Cfix burnout of the coarser coal grains.

18.8	10000	22	70	102
46.2	6000	47	140	71
56.1	5000	46	134	91
63.3	4400	40	121	91
77.2	2600	35	138	108
nb	nb	52*)	112	100



In the lower grain size range, as can be seen to read an increase in Hg-content with the C content; in the upper grain size range, however, the The question arises as to why this might be the case, since it is well known that “Carbon” leads to increased mercury adsorption compared to “quicklime” cf. e.g. Hocquel.



Why is there not increased mercury in the C-rich coarse fractions?

The divergence of the two curves in the upper grain size range can be explained:

It can be assumed that the fly coke (compared to activated carbon) has only a small internal surface surface area and offers the Hg hardly any access to them (small BET surface area), so that the Mercury is predominantly adsorbed on the outer grain surface.*)

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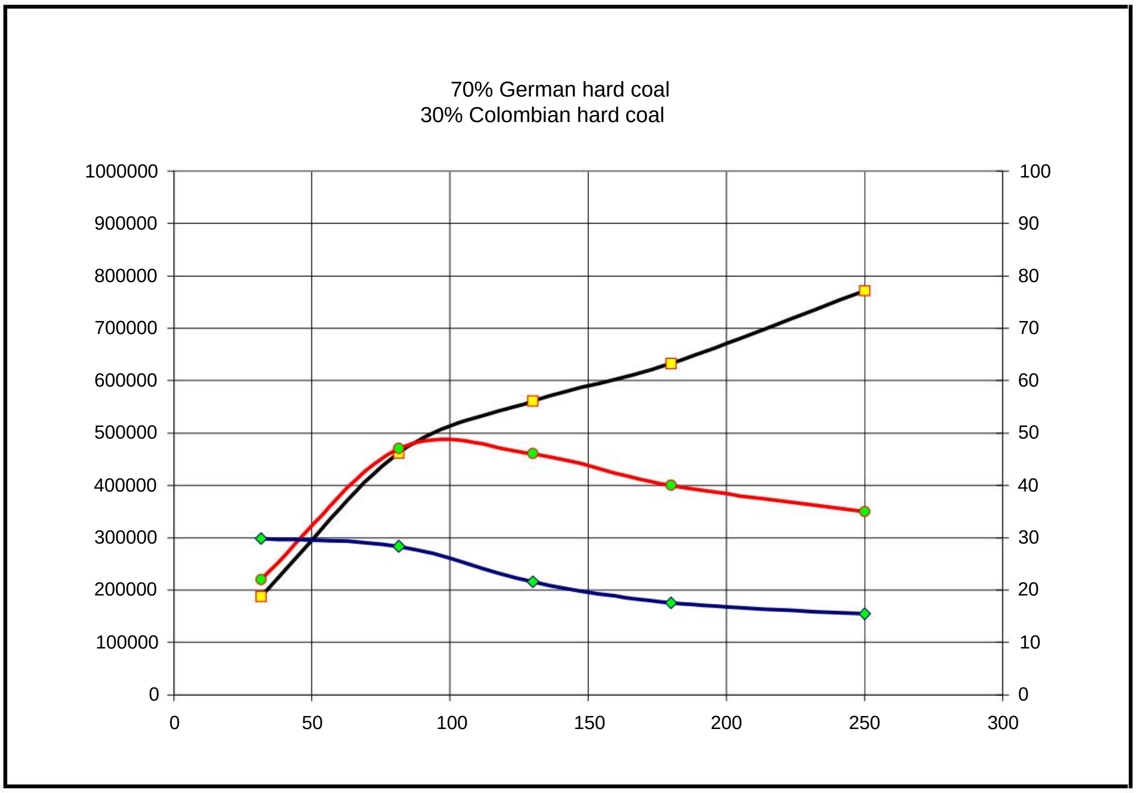
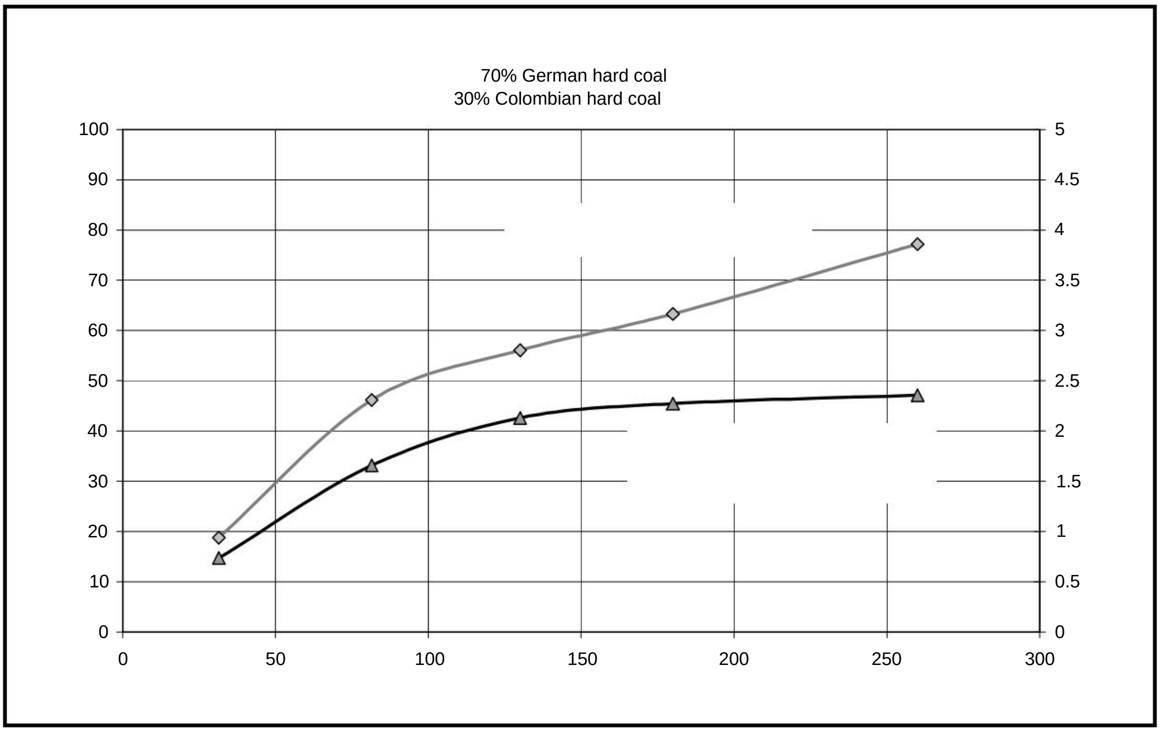
*) Already in the context of the experiments on chlorine-induced Hg separation in 1993, the first considerations on Hg Adsorption on the fly coke. Therefore, a measurement of the BET surface area of the fly coke was carried out at that time. It was shown that the specific BET surface areas in the order activated carbon, hearth furnace coke, and fly coke decrease by orders of magnitude. In principle, therefore, one would not make a major mistake if the inner surface of the fly coke was ignored.

In In addition to the contents of Rest-C and Hg also the calculated outer surface of the dust contained Coke grains are applied. The calculation of the outer surface available in a grain fraction area was carried out, as explained in Noltenäher, with simplifying assumptions (spherical Coke particles (coke density approx. 1.2 g/cm³). Above an average grain size (approx. 100 µm) the Hg content of the dust fractions decreases, but at the same time the calculated outer surface surface area of the coke grains contained in the screen fraction. Although the residual C content increases with As the particle size increases, the available outer C-grain surface decreases and thus the total amount of Hg adsorbed there. Under the assumption made above that the Hg adsorption is more or less limited to the outer coke grain surface, so understandable why less adsorbed mercury is found with increasing grain size.

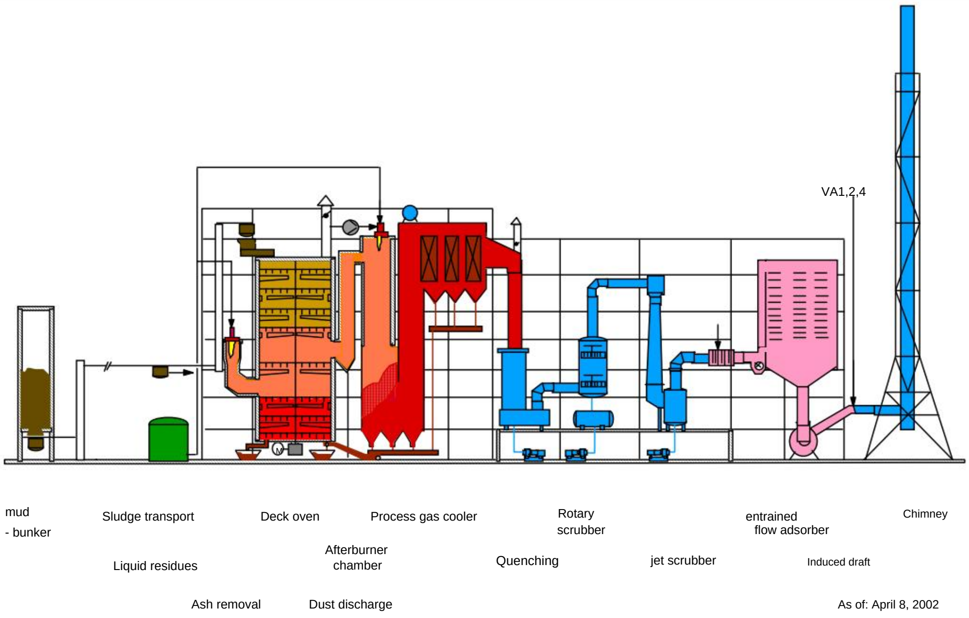


In Finally, the residual C content and the Hg loading of the calculated outer C-grain surface. This Hg loading increases with increasing Grain size to a “saturation value” of approx. 2.5 mg Hg/m².



Common sorbent mixtures with PAC, HOK or carbon black additives have a different larger accessible internal surface, namely the "BET-Surface". If one applies the models described above to such C-based sorbent mixtures, it is not surprising that these in connection with "bromine" have a considerable Hg adsorption capacity, see Nelson /18/, /19/ on Hg-Adsorption on externally brominated sorbent mixtures with such additives (activated carbon, carbon black).

shows another incineration plant in the BAYER waste disposal center Leverkusen-Bürrig. This VA 3 is used for the co-combustion of lime-conditioned raw Sewage sludge (in the multi-story furnace) with chlorinated hydrocarbons (in the afterburner chamber mer) as “support fuel” /, The vast majority of CaO-rich sewage sludge Ash is discharged at the foot of the deck furnace and thus remains in the This is particularly advantageous (reduced Boiler fouling due to reduced formation of calcium chloride hexahydrate).



Multi-story furnace (throughput approx. 11 t wet solids/h with 43% dry matter), ceiling-fired NBK (support fuel CHC), Waste heat boiler (steam 40 bar, 320 °C), multi-stage wet scrubber, entrained flow adsorber (LÜHR fabric filter)

(Source: BAYER-Industry-Services GmbH (2002)

During normal plant operation (CHC co-combustion), mercury oxidation is always ensured due to the high Cl load in the boiler flue gas, and thus, wet mercury separation in the multi-stage flue gas scrubber (RGW) was not a problem anyway.

(“Heating oil operation”) or with occasional co-combustion of only slightly chlorinated liquid waste However, noticeable traces of Hgmet could occur, which – as explained in Chapter 2 – pass through the flue gas scrubber.

At that time, the process for bromine-assisted Hg deposition was not yet known.

In 1996/97, a so-called entrained flow adsorber, namely a fabric filter from the company LÜHR, Stadthagen, for dry flue gas post-treatment (residual dust, PCDD/F residual traces, Hg residual traces); a PAC / $Ca(OH)_2$ / $CaCO_3$ adsorbent is used as adsorbent.
Sorbent mixture, see Vosteen , School .

As part of extensive preliminary investigations into various aspects of this During the upgrade in 1995, tests were conducted with a "fixed-bed mini-reactor" from LÜHR. The dry mercury separation on various sorbent mixtures was to be investigated. The reactor was a system designed by Dr. Kelterborn of LÜHR.
tempered measuring section made of glass with a solid flow from top to bottom bed. The fixed bed consisted of a "lean mixture" of the respective Coal component and calcium hydroxide with pure quartz sand ("sea sand").*) Operational clean gas, which was taken from the plant after the alkaline scrubber in the bypass, was fed directly or (alternatively) via an SO_2 scrubber to the mini-reactor.
Of particular interest to us was the question of whether the usually low residual SO_2 levels in washed clean gas after alkaline jet scrubber (cf.) for a "self-doping" of the "activated carbon components" in the sorbent mixture. Before and after the reactor were carried out over the entire test period (15 - 20 h) for one-hour Sampling (Braun tube method) to determine elemental and ionic Mercury, cf. Gutberlet et al. .

The following sorbents were investigated:

- undoped Norit activated carbon (type G50) with $Ca(OH)_2$ (mixture with 33% and 10% activated carbon split)
- undoped hearth furnace coke (HOK) with $Ca(OH)_2$ (mixture with 10% HOK content)
- pure quartz sand

We will only select a typical test procedure that illustrates the basic behavior and limit ourselves to an overview of the separation efficiencies achieved.

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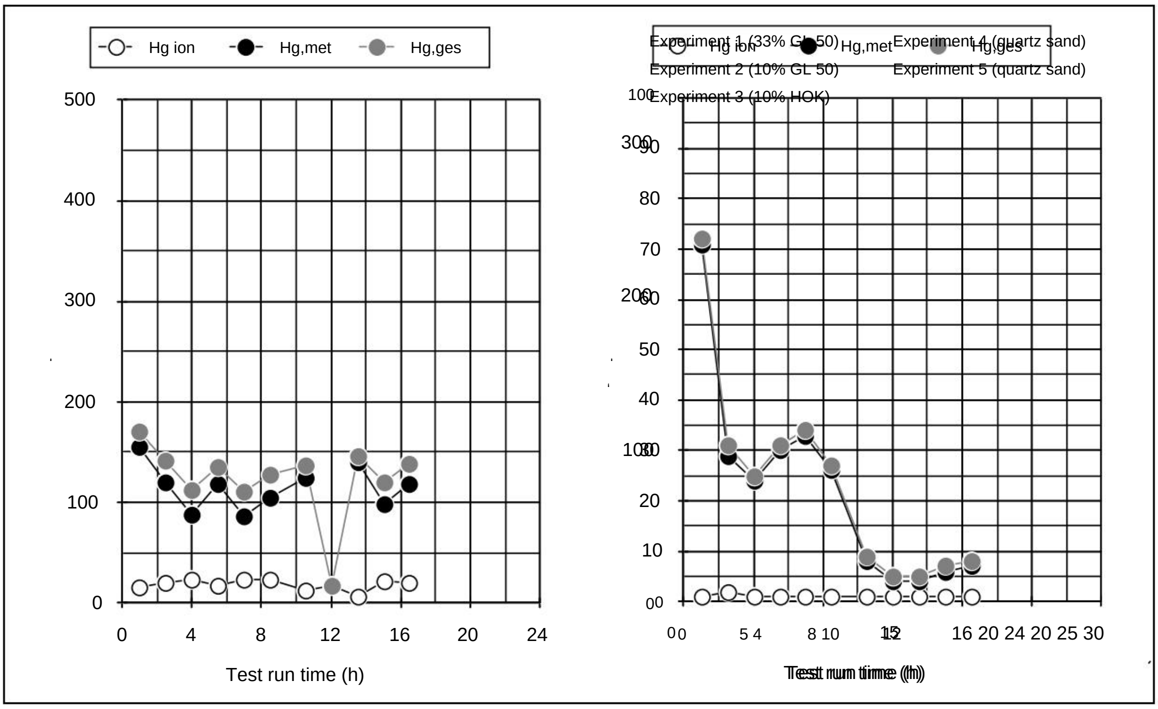
*) The LÜHR mini reactor consisted of a DN 100 glass cylinder (approx. 500 mm high), in which adsorbent/quartz sand mixtures (adsorbent weight: 10 g, total weight: 350 g) were placed on a PTFE filter disc.
The quartz sand only had an equalizing function, since the small amount of adsorbent alone cannot be filled in a satisfactorily uniform manner (layer thickness, bulk density).

The mini-reactor was installed in the clean gas downstream of the alkaline jet scrubber (behind the droplet eliminator). After passing through a heated pre-filter, the partial gas stream (approx. 0.8 m^3/h) extracted in the bypass entered the mini-reactor, which was operated at an operating temperature of 120 °C.

In the main stream after the jet scrubber, the following parameters were measured: gas temperature, humidity, pressure, oxygen content, SO_2 concentration and, at times, Hg_{met} content (Hg_{met} monitor).



concerns the Hg dry sorption in experiment 2 (date: 17. 7. 95, 12:00 - 18. 7. 95, 05:30) on a lean bed of activated carbon, $Ca(OH)_2$ and sand.*)

On the left, you can see the mercury content in the raw gas partial stream before the mini-reactor. The raw gas contained 20 - 40 mg/Nm^3 d. of residual SO_2. Its Hg content was due to the previous smoke gas scrubbing in the plant was relatively low (approx. 25 µg /Nm^3 tr.), but its content was at the the non-leachable Hgmet is quite high (approx. 100 … 150 µg/Nm^3 d.); note that these input values refer to a low-chlorine operation with insufficient Hg-Chlorination. On the right you can see the clean gas values after the mini reactor. Hgion content in the clean gas after the mini reactor immediately drops to practically zero (good adsorbability of the ionic mercury). In contrast, the Hgmet content in the clean gas after the mini-reactor decreases only slowly (gradual self-doping of the activated carbon due to SO_2/SO_3 conversion and pore condensation), i.e. delayed over several hours (low supply of residual SO_2). The increase towards the end of the experiment indicates the beginning of a Hgmet-breakthrough.

gives a brief overview of the results of the four experiments. In one experiment (No. 4), the mini-reactor was filled with sodium hydroxide solution. driven SO_2 absorber column (DN 50, 1 m high) upstream to increase the efficiency of the subsequent Hgmet removal in a fixed bed at extremely low SO_2 contents (<< 5 mg/Nm^3 dry) to be determined. Of course, this absorber column also largely removed the Hg ion ; therefore, no data regarding the dry separation of ionic mercury are available for this experiment.

The left part of the image shows the contents of Hgion, Hgmet and Hgges (as sum

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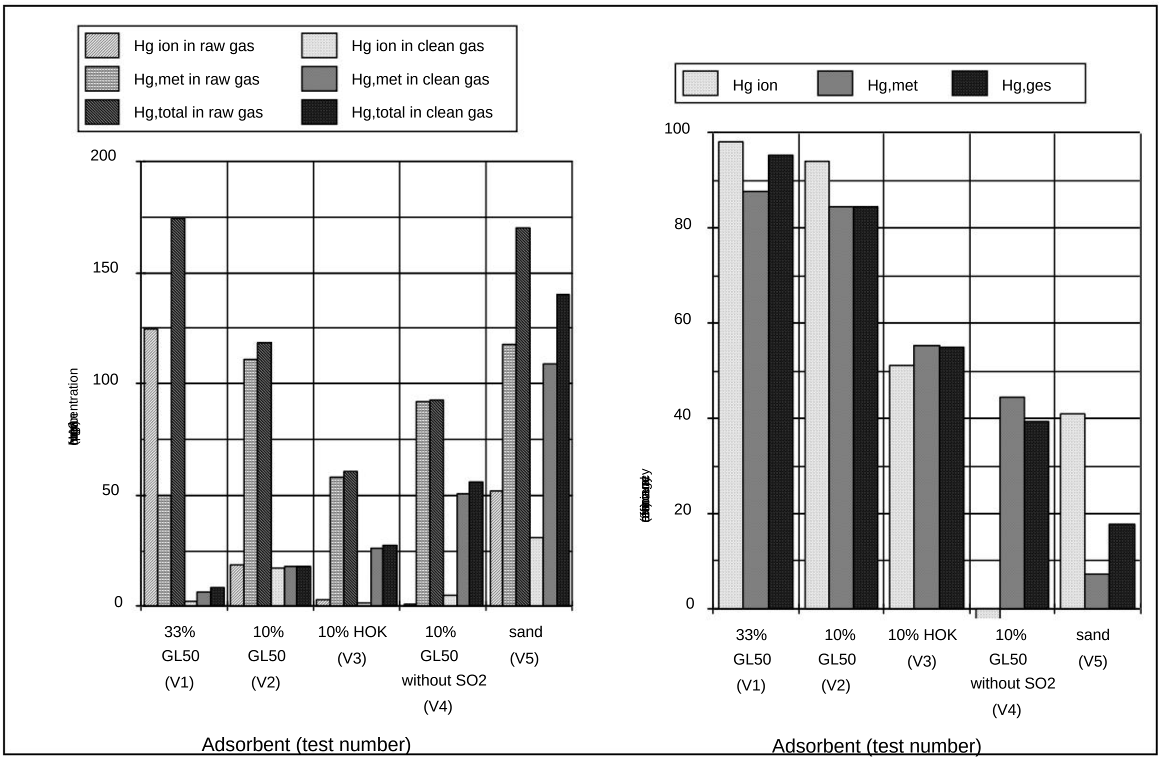
*) The 350 g of the total mixture with sand contained 1.0 g GL 50, 9.0 g $Ca(OH)_2$, rest sand.

both) in the raw gas before the mini-reactor and also in the clean gas after the mini-reactor. Interestingly, the sand seems to adsorb some ionic mercury; perhaps it was not quite as washed clean, as was to be expected (remaining traces of humus?). Otherwise, The expected picture of good Hgion and Hgmet adsorption in the SO2-containing gas stream (depending on the coal type and quantity) emerges . Note how the HgMe removal efficiency in test no. 4 ("almost no residual SO2") drops to just under 40%.



The experimental observations described above are qualitatively also from other earlier The core of this work is the fact that Hgmet dissolves in sulfuric acid and reacts with it to form the almost insoluble HgSO4 .

As explained towards the end of this work, free bromine and SO2 can be released as a result of Bromine-Bunsen reaction in the laundry and possibly also at the higher temperature sorbenskorn (capillary condensation) can lead to an “accelerated self-doping”, especially on the carbon surfaces (no sudden neutralization of the locally formed Sulfuric acid).

BImSchV	Federal Immission Control Ordinance
UNTIL	Bayer Industry Services GmbH, Leverkusen
DeNOx	Denitrification
DR	rotary kiln
DR-SVA	rotary kiln hazardous waste incineration plant
EGR	Electrostatic gas cleaning (electrostatic precipitator)
DOE	US Department of Energy
KEGR	Condensation electrostatic precipitator (wet EGR)
LuVo	Air preheater
MLU	Martin Luther University Halle-Wittenberg
NBK	Afterburner chamber
PCDD	polychlorinated dibenzodioxins
PCDF	polychlorinated dibenzofurans
REA	Flue gas desulfurization plant
RGR	Flue gas cleaning
SCR	selective catalytic reduction
SKK	Melting chamber boiler
SRI	Southern Research Institute in Birmingham, Alabama/USA
SVA	hazardous waste incineration plant
TEQ	Toxicity equivalents
VA	incineration plant