RESEARCH ARTICLE

Effect of additives on mercury partitioning in wet-limestone flue-gas desulfurization

Ida Masoomi[1,*], Barna Heidel[2], Marc Oliver Schmid[1] and Günter Scheffknecht[1]

[1]Institute of Combustion and Power Plant Technology—IFK, Department Fuels and Flue Gas Cleaning, University of Stuttgart, Pfaffenwaldring 23, D-70569 Stuttgart, Germany
[2]Faculty Building service, Energy, Environment, Hochschule Esslingen, University of Applied Science, Flandernstraße 101, D-73732 Esslingen, Germany

*Corresponding author. E-mail: ida.masoomi@ifk.uni-stuttgart.de

Abstract

The wet-flue-gas desulfurization (FGD) process plays an important role in removing water-soluble flue-gas components such as sulphur dioxide (SO_2) and oxidized mercury compounds. Under the reducing environment of the FGD, there is the possibility of re-emission of the already absorbed mercury (Hg) to the gas phase, which may be diminished by the utilization of specific additives. In this study, the effect of two different additives on Hg re-emission from the aqueous phase and Hg partitioning in gypsum and filtrate of a lab-scale wet-limestone FGD is investigated. Furthermore, the behaviour of additives in the presence of different halides is studied. The studied additives are TMT 15® as a sulphidic precipitating agent, which forms non-soluble mercury compounds, and activated lignite (AL) as a carbon-based sorbent, which adsorbs Hg compounds from the aqueous phase. TMT 15® has no significant effect on SO_2 absorption; on the other hand, addition of AL improves the SO_2-removal efficiency by up to 30%. Using both additives, Hg re-emission is suppressed in all the experimented cases except for AL in the absence of halides, in which Hg re-emission shows no change. Thus, the need to form nucleophilic oxidized mercury compounds in the slurry for the adsorption of oxidized mercury on AL can be concluded. Usage of both additives improves Hg retention in the slurry to different extents. It is shown that, for the additive-free slurries, the Hg-adsorption capacity of the solid fraction of the slurry is the limiting parameter. Moreover, the utilization of both additives results in a significant increase in the Hg concentration of solid fraction. The correlation between redox potential and partitioning of Hg in the slurry is presented by comparing the change in the redox potential of slurries when additives are used.

Graphical Abstract
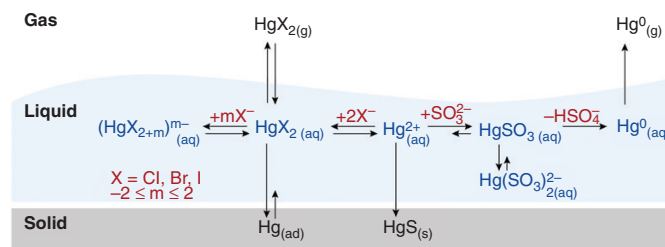
Keywords: fossil energy; flue-gas cleaning; flue-gas desulfurization; mercury; additives
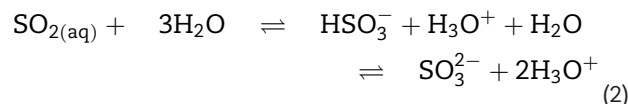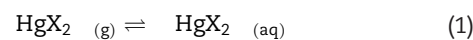
Introduction

Mercury (Hg) is widely known as a global pollutant due to its long life and long range of transport in the atmosphere. Its high vapour pressure is responsible for its evaporation through natural sources or human activities such as the combustion of fuels [1]. The mercury content of different fuels varies between 0.01 and 2 µg/g, which results in an Hg concentration of 1–200 µg/m^3 in flue gas [2]. Hg is highly toxic and has negative effects on human health and on the environment; thus, several regulations have been set worldwide to control and reduce mercury emissions from anthropogenic sources. For instance, within the Mercury and Air Toxics Standards, the limits have been set as a 30-day rolling average on a lb/GWh or Ib/TBtu basis, which, for the state-of-the art European power plants, is equivalent to values of <2.2 µg/m^3 for hard coal-fired plants and <5.4 µg/m^3 for lignite-fired plants [3]. The new large combustion plant best available techniques reference documents (LCP-BREF), which was finalized in 2017, sets the emission bandwidths for the existing coal-fired power plants in the European Union with a capacity >300 MW$_{el}$ to <1–4 µg/m^3 for hard coal and <1–7 µg/m^3 for lignite plants [4]. Considering the strict regulation on Hg emission, significant efforts have been undertaken during recent years to reduce Hg emission. Existing air-pollution-control devices play an important role in Hg removal from the flue gas.

In flue gas, Hg exists in different forms: gaseous elemental mercury (Hg^0), gaseous oxidized mercury species and particulate-bound mercury (Hg$_p$). Within the group of oxidized mercury species, mercuric (Hg^{2+}) compounds are the most abundant [5]. The speciation of Hg strongly depends on different parameters such as the combustion system, fuel types and the flue-gas pathway. In the combustion process, Hg is released mostly as Hg^0, which is the thermodynamically favoured form for high temperatures [6]. As the flue-gas temperature drops, Hg can undergo different reactions with the other flue-gas constituents. It can be oxidized homogenously by halogen radicals at higher temperatures of around 500–700°C, as halogen radicals are more abundant at this temperature range [5]. Even though the concentration of chlorine in coal is much higher than the concentration of bromine, Br-radical formation is kinetically more favoured. That is why bromine is more effective than chlorine in the homogenous oxidation of Hg [7, 8]. However, the homogenous oxidation of Hg is kinetically limited [5, 9]. The heterogeneous oxidation of Hg occurs at the selective catalytic reduction (SCR) catalyst and fly ash surface at lower temperatures of flue gas. SCR catalysts have been used widely for the reduction of nitrogen oxides (NO$_x$) from flue gas; however, they exert a significant impact on increasing the share of Hg^{2+} in the flue gas [9–11].
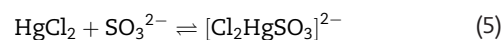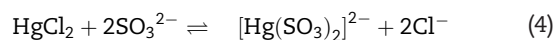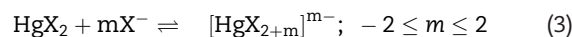
At a lower temperature of flue gas, Hg is adsorbed physically or chemically on the surface of fly ash or carbon-based sorbents to some extent and is removed consequently in the electrostatic precipitator or fabric filter (FF) [12]. The composition and surface area of the sorbents, as well as the composition and temperature of the flue gas, play important roles in the adsorption of Hg [13, 14]. It has to be considered that the Hg ends up in the fly ash, which may restrict in the use of fly ash as a by-product.

In the wet-flue-gas desulfurization (FGD) system, soluble flue-gas components such as sulphur oxides (SO$_x$) and acid gases such as hydrogen halides (HCl, HBr and HI) are absorbed in a scrubbing process. One of the most commonly used processes for the removal of SO$_x$ is the wet-limestone FGD, in which limestone (CaCO$_3$) is used as a neutralization agent. By implementing a forced-oxidation process in the scrubber, gypsum (CaSO$_4$·2H$_2$O) is produced as the final product, which is utilized in the wallboard-construction industry [15]. In contrast to Hg^0, which has low water solubility, gaseous bivalent mercury halides are more readily water-soluble, as shown in Reaction (1) [16]. Therefore, they can be absorbed and interact further with other components in the wet-FGD slurry [17]. Hg^{2+} is a soft acid; therefore, it can form stable complexes with soft bases according to the hard and soft acid-base theory (HSAB) [18]. According to Reaction (2), the absorbed SO$_2$ (S(IV)) may exist in different forms depending on the pH of the slurry [19].
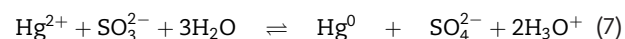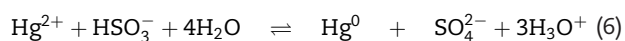
$$HgX_{2\ (g)} \rightleftharpoons HgX_{2\ (aq)} \tag{1}$$

$$SO_{2(aq)} + 3H_2O \rightleftharpoons HSO_3^- + H_3O^+ + H_2O$$
$$\rightleftharpoons SO_3^{2-} + 2H_3O^+ \tag{2}$$

Halides and S(IV) are existing ligands in the slurry and possible reagents for the formation of Hg^{2+}-complexes. Depending on the concentration of the relevant ligands and the formation constant of complexes, homoleptic and heteroleptic complexes of Hg^{2+} can be formed [20, 21]. Homoleptic complexes are complexes containing only one type of ligand such as Reactions (3) and (4) and heteroleptic complexes contain different types of ligands as shown in Reaction (5). Reaction (3) shows the formation of halidomercurate complexes, in which X represents any of the halides Cl, Br and I. The numeric value of m depends on the position of the complex formation equilibria. According to the formation constant of halidomercurate complexes, the higher the concentration of the individual halide, the higher the coordination number of the complex. And, among different halides, the formation constant increases in the order of Cl < Br < I [22, 23]. Therefore, the distribution of mercury complexes in the slurry depends on the concentration of ligands [24].

$$HgX_2 + mX^- \rightleftharpoons [HgX_{2+m}]^{m-}; \ -2 \leq m \leq 2 \tag{3}$$

$$HgCl_2 + 2SO_3^{2-} \rightleftharpoons [Hg(SO_3)_2]^{2-} + 2Cl^- \tag{4}$$

$$HgCl_2 + SO_3^{2-} \rightleftharpoons [Cl_2HgSO_3]^{2-} \tag{5}$$

It has to be mentioned that bivalent mercury compounds (HgX_2) are formed with covalent bonds. Thus, they are not easily dissociated in water. Due to their Henry coefficients and gas–liquid equilibrium, they have the ability to evaporate back to the gas phase, which results in HgX_2 re-emission. Reaction (1) shows the gas–liquid equilibrium of the bivalent mercury compounds. The volatility of the bivalent mercury compounds increases in the order of Cl < Br < I [24].

Depending on the oxidation-reduction (redox) potential and the pH of the slurry, all of the Hg^{2+}-complexes can be reduced to Hg^0, which is emitted to the gas phase [25, 26]. The driving force of the reaction depends on the half-cell potentials of the Hg^{2+}-complex and that of the reducing agent [16]. As SO_2 is readily absorbed into the slurry, S(IV) is the most abundant reducing agent for Hg^{2+}-complexes in typical wet-FGD units. The redox reaction may occur according to the reactions below:

$$Hg^{2+} + HSO_3^- + 4H_2O \rightleftharpoons Hg^0 + SO_4^{2-} + 3H_3O^+ \quad (6)$$

$$Hg^{2+} + SO_3^{2-} + 3H_2O \rightleftharpoons Hg^0 + SO_4^{2-} + 2H_3O^+ \quad (7)$$

It has been reported that the rate of the reduction reaction with HSO_3^- is smaller than the reduction reaction with SO_3^{2-} by orders of magnitude [19, 27]. The standard electrode potential of individual halidomercurate complexes decreases with increasing values of the formation constant [28]. It means that, considering different halides, the driving force of the reduction reaction increases in the order of I < Br < Cl and, for a particular halide, the higher the coordination number, the lower the possibility of reduction [29].

In order to reduce the amount of re-emitted Hg from the slurry, it is important to keep Hg^{2+} in a stable form, which decreases the possibility of its reduction. Adjusting the concentration of halides or using additives in the slurry could help to prevent the reduction reactions.

Additives are categorized into two groups: precipitating agents, which normally form a more stable Hg compound; and sorbents, which adsorb Hg physically or chemically. In both cases, Hg is transformed into a stable form and is more difficult to remobilize, due to reduction reactions. Some studies suggest the utilization of these additives in the slurry of the wet FGDs, in order to prevent Hg^{2+} reduction [30–32].

One of the precipitating agents that are used commonly to remove heavy metals from industrial waste water is 2,4,6-trimercaptotiazine, trisodium salt ($Na_3S_3C_3N_3$) or TMT. According to the reaction below, 3 moles of Hg^{2+} chemically bonds with 2 moles of TMT and forms weakly water-soluble macromolecular organo-metallic compounds. Therefore, they can be separated as they precipitate as solid substances [33].

$$2Na_3C_3N_3S_3 + 3Hg^{2+} \rightarrow Hg_3(C_3N_3S_3)_2 + 6Na^+ \quad (8)$$
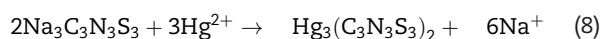
TMT is mostly available as a 15% aqueous solution (TMT 15®) and has been already used widely in waste-water-treatment plants. It is easy to handle due to its non-toxicity and is environmentally friendly. Using TMT in a wet-FGD scrubber may transfer the Hg–TMT compound to the waste-water-treatment plant as well as to the gypsum. The compounds are chemically and thermodynamically stable, with their thermal decomposition taking place at temperatures higher than 210°C [33].

Activated lignite (AL) is produced in rotary hearth furnaces and exists in different grain sizes. Its specific surface area is ~300 m^2/g and it covers the pore radii distribution in the macro- and micropore ranges [32]. In general, large macropores are required to transport pollutants into the sorbent and the smaller micropores with their high adsorptive energies are responsible for adsorbing the pollutants and preventing them from diffusing back to the gas or liquid phase. Therefore, the structure of AL can make it possible for a molecule with a bigger diameter to be absorbed more easily [34].

In this study, the utilization of these two additives in different synthetic slurries has been studied in order to investigate the effect of additives on preventing Hg re-emission and their performance in the presence of different halides.

1 Materials and methods

1.1 Lab-scale experimental plant

The experiments were carried out in a lab-scale FGD system presented in Fig. 1, which consisted of two sections: synthetic-gas preparation and the FGD system. Required gases were injected into the system using mass flow controllers. The synthetic flue gas was a mixture of 15 vol.-% CO_2, 3.5 vol.-% O_2 and the rest N_2; it was fed by the flow of 4 l $_{STP, dry}$/min to the gas preparation section, where its SO_2 concentration was adjusted to 3000 mg/m$^3_{STP, dry}$ by the addition of SO_2 gas. Hg^0 was dosed directly upstream of the catalyst using N_2 as a carrier gas passing through metallic Hg and its concentration in the flue gas was adjusted to 50 µg/m$^3_{STP, dry}$. A constant flue-gas humidity of 7 vol.-% and hydrogen-chloride (HCl) concentration of 50 mg/m$^3_{STP, dry}$ were adjusted using a peristaltic pump to inject the diluted HCl solution into the reactor. All gaseous concentrations in this work are provided at a reference oxygen concentration of 3.5 vol.-% O_2. The mixing zone was heated up, in order to reach the gas temperature of 300°C at the inlet of the SCR catalyst. A honeycomb SCR catalyst was used to generate the required share of oxidized mercury in the flue gas. The operating parameters were adjusted in a way to generate ~50% oxidized mercury in the SCR catalyst. The catalyst was heated to 300°C as well, in order to keep the temperature of the gas in the reactor constant. The temperature of the gas entering for FGD was adjusted to ~120°C. Heating of the gas-mixing section was carried out using adjustable heating bands.
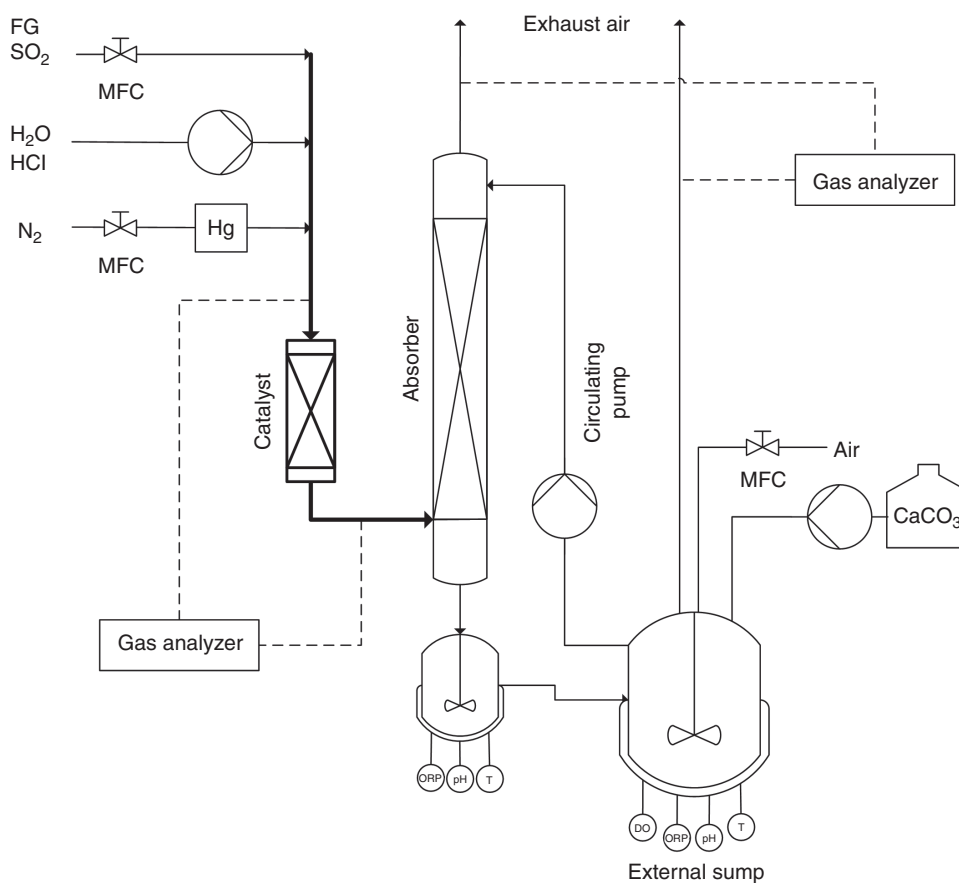
Fig. 1: Flow diagram of the lab-scale flue-gas desulfurization system and measurement points (with dashed lines)

The heated section of the plant is marked by a thick line strength in Fig. 1. In order to minimize the interaction of the surface, the whole reactor was made of glass.

The FGD system consisted of an absorber and an external sump. The gas mixture entered the bottom of the absorber and was brought into contact counter currently with the limestone slurry, which was pumped to the top of the absorber from the external sump using a peristaltic pump. The liquid-to-gas ratio was set at 20 l/m³. The collected slurry at the bottom of the absorber was transferred through a siphon to the external sump, hence no synthetic flue gas could enter the external sump. The volume of the slurry was 1.5 l. It consisted of an aqueous 10 wt.-% $CaSO_4 \cdot 2H_2O$ solution, with an experiment-specific halide concentration. In order to simulate the accumulation of halides in the slurry using flue gases with different halogen content, synthetic slurries were prepared. The runs were conducted using no halides, 10 g/l chloride (Cl^-), 1 g/l bromide (Br^-) and 0.1 g/l iodide (I^-). The concentrations of halides were adapted using the corresponding sodium (Na^+), potassium (K^+) or magnesium (Mg^{2+}) salts. The Hg^{2+} concentration in the slurry was adjusted at 300 μg/l before starting the measurement. The tested additives were injected into the slurry at the beginning of the runs to check their effect on the whole process. TMT 15® was provided by Evonik Industries AG and the AL by Rheinbraun Brennstoff

GmbH. The concentration of the injected TMT 15® was adjusted to have 10× the stoichiometric value of the needed TMT 15® to react with the initial Hg in the slurry and 0.2 g of AL was added to 1 l of the slurry. The used AL was in the form of slurry with a 19.4 wt.-% share of solid fraction and a particle size of $d_{50} \sim 8$ μm.

The redox potential, pH and temperature of the bottom of absorber and external sump were measured. The temperature of the slurry at the external sump was adjusted to 60°C using a heating plate. Due to heat loss and evaporation, the temperature of the slurry decreased slightly over the height of the absorber from 60°C at the top to ~50°C at the bottom. The pH of the external sump was controlled at 5.6 using a PID controller and the addition of fresh $CaCO_3$ solution. Forced oxidation occurred by the introduction of oxidation air with the flow of 2 l $_{STP,\,dry}$/min into the external sump and the amount of dissolved oxygen was measured continuously. Table 1 summarizes all the main parameters of the study for the synthetic flue gas as well as the synthetic slurry. Case-relevant compositions of the slurry are provided separately.

The gas concentration was measured at the inlet and outlet of the catalyst and absorber as well as in the outlet of the external sump. The measurement points are shown with a dashed line in Fig. 1. Using the external sump made it possible to be able to differentiate between the

Table 1. Summary of the main parameters of the experimental study (all gaseous concentrations @ STP and 3.5 vol.-% O_2)

Flue gas	Lab-scale
Flue-gas flow, $l_{STP, dry}$/min	4 ± 0.1
H_2O, vol.-%	7.0 ± 0.1
CO_2, vol.-%	15.0 ± 0.1
O_2, vol.-%	3.5 ± 0.1
SO_2, mg/m³ $_{STP, dry}$	3000 ± 50
Hg, μg/m³ $_{STP, dry}$	50 ± 10
Hg^{2+}/Hg^0	50 % ± 5
HCl, mg/m³ $_{STP, dry}$	50 ± 3.2 %
Flue-gas inlet FGD, °C	120 ± 6
FGD	
L/G, l/m³	20
Oxidation air flow, $l_{STP, dry}$/min	2 ± 0.1
Slurry temperature, °C	60 ± 2
pH	5.6
$CaSO_4{\cdot}2H_2O$, wt.-%	10
Hg^{2+}-slurry, μg/l	300 ± 30
Case dependent compositions	
Cl^--slurry, g/l	10 ± 0.01
Br^--slurry, g/l	1 ± 0.01
I^--slurry, g/l	0.1 ± 0.01
TMT 15®	10 x stoichiometric
AL, g/l	0.2 ± 0.01

re-emitted Hg and the Hg that was not absorbed in the first place. For each experiment after reaching steady state, the concentrations of Hg^{tot} and Hg^0 were measured at the inlet and outlet of the absorber and at the exhaust air of the external sump. The system was considered to run in a steady state when operating parameters such as the pH, redox potential and dissolved oxygen were constant over a longer period. A slurry sample was taken at the end of each run and filtered using a paper filter, with a particle retention of 5–13 μm, to separate the filtrate and gypsum from each other. Filtrate samples were stabilized by the addition of 10 vol.-% hydrochloric acid and gypsum samples were dried at 40°C and ground to have a homogenized sample. The concentration of Hg in the samples was measured in the laboratory.

1.2 Analysis methods

Dissolved-oxygen measurement was carried out using a 'VisiFerm DO Sensor' from Hamilton® with the luminescence quenching measurement principle. The redox potential was measured using silver/silver chloride electrodes. The redox potential values provided in this work represent the potential difference of the slurry to the silver/silver chloride electrode. Gas-component concentrations were measured using an online gas analyser 'ABB EL 3020', in which the oxygen (O_2) was measured using a paramagnetic method, and SO_2 and carbon dioxide (CO_2) using the non-dispersive infrared (NDIR) principle.

Mercury speciation was determined by measuring the concentration of Hg^{tot} (elemental and oxidized) and of Hg^0 with a continuous mercury analyser 'Lumex RA 915 AMFG' working with cold vapour atomic absorption spectroscopy (AAS) with Zeemann-background-correction. A reducing solution of Tin (II) chloride ($SnCl_2$) ensured the reduction of oxidized mercury. The measurement of elemental mercury was realized by selectively trapping the oxidized mercury using ion exchange resin. The difference between the total and elemental mercury is calculated as Hg^{2+}.

Filtrate and gypsum samples were analysed for their Hg content with the Hg analyser 'MLS Company DMA-80', using the direct thermal principle.

2 Results and discussion

The aim of this study is to reveal the effect of additives on the major wet-FGD-process parameters and pollutant removal for various halide contents of the slurry. Hence, the runs in the absence of additives represent the baseline scenario. In order to reveal the impact of the concentration of different halides, in each run, one specific halide was added to the slurry. After reaching steady-state operating conditions, major process parameters such as SO_2 removal, dissolved-oxygen concentration, redox potential, Hg re-emission and Hg partitioning were determined. The procedure was repeated in two similar runs, once in the presence of TMT as a precipitating agent for Hg and once in the presence of AL as a sorbent. Therefore, the effect of using additives in the slurry containing different halides could be derived.

2.1 Effect of additives on SO2-removal efficiency and dissolved-oxygen concentration

In order to investigate the effect of the additives and halides on SO_2 removal in the FGD, the SO_2 concentration at the inlet and outlet of the FGD was measured at the steady state. Fig. 2 illustrates the SO_2-removal efficiency of the absorber without using additives in the presence of different halides and in the case that additives were added to the system.

It can be seen that, for the baseline case in the absence of additives and halides, the SO_2-removal efficiency of the FGD is around 60%. The presence of halides for the concentrations investigated shows no significant impact on the SO_2-removal efficiency. It could be speculated that the increase in ionic strength and corresponding change in the diffusion rate in the presence of halides could have a positive effect on SO_2 removal. However, the actual removal efficiency of the scrubber depends not only on the chemical parameters, but also on the thermodynamic properties of the phases (e.g. surface tension), which could be affected adversely by the addition of halides.

The addition of TMT to the slurry does not change the SO_2-removal efficiency in a pronounced way. Hence, the removal of ~60% is also observed in the presence of TMT for
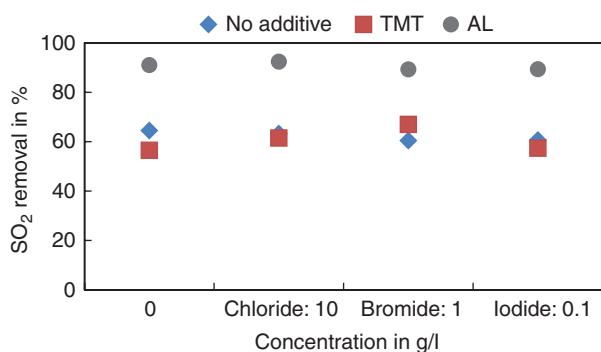
Fig. 2: Percentage of SO₂-removal efficiency at different halide contents of the slurry by using TMT or AL

Fig. 3: Dissolved-oxygen concentration in parts per million (ppm) at different halide contents of slurry by using TMT or AL

all halide-containing slurries. On the other hand, using AL for Hg adsorption significantly improves the SO_2-removal efficiency. For all halide concentrations investigated and in the presence of AL, the FGD shows a SO_2 removal of around 90%. It has to be emphasized that the significant increase in SO_2-removal efficiency may not be transferred to full-scale plants without caution. In contrast to full-scale FGDs, the baseline operating conditions of the lab-scale test rig are not optimized for SO_2-removal efficiency. In a full-scale FGD, the increase may be less pronounced, as the efficiency of the plant is already >90%.

As presented in Fig. 3, the dissolved-oxygen content of the slurry is hardly impacted by the additives in the absence of halides. The results of the additive-free slurry show an increase in the dissolved oxygen in the presence of bromide, while dissolved chloride and iodide lead to a decrease in dissolved oxygen. The addition of TMT or AL to the chloride-containing slurry causes only a small effect on the dissolved oxygen. In contrast, a more pronounced effect on the oxygen concentration is observed when AL is added to the slurry in the presence of bromide and iodide. For TMT, the impact of the halides on both the SO_2-removal efficiency and dissolved oxygen is qualitatively comparable with the additive-free baseline case. It can be concluded that the co-existence of TMT in the slurry does not lead to fundamental changes in the context of the SO_2 mass transfer and corresponding reaction pathways. This statement is not true for the additive AL. Based on the overall significantly increased SO_2 removal efficiency for all test runs including AL and the great difference between the amount of dissolved oxygen by using AL compared to the baseline slurry, it can be deduced that Al introduces further pathways for sorption and/or reaction processes involving SO_2.

Dissolved oxygen is an indicator of the quantitative amount of oxygen present in the slurry. As for any other gas, the dissolution depends on the temperature and the partial pressure of the system. In addition, the reactions taking place in the slurry may consume dissolved oxygen and change the equilibrium. One of these reactions is the oxidation of sulphite to sulphate. In case of the inhibited oxidation of sulphite, the level of dissolved oxygen
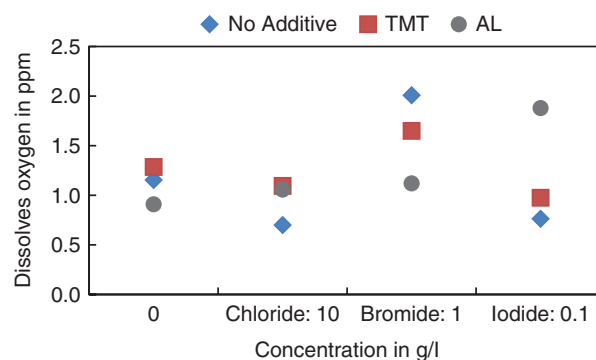
should have been at higher levels, as dissolved oxygen is the indirect indicator of dissolved sulphite in the slurry. However, this correlation is no longer valid if the adsorption sites for SO_2 are introduced into the system. It could be speculated that AL provides suitable adsorption sites for SO_2, decreasing dissolved SO_2 concentration while simultaneously increasing the driving force for SO_2 removal from the gaseous phase without consumption of dissolved O_2. Increased adsorption of SO_2 from the flue gas using AL has been already proven by previous works [32].

2.2 Effect of additives on Hg re-emission

After reaching the steady state, concentrations of Hg^{tot} and Hg^0 were measured at the external sump. Due to the siphon barrier, the Hg content of the external sump exhaust air represents re-emitted Hg exclusively. Fig. 4 shows the mass flow of the total re-emitted Hg from the external sump in all the studied cases. For the baseline case without additives, the presence of halides leads to decreased re-emission of Hg. Fig. 5 illustrates the distribution of the corresponding Hg re-emission mass flow between Hg^0 and Hg^{2+}. From the analysis of the distribution, it can be concluded that the highest Hg^0 re-emission belongs to the slurry containing no halides at all and the lowest to the slurry containing 0.1 g/l iodide. The results are in agreement with previous studies [29, 35], as the presence of halides plays an important role in the formation of Hg complexes. The individual half-cell standard electrode potentials of the various halidomercurate complexes correspond to different reaction rates of the chemical reduction of the Lewis acid Hg^{2+}. Thus, the effect of the type of halide on the re-emission of Hg^0 is in the order of Cl > Br > I.

Comparing the total Hg re-emission in Fig. 4, the slurry containing iodide shows higher re-emission than the slurry with bromide. However, by analysing the distribution of Hg^0 and Hg^{2+}, it can be seen that >90% of the total mercury re-emitted consists of Hg^{2+} species in the presence of iodide. The corresponding emitted volatile Hg^{2+} compound is likely to be HgI_2. This compound has the highest vapour pressure when compared to the other bivalent Hg^{2+} species

as discussed earlier. For the halide-free baseline case and the chloride-containing slurry, the re-emitted Hg mass flow consisted of Hg^0 exclusively and, for the bromide-containing slurry, only 2% of the total re-emitted Hg consisted of Hg^{2+} in the form of $HgBr_2$. These findings are in agreement with previous studies regarding Hg re-emission from the FGD slurries [35, 36]. It has to be mentioned that the amount of re-emission during the measurement time was around 9.5% of the initial Hg inventory in case of no halides being present in the slurry. For the halide-containing slurries, the value declines between 0.8% and 2.5%, depending on the utilized halide.
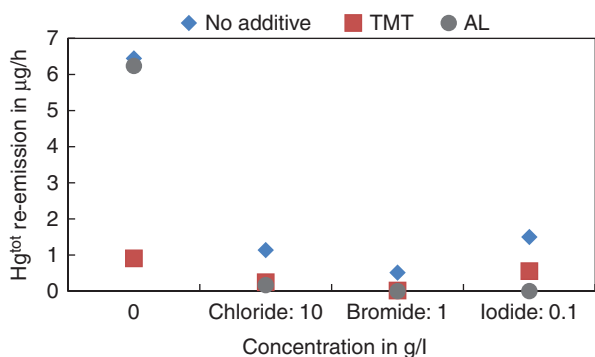

Fig. 4: Hg^{tot} re-emission from the external sump at different halide contents of the slurry by using TMT or AL
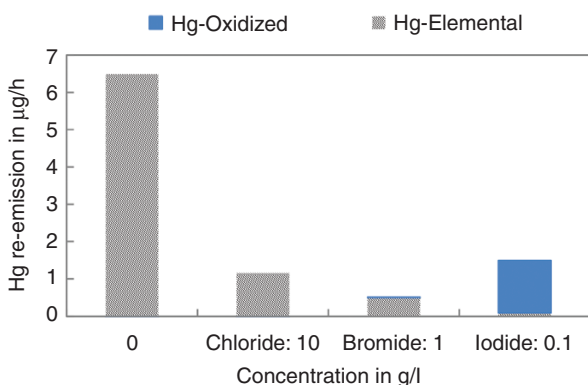

Fig. 5: The share of Hg^0 and Hg^{2+} in the total Hg re-emission from the external sump at different halide-containing slurries
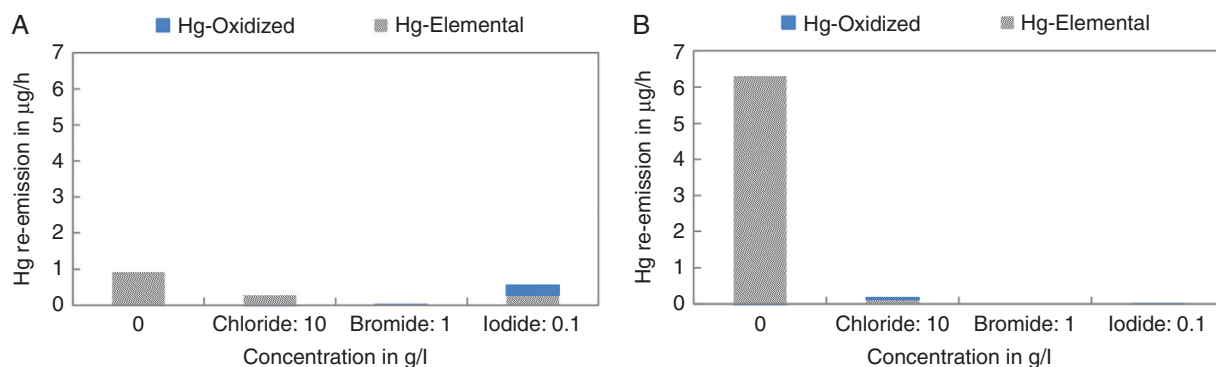
When TMT is added to the slurry, the total Hg re-emission in Fig. 4 decreases in all cases to <1.5% of the initial Hg of the slurry. The bromide-containing slurry achieves almost zero Hg re-emission. In the presence of iodide, the total Hg re-emission decreases by ~60%. As depicted in Fig. 6a, in contrast to the suppressed Hg^0 re-emission, the Hg^{2+} re-emission is not inhibited completely. As mentioned before, TMT is a sulphidic precipitating agent. It bonds with Hg^{2+} in the slurry and forms macromolecular organo-metallic compounds, which removes dissolved Hg^{2+} from the aqueous phase and therefore prevents its reduction to Hg^0 and subsequently its re-emission. However, TMT and halides compete for the Hg^{2+} inventory of the slurry. Due to the large formation constants of Hg^{2+}-complexes with iodide ligands, a fraction of the Hg^{2+} remains inaccessible for reaction with TMT, although, at low levels, this leads to ongoing re-emissions of Hg^0 and HgI_2 in the presence of both TMT and iodide.

Interestingly, the data in Fig. 6b reveal that the inhibition of Hg re-emissions by addition of AL to the slurry requires the co-existence of halides. As can be derived by comparing the baseline case in Fig. 5 and Fig. 6b, the total Hg re-emission is almost the same in the absence of halides, regardless of AL being present or not, and it is measured to be at ~8.6% of the initial Hg in the slurry during the steady-state period. In contrast, for the case of bromide- and iodide-containing slurries, the total Hg re-emission reaches zero. In addition, there are also no Hg^{2+} re-emissions, even when iodide co-exists in the slurry. From these observations, two different conclusions may be derived. First, the adsorption of Hg^{2+} on AL implicitly requires the formation of nucleophilic Hg^{2+} compounds, such as bivalent Hg^{2+} halides or negatively charged halide complexes of Hg^{2+}. Hence, the larger the formation constant of the corresponding complex and the higher the concentration of the ligand respectively, the higher the share of overall adsorbed Hg^{2+} on the AL surface. Second, the adsorbed Hg^{2+} species show very high affinity towards the sorbent and very low reactivity after adsorption. Consequently, re-emissions of both Hg^0 and Hg^{2+} are close to zero if halides and AL co-exist in the slurry.

Fig. 7 shows the redox potential of the slurry for all experimental conditions investigated. In general, the addition of chloride and bromide to the slurry increases its

Fig. 6: The share of Hg^0 and Hg^{2+} in the total Hg re-emission at different halide-containing slurries by using (a) TMT or (b) AL

redox potential. In contrast, the presence of iodide leads to a more reducing environment, indicated by the lowest individual redox potential of the interrelated test runs. Furthermore, the presence of TMT or AL also decreases the redox potential, with the reducing effect of AL being less distinct. It is widely accepted that the sorption equilibria of Hg compounds are shifted towards the adsorbed species for reducing conditions [37]. Stable adsorbed Hg^{2+}-species are hardly available to redox reactions, hence the more reducing environment in the presence of the additives investigated in this study does not promote Hg^{2+} reduction to Hg^0. It is important to stress that the redox potential may only be used as an indicator for Hg^{2+} reduction for comparable slurry compositions. This is especially relevant for processes involving adsorption equilibria.

2.3 Effect of additives on Hg partitioning in slurry

Fig. 8 shows the Hg concentration of the slurry for steady-state operation of the system, considering the measured Hg concentration in gypsum and filtrate. A low Hg content in the slurry indicates high-transient Hg re-emission from the slurry in the whole process until reaching steady state. As the Hg re-emission measurements evaluated previously were carried out after the FGD had reached steady state, the data in Figs 4–6 may not be compared directly with the
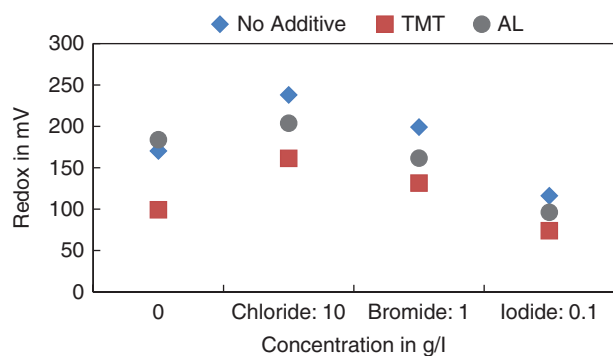
Hg concentration of the slurry in Fig. 8. It can be seen that, when no additives were used and in the absence of halides, the slurry contained ~50 µg Hg, which amounts to ~10% of the initial Hg^{2+} inventory of the synthetic slurry. The corresponding re-emission of 90% of the initial Hg^{2+} content of the slurry underlines the high rate of re-emissions at the absence of halides. When comparing halide-containing slurries, the one containing 0.1 g/l iodide has the lowest Hg content of slurry due to the high re-emission of Hg^{2+}, even though the re-emission of Hg^0 was comparably low for this case, as evaluated previously. The addition of TMT to the slurry improves the ability of the slurry to retain its Hg inventory and suppresses the re-emission of Hg to an extent that depends on the specific composition of the slurry. The existence of AL in the slurry leads also to improved Hg retention. In the absence of halides, the stabilizing effect of AL is less pronounced. However, the Hg content of the AL-containing slurry is still six times higher than for the baseline case without halides. This is worth pointing out, since, for the steady-state conditions in Fig. 4, the flow of re-emitted Hg from the halide-free slurry is not reduced by the addition of AL. Hence, it can be concluded that, even for the halide-free slurry, the presence of AL decreases transient re-emissions of Hg until reaching the steady-state operation of the FGD. As a further important conclusion of the data in Fig. 8, it should be stressed that, for transient conditions during start-up of the FGD, even for the best-performing cases, ~10% of the Hg^{2+}-inventory of the slurry was re-emitted to the gas phase.

The share of Hg in the solid phase of the slurry at different halide contents and with the use of additives is depicted in Fig. 9. The values represent the relative share of Hg associated with the solid phase with respect to the total Hg content of the slurry. In the absence of additives, the absolute quantity of Hg in the gypsum for all slurries investigated is ~25 µg, which amounts to 50% of the total Hg content of the slurry when no halides are present. For the slurries with halides, the same absolute quantity of Hg is analysed in the solid phase, resulting in a share of <10% due to the higher total Hg content of the slurry. From this observation, it could be concluded that the adsorption capacity of the solid-particle content of the slurry is the

Fig. 7: Redox potential in the external sump at different halide-containing slurries by using TMT or AL

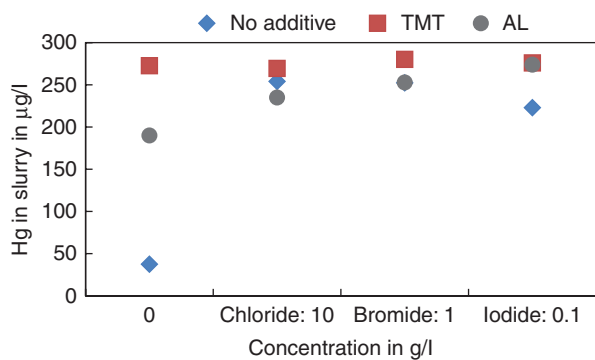**Fig. 8:** Total Hg concentration of slurry at steady state at different halide contents and using TMT or AL
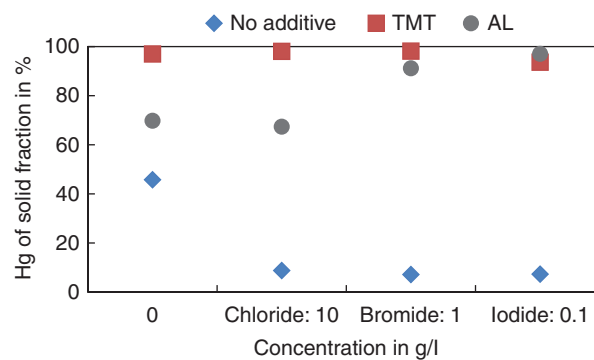

Fig. 9: Hg share of solid fraction in the slurry at different halide contents and using TMT or AL

limiting parameter for the additive-free slurries investigated. Hence, increasing the total Hg content of the slurry would not result in elevated Hg content of the solid phase, since the maximum adsorption capacity of the gypsum particle inventory is already exceeded for a Hg^{2+} concentration in the aqueous phase as low as 20.8 μg/l.

Using TMT results in a shift in the partitioning to almost 100% of the Hg in the solid fraction for all halide-containing slurries. For the slurries containing AL, Hg in the solid fraction increases as well. However, the extent of the increase in the share of Hg in the solid fraction is less distinct for AL in co-existence with chloride, when compared to the TMT slurry. This observation is in line with the corresponding redox potential data of the experiments in Fig. 7. For all slurries, there is a correlation between redox potential and share of Hg in the aqueous phase. Since the additive AL causes a less distinct decrease in the redox potential, the share of particle-bound Hg content of the slurry is also less pronounced.

However, it has to be stressed that the separation process was conducted by filtration through a paper filter. Therefore, the solid residue contained the entire particle content of the slurry, including the very small particle-size fractions. Hence, these results may not be transferred to predict the gypsum properties produced by full-scale FGD plants. Full-scale FGDs in power plants use hydro cyclones for the separation of gypsum from the slurry. The separation particle size of hydro cyclones is much higher than that of the cake-filtration process. Hydro cyclones are designed to remove the coarse-particle fraction for gypsum production. The fine particles with the highest surface area, containing most of the adsorbed Hg, are fed back to the FGD or subsequently to the waste-water-treatment plant. In order to investigate the actual gypsum Hg content using additives, the separation process has to be carried out using hydro cyclones. This remark is also important for the interpretation of the results using the second additive investigated. AL has a lower density in comparison with gypsum. Therefore, AL is also mainly transferred to the aqueous fraction including the fine particles in the hydro cyclone. In contrast, the particle density is of negligible importance for the cake filtration conducted in this study. The results derived from Fig. 9 provide insight into the sorption equilibria, but may not be used for the prediction of gypsum-quality parameters.

3 Summary and conclusion

In this study, the behaviour of Hg in a lab-scale wet-limestone FGD system using two different additives was investigated. The impact of halides on the performance of the additives was studied as well using synthetic slurries containing different halides. The experiments were conducted using TMT 15® as a sulphidic precipitating agent for Hg, which forms a weakly water-soluble Hg compound, and AL as a carbon-based sorbent with a wide range of pore radii. The presence of AL in the slurry resulted in a higher

SO_2-removal efficiency up to 90%, but using TMT 15® did not have a significant effect. The obtained results reveal the improving effects of both additives on suppressing Hg re-emission from the slurry. At the steady state for the slurry containing no halides, usage of AL did not lead to any positive effect regarding the diminishing Hg re-emission. On the other hand, the co-existence of halides and AL resulted in Hg re-emission of almost zero, which shows the need to form nucleophilic Hg^{2+} compounds in the slurry for adsorption of Hg^{2+} on AL. Even though using additives improves Hg retention in the slurry, during the start-up process, even for the best case, the loss of ~10% in the Hg^{2+} inventory was measured. In the absence of additives and halides, the slurry retained only 10% of its inventory due to the high Hg re-emission. For the iodide-containing slurry, the high Hg^{2+} re-emission led to a high loss of the Hg inventory compared to the other halides, although the Hg^{0} re-emission was quite low. The adsorbed Hg on the gypsum was almost the same for all the investigated slurries in the absence of additives, although the total concentration of Hg was different. Thus, it could be concluded that the adsorption capacity of the solid particles in the slurry was the limiting parameter for the slurries without additives. Both additives contributed significantly to the increase in Hg concentration in the solid fraction. However, the filtration process was conducted using a paper filter, which resulted in removing all particle sizes of the gypsum. As hydro cyclones are used to separate the solid fraction for gypsum production in the full-scale FGDs, the gypsum quality using additives cannot be predicted using the result of this study. The correlation between the redox potential and sorption equilibria of Hg compounds could be derived from the results obtained from the share of Hg in the aqueous phase. The reducing environment of the slurry using TMT 15® shifted the sorption equilibria towards particle-bound Hg.

Conflict of Interest

None declared

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