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Reemission of elemental mercury and mercury halides in wet flue gas desulfurization

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ABSTRACT

The wet flue gas desulfurization process enables the removal of sulfur dioxide (SO₂) and water soluble mercury compounds (e.g. HgCl₂) from coal derived flue gas. The aim of this study is to improve the state of science about subsequent processes in the liquid phase of the slurry, leading to the undesired reemission of mercury. For that purpose, experiments are carried out on a continuously operated lab-scale wet flue gas desulfurization test-rig. The parameters investigated include slurry temperature, pH-value, individual halide concentration and slurry aeration flow rate. The results indicate that the reemission of elemental mercury results from the chemical reduction of dissolved oxidized mercury species with sulfite being the reducing agent. For increased slurry temperature and within individual concentration ranges of the halides bromide and iodide, simultaneous desorption of both, elemental mercury and oxidized mercury compounds into the clean gas is observed. The underlying mechanism is proposed to be the formation of the volatile uncharged oxidized mercury species HgBr₂ and HgI₂ respectively. Reemissions of both elemental and oxidized mercury species decrease with decreasing temperature and increasing share of charged halogenidomercurate(II)-complexes. Formation constants, inert redox character and volatility of halogenidomercurate(II)-complexes increase in the order Cl⁻ < Br⁻ < I⁻.

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1. Introduction

It is widely recognized, that mercury (Hg) is a pollutant of global concern due to its toxicity and long-range transport in the atmosphere. Combustion processes account for a significant share of anthropogenic Hg emissions into the atmosphere (UNEP, 2013), (Yudovich and Ketris, 2005). Thus, during the last decades, significant efforts are being undertaken to reduce the emission of Hg by coal fired power plants. In this context, co-removal of Hg by existing air pollution control devices (APCD) plays an important role.

Mercury enters the furnace of power plants as a trace element of coal and secondary fuels. Due to its chemical and physical properties, for typical combustion chamber temperatures, it is almost exclusively released as elemental mercury vapor (Hg⁰) into the flue gas (Martel and Rentz, 1988). Subsequently, as the flue gas passes the flue gas cleaning chain, Hg⁰ undergoes chemical and physical interactions with further flue gas constituents. For decreasing temperature, Hg⁰ is oxidized in presence of hydrogen halides to Hg²⁺-compounds, such as HgCl₂, HgBr₂ and HgI₂ (Senior et al., 2000), (Galbreath and Zygarlicke, 2000), (Hall et al., 1991), (van Otten et al., 2011), (Chi et al., 2009), (Wilcox et al., 2012). In addition to the homogeneous gas phase oxidation of Hg⁰ by

hydrogen halides, the heterogeneous oxidation of Hg⁰, catalyzed by SCR-DeNO_x catalysts, increase the share of oxidized Hg²⁺-compounds in total Hg-content of the flue gas downstream of the SCR-DeNO_x unit (Gutberlet et al., 1992), (Laudal et al., 2003), (Kamata et al., 2009), (Eswaran and Stenger, 2008), (Rallo et al., 2012), (Wilcox et al., 2012). Due to the usual proportioning of the individual halogens in coal, HCl represents the dominant hydrogen halide in flue gas. Thus, HgCl₂ is the major oxidized Hg²⁺-compound in typical coal derived flue gases (Acuña Caro, 2013), (Wu et al., 2010), (NESCAUM, 2010), (Yudovich and Ketris, 2005). However, the oxidation of Hg⁰ by HBr and HI is favored at higher temperatures and proceeds at higher reaction rates, when compared to the reaction of Hg⁰ with HCl (Vosteen and Kanefke, 2003), (Eswaran and Stenger, 2008), (Niksa et al., 2009), (Qu et al., 2010). Therefore, actual speciation of Hg downstream of the SCR-DeNO_x unit depends not only on temperature, but also on individual hydrogen halide concentrations. For specific coals with uncommon distribution of halogen content and for the addition of halide-based additives to the fuel as a measure to increase Hg⁰-oxidation, the formation and fate of all relevant Hg²⁺-halides has to be considered in order to predict the Hg co-removal efficiency of APCDs.

Several studies reveal, that the co-removal of Hg from flue gas by electrostatic precipitators and fabric filters benefits from high share of Hg²⁺-compounds in total Hg-content in flue gas due superior sorption properties of Hg²⁺-halides on fly ash particles as well as on activated carbon based sorbents when compared to the adsorption of Hg⁰

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(Wang and Wu, 2006). Moreover, the composition and the surface area of the fly ash particle are of crucial importance (Kostova et al., 2013), (Goodarzi, 2005). However, the by-product fly ash is often further utilized as a raw material in the construction industry. Thus, high Hg content of fly ash may restrict its usability.

The final stage of the typical flue gas cleaning chain in coal fired power plants is the wet flue gas desulfurization (FGD) unit. The state of the art technology for the removal of SO₂ from flue gases is the wet FGD process utilizing limestone CaCO₃ as neutralization agent. In a countercurrent spray scrubbing process, the circulating slurry is atomized and the spray is brought into contact with the flue gas in the absorber tower. Water soluble gases, such as SO₂, are absorbed by the slurry. Final product of the wet FGD process in natural oxidation configuration is CaSO₃ sludge, which has to be landfilled. Plants operated in forced oxidation configuration produce commercial grade gypsum (CaSO₄·2H₂O), which is utilized in the construction materials industry (e.g. wallboard production) (Kairies et al., 2006), (Leiva et al., 2010), (Hamm et al., 2004). In contrast to Hg⁰, gaseous HgX₂-compounds (X = Cl, Br, I) are more readily water-soluble (Haynes, 2016). Thus, the wet FGD process offers the benefit of removing not only sulfur oxides and hydrogen halides, but also HgX₂-species from flue gas. From a sustainable point of view, the desired sink of Hg in the flue gas cleaning chain is the FGD waste water effluent. In the subsequent waste water treatment section, dissolved Hg²⁺-compounds are precipitated by sulfide based reagents. Hence, the resulting highly concentrated solid waste stream of insoluble heavy metal salts (e.g. HgS) can be disposed safely. Numerous lab- to full-scale investigations demonstrate that wet FGD is capable of absorbing the oxidized Hg²⁺-fraction from flue gas almost quantitatively (Wu et al., 2010), (Font et al., 2009), (Niksa and Fujiwara, 2005). However, many of those investigations also reveal the reemission of previously absorbed Hg to the clean gas for unfavorable operating conditions (Omíne et al., 2012), (Heidel et al., 2014), (Wo et al., 2009). Hence, it is widely accepted, that reemission phenomena of Hg in wet FGD of coal fired power plants are triggered typically by redox reactions in the liquid phase, leading to the formation and desorption of Hg⁰. Being the dominant halide in FGD slurries, usually the isolated impact of chloride concentration on the Hg⁰ reemission mechanism is investigated. However, for specific plants, it is observed, that despite their good aqueous solubility, gaseous HgX₂-compounds are detected downstream of the FGD at relevant concentrations (Córdoba et al., 2012), (Bittig, 2010), (Schwämmle et al., 2015). In this context, limited data is available in literature. Thus, this paper investigates the reemission of both Hg⁰ and HgX₂-compounds and illuminates the impact of the halides Cl⁻, Br⁻ and I⁻ on the HgX₂-reemission mechanism.

2. Materials and methods

Experiments were carried out in a fully automated, continuously working lab-scale FGD, which was already described previously (Heidel et al., 2014), (Scheffknecht et al., 2012). Fig. 1 shows a scheme of the applied test rig. The lab-scale FGD consists of an absorber column and an external FGD sump. The synthetic flue gas can be adjusted according to the desired investigated parameters and consists of a carrier gas flux containing 15 vol% CO₂, 3.5 vol% O₂ and balance N₂. Further components as SO₂, HCl, H₂O, Hg⁰ and HgCl₂ can be added in wide concentration ranges via mass flow controller and dosing valves. The synthetic flue gas is preheated to 150 °C before it is led into the bottom of the absorber column, where it is counter currently contacted with the circulating scrubber slurry, which is fed into the absorber top by a peristaltic pump. Measurement devices along the absorber column allow the investigation of gas phase concentrations and the extraction of liquid samples along the column heights. The loaded scrubber slurry is collected in the bottom of the absorber column and subsequently transferred through a siphon into the external sump. There, forced oxidation of dissolved sulfite species is ensured by the aeration of the

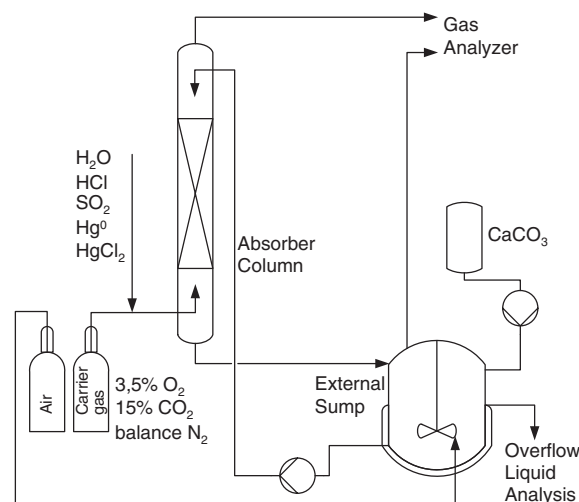


Fig. 1. Functional principle of the lab-scale wet FGD test-rig.

stirred slurry. The aeration air flux and the slurry temperature can be adjusted according to the desired investigations. Redox-potential and pH-value in the external sump as well as in the bottom of the absorber column are continuously measured and logged. Moreover, thermocouples are installed in the external sump, the bottom of the absorber column, the gas in- and outlet and at different heights along the column.

Solid content of the circulating scrubber slurry is adjusted to 3.5 wt% and the addition of fresh limestone slurry via hose pump is triggered when pH in the external sump falls below the adjusted pH value. Hence, the test-rig is operated at constant pH-value. An overflow pipe in the external sump enables the discharge of reaction products and ensures a constant slurry volume. Slurry composition can be adjusted to the desired concentrations by the addition of pure substances prior to the experiments.

Gas concentrations are measured continuously at the outlet of the absorber column as well as in the aeration air flux leaving the external sump, which enables the differentiation between reemitted Hg and Hg which was not absorbed at all in the first place. Measurements of O₂, SO₂ and CO₂ were carried out with on-line gas analyzers (paramagnetic and NDIR sensors) and total mercury (Hg^T) was measured according to the principles of atomic absorption spectroscopy (AAS) combined with a SnCl₂ reduction unit upstream the analyzer. Hg⁰-concentration is measured by the application of a selective adsorbent for gaseous Hg²⁺-components upstream the analyzer. Thus, Hg^T and Hg⁰ are measured directly while Hg²⁺-concentration is calculated by mass balance. Concentrations of anions in the scrubber slurry are determined by ion chromatography and dissolved Hg²⁺-species are measured via cold vapor AAS. Sulfite concentration of the slurry is titrated iodometrically.

For the experiments in the present work standard experimental conditions were defined to be 2000 mg/m³ SO₂-concentration at the inlet of the absorber, 3 l_{STP}/min flue gas flow rate and 60 ml/min slurry circulation flow rate. The investigated parameters include aeration flow rate, slurry temperature, pH-value and halide concentration.

3. Thermodynamics of Hg²⁺-compounds

The compounds HgCl₂, HgBr₂ and HgI₂ are characterized by covalent bonds. The linear shape molecules are hardly dissociated in aqueous solutions. As can be derived from their Henry-coefficients, those compounds are to be regarded as volatile species. In dependence on gas-liquid equilibrium, they are able to desorb into the gas-phase (Schuetz et al., 2012). Covalent characteristic and volatility of the individual HgX₂-compounds (X = Cl, Br, I) increase in the order Cl < Br < I (Fleming, 2010), (Riedel and Alsfasser, 2007). If multiple ligands are present in solution, several dissolved HgX₂-compounds coexist due to

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