

Impact of additives for enhanced sulfur dioxide removal on re-emissions of mercury in wet flue gas desulfurization



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HIGHLIGHTS

- Mercury removal in wet FGD.
- Re-emission of mercury.
- Additives for enhanced SO₂ removal in wet FGD.
- Reaction mechanisms of mercury re-emissions.
- Multi pollutant control by wet FGD.

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ABSTRACT

The wet flue gas desulfurization process (FGD) in fossil fired power plants offers the advantage of simultaneously removing SO₂ and other water soluble pollutants, such as certain oxidized mercury compounds (Hg²⁺). In order to maximize SO₂ removal efficiency of installed FGD units, organic additives can be utilized. In the context of multi-pollutant control by wet FGD, the effect of formic and adipic acid on redox reactions of dissolved mercury compounds is investigated with a continuously operated lab-scale test-rig. For sulfite (SO₃²⁻) concentrations above a certain critical value, their potential as reducing agent leads to rapidly increasing formation and re-emission of elemental mercury (Hg⁰). Increasing chloride concentration and decreasing pH and slurry temperature have been identified as key factors for depressing Hg⁰ re-emissions. Both organic additives have a negative impact on Hg-retention and cause increased Hg⁰ re-emissions in the wet FGD process, with formic acid being the significantly stronger reducing agent. Different pathways of Hg²⁺ reduction were identified by qualitative interpretation of the pH-dependence and by comparison of activation enthalpies and activation entropies. While the first mechanism proposed identifies SO₃²⁻ as reducing agent and is therefore relevant for any FGD process, the second mechanism involves the formate anion, thus being exclusively relevant for FGDs utilizing formic acid as additive.

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1. Introduction

Sulfur (S) and Mercury (Hg) enter the combustion chamber as constituents of coal and secondary fuels [1]. The dominant gas phase compound of sulfur is sulfur dioxide (SO₂). However, due to subsequent reactions with other flue gas constituents and in dependence of the configuration of the installed air pollution control devices (APCD), the formation of SO₃ can be promoted, leading to cold-end corrosion phenomena. The most common technology for SO_x-removal in Europe is the wet flue gas desulfurization (FGD) process with limestone, enabling SO_x-removal rates of >95%. An overview about available SO₂ control technologies and the corresponding abatement costs can be found in [2].

The reactions of the trace element Hg in the flue gas and its interaction with other flue gas components are of complex nature. Due to the high temperatures in the combustion chamber, the thermodynamic equilibrium of Hg-reactions is shifted to its elemental form (Hg⁰). With decreasing temperature and affected by the flue gas composition, gaseous Hg⁰ undergoes oxidation to bivalent mercury (Hg²⁺), leading to the formation of HgCl₂ in the presence of HCl, which is the dominant hydrogen halide in coal derived flue gas without additives. The heterogeneous oxidation of Hg⁰ is catalyzed by high-dust SCR DeNOx systems, resulting in higher shares of HgCl₂. A certain fraction of mercury is bound to particulate matter (Hg^p), due to sorption on the surface of ash particles. While elemental mercury is considered not to be affected by conventional flue gas cleaning systems, Hg^p is removed by particle filters [3]. Due to the high solubility of HgCl₂ in water, wet FGD offers the possible side benefit of removing HgCl₂ from

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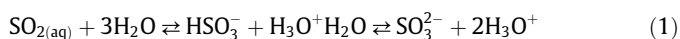
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the flue gas efficiently. Therefore, wet FGD systems have considerable influence on mercury removal [4]. However, due to the utilization of high-sulfur coal blends, the efficiency of installed FGD units is often driven to its limits. A reasonable strategy for the optimization of the process with low investment costs is the addition of organic pH-buffer systems to the slurry. These additives lower the pH-drop caused by the absorption of SO₂ in the slurry droplets, leading to an increased mass transfer during the whole contact time between slurry and flue gas and subsequently improved SO₂ removal efficiency. For this purpose, carboxylic acids are often utilized, such as formic and adipic acid. It is known that under unfavorable FGD operational conditions and in presence of suitable reducing agents in the liquid phase, dissolved Hg²⁺ can be reduced to Hg⁰, which is released to the clean gas [5]. Besides compounds of sulfur with the oxidation number of +IV (S(IV)), (di-) carboxylic acids are known to be possible electron donors [6]. Thus, these organic compounds are able to act as reducing agents under specific conditions. Therefore, their presence in the liquid phase of the slurry could lead to the previously described chemical reduction of dissolved HgCl₂, restricting the benefit of co-removal of mercury by the wet FGD system. In FGD slurries, there is a permanent interaction of complex formation and redox reactions of mercury compounds. Considering the large volume of the circulating slurry containing dissolved HgCl₂, re-emissions of Hg⁰ are able to negatively impact the overall Hg removal efficiency of the FGD. Thus, factors leading to stable dissolved mercury compounds are essential for overall high Hg removal rates. Previous studies indicate that the optimization of operational parameters can lead to significantly lower Hg-emissions [7,8].

2. Reactions of SO₂ and Hg compounds in wet FGD

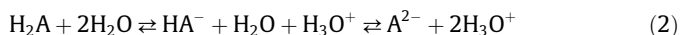
There are several parameters determining the rate of SO₂-absorption in wet FGD slurries. The impact of numerous operating parameters can be found in [9]. However in this work, main focus is put on temperature and pH-value of the slurry. Considering Henry's Law, there is an exponential dependence of the solubility of SO₂ on temperature.

Dissociation of SO_{2(aq)} and relevant S(IV) compounds



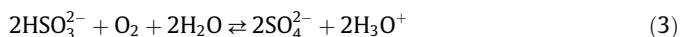
Dissociation product of SO₂ is the (bi-) sulfite anion and (one) two proton(s), which explains the impact of pH on SO₂ mass transfer. By raising pH, the equilibrium is shifted to the deprotonated sulfite side.

pH-buffer effect of di-carboxylic acids



In presence of the organic additives investigated in this study, both being weak organic acids and co-existing with their conjugated base in the solution, the drop of pH-value in the circulating slurry caused by the uptake of SO₂ is reduced. The buffering capacity is directly linked to the operational slurry pH-value of the process. From the Henderson–Hasselbalch equation it can be derived, that the maximum buffering capacity is obtained for identical pH- and pK_A-values of the carboxylic acid utilized. Being the negative logarithm of the acid constant, the pK_A-value of suitable organic additives should be within the range of applicable operating pH-values in the FGD process.

Oxidation of S(IV)



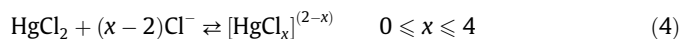
The oxygen content of the flue gas enables partial oxidation of S(IV)-compounds in the absorber section of the FGD. In forced oxidation mode, S(IV)-oxidation is enhanced by blowing an airflow

into the sump of the FGD. The overall reaction product of the described process is gypsum. Therefore, the pH of the slurry is controlled to a constant value by dosing fresh limestone slurry in order to replace the consumed CaCO₃ and to neutralize the acidic slurry. Limestone has a low solubility in water; however the Ca²⁺ concentration in the slurry increases for decreasing pH-value. Hence, the influence of pH on the FGD-process is ambivalent: acidic slurries enhance limestone solubility on the one hand, but inhibit H₂SO₃ dissociation and overall reaction rate on the other.

The previously described operational parameters and additional dissolved compounds have a strong impact on the fate of Hg compounds entering the scrubber. Due to the high solubility of HgCl₂ in water and its low gaseous mass flow compared with SO₂, FGD units are able to remove HgCl₂ almost quantitatively. Because of its very low solubility and high volatility, the elemental form of gaseous mercury is usually not absorbed by the slurry in the scrubber. Former studies show rather an increase of the concentration of Hg⁰ at the outlet of wet FGD systems [5]. To clarify this phenomenon, it is necessary to identify possible reaction pathways leading to the reduction of previously absorbed Hg²⁺-compounds to Hg⁰.

HgCl₂ is a compound with covalent bonds; the linear shape molecule is hardly dissociated in aqueous solutions [10]. Dissolved HgCl₂ has the affinity to form complexes in solution with suitable electron donor ligands. An approach in predicting the complex chemistry of mercury is the hard and soft acid bases theory (HSAB), which introduces two classes (and intermediates) of acids and bases. It states that complexes formed by combination of acceptors and donors of the same class show strong bindings and high stability [11]. Hg²⁺ is classified as a typically soft acid, thus forming stable complexes with soft bases. Regarding the composition of the aqueous phase in FGD slurries, possible complexing agents for Hg²⁺ considered in this work are HSO₃⁻/SO₃²⁻ and Cl⁻. Both being classified as borderline bases between hard and soft, while SO₄²⁻, OH⁻ and CO₃²⁻ are regarded as classic hard bases and therefore unsuitable to combine with Hg²⁺ under typical FGD conditions. The formation of stable complexes is essential to permit the reduction of uncomplexed HgCl₂ by electron donors. For increasing halide content (e.g. Cl⁻) of the slurry, HgCl₂ coexists with [HgCl₃]⁻ and [HgCl₄]²⁻ complexes. According to the stability diagram in [12], [HgCl₄]²⁻ is the dominating complex when the Cl⁻ concentration is higher than 0.2 mol/l. This is in good agreement with calculations in [13]. It is stated, that increasing the activity of chloride ions greatly extends the stability of Hg₂²⁺ and Hg²⁺ ions by the formation of Hg₂Cl₂ and [HgCl₄]²⁻ complexes. These statements are also true when exchanging Cl⁻ by Br⁻. The stability constants of compounds consisting of Hg²⁺ with Br-ligands are even higher than of those with Cl⁻. Therefore, for power plants using both wet FGD and bromide based Hg control strategies, the impact of Br⁻ concentration of the slurry has to be considered [14].

Formation of Hg²⁺-Cl⁻ complexes in FGD slurries



Also, multi-ligand complexes consisting of Hg²⁺ as central ion and with several different ligands (e.g. Cl⁻, Br⁻ and S(IV)-compounds) are suggested by several authors [15,16]. Mercury is a relatively noble element, the Hg²⁺/Hg⁰ half cell reaction is listed with a standard electrode potential of +0.85 V [10]. Therefore, redox reactions with participation of dissolved HgCl₂ are likely to occur in FGD slurries. The equilibrium of dissociation of the covalent molecule is strongly dependent on pH and oxidation–reduction potential (ORP) [17]. However, a certain amount of dissociated Hg²⁺ can be expected in FGD slurries [18]. Reaction products of the chemical reduction of Hg²⁺ by S(IV) are sulfate and elemental mercury, which is emitted to the gas phase.

Chemical reduction of Hg²⁺

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