

**Effect of adding aluminium salts to wet FGD systems upon
the stabilization of mercury**

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Abstract

This paper evaluates the effect of using aluminium salts in wet Flue Gas Desulphurization Plants (FGD) upon mercury reemission. Aluminium sulfate is employed to increase the SO₂ retention capacity of low porosity limestone. However, its presence in the FGD system also influences the chemical reactions of the species in the scrubber. This study, performed at lab-scale to assess the reduction of mercury from aqueous solutions and gypsum slurries, has demonstrated that the addition of aluminium sulfate mainly affects the pH of the solution and the formation of sulfite ions, which in turn affects the mechanisms of mercury re-emission.

Keywords: Mercury, FGD, Additive

Introduction

The problems arising from SO₂ emissions in energy production from coal are controlled by means of different kinds of Flue Gas Desulphurization systems (FGD), among which the most popular are wet FGD or scrubbers. These systems can achieve SO₂ removal efficiencies higher than 99 % depending on operation conditions. The use of highly efficient scrubbing solutions allows the process to be optimized. In order to increase the retention capacity of limestone slurry, additional solid compounds, such as aluminium sulfate, can be employed. However the use of these additives in the FGD system may also influence the chemical reactions occurring in the scrubber.

In a study performed by Alvarez-Ayuso et al. (2006) [1] on the environmental characteristics of combustion by-products from a specific FGD plant, it was found that

fluoride was a critical element for admitting FGD gypsum for disposal at landfill sites as a non-hazardous waste. It was observed that the amount of fluoride leached was very close to the limit (150 mg kg^{-1}) established in EU by the Council Decision 2003/ 33/EC, making it necessary to introduce measures to control the fluoride content in FGD gypsum. Various procedures were evaluated [2-4] for stabilizing this by-product for its disposal and for minimizing the leaching of fluoride. Among the different possibilities for waste stabilization, the incorporation of additives to the FGD for fluoride retention was considered as an appropriate option and of the materials with the most suitable features for retaining fluoride, aluminum sulfate proved to be the most effective. By adding aluminum sulfate a substantial reduction in fluoride leaching was achieved at lab scale [3] where the formation of an insoluble species of Al-F was observed and consequently a reduction of CaF_2 . When this additive was used at industrial scale [5] it also caused the stabilization of the fluorine in the water and a greater efficiency of the limestone on the reaction with sulfur.

In the studies mentioned above [2-5] the effects of adding aluminium sulfate to an industrial wet FGD plant were assessed on the basis of the quality of the gypsum produced, the possible future lixiviation of fluorine and the efficiency of sulfur capture. However, the effect of adding the aluminium salt to the limestone slurry upon the chemistry of other compounds present in the system also needs to be considered. In particular, the effect of aluminium sulfate on mercury behavior in the scrubber needs to be evaluated.

FGD systems can be considered as gas cleaning systems for elements other than sulfur [6,7]. However for these systems to be employed for the retention of toxic trace elements, the elements entering the plant, either in gas phase or as particulate matter, must be distributed among the sub-products (water, gypsum and flue gases) in non-

hazardous levels. Mercury enters the FGD plant mainly in gas phase as both elemental (Hg^0) and oxidized mercury (Hg^{2+}) and may also be found in relatively small amounts as particulate matter (Hg^p). Whereas Hg^{2+} species are soluble in water, Hg^0 is insoluble and leaves the system in gas phase [8-10]. Depending on several conditions and variables, Hg^{2+} may remain in solution, be retained in the gypsum or be reduced and reemitted as $\text{Hg}^0(\text{g})$. Re-emission as Hg^0 is undesirable and needs to be avoided in so far as is possible. To this end, it is essential to control all the reactions and mechanisms that take place in the scrubber liquor. In this study, the effect of adding aluminium sulfate to the scrubber to enhance SO_2 removal upon the reduction of mercury was evaluated. Although the study was carried out at lab-scale, the results are in agreement with those of industrial scale evaluations of mercury behaviour in plants that use this additive.

Experimental

To investigate the re-emission of Hg^0 from simulated scrubber solutions comparable to those of FGD plants a lab-scale device consisting of 3 parts was used (Figure 1). Each part was built with a different purpose (i) to prepare the simulated gas, (ii) to conduct the reactions and to capture the mercury and (iii) to analyse the reemitted Hg^0 . The mercury species in the simulated flue gas were generated in a commercial gas evaporator (HovaCAL, IAS GmbH) from an aqueous mercury solution stabilized in a hydrochloric acid medium and evaporated at 200°C . In these conditions HgCl_2 is the most probable species to be formed in the flue gas. The gas containing $50 \mu\text{g}/\text{m}^3$ of Hg^{2+} or $130 \mu\text{g}/\text{m}^3$ of a mixture of Hg^{2+} and Hg^0 in N_2 (3 L/min) was conducted to the reactor along PFA pipes which were heated at 120°C with a temperature-controlled heating tape to prevent the condensation of moisture and absorption of mercury onto its surface.

The reactor consisted of a 500 ml glass flask fitted with three connections: a flue gas inlet, an outlet and an additional connection for the pH electrode. The gypsum slurry inside the flask was stirred to favour the mixing of the mercury with the reactants and was kept at constant temperature (40°C). The pH was recorded with a Mettler Toledo DL53 Titrator. Two series of tests were performed. The first series was carried out in an aqueous solution containing sulfite ions (sodium sulfite) and sulphate ions (sulfuric acid), in addition to the Hg^{2+} captured from the flue gas. The second series was carried out in a suspension containing gypsum slurry prepared with 1 % of natural limestone and 0.1 mol/L of sulphuric acid. Different concentrations of aluminium sulfate ranging from 0 to 10 mM of sulfate ions were used in both series of tests.

A continuous mercury emission monitor (VM 3000, Mercury Instruments) was employed to measure the Hg^0 generated as the oxidised mercury species (designated as Hg^{2+}) underwent reduction. The mercury content of the limestone, gypsum and liquid samples produced in the tests was determined by means of an Advanced Mercury Analyser (AMA 254). The gypsum samples were first dried for 48 h at 40°C to prevent the decomposition of the samples and the loss of mercury.

Results

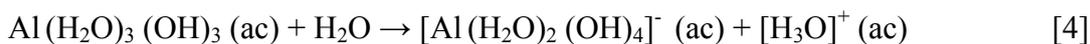
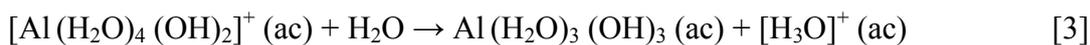
Figure 2 illustrates the reemission of Hg^0 during the time of the experiments. In this Figure the Hg^0 emitted from the reactor during the experiment is represented against time for each of the five tests, using different amounts of aluminium sulfate in the scrubbing solution. The total amount of mercury passed through the reactor was in all cases $130 \mu\text{g}/\text{m}^3$. A small fraction of the mercury evaporated was $\text{Hg}^0(\text{g})$, the $\text{Hg}^{2+}(\text{g})/\text{Hg}^0(\text{g})$ ratio of the gas entering the reactor being 96/4. This ratio was confirmed by means of the Ontario Hydro Method and corresponds to the baseline value of the

Hg⁰(g) leaving the reactor (8 µg/m³) (Figure 2). The blank test without aluminum sulfate was performed in a solution containing 1 mM sulfite ions. The second solution tested contained the 10 mM of aluminium sulfate in the absence of sulfite ions, just to check the effect of the additive. Then, a sequence of tests has been carried out at a pH of 4.0, with a concentration 1mM of sulfite ions and increasing amounts of Aluminium sulfate (Figure 2).

The Hg²⁺ present in the gas was retained in the solution inside the reactor, as it was confirmed by an analysis of this solution at the end of the experiment. It can be observed (Figure 2) that in these solutions containing sulfite ions, the presence of aluminum sulfate favors the reduction of mercury and that the kinetics of the process depends on the amount of aluminium sulfate. The same figure shows that there is a relation between the concentration of aluminum sulfate and the amount of elemental mercury reemitted to the atmosphere. When the concentration of aluminium sulfate reaches 10 mM in the presence of sulfite ions, reduction of the oxidized mercury species occurs quickly. However, when aluminium sulfate is added in the absence of sulfite ions, reduction of Hg²⁺ does not occur, which explains why the background curve overlaps that of the blank experiment.

The correlation between aluminium sulfate and mercury reduction may be due to the presence of aluminium ions in the scrubber solution. The aluminium ions are hydrolyzed in aqueous solutions to form hydrated aluminium ([Al(H₂O)₆]³⁺) which generate protons according to Eq. 1 to 4. As a result, the pH decreases and the stability of the mercury in solution is diminished.





The role of aluminium in this process can be confirmed by conducting different experiments with solutions containing the same quantity of sulfite and adding 10 mmol/L of sulfate ions in the form of sodium sulfate instead of aluminium sulfate. No significant differences were observed (Figure 3) in mercury behaviour in the presence of sodium sulfate when compared to the blank. In all cases Hg^{2+} dissolved inside the reactor until the concentration reached a value of $0.4 \mu\text{g ml}^{-1}$, the mercury reduction occurring in all cases at the same velocity. In these solutions the pH decreased during the experiment and the point of reduction was established as taking place at a pH lower than 6.0. These data prove that the addition of aluminium sulfate in the presence of high sulfite concentrations favours the reduction of Hg^{2+} which is due to the decrease in pH, since mercury forms stable complexes with sulfite ions such as HgSO_3 or $\text{Hg}(\text{SO}_3)_2^{2-}$ at pH values higher than 6. However, it cannot be discarded that the formation of Al^{3+} complexes prevents the formation of stable complexes of Hg^{2+} in solution.

These findings were verified in the second series of experiments carried out in gypsum slurries instead of in aqueous solutions when the flue gas contained a lower concentration of mercury. In these experiments 10 mM of sulfate ions were introduced as aluminium sulfate or sodium sulfate into the reactor which contained 100 g of gypsum slurry prepared from natural limestone. Fig. 4 shows the behaviour of mercury in the different slurry compositions. When aluminium sulfate was absent in the slurry, most of the oxidized mercury species were reduced to Hg^0 in a short time, the pH of the suspension being 7. The same behavior was observed in the experiment in which a similar amount of sulfate ions (sodium sulfate) was added to the natural limestone.

When sodium sulfate was used in these conditions instead of aluminium sulfate, the reduction of oxidized mercury was detected, as in the case of the aqueous solutions. When in a second test the aluminium additive was incorporated to the reactor, it was observed that the pH of the suspension decreased drastically and that no Hg^{2+} was reemitted. This result appoints that the aluminium additive in these conditions prevents the reemission of the Hg^0 originating from the reduction of the mercury dissolved by the sulfite ions. It can be inferred therefore that if aluminium sulfate prevent the re-emission of mercury only if it is added in such a high quantity that decreases the pH at which no sulfite ions could be formed in the slurry.

The percentages of mercury found in the liquid and solid fractions on completion of the experiments are given in Table 1. The values indicate that in the absence of aluminum sulfate (experiments A and D) there is a very low retention of mercury in the byproducts, since most of the mercury is reduced to Hg^0 leaving the reactor. However, when aluminum sulfate is present in the reactor, either with gypsum (experiment B) or with limestone (experiment C) the mercury is primarily retained in the liquid fraction, since soluble mercury species such as HgCl_2 are formed.

It can be therefore concluded that the presence of aluminum sulfate could prevent the reduction of Hg^{2+} in the liquid fraction by causing a decrease in the pH, and that the pH is the key to control the reemission of mercury. In other words, mercury retention depends on the amount of aluminium sulfate added to the scrubber slurry, since the greater the amount of $\text{Al}_2(\text{SO}_4)_3$ added, the lower the pH. The pH can be easily controlled by adjusting the liquid and gas ratio. When $\text{Al}_2(\text{SO}_4)_3$ is added it is necessary to maintain a strict control over this ratio.

Conclusions

The use of aluminium sulfate as an additive in wet FGD systems prevents the reduction of mercury and its subsequent reemission. Aluminum sulfate decreases the pH of the slurry to a level where the sulfite ions, responsible for the mercury reduction, cease to form. The incoming mercury remains in solution and is discharged with the wastewater.

Acknowledgements

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Table 1. Mercury partitioning in the byproducts.

<i>Experiment</i>	<i>Hg retention solid fraction (%)</i>	<i>Hg retention liquid fraction (%)</i>
A (gypsum CaC)	2	n.d.
B (limestone CaC, Al ₂ (SO ₄) ₃)	3	97
C (gypsum CaC, Al ₂ (SO ₄) ₃)	2	98
D (gypsum CaC, Na ₂ SO ₄)	3	n.d.

Figure Captions

Figure 1. Scheme of the system and FGD reactor.

Figure 2. Elemental mercury emission for different concentrations of aluminium sulfate (SO_4^{2-}); $[\text{S(IV)}]=1 \text{ mM}$; flue gas composition: N_2 , $130 \mu\text{g}/\text{m}^3 \text{ Hg}$.

*** In the absence of sulfite ions.**

Figure 3 Elemental mercury emission for different concentrations of sodium sulfate. $[\text{S(IV)}] = 1 \text{ mM}$; flue gas composition: N_2 , $130 \mu\text{g}/\text{m}^3 \text{ Hg}$.

Figure 4. Influence of aluminium sulphate on elemental mercury re-emission. 1 mmol SO_4^{2-} ($\text{Al}_2(\text{SO}_4)_3$ or Na_2SO_4). Flue gas composition: N_2 , $50 \mu\text{g}/\text{m}^3 \text{ Hg}$.

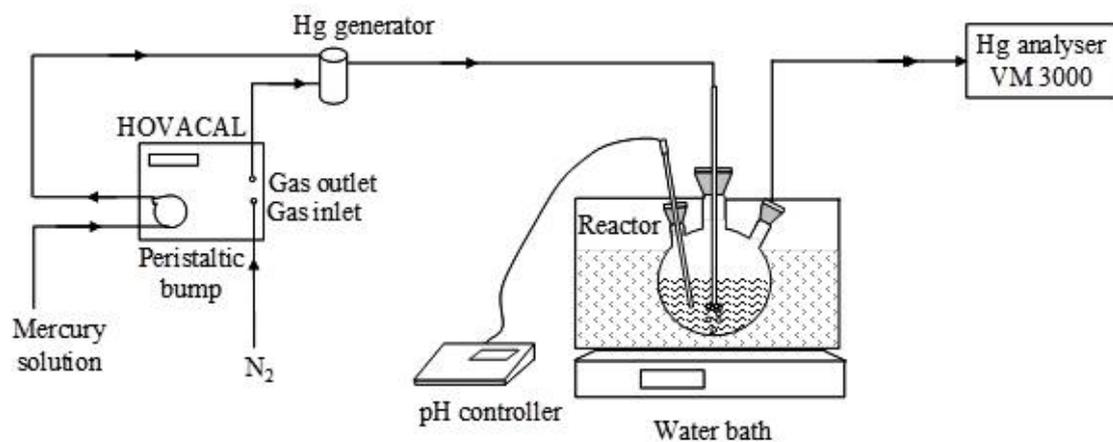


Figure 1

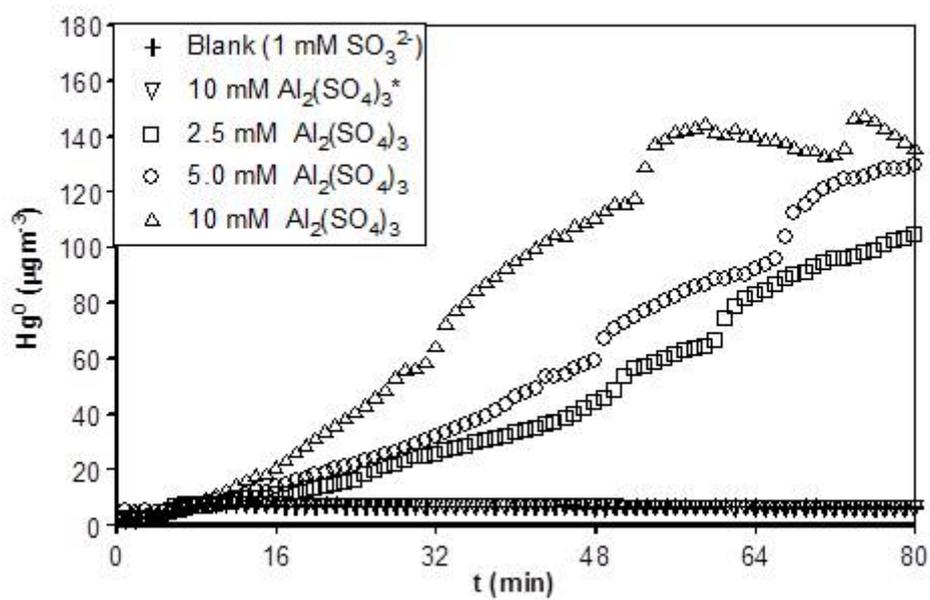


Figure 2

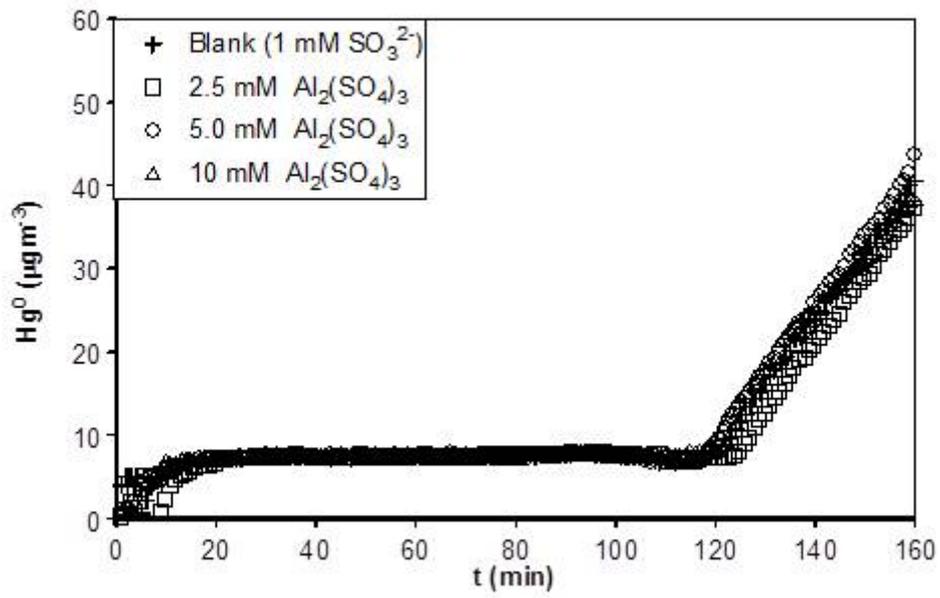


Figure 3

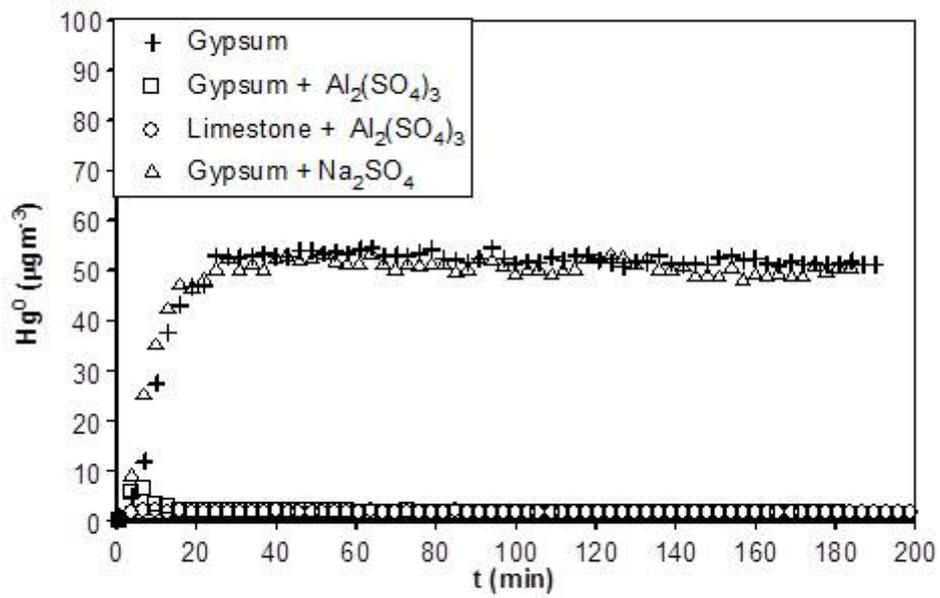


Figure 4