Control of Hg$^0$ re-emission from gypsum slurries by means of additives in typical wet scrubber conditions

Raquel Ochoa-González*, Mercedes Díaz-Somoano and M. Rosa Martínez-Tarazona

Instituto Nacional del Carbón (INCAR), CSIC. C/ Francisco Pintado Fé, 26, 33011, Oviedo, Spain

*Corresponding author

Phone: +34 985119090
Fax: +34 985297662
e-mail: rmtarazona@incar.csic.es
Abstract

The effect of different additives on the re-emission of Hg\(^0\) in wet limestone-based flue gas desulphurisation (WFGD) conditions is assessed. Because re-emission of elemental mercury from natural limestone is dependent on the pH of the gypsum slurry, re-emission of elemental mercury was evaluated for different additives using gypsum slurry with a constant pH value of 7. The additives investigated included oxidizing and reducing agents (Fenton reagents and sodium thiosulphate) and also chelating agents (2,4,6 trimercaptotriazine trisodium and sodium hydrosulfide). Fenton reagents were added to prevent the reduction of oxidized mercury species as H\(_2\)O\(_2\) was the precursor used to convert sulfite ions into sulphate or to oxidize Hg\(^0\). Thiosulphate were added so that mercury could be retained in the gypsum at low concentrations as insoluble HgS, while mercury is being stabilized in the liquid fraction at higher additive doses. The addition of 2,4,6 trimercaptotriazine trisodium (TMT) and NaHS in low doses prevented the reduction of oxidized mercury species as insoluble HgS and Hg\(_3\)(TMT) precipitate onto the gypsum slurry. TMT was found to be most effective additive for Hg\(^{2+}\) capture.

Keywords: wet FGD, additives, mercury capture

1. Introduction

Mercury and its compounds are highly toxic species which have a considerable impact on human health. Among the different mercury species, methylmercury is known to be the most toxic. What is more, there is clear evidence of the bioaccumulation and biomagnification of this neurotoxin in the aquatic food chain. Recent investigations have demonstrated that exposure to high levels of mercury may damage the brain, heart, kidneys, lungs and immune
systems [1-2] and harmful effects have also been detected even at low concentrations [3]. Children are especially vulnerable to the effects of mercury since it interferes in the development of their reasoning and learning processes. For example, prenatal methylmercury exposure has led to skin disorders and autism in Hong Kong children [4]. In terms of human exposure to mercury, fish consumption is the major exposure pathway, although inhalation may be another important source in areas with high concentrations of mercury in the air [5].

A large proportion of mercury is emitted to the environment by the burning of coal. This process is responsible for about one-third of anthropogenic mercury emissions [6]. Mercury may be present in flue gas as elemental mercury (Hg\(^0\)) or oxidized mercury (Hg\(^{2+}\)). It may also be retained in fly ash particles, in which case it is referred to as particle-bound mercury (Hg\(^p\)). The proportion of the different mercury species varies throughout the system. As the temperature of the flue gases decreases, mercury remains mainly as Hg\(^{2+}\) [7-8]. However, selective catalytic reduction (SCR) systems, which are used in some power plants to reduce NO\(_x\) emissions, have been shown to cause an increase in the proportion of Hg\(^{2+}\)(g) in flue gases [9-10]. Whereas Hg\(^p\) is retained in the electrostatic precipitators or bag filters, both Hg\(^{2+}\) and Hg\(^0\) species from the flue gas are emitted to the atmosphere in power plants without undergoing any post-combustion processes to reduce emissions. In some cases, wet flue gas desulphurization (WFGD) systems or scrubbers installed in coal fired power plants to control SO\(_2\) emissions have been used to decrease mercury emissions [11-12]. In such systems, SO\(_2\) reacts usually with the limestone slurry to produce insoluble gypsum. Hg\(^{2+}\) can be efficiently captured in WFGD by taking advantage of its high solubility in water [13]. In fact, it has been calculated that the mercury removal efficiency of FGD systems ranges from 51 to 90% [11-12;14-15] and these values increase up to 89% if SCR systems are installed [16]. Hg\(^{2+}\) may follow one of three pathways in WFGD systems. It may react with
other species to form Hg\(^0\) which is then re-emitted from the scrubber. It may be retained in the sludge and recirculated through the system or it may be captured in the grained fraction of solid by-products or gypsum. In the first case, oxidized mercury may be reduced by the aqueous S(IV) species (sulfite and/or bisulfite) resulting from the absorption of SO\(_2\) in the slurry [17]. In the second case, if the liquid fraction of the limestone slurry is recirculated, high concentrations of mercury may accumulate throughout the system giving rise to a new risk [18]. The last option appears to be the most suitable for desulphurization system which dispose of solid products at landfill sites if the spread of mercury is to be avoided. This involves using special additives for mercury capture as a mean of improving the efficiency of the WFGD system for the retention of mercury species in the solid fraction.

Another means of capture mercury involves the oxidation of Hg\(^0\) by chlorine and bromine species present in the flue gases [19-20], as well as the use of FGD oxidation additives, such as potassium permanganate and Fenton reagents. The oxidation rates of potassium permanganate are very high [21]. However, its application in desulphurization systems is not feasible due to its toxicity and ability to stain the gypsum. The Fenton process is based on the catalytic generation of hydroxyl radicals (\(\mathrm{OH}^\cdot\)) from H\(_2\)O\(_2\) and metal ions such as copper or iron. Previous studies have shown that \(\text{Fe}^{3+}\) salts (FeCl\(_3\) and Fe\(_2\)(SO\(_4\))\(_3\)) have a greater capacity to oxidize Hg\(^0\) than the salts of other metal ions such as Cu\(^{2+}\) [22], but their effect on the re-emission of mercury has not yet received much attention. The reagents involved in this process are not only able to oxidize Hg\(^0\) but may also inhibit the reduction reactions of the oxidized mercury species.

Oxidation inhibition is necessary in a dual alkali FGD system to improve reliability. Sodium thiosulfate has been demonstrated to be an effective oxidation inhibitor of sulphite in lime or
limestone slurry or in highly diluted sulfite solutions [23]. However, its effect on mercury removal has not been studied until now.

The most recent research focussed on the chelating capacity of Hg\(^{2+}\) sequesters such as 2,4,6 trimercaptotriazine trisodium (TMT) and sulphides. The results indicate that TMT has a lower chelating capacity than Na\(_2\)S [24] and that the dose of TMT should be kept to the minimum in order to limit emissions of mercury since doses that are too high could lead to the reduction of mercury instead of its precipitation [25]. However, these results have not been demonstrated in wet scrubber conditions with limestone slurry as the sorbent.

The objective of the present work was to evaluate the effectiveness of different additives in reducing mercury re-emission in gypsum slurries derived from natural limestone and to study the partitioning of this element in the solid and liquid byproducts. The effect of using iron-based Fenton-type additives and sodium thiosulphate to improve mercury retention in FGD systems was also assessed. The mercury capture efficiency of sodium hydrosulphide was compared with that of TMT in wet scrubber conditions.

2. Experimental

To investigate the reactions involved in Hg\(^0\) re-emission in wet flue gas desulphurization facilities, a FGD lab-scale device was set up [26]. A commercial evaporator (HovaCAL, IAS GmbH) was used to generate mercury species from an aqueous mercury solution, which was stabilized in a hydrochloric acid medium and allowed to evaporate continuously at 200°C. The mercury in gas phase was conducted to a N\(_2\) atmosphere. This resulted in a flue gas containing N\(_2\) and 50 \(\mu\)g/m\(^3\) of Hg\(^{2+}\) which was maintained at 3 L/min by means of a mass flow controller.
The reactor consisted of a 500 ml flask made of glass with three connections: an inlet and an outlet for the flue gas and an additional connection for the pH electrode and a titrator. The reactor was stirred to favour the mixing of the mercury with the sorbent and the reactants, and kept at constant temperature (40°C) during the tests since mercury reduction is sensitive to the operating temperature. The pH was kept constant at 7 to favour the formation of sulphite ions in the slurry. The pH was adjusted continuously by adding sulphuric acid 0.1 N with a continuous titrator. For each test, a slurry containing 1% of natural limestone and 0.1 mol/L of sulphuric acid was placed in the reactor. The gas before and after the reactor was conducted through PFA pipes which were heated at 120°C by means of a temperature-controlled heating tape to prevent the condensation of moisture and the adsorption of mercury on its surface.

A continuous mercury emission monitor (VM 3000, Mercury Instruments) was used to measure the elemental mercury generated through the reduction of oxidised mercury species during the experiments. The mercury content of the gypsum and aqueous samples generated in the lab-scale tests was determined by means of an Advance Mercury Analyser (AMA-254). The gypsum samples were dried for 48 h at 40°C prior to analysis to avoid decomposition of the samples and loss of mercury.

The stability of the mercury in the gypsum samples obtained from the laboratory-scale tests was evaluated in water in accordance with the UNE-EN 12457-2 norm. Leaching tests were performed in duplicate using a 1:40 solid:liquid ratio. The samples were mixed with water for 24 hours after which the gypsum slurry was filtered. The mercury dissolved in the liquid fraction was analyzed using the AMA.

For the analysis of Fe in the gypsum, the samples were previously digested with HNO₃:HCl at a ratio of 3:1 in a microwave oven. The analyses were carried out in a ICP-MS 7700x Agilent device equipped with a He collision cell to eliminate matrix interferences.
3. Results and discussion

Optimization of the pH for the re-emission of Hg$^0$

The effect of the pH on mercury re-emission was evaluated. Fig. 1 shows that the re-emission of Hg$^0$ from the reactor containing limestone and gypsum slurries is dependent on pH values. These were adjusted by using diluted sulfuric acid. It can be seen that the mercury concentration detected corresponds to the amount of Hg$^0$ re-emitted and increases at pH values higher than 5. More than 50% of the Hg$^0$ was produced when pH was kept constant at 6 and at pH=7 nearly 100% reduction was achieved. These results confirm that mercury capture in FGD systems depends on the pH of the slurry as the formation of sulfite ions is a function of the pH (Eq.1).

$$\text{Hg}^{2+} + \text{SO}_3^{2-} + \text{H}_2\text{O} \leftrightarrow \text{Hg}^0 + \text{SO}_4^{2-} + 2\text{H}^+ \quad [\text{Eq. 1}]$$

For pH values between 4 and 5 more than 90% of the mercury captured was retained in the liquid fraction of the slurry, as HgCl$_2$ is the main mercury species in the flue gas. A pH value of 7 was selected to carry out the retention experiments since the highest degree of Hg$^{2+}$ reduction was achieved in these conditions.

Fenton additives

When using a Fenton reactive, most of the mercury will be retained in the slurry in a pH range of 3-4 in which the oxidant radicals are formed. However, at the high pH values typical of FGD plants, the formation of such radicals is more difficult. In these more unfavorable conditions, mercury behavior was compared introducing Fe$^{3+}$ additives (FeCl$_3$ and Fe$_2$(SO$_4$)$_3$) into the slurry.

The re-emission of Hg$^0$ was evaluated employing different concentrations of Fe$_2$(SO$_4$)$_3$ in the absence and presence of H$_2$O$_2$ (Fig. 2a). It was found that Fe$_2$(SO$_4$)$_3$ does not affect the
reduction of mercury. However, when 200 mg/mL of H₂O₂ was added, the mercury in the slurry stabilized. It was also observed that the partitioning of mercury among the products is modified as a function of the concentration of Fe₂(SO₄)₃. Although the re-emission of Hg⁰ is similar for the different concentrations of Fe₂(SO₄)₃ tested (Fig. 2a), the presence of high concentrations of Fe₂(SO₄)₃ in the slurry increases the mercury retained in the solid fraction (Fig. 2c). This may be due not only to the adsorption of Hg²⁺ onto the gypsum particles but also to the formation of HgSO₄, which decomposes into HgO(s) at pH values of around 7. Moreover the addition of Fe³⁺ may favor the co-precipitation of mercury with Fe(OH)₃ particles.

With the FeCl₃ additive the results obtained by varying the concentration of Fe³⁺ between 25 and 200 mg/mL (Fig. 2b) also show that the combination of FeCl₃ and H₂O₂ prevents the re-emission of Hg⁰. As in the case of Fe₂(SO₄)₃, this is a consequence of the stabilization of mercury in the solution in the presence of H₂O₂. These results also suggest that under the experimental conditions of this study chloride ions resulting from the dissolution of FeCl₃ are unable to enhance mercury capture in the gypsum slurry because the reduction of Hg²⁺ by sulfite ions is thermodynamically more favored. The mercury partitioning in the byproducts indicates that an increase in mercury retention in the solid fraction occurs at higher concentrations of FeCl₃ (Fig. 2d), although the amount of mercury retained in the solid is lower than in the case of Fe₂(SO₄)₃ (Fig. 2c). This suggests that sulfate ions may be contributing to the formation of a small amount of mercury sulfate which then precipitates with the gypsum particles or decomposes into HgO(s). This would reinforce the main mechanism proposed above whereby mercury is adsorbed onto the particles of gypsum or Fe(OH)₃. The iron content in the gypsum samples varies between 0.26 (25 mg/L Fe³⁺) and 1.5% (200 mg/L Fe³⁺), indicating there may be a correlation between the concentration of
Fe$^{3+}$ and Hg capture. It is also possible that the high concentration of mercury that accumulates in the liquid fraction with the addition of FeCl$_3$ may be due to the stabilization of Hg$^{2+}$ as HgCl$_2$ in solution.

When the effect of different concentrations of H$_2$O$_2$ in the slurry was evaluated in the absence of iron salts (Fig. 3a) it was found that for low concentrations of H$_2$O$_2$ (1 mg/mL), mercury stabilizes in the gypsum slurry. However, if the partitioning between the solid and liquid fractions is evaluated (Fig. 3b), there is a significant reduction in the amount of mercury captured in the solid compared to that retained using iron salts. Only 2% of the mercury was retained in the absence of H$_2$O$_2$ due to the high amount of Hg$^{2+}$ converted to Hg$^0$ in the gypsum slurry, while no mercury was found in the liquid fraction. In contrast, when H$_2$O$_2$ is added in concentrations in the range of 1 to 300 mg/mL (Fig. 3b), the percentage of mercury retained in the solid increases to 20% for different concentrations of H$_2$O$_2$, even though most of the mercury is retained in the liquid fraction of the slurry as HgCl$_2$.

The possible leaching of mercury from the gypsum samples was also evaluated by carrying out leaching tests in water. As can be seen from Table 1, 3% of soluble mercury was detected in the leaching experiments using the gypsum obtained in the presence of FeCl$_3$. As the mercury concentrations in the gypsum samples obtained by adding Fe$_2$(SO$_4$)$_3$ and FeCl$_3$ are similar, it is likely that when FeCl$_3$ is used mercury is absorbed as HgCl$_2$, which then dissolves in water. No leaching of mercury occurred in the gypsum samples obtained when only H$_2$O$_2$ was used. However, this may be due to the low concentration of mercury in the sample or to the presence of other mercury species of lower solubility such as HgSO$_4$ and HgO.

The results obtained in Figures 2 and 3 indicate that the addition of H$_2$O$_2$, whether in the presence or absence of Fe$^{3+}$ salts, prevents Hg$^0$ re-emission. It appears that H$_2$O$_2$ not only
oxidizes the Hg\(^0\) formed in the scrubber, but it also reduces the generation of sulfite ions. This shows that the stability of mercury in the reactor is essentially due to the oxidizing effect of H\(_2\)O\(_2\). However, as the flue gas from coal combustion contains high concentrations of SO\(_2\), H\(_2\)O\(_2\) could be consumed by the sulphur species in the scrubber system.

**Thiosulphate**

The thiosulfate ion is a reductor species which prevents the oxidation of sulfur species present in the slurry and, as a consequence, it alters the sulfite/sulfate ratio. However, its reducing effect is not strong enough to convert oxidised mercury species into elemental mercury. This additive has several advantages over the other additives used, including its non-toxicity and its low cost. In the experimental conditions of this work, it was observed that the re-emission of Hg\(^0\)(g) decreases as the sodium thiosulfate concentration increases (Fig. 4a). However, for concentrations of thiosulfate between 10 and 20 mM, the retention of oxidized mercury does not reach 100%. Mercury capture in the gypsum increases when the amount of thiosulfate added is in the concentration range of 1 and 5 mM (Fig. 4b) due to the formation of HgS, as shown by Eq.2:

\[
\text{HgCl}_2 + S_2O_3^{2-} + H_2O \rightarrow \text{HgS} + SO_4^{2-} + 2Cl^- + 2H^+ \quad \text{[Eq. 2]}
\]

For higher concentrations of thiosulfate ions (10 and 20 mM), the mercury is mainly retained in the liquid fraction because it forms complexes such as HgS\(_2\)O\(_3\) and Hg(S\(_2\)O\(_3\))\(_2\)\(^{2-}\) which are stable in solution (Blythe et al., 2008). In short, the partitioning of mercury into liquid and solid fractions depends on the concentration of thiosulphate.

Leaching tests carried out with gypsum generated in the presence of Na\(_2\)S\(_2\)O\(_3\) indicate that, despite the high concentrations of mercury in the gypsum, the mercury species are insoluble in water, which is agreement with the reaction mechanism of Eq 2.
Hydrosulphide

Fig. 5a shows the $\text{Hg}^0(g)$ curves when the gypsum slurry contains different amounts of sodium hydrosulphide. $\text{Hg}^0$ emissions decrease as the sodium hydrosulphide concentration increases. However, a concentration of at least 1 mmol/L of sodium hydrosulphide is required to produce any significant reduction in mercury emission. Fig. 5b shows the distribution of mercury in the gas, liquid and solid byproducts for different concentrations of sodium hydrosulphide. It can be seen that mercury retention by the gypsum is enhanced by high concentrations of sodium hydrosulphide. With this additive, mercury forms $\text{HgS}$ in the slurry in accordance with Eq.3. $\text{HgS}$ is then adsorbed onto the gypsum particles.

$$\text{NaHS} + \text{Hg}^{2+} \rightarrow \text{HgS} + \text{H}^+ + \text{Na}^+ \quad \text{[Eq. 3]}$$

Leaching tests using the gypsum produced in the presence of NaHS show that the mercury species present in the solid fraction are insoluble in water, which indicates the formation of $\text{HgS}$.

TMT

Fig. 6a represents the emission of $\text{Hg}^0(g)$ for different concentrations of TMT. No re-emission of $\text{Hg}^0$ occurs for concentrations of additive higher than $8.0 \times 10^{-5}$ mmol/L. The amount of $\text{Hg}^0$ generated was significant only for $4.0 \times 10^{-5}$ mmol/L of TMT. Fig. 6b shows the proportion of mercury retained in the gypsum and flue gas. All of the mercury precipitates as $\text{Hg}_3\text{TMT}$ with the gypsum as no mercury was detected in the liquid fraction. The leaching tests carried out with the gypsum generated in the presence of TMT demonstrate that the mercury species formed are insoluble in water. A comparison of the additives NaHS and TMT based on the
The stoichiometry of Eq. 3 and 4 (1 and 1.5 respectively) shows that TMT has a higher mercury capture capacity than NaHS.

\[ \text{Na}_3 \text{Na} + \frac{3}{2} \text{Hg}^{2+} \rightarrow \text{Hg}_3(\text{TMT}) \]  

**4. Conclusions**

The effect that different additives have on elemental mercury re-emission has been studied under conditions in which the pH of the gypsum slurry is kept constant. The simulation of FGD wet scrubber slurries, where most of the oxidized mercury is reduced by sulfite ions or metals derived from limestone, demonstrated the ability of these additives to stabilize mercury in the solid and liquid fractions. Fenton reagents were added to prevent the reduction of oxidized mercury species. The oxygenated water in the Fenton reagent converts the sulfite ions into sulphate. OOH$^*$ radicals were observed to have no effect on Hg$^0$ oxidation at the pH of the experiments. When sodium thiosulphate is added mercury is retained in the gypsum at low concentrations while with higher doses of additive mercury is stabilised in the liquid fraction. The addition of TMT and NaHS prevents the reduction of oxidized mercury species into insoluble HgS and Hg$_3$(TMT). TMT is more effective for Hg$^{2+}$ capture and has the advantage that only a small proportion of additive is necessary to stabilize the mercury in WFGD systems.

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Table 1. Mercury concentrations in gypsum samples (μg/g) and leaching mercury.

<table>
<thead>
<tr>
<th>Test</th>
<th>Hg concentration (μg/g)</th>
<th>Leaching of Hg (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Blank (gypsum)</td>
<td>0.34</td>
<td>n.d.</td>
</tr>
<tr>
<td>50 mg/mL H₂O₂</td>
<td>1.80</td>
<td>n.d.</td>
</tr>
<tr>
<td>50 mg/mL FeCl₃ + 200 mg/mL H₂O₂</td>
<td>6.37</td>
<td>3</td>
</tr>
<tr>
<td>50 mg/mL Fe₂(SO₄)₃ + 200 mg/mL H₂O₂</td>
<td>5.20</td>
<td>n.d.</td>
</tr>
<tr>
<td>5 mM NaHS</td>
<td>14.0</td>
<td>n.d.</td>
</tr>
<tr>
<td>5 mM Na₂S₂O₃</td>
<td>12.3</td>
<td>n.d.</td>
</tr>
<tr>
<td>2 10⁻⁴ mM TMT</td>
<td>19.5</td>
<td>n.d.</td>
</tr>
</tbody>
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Figure captions

Figure 1. Influence of the pH of the gypsum slurry on Hg⁰ re-emission.

Figure 2. Effect of Fe₂(SO₄)₃ on mercury retention ([H₂O₂] = 200 mg/mL) (a). Relationship between the proportion of mercury retained in the solid and liquid fraction of the slurry and the concentration of Fe₂(SO₄)₃ ([H₂O₂] = 200 mg/mL) (b). Effect of FeCl₃ concentration on the retention of mercury ([H₂O₂] = 200 mg/mL) (c). Relationship between the proportion of mercury retained in the solid and liquid fraction for different concentrations of FeCl₃ ([H₂O₂] = 200 mg/mL) (d).

Figure 3. Effect of H₂O₂ concentration on mercury retention (a) and relationship between the proportion of mercury retained in the solid and liquid fractions and the concentration of H₂O₂ (b).

Figure 4. Elemental mercury emission when different quantities of Na₂S₂O₃ are added to the gypsum slurry (a) and the distribution of mercury in the gas and desulfurization products for different concentrations of sodium thiosulfate (b).

Figure 5. Elemental mercury emissions for different concentrations of NaHS (a) and the distribution of mercury in the gas and the solid fractions as a function of the concentration of sodium hydrosulphide (b).

Figure 6. Effect of the concentration of TMT on the retention of mercury (a) and relationship between mercury distribution and the concentration of TMT (b).
Figure 1. Influence of the pH of gypsum slurry on Hg$^0$ re-emission.
Figure 2. Effect of Fe$_2$(SO$_4$)$_3$ and FeCl$_3$ on mercury retention ([H$_2$O$_2$] = 200 mg/mL) ((a) and (b), respectively) and relationship between the proportion of mercury retained in the solid and liquid fraction of the slurry and the concentration of Fe$_2$(SO$_4$)$_3$ and FeCl$_3$ ([H$_2$O$_2$] = 200 mg/mL) ((c) and (d), respectively).
Figure 3. Effect of the H$_2$O$_2$ concentration on mercury retention (a) and the relationship between the proportion of mercury retained in the solid and liquid fractions and the concentration of H$_2$O$_2$ (b).
Figure 4. Elemental mercury emission when different quantities of Na$_2$S$_2$O$_3$ are added to the gypsum slurry (a) and distribution of mercury in the gas and desulfurization products for different concentrations of sodium thiosulfate (b).
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Figure 6. Effect of the concentration of TMT on the retention of mercury (a) and the relationship between mercury distribution and the concentration of TMT (b).
References

[1] EPA: [http://www.epa.gov/hg/effects.htm](http://www.epa.gov/hg/effects.htm)


