

# A comprehensive evaluation of the influence of air combustion and oxy-fuel combustion flue gas constituents on Hg<sup>0</sup> re-emission in WFGD systems

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## **Keywords**

Oxy-fuel combustion, re-emission of mercury, wet flue gas desulphurization

## **Abstract**

This paper evaluates the influence of the main constituents of flue gases from coal combustion ( $\text{CO}_2$ ,  $\text{O}_2$ ,  $\text{N}_2$  and water vapor), in air and oxy-fuel combustion conditions on the re-emission of  $\text{Hg}^0$  in wet scrubbers. It was observed that the concentration of water vapor does not affect the re-emission of mercury, whereas  $\text{O}_2$  and  $\text{CO}_2$  have a notable influence. High concentrations of  $\text{O}_2$  in the flue gas prevent the re-emission of  $\text{Hg}^0$  due to the reaction of oxygen with the metals present in low oxidation states. High concentrations of  $\text{CO}_2$ , which cause a decrease in the pH and the redox potential of gypsum slurries, reduce the amount of  $\text{Hg}^0$  that is re-emitted. As a consequence, the high content of  $\text{CO}_2$  in oxy-fuel combustion may decrease the re-emission of  $\text{Hg}^0$  due to the solubility of  $\text{CO}_2$  in the suspension and the decrease in the pH. It was also found that  $\text{O}_2$  affects the stabilization of  $\text{Hg}^{2+}$  species in gypsum slurries. The results of this study confirm that the amount of metals present in limestone as well as the redox potential and pH of the slurries in wet desulphurization plants need to be strictly controlled to reduce  $\text{Hg}^0$  re-emissions from power plants operating under oxy-fuel combustion conditions.

## 1. Introduction

According to data supplied by the International Energy Agency coal-fired power plants produced more than 41% of the global electricity supply in 2011 [1]. Although efficiency and pollution control in power plants have been considerably improved, coal combustion still remains the main source of CO<sub>2</sub>, SO<sub>2</sub>, NO<sub>x</sub> and mercury emissions to the air [2]. Clearly, these emissions need to be regulated so that coal can continue to be used as an energy source [3–5].

Among the available technologies for avoiding CO<sub>2</sub> emissions, oxy-fuel combustion has attracted renewed interest as a means to decrease CO<sub>2</sub> emissions from coal-fired power plants. Oxy-fuel combustion involves the burning of coal using O<sub>2</sub> diluted with a recycled flow of flue gas from the combustion process. The flue gas at the exit of the boiler mainly consists of CO<sub>2</sub> (20–80 vol.%), water vapor (approx. 20 vol.%) and a small proportion of O<sub>2</sub> (2–7 vol. %) [6–10]. The water vapor is condensed to produce a stream of high purity CO<sub>2</sub> which can be cooled and compressed for subsequent storage.

Research on oxy-fuel combustion technology has focused on producing a rich stream of CO<sub>2</sub> for subsequent capture [11]. Although no full-scale plants are operating yet under oxy-fuel conditions, pilot plant experience and theoretical studies have shown that this technology will substantially diminish NO<sub>x</sub> emissions by 50–75% due to the low concentration of N<sub>2</sub> in the oxidant gas and interactions between the NO<sub>x</sub> in the recycled stream and the fuel. However, the concentration of SO<sub>2</sub> is expected to be 3 or 4 times higher than that of conventional air firing [8,9,12,13]. For this reason, the removal of sulphur species (SO<sub>3</sub> and SO<sub>2</sub>) by wet flue gas desulphurization systems (WFGD), commonly referred to as scrubbers, is necessary to enable CO<sub>2</sub> to be stored and to

prevent corrosion of the equipment. Therefore, from an environmental point of view, oxy-fuel combustion could provide a cleaner energy than air firing. However, problems arising from the presence of mercury in the gas need to be addressed.

Mercury (Hg) is an element of primary concern in oxy-coal combustion not only from an environmental point of view, but also because it forms an amalgam with aluminum which produces corrosion inside the CO<sub>2</sub> compression units and the failure of components in the aluminum heat exchangers [14–16]. Although some research is being carried out to improve oxy-coal combustion technology, information on the behavior of Hg in oxy-combustion processes is still scarce. The main Hg species present in air combustion flue gas are elemental mercury (Hg<sup>0</sup>), oxidized mercury (Hg<sup>2+</sup>) and particle bound mercury (Hg<sup>p</sup>). It has been demonstrated that minor constituents of the gas (NO<sub>x</sub>, SO<sub>x</sub>, HCl) play an important role in the oxidation of Hg<sup>0</sup> to Hg<sup>2+</sup> and consequently in the speciation of Hg [17,18]. Various studies have evaluated the speciation of Hg in air and CO<sub>2</sub>-rich flue gas. O<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/CO<sub>2</sub> atmospheres have been reported to have little effect on Hg<sup>0</sup> oxidation in several works, whereas in other studies, Hg<sup>0</sup> oxidation has been observed to increase in oxy-coal combustion [21,22]. This enhancement of Hg<sup>0</sup> oxidation is attributed by some researchers to the accumulation of chlorine in the recycled flue gas as it enters the boiler [20]. Regarding the retention of Hg in fly ashes (Hg<sup>p</sup>), model predictions suggest that the capture of particle-bound Hg might be more effective in oxy-fuel combustion conditions due to the larger amount of unburned carbon in the particles [23].

It has been demonstrated that WFGD systems act as a sink for some Hg species present in the gas in conventional coal combustion plants. Hg<sup>2+</sup> species, which are soluble in water, can be retained in these systems [24–27]. However, the reactions that occur in the scrubbers are complex, and the chemical reduction of dissolved Hg<sup>2+</sup>,

which is known as re-emission, diminishes Hg capture efficiency [24,25,28]. Several studies have identified sulphur anions ( $\text{SO}_3^{2-}$ ,  $\text{HSO}_3^-$ ) and metals in the limestone used in the WFGD process as the species responsible for the re-emission of  $\text{Hg}^0$  [21,25,28,29]. Recent field data collected from two coal combustion power plants suggest that re-emissions of Hg are affected by the ratio between the amount of sulphur and the oxidation air flow rate, among other factors [30]. There is also a convincing body of evidence to suggest that re-emissions of Hg are influenced by the pH and composition of the slurry and the operating temperature in the scrubber [19,22,24]. Previous data indicated that the re-emission of Hg is increased by high pH values of the suspension in the scrubber and the presence of metals coming from the limestone [24,25]. In addition, higher re-emissions of Hg have been related to higher operating temperatures in the scrubber [24,26,28]. However, these studies were conducted under typical air combustion conditions. It was Omine et al. who performed the first lab-scale study using a flue gas enriched in  $\text{CO}_2$  and their results indicate that the enrichment of  $\text{CO}_2$  in the flue gas has no impact on  $\text{Hg}^0$  re-emission in oxy-coal firing [24]. However the study by Omine et al focuses on re-emission produced by the reduction of sulfite ions rather than on the mechanisms involving the reduction of the Hg produced from limestone impurities or on the partitioning of the Hg present in the by-products of the scrubber. No additional laboratory-scale studies have been conducted to obtain a comprehensive understanding of the behavior of Hg in oxy-fuel combustion conditions. Clearly, further research is necessary to assess the impact of the constituents of the oxy-fuel gas stream on  $\text{Hg}^0$  re-emission in scrubbers. This will facilitate the design of an appropriate strategy for removing Hg from the  $\text{CO}_2$ -rich stream. The present study focuses on the effect of the  $\text{O}_2$ ,  $\text{CO}_2$  and water vapor concentrations in the oxy-fuel gas and the influence of the WFGD operating parameters on the re-emission of Hg

produced by the metals originating from limestone under typical wet scrubber conditions.

## 2. Experimental

Hg<sup>0</sup> re-emission under oxy-fuel and air combustion conditions was evaluated in a lab-scale device, a detailed description of which has been provided elsewhere [25,31]. The system was assembled with a reactor consisting of a three-necked round bottom glass flask thermostated at 40°C. The gas mixing station used to generate a synthetic flue gas included a calibration gas generator (HovaCAL, IAS GmbH) coupled to an evaporator. Hg<sup>2+</sup> species were added to the gas phase by evaporating of a 1 µg mL<sup>-1</sup> Hg solution in 10 mmol L<sup>-1</sup> of hydrochloric acid at 200°C. A Gypsum slurry was prepared by mixing a natural limestone and sulphuric acid inside the reactor. The initial concentration of the limestone in the slurry was fixed at 1% to generate gypsum samples with Hg concentrations high enough for analysis. The system was designed to operate without recirculation of the slurry in order to avoid the adsorption of the Hg<sup>2+</sup> on the pipes and to obtain reliable data for determining the partitioning of the Hg. An Orion electrode 9678BNWP was employed to measure the redox potential (Eh) of the suspensions and its values were time recorded continuously on an Orion Meter Model 720A+. The pH was measured using an Orion electrode 8102BNWP and the data were recorded on a Mettler Toledo DL53 titrator.

A simulated flue gas containing 50 µg m<sup>-3</sup> of Hg<sup>2+</sup>, 8 vol.% of H<sub>2</sub>O and O<sub>2</sub> (N<sub>2</sub> balance), CO<sub>2</sub> (N<sub>2</sub> balance) or CO<sub>2</sub> (O<sub>2</sub> balance) was passed through the gypsum slurry at a total mass flow rate of 3 L min<sup>-1</sup>. The flue gas did not contain any SO<sub>2</sub> since the sulphur species were added directly during the preparation of the slurry. The flue gas before and after the reactor was conducted through perfluoroalkoxy pipes which were

maintained at 120°C to prevent the adsorption of Hg on their surface. The Hg<sup>0</sup> generated in the scrubbing solution was measured by a continuous Hg emission monitor VM 3000 (Mercury Instruments) at the outlet of the reactor at 120°C and 1bar. The VM 3000 analyzer, which functions on the basis of UV absorption, has a detection limit of 0.1 µg m<sup>-3</sup>. Different tests were carried out to ensure the absence of interference in the Hg analyzer from the presence of CO<sub>2</sub>. No interference in the measurement of Hg in the flue gas at 120°C was detected for the different concentrations of CO<sub>2</sub> tested.

The experiments were performed over periods of 150 min in duplicate. The concentrations of Hg<sup>0</sup>, representing the re-emitted Hg from the reactor, were recorded every 3 minutes. The partitioning of the Hg was determined by analyzing the Hg retained in the solid and liquid by-products while the amount of Hg<sup>0</sup> in the flue gas was calculated by integrating the area below the plots of concentration of the Hg<sup>0</sup> concentration versus time. The Hg retained in the gypsum and liquid fractions was determined by means of a LECO Automatic Mercury Analyzer (AMA 254), which operates on the basis of atomic absorption principles. The gypsum samples were prepared and analyzed by the same procedure as that used in previous investigations [17].

Different flue gas compositions were employed to investigate the influence of the flue gas constituents on Hg<sup>0</sup> re-emission. These included mixtures of Hg<sup>2+</sup> and i) O<sub>2</sub> (N<sub>2</sub> balance), ii) CO<sub>2</sub> (N<sub>2</sub> balance) and iii) a mixture of CO<sub>2</sub> and O<sub>2</sub> used to simulate a typical oxy-coal combustion flue gas. The influence of the water vapor in the flue gas entering the scrubber was also assessed.

### **3. Results**

This study is partly based on data obtained from previous laboratory investigations carried out using the same experimental device and operating conditions [25]. The results of the previous research showed that in a slurry composed of a solid mixture of gypsum (98%) and unreacted limestone (2%), Hg reduction can be caused by: i) sulphite ions formed at pH values higher than 6 or ii) metals resulting from limestone impurities. In the experimental conditions of this work, the presence of sulphites would be unlikely since such ions are unstable and would be immediately consumed in the production of gypsum. Even if sulphites were present in the solution, the reduction of Hg by the sulphites would not be likely since, when high purity reactive calcium carbonate is used, no  $\text{Hg}^0$  re-emission occurs [25]. On the other hand, significant re-emission takes place if limestone with a high content in iron and manganese is used [25]. The aim of this paper is to assess the influence of gas composition on the re-emission of  $\text{Hg}^0$  under wet scrubber conditions when the limestone used in the scrubber contains iron and manganese impurities.

### **3.1. Effect of the oxygen concentration in the flue gas**

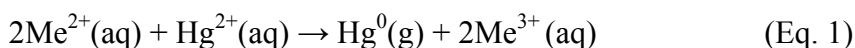
The concentrations of  $\text{O}_2$  in combustion and oxy-coal combustion are typically lower than 10 vol.%. To assess the influence of the presence of  $\text{O}_2$  in the flue gas entering the lab-scale scrubber, different concentrations of  $\text{O}_2$  within a range of 0-15 % vol. were tested.

Figure 1a shows  $\text{Hg}^0$  concentration in the flue gas at the outlet of the reactor for an input gas containing a fixed amount of  $\text{Hg}^{2+}$  and different concentrations of  $\text{O}_2$  balanced with  $\text{N}_2$  when passed through the slurry. The percentage of water vapor in the flue gas was kept constant at a value of 8 % vol. In the absence of  $\text{O}_2$ , a significant reduction in the  $\text{Hg}^{2+}$  species entering the reactor occurred, whereas in the presence of



O<sub>2</sub>, the re-emission of Hg<sup>0</sup> decreased significantly. As it can be seen from Figure 1b, the pH of the gypsum remained constant at 7.9±0.3 throughout all the experiments conducted with a flue gas containing O<sub>2</sub> in proportions ranging between 0 and 15 vol.% balanced with N<sub>2</sub>. This confirms that it was the presence of oxygen in the flue gas that determined the stabilization of the Hg.

When the gaseous species of Hg<sup>2+</sup> reached the slurry in a N<sub>2</sub> atmosphere, Hg was possibly stabilized in the suspension by the formation of Hg(OH)<sup>+</sup> and Hg(OH)<sub>2</sub>. A significant amount of Hg was reduced to Hg<sup>0</sup> since the pH was close to 8 and according to previous results, reduction occurs at high pH values [25]. However, when the gaseous Hg<sup>2+</sup> reached the slurry in a flue gas containing O<sub>2</sub> in a proportion higher than 5 vol. %, the amount of re-emitted Hg<sup>0</sup> was less than 9%. To explain the effect of O<sub>2</sub> it needs to be remembered that O<sub>2</sub> in contact with the gypsum slurry can modify the oxidation state of metals. The presence of O<sub>2</sub> might therefore favor the oxidation of metals dissolved in the slurry and increase the stabilization of the Hg<sup>2+</sup> species in the reactor. Since the reactor only contained the gypsum slurry generated from the reaction between natural limestone and sulphuric acid, it can be assumed that the Hg<sup>2+</sup> species in the slurry were reduced to Hg<sup>0</sup> by the metals derived from the limestone (Me), according to Eq.1:



This assumption was supported by the ICP-MS analysis of the liquid fraction in the reactor which revealed significant quantities of iron and manganese in the slurry (1.9 and 1.0 mg L<sup>-1</sup>, respectively) [25]. The presence of O<sub>2</sub> in the gas would favor the oxidation of the metals and promote the stabilization of the Hg<sup>2+</sup> species, resulting in an increase in Hg retention in the scrubber (Figure 1a). It can be inferred from these results that aeration of the slurry in the scrubber might inhibit the formation of intermediate metals in low states of oxidation and increase the re- emission of Hg<sup>0</sup>. This outcome is

in good agreement with the results obtained in previous works at a lower pH [24]. Omine et al. proposed a mechanism of stabilization of Hg for higher concentrations of O<sub>2</sub> in the flue gas based on a chemical reaction between sulfite ions and O<sub>2</sub> [24].

The partitioning of Hg in the by-products of the reactor is illustrated in Figure 1c. A proportion higher than 80% of the Hg was retained in the by-products of the scrubber (water and gypsum) when the concentration of O<sub>2</sub> was higher than 10 vol.%. The fraction of Hg retained in the gypsum ranged from 6 to 7% for concentrations of O<sub>2</sub> higher than 5 vol.%. This suggests that O<sub>2</sub> influences the reduction of Hg by metals but not the chemical form of the Hg species in the slurry or the adsorption of Hg by the gypsum.

Although the proportion of O<sub>2</sub> in the flue gas at the exit of the boiler is similar under both air combustion and oxy-coal combustion conditions, the results of this study indicate that the concentration of O<sub>2</sub> plays an important role in the stabilization of Hg in WFGD systems.

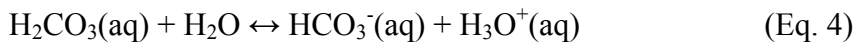
### **3.2. Effect of carbon dioxide concentration in the flue gas**

Based on the experimental results discussed in the previous section, a possible mechanism of Hg<sup>0</sup> re-emission can be proposed (Figure 2). These reactions include the reduction of the Hg<sup>2+</sup> by metals originating from the limestone that is also shown in Eq. 1. Since the re-emission of the Hg occurs at pH close to 8, Hg(OH)<sub>2</sub> would be the most probable species to be formed in these conditions. Figure 2 also illustrates the equilibrium reactions of the chemical species produced from the dissolution of CO<sub>2</sub>, SO<sub>2</sub> and SO<sub>3</sub> species in the slurry. It can be seen that the dissolution of SO<sub>2</sub>, SO<sub>3</sub>, and CO<sub>2</sub> generates protons in the suspension that cause a decrease in the pH of the slurry. Although the solubility of CO<sub>2</sub> in water is much lower than that of SO<sub>2</sub> and SO<sub>3</sub>,

changes in the pH produced by high concentrations of CO<sub>2</sub> in the flue gas in plants operating under oxy-fuel combustion conditions may occur. It is also clear from Figure 2 that the chemical equilibrium involved in the stabilization of Hg<sup>2+</sup> species is influenced by the pH of the slurry.

The effect of CO<sub>2</sub> is illustrated in Figure 3a which shows Hg<sup>0</sup> re-emissions for input gases with the same concentration of Hg<sup>2+</sup> as in the previous experiments and different percentages of CO<sub>2</sub> within the range of 0–90 vol.% balanced with N<sub>2</sub> (without O<sub>2</sub>). It can be seen that the proportion of Hg<sup>0</sup> generated in the gypsum slurry decreases as the CO<sub>2</sub> concentration in the flue gas increases. Nevertheless, Hg retention capacity remains constant for percentages of CO<sub>2</sub> higher than 50%.

The pH of the gypsum slurry decreases from 7.9±0.3 when the flue gas does not contain CO<sub>2</sub>, to 5.3±0.3 when the concentrations of CO<sub>2</sub> are in the range of 70–90 vol.% (Figure 3b). According to the model proposed (Figure 2), this modification in the pH value is a consequence of the equilibrium conditions between the species in the gas and the aqueous slurry (Eq. 2–4).



The positive effect of the decrease in pH in these conditions could be due to the formation of stable Hg<sup>2+</sup> species which are not easily reduced by the mechanism shown in Eq 1. The decrease in the pH produced by the dissolution of CO<sub>2</sub> is consistent with the destabilization of the complexes between Hg<sup>2+</sup> and hydroxide ions shown in the mechanism of Figure 2 and with the decrease in the re-emission of Hg<sup>0</sup>.

The partitioning of the Hg represented in Figure 3c indicates that the fraction of Hg retained in the liquid increases from 28 to 50% for concentrations of CO<sub>2</sub> in the range of 20 to 90 vol.%. This shows that, in the presence of CO<sub>2</sub>, Hg is captured as

soluble  $\text{Hg}^{2+}$  species in the liquid fraction rather than in the gypsum. These data, which are in accordance with the formation of  $\text{Hg}(\text{OH})_x$  complexes, support the mechanism proposed for the re-emission of Hg (Figure 2).

### **3.3. Effect of the carbon dioxide concentration in the flue gas containing oxygen**

To simulate oxy-combustion conditions,  $\text{O}_2$  was added to the flue gas to generate synthetic atmospheres containing  $\text{H}_2\text{O}$ ,  $\text{Hg}^{2+}$ ,  $\text{CO}_2$  and  $\text{O}_2$ . In these tests, the concentration of water vapor was kept constant at 8 vol.% while the concentration of  $\text{CO}_2$  was varied within a range of 0–90 vol.%. The balance in the flue gas was performed adding  $\text{O}_2$  to the synthetic flue gas entering the reactor.

When the atmosphere that contained  $\text{Hg}^{2+}$  and  $\text{O}_2$  as the main constituents (0 vol.%  $\text{CO}_2$ ) was passed through the reactor, it was found that only insignificant amounts of Hg were re-emitted from the reactor (Figure 4a). When the gas contained  $\text{O}_2$ , the stability of the metals in low oxidation states such as  $\text{Fe}^{2+}$  decreased, favoring the stabilization of  $\text{Hg}^{2+}$  species in the slurry according to Eq. 1. When  $\text{CO}_2$  was added to the gases in concentrations higher than 20 vol.%, Hg was re-emitted from the reactor in similar proportions, i.e. lower than 30% of the total amount of Hg introduced into the reactor. Under these experimental conditions, the partitioning behavior of the Hg indicates that more Hg was retained in the liquid fraction than in the gypsum (Figure 4c) which confirms the formation of mainly soluble-Hg species in the suspension of the scrubber. Omine et al. did not observe any significant effect from the concentration of  $\text{CO}_2$  upon the re-emission of Hg, probably due to the higher liquid-to-gas ratio of the employed experimental device. This shows that the limitations of the experimental devices used also need to be taken into account when comparing the results of Hg re-emission.

A comparison of Figures 3 and 4 shows the important influence that O<sub>2</sub> has on the stabilization of Hg. For similar gypsum slurry pH when the gases reaching the reactor contain CO<sub>2</sub>+O<sub>2</sub>, Hg is consistently more stable than when they contain CO<sub>2</sub>+N<sub>2</sub>. In addition to the pH, the redox potential of the gypsum slurries was monitored simultaneously throughout the experiments in a typical air combustion atmosphere (10 vol.% O<sub>2</sub>) and in gas atmospheres containing 70 vol.% CO<sub>2</sub> balanced in N<sub>2</sub> and 70 vol.% CO<sub>2</sub> balanced in O<sub>2</sub> (Figure 5). When the flue gas stream only contains O<sub>2</sub> and N<sub>2</sub>, the pH comes close to 8 and the redox potential reaches 400 mV. These redox conditions limit the tendency of the Hg to be reduced and explain the low amount of Hg re-emitted. Despite the high pH, the presence of O<sub>2</sub> leads to a decrease in the re-emission of Hg compared to the atmosphere with only N<sub>2</sub>. These results are consistent with previous investigations in which a low abatement of Hg re-emissions was reported for low values of redox potential [24,25]. When the gas entering the reactor contains 70 vol.% CO<sub>2</sub> in N<sub>2</sub> or a mixture of 70 vol.% CO<sub>2</sub> and O<sub>2</sub>, the amount of generated Hg<sup>0</sup> decreases as a consequence of the low pH and redox potential (Figures 5a and 5b). This shows that in CO<sub>2</sub>-rich atmospheres it is the concentration of CO<sub>2</sub> that controls the mechanism of Hg<sup>0</sup> re-emission and the effect of the presence of O<sub>2</sub> becomes less important.

The data in Figure 5 confirm that CO<sub>2</sub> has a significant influence on the redox potential and the pH of the gypsum slurries in the scrubber. Consequently, in order to reduce Hg<sup>0</sup> re-emissions at power plants operating under oxy-fuel combustion conditions, the pH or ORP needs to be strictly controlled.

### **3.4. Water vapor concentration**

To investigate the influence of the concentration of water vapor, a flue gas containing CO<sub>2</sub> (70 vol.%) and O<sub>2</sub>, similar to the composition of a conventional oxy-fuel flue gas was used [6]. The data for Hg<sup>0</sup> reemission and the partitioning of the Hg between the liquid and solid fractions (Figures 6.a and 6.c) showed no significant differences when the water vapor content was varied within a range of 8 to 20 vol.%. Indeed, the pH of the gypsum slurries remained constant at 5.6±0.2 throughout these experiments (Figure 6b). In addition, most of the Hg was retained in the liquid fraction of the suspension, which again confirms the presence of soluble Hg<sup>2+</sup> species. It can be concluded therefore that the concentration of water vapor in the flue gas does not significantly influence the re-emission of Hg in oxy-fuel combustion plants.

#### **4. Conclusions**

The composition of the flue gas produced from oxy-coal combustion systems significantly influences the re-emission of Hg<sup>0</sup> in lab-scale wet scrubber test rigs as a consequence of the modification of the pH and redox potential of the gypsum slurry. Although the O<sub>2</sub> concentrations in air combustion and oxy-coal combustion flue gas are generally similar, O<sub>2</sub> has a positive effect on the stabilization of the Hg in the slurry when re-emission is a consequence of the metal impurities in the limestone. High concentrations of CO<sub>2</sub>, which reduce the pH and the redox potential of the gypsum slurries, lead to a decrease in the re-emission of Hg. Consequently, under potential oxy-fuel combustion conditions the impact of the CO<sub>2</sub> concentration not only on the re-emission of Hg but also on the pH of the suspension in the scrubber is considerable. It follows that by adjusting the liquid-to-gas ratio in the scrubbers it should be possible to increase the capture of Hg and sulphur species in these CO<sub>2</sub> capture systems.

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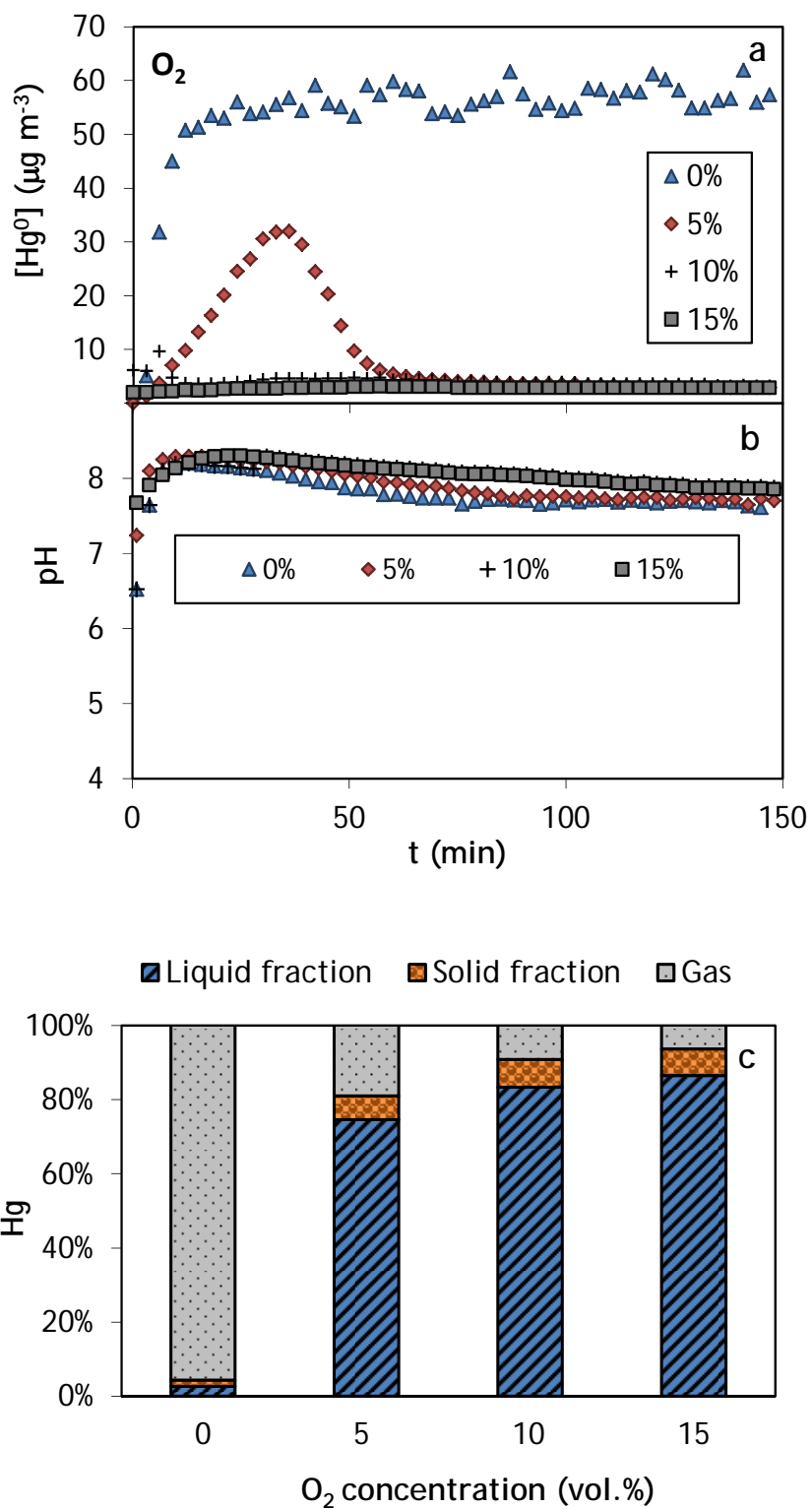
**Figure 2.** Equilibrium reactions of the aqueous species produced from the dissolution of the Hg<sup>2+</sup> species, CO<sub>2</sub>, SO<sub>2</sub> and SO<sub>3</sub> in the scrubber and their influence on the pH.

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**Figure 5.** Correlation between the re-emission of Hg in 10 vol.% O<sub>2</sub> (N<sub>2</sub>/O<sub>2</sub>), 70 vol.% CO<sub>2</sub> (CO<sub>2</sub>/N<sub>2</sub>) and 70 vol.% CO<sub>2</sub> (CO<sub>2</sub>/O<sub>2</sub>) and the redox potential (a) and the pH (b). T<sup>a</sup>= 40 °C; flue gas composition: O<sub>2</sub> (N<sub>2</sub> balance) or CO<sub>2</sub> (N<sub>2</sub> balance) or CO<sub>2</sub> (O<sub>2</sub> balance), 50 µg m<sup>-3</sup> Hg<sup>2+</sup> and 8 vol.% H<sub>2</sub>O.

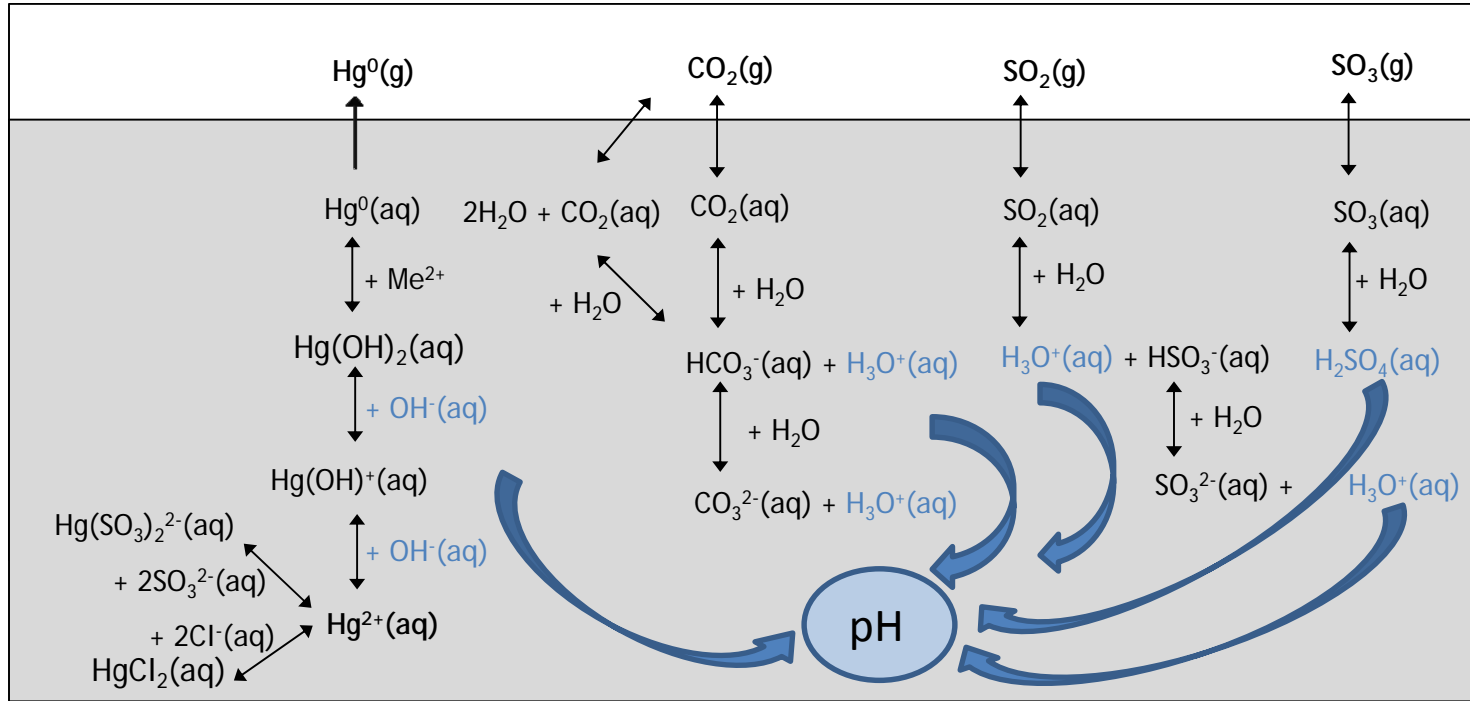
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**Figure 1.** Influence of the oxygen concentration (vol.%) in the flue gas ( $\text{N}_2$  balance) on (a)  $\text{Hg}^0$  re-emission, (b) the pH of the gypsum slurry and (c) the partitioning of the Hg in the gas, solid and liquid by-products of the scrubber.  $T^a = 40\text{ }^\circ\text{C}$ ; flue gas composition:  $\text{O}_2$ ,  $\text{N}_2$ ,  $50\text{ }\mu\text{g m}^{-3}$   $\text{Hg}^{2+}$  and 8 vol.%  $\text{H}_2\text{O}$ .

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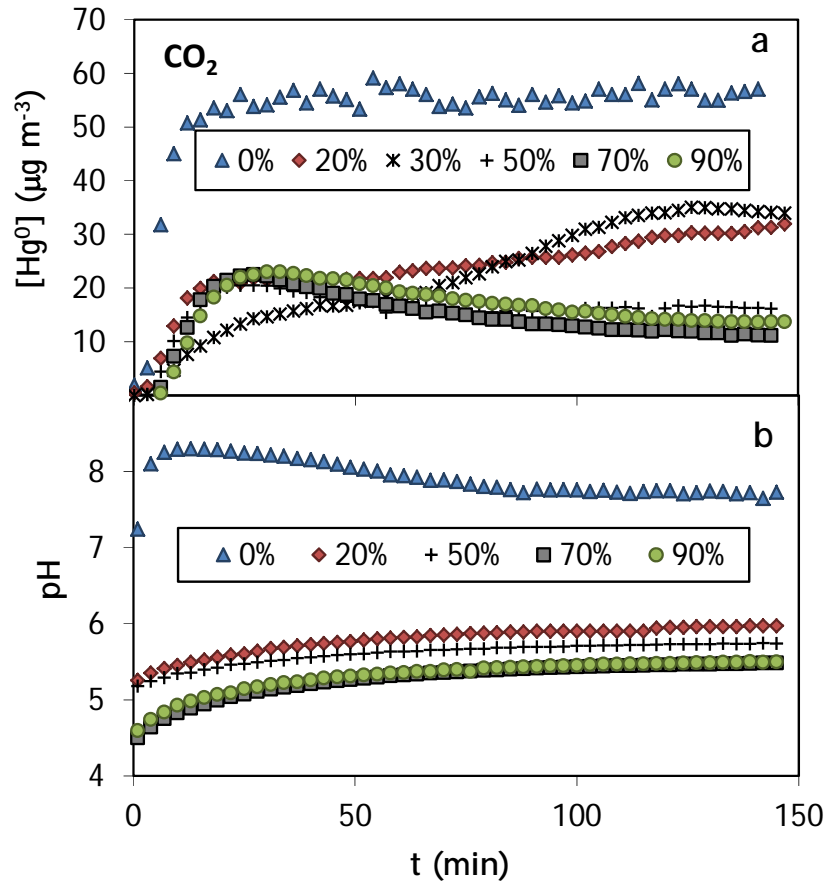
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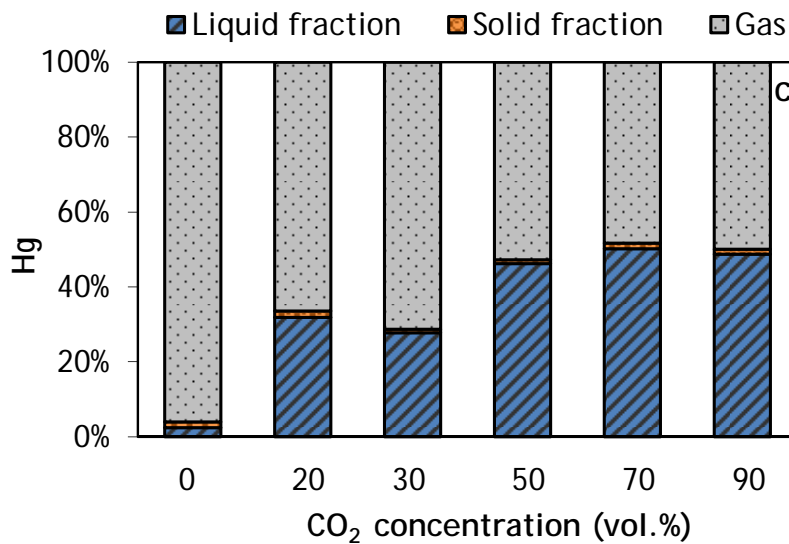
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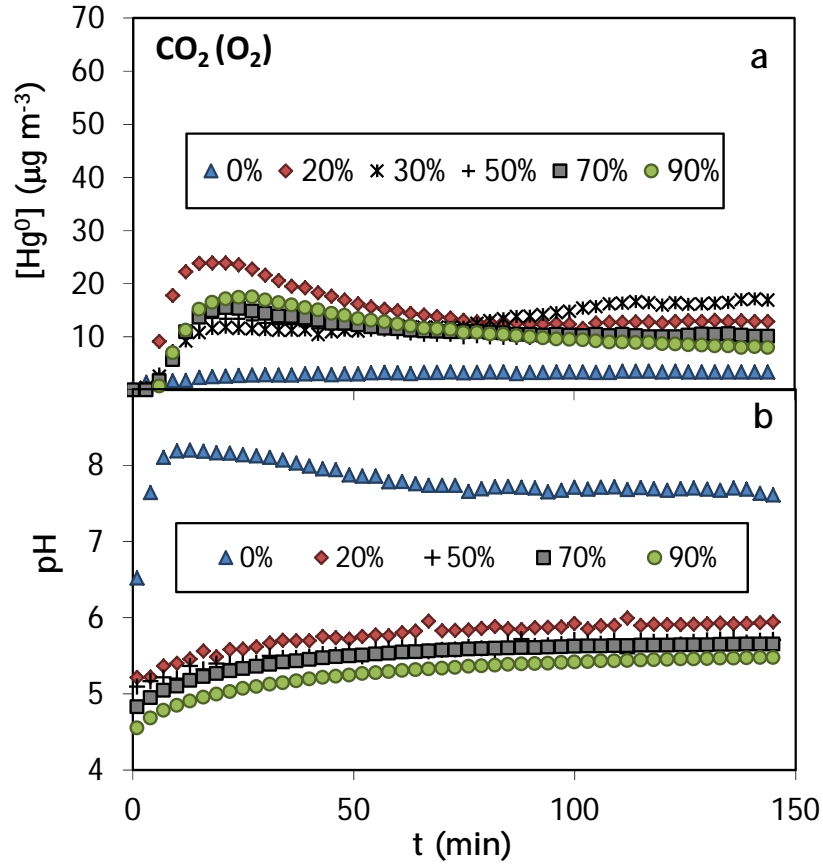


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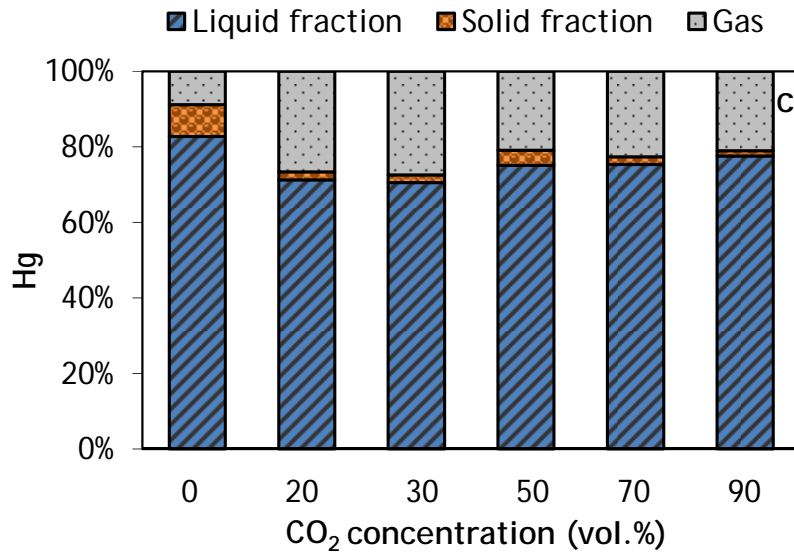


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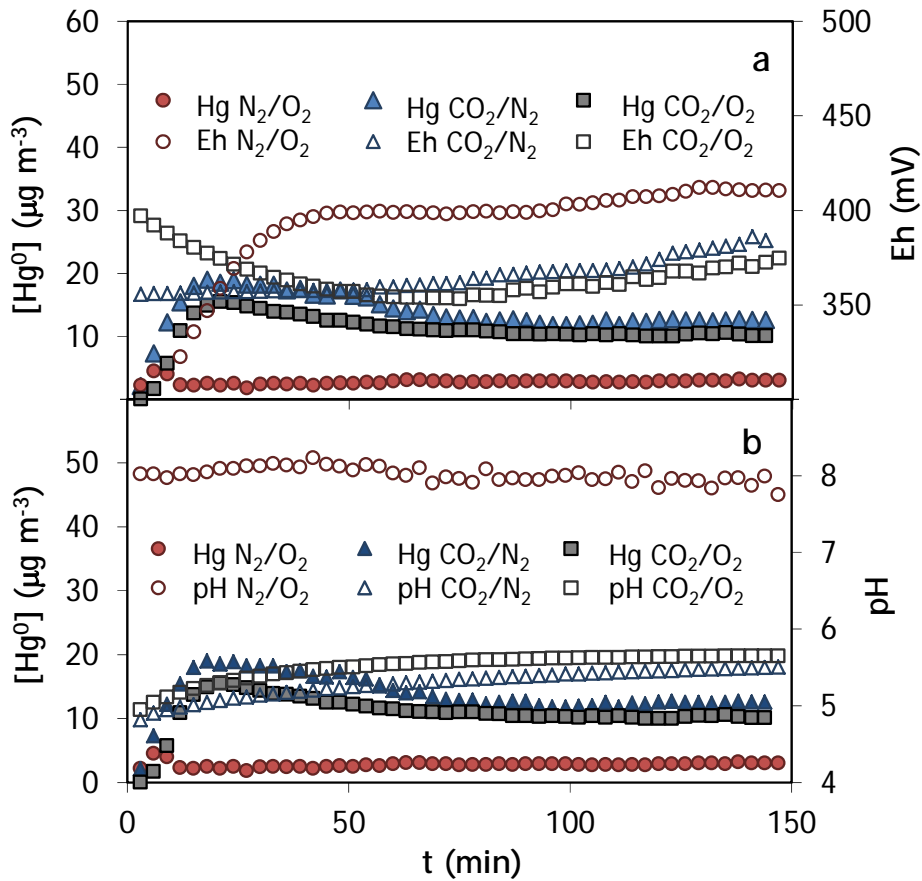
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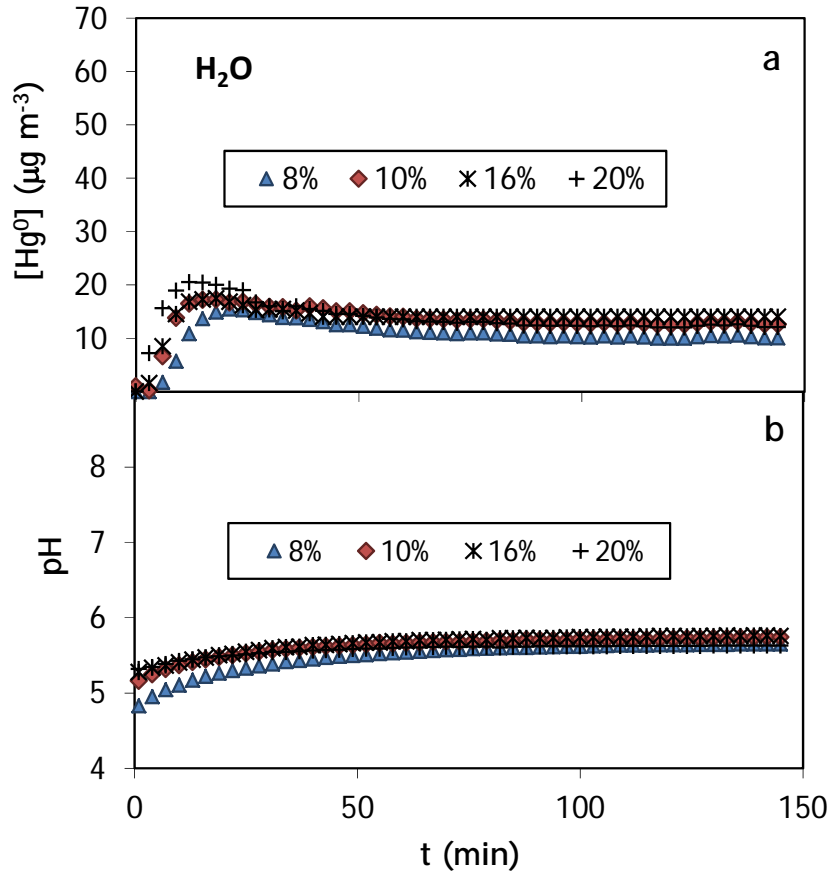
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21 **Figure 5.** Correlation between the re-emission of Hg in 10 vol.%  $\text{O}_2$  ( $\text{N}_2/\text{O}_2$ ), 70 vol.%

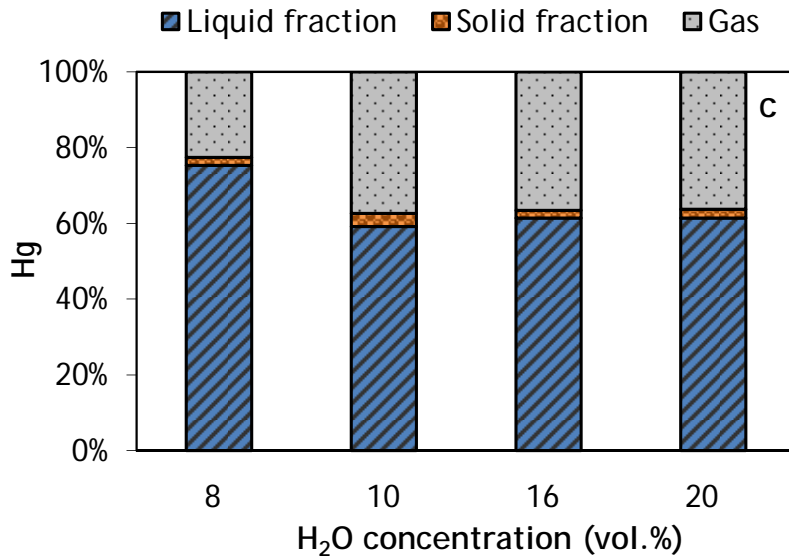
22  $\text{CO}_2$  ( $\text{CO}_2/\text{N}_2$ ) and 70 vol.%  $\text{CO}_2$  ( $\text{CO}_2/\text{O}_2$ ) and the redox potential (a) and the pH (b).

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