Effect of anion concentrations on Hg^{2+} reduction from simulated desulphurization aqueous solutions

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Keywords

Abstract

The influence of different anions on the stability of mercury in absorbing solutions containing sulphite ions was investigated. The re-emission of gaseous mercury in the presence of fluoride, chloride, bromide, nitrate, carbonate and sulphate ions from the scrubbing solution was determined. Fluoride, chloride and bromide ions contribute to mercury stabilization, bromide being the most efficient anion for retaining mercury in sulphite aqueous solutions. High carbonate concentrations prevent the reduction of mercury by sulphite ions due to the stabilization of the complexes formed between oxidised mercury, hydroxide and sulphite ions or through the formation of mercury carbonate species. However, nitrate and sulphate ions do not influence the equilibrium between mercury and sulphite ions and, as a consequence, the re-emission of mercury is not modified. The results of this study suggest that the pH is one of the most important parameters for achieving an efficient control of mercury pollution in desulphurization systems. The re-emission of mercury was observed to increase when the pH value of the slurries was higher than 6 due to the stabilization of the mercury in the form of $Hg(SO_3)_2^{2-}$, $Hg(OH)^+$, $Hg(OH)_2$, $HgHCO_3^+$, $HgCO_3$ or $Hg(CO_3)_2^{2-}$. Since the pH depends on the concentration of SO_2 in the flue gas and the type of limestone, the alkalinity that comes from the sorbent used in the scrubber may play an important role in mercury capture in such systems.

1. Introduction

Due to the high volatility of its compounds and long time residence in the atmosphere, mercury is one of the most toxic metals found in the environment. Mercury is easily bioaccumulated through the food chain and poses a great threat for human health via the route of fish consumption.[1,2] Energy production is responsible for more than 50% of mercury emissions to the air according to the European Pollutant Release and Transfer Register.[3] The mercury species present in coal are evaporated during combustion and subsequently transformed into a number of other forms which include elemental mercury (Hg^0) and other compounds generally referred to as oxidised mercury (Hg^{2+}). Both species are emitted to the environment in different proportions depending on the characteristics of the coal, combustion conditions and pollution control devices.[4,5] This has led to growing interest in developing and improving methods of reducing such emissions, including the upgrading of some gas cleaning processes already installed in power plants.

Existing modern combustion plants with Flue Gas Desulphurization (FGD) systems allow the reduction of sulphur emissions to the atmosphere, but at the same time they can also be used to modify the rate and speciation of the mercury emitted into the atmosphere. To take advantage of the potential of these systems for mercury retention it is necessary to have a good in-depth knowledge of all the possible reactions involving mercury species that may occur under the operating conditions of desulphurization systems.

Among the different FGD plants installed in power stations, Wet Flue Gas Desulphurization (WFGD) systems or scrubbers are the most common. Sulphur dioxide is retained in WFGD systems with a high degree of efficiency by slurries of CaO or limestone, limestone being the most frequently used due to its low price and its ready availability. The Hg^0 entering the scrubber, because of its low solubility in water, is not

retained in WFGD systems.[6] However, due to the high solubility of Hg^{2+}, the oxidised mercury species may be retained in these systems in percentages ranging from 51 to 75%.[7] This behavior favours the co-capture of Hg^{2+} present in the flue gases entering the scrubbers where a gypsum slurry is produced. Capture of mercury in gypsum is advisable only if the mercury is not likely to leach. The liquid fraction is recirculated in the plant and as a result reaches high concentrations in most cases.[8]. However, certain processes involving aqueous phase reactions with mercury inside the scrubber are not always positive for mercury retention. In WFGD plants, reduction processes which transform Hg^{2+} into insoluble Hg^0 occur via aqueous reactions. There is now a convincing body of evidence that such reactions involve sulphite ions, which are produced in the desulphurization process, and result in the re-emission of mercury.[9-11] On the other hand, complexes of Hg^{2+} and sulphite ions are known to be stable. V. Loon at al. measured kinetic and thermodynamic parameters for the aqueous mercuric ion-sulphite system.[10] Under conditions where $Hg(SO_3)_2^{2-}$ predominated, the rate of reduction of the mercuric ion to Hg^0 via coordinated sulphite showed an inverse dependence with the concentration of uncoordinated sulphite, whereas it was unaffected by the amount of sulphite liberated by dissociation. In addition to the influence of sulphur species, the kinetics of mercury reduction reactions in the scrubber are affected by the pH of the slurry. Wo et al. demonstrated that high pH values favoured mercury capture through the formation of $Hg(OH)^+$ or $Hg(OH)_2$ in sulphite solutions[13] while Wu and Omine et al. found that the highest re-emission of mercury occurred in basic suspensions of calcium sulphite and a mixture of limestone and gypsum, respectively.[14,15] They attributed this to the reduction of Hg^{2+} by sulphite ions at pH values greater than 5. Schuetze et al. also found a pronounced enhancement in the concentration of Hg^0 when the pH of the gypsum slurry rose above 7 due to the

disproportionation of $Hg_2(OH)_2$ into $Hg(OH)_2$ and Hg^0.[16] However, the chemistry of the scrubber is also influenced by other species present, and their behaviour under different conditions needs to be thoroughly understood. Among the possible reactions that may influence mercury speciation in WFGD conditions are those involving anions.

Different anions may be present in the scrubber solutions, most of them originating from the combustion of gases. Some of these anions are used as additives in the WFGD or in other devices of the plant.[17] Coal is the main source of gaseous species that may give rise to anions in suspension in the scrubber. Chlorine and fluorine are present in coal combustion flue gases as HCl and HF in proportions that depend on the composition of the coal. These halide species, which are captured in the scrubbers with an efficiency of about 100% [17-19], may affect the stability of the mercury species in solution. Nitrates and sulphates are also present in the WFGD slurry from the dissolution of the NO_x and SO_2 present in the gases and carbonates originate from the limestone used in the desulphurization process. Other additives also contribute to the presence of anions. With the aim of increasing the proportion of Hg^{2+} in the gases entering the scrubbers, different procedures have been tested, including the injection of chlorine into the gas stream[20] and more recently the injection of bromine.[21] Both methods have led to good results and provided an additional source of anions to the WFGD systems. As the liquid fraction of the slurry is usually recirculated in these systems, concentrations of fluorine, chlorine, nitrate and sulphate ions present in these fractions increase with time.[22,23] All of the above mentioned ions could affect the chemistry in the slurries in WFGD plants and, as a consequence, the stability of the mercury by means of reactions and processes that need to be controlled. Some researchers studying the influence of chlorine, nitrate, fluoride and sulphate ions in scrubber liquors observed a delay in the re-emission of mercury as concentration of

these ions increased.[13,24,25] However, given the complexity of the chemical reactions in WFGD systems, little work has been conducted on reactions involving other anions taking into account the re-emission of mercury, the pH and the redox potential in continuous mode. In addition, most of the studies in the literature have been carried out without a continuous flow of the Hg^{2+} entering the WFGD lab-scale reactor.[13,15,16]

In this paper the stability of Hg^{2+} in the absorbing solutions with sulphite ions and different anions was evaluated by analyzing the re-emission of mercury, pH and redox potential simultaneously. The objective of this work was to assess the role of sulphate, nitrate, chloride, fluoride and carbonate anions on the re-emission of mercury.

2. Experimental

In order to investigate Hg^{2+} absorption and its reduction by sulphite ions, a lab-scale device that simulates WFGD conditions was used. A schematic diagram of the device is shown in Figure 1. This system consisted of three parts: i) the mercury and flue gas generation units, ii) the reactor containing the scrubber slurry or absorption solution and iii) a continuous mercury emission monitor to measure the Hg^0 at the outlet of the reactor.

The mercury species in the flue gas were generated by using a commercial evaporator (HovaCAL, GmbH). In this device, an aqueous mercury nitrate solution, stabilized in a hydrochloric acid medium, was evaporated continuously at a temperature of 200ºC. The concentration of hydrochloric acid was kept constant at 0.6 mg·L^{-1} to achieve the desired proportions of Hg^0 and Hg^{2+} in the gases. The addition of hydrochloric acid to the mercury nitrate solution allowed the formation of mercury chloride complexes such as $HgCl_2$. The flow gas composition was regulated by mass flow controllers and set to 3 L·min^{-1}. The gas was conducted to the reactor through PFA pipes heated with a

temperature-controlled heating belt at 120°C to avoid the condensation of moisture and the adsorption of the mercury on the surface.

The reactor consisted of a 500 ml flask made of glass with three connections: an inlet and an outlet for the flue gas, a pipe for the pH and redox potential electrodes. The flask, which contained limestone slurry and/or S(IV) species to simulate a real wet scrubber composition, was stirred and kept at 40ºC during the tests. The pH of the solutions and the redox potential were recorded continuously. The pH was measured with an Orion electrode (8102BNWP) and data were recorded with a Mettler Toledo DL53 titrator. The redox potential (Eh) measurements were recorded to distinguish the reducing or oxidizing effect of the sulphur species in the scrubbing solution. The redox potential against normal hydrogen electrode, which was measured with an Orion electrode (9678BNWP), was recorded approximately every 50 min on an Orion Meter (Model 720A+). For each test, 100 mL of slurry or aqueous solution containing 1 mM of sodium sulphite was used. The flue gas containing 130 $\mu g \cdot m^{-3}$ of mercury in nitrogen or in nitrogen plus oxygen was introduced into the reactor through a glass stem which had a glass fritted disc at its end to favour mixing of the gas and the liquid. A mercury analyser (VM 3000, Mercury Instruments) was used to measure the Hg^0 at the outlet of the reactor. The Hg^0 concentration was recorded continuously as a function of time. The Hg^0/Hg^{2+} ratio in the flue gas was calculated by continuous recording of the Hg^0 concentration in the synthetic flue gas and it was confirmed by means of the Ontario Hydro Method. In this method, three impingers containing a 1 M KCl solution were used to absorb Hg^{2+}. A fourth impinger was filled with acidified H_2O_2, which served to absorb Hg^0. Hg^0 was mainly captured in the last three impingers, which contained solutions of acidified $KMnO_4$. Mercury concentration in the solution after reaction was tested by means of an Advance Mercury Analyser (AMA-254).
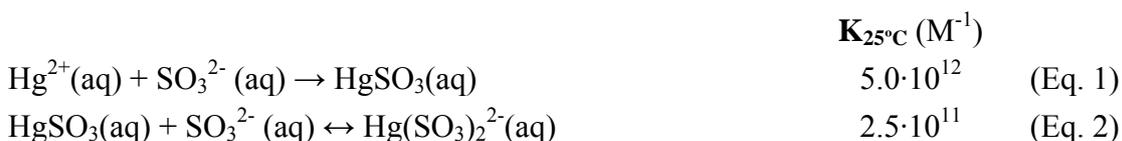
Hg^0 re-emission was evaluated in solutions containing chloride, fluoride, bromide, nitrate, sulphate ions for 200 min and in suspensions containing carbonate ions for 400 min.

HSC Chemistry 6.1 software was used to predict the reaction mechanisms and to identify the sulphur species in the experimental conditions.

3. Results and discussion

The gas composition used in the experiments contained 130 $\mu g \cdot m^{-3}$ of total mercury in the form of a mixture of Hg^{2+} and Hg^0. In this mixture, the concentration of Hg^0 at the outlet of the reactor, measured with a continuous monitoring analyzer, was 7 $\mu g \cdot m^{-3}$ which is consistent with the speciation calculated by using the Ontario Hydro Method. Thus, the flue gas contained 5% of Hg^0, the predominant mercury species in the synthetic flue gas being Hg^{2+}.
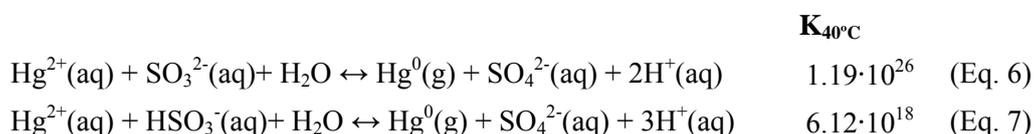
The Hg^0 curve obtained when the solution only contained sulphite ions showed that the re-emission of $Hg^0(g)$ ocurred after 120 min of experimentation (Figure 2a). At this fixed point in time the concentration of mercury in solution was 0.4 $\mu g \cdot g^{-1}$; the molar ratio of $Hg^{2+}:SO_3^{2-}$ was 1:400 and the pH 6. Under the experimental conditions evaluated in which the concentration of sulphites was 1 mM the Hg^0 concentration was constant. Hg^{2+} was stabilised in the solution due to the formation of complexes with chloride ($HgCl_x^{2-x}$) or even with sulphite ions ($HgSO_3$ and $Hg(SO_3)_2^{2-}$) which can be considered stable according to previous thermodynamic data calculated at 25ºC (Eq. 1 and 2).[11]

	$K_{25ºC}$ (M^{-1})	
$Hg^{2+}(aq) + SO_3^{2-}(aq) \rightarrow HgSO_3(aq)$	$5.0 \cdot 10^{12}$	(Eq. 1)
$HgSO_3(aq) + SO_3^{2-}(aq) \leftrightarrow Hg(SO_3)_2^{2-}(aq)$	$2.5 \cdot 10^{11}$	(Eq. 2)

The retention of the mercury may also have been due to the formation of $Hg(OH)^+$ or $Hg(OH)_2$ through Eq. 3-5 whose equilibrium constants predicted with HSC Chemistry range from $2.4 \cdot 10^{10}$ to $3.4 \cdot 10^{20}$ at 40°C.

$$K_{40°C}$$

$$SO_3^{2-}(ac) + H_2O \leftrightarrow HSO_3^-(aq) + OH^-(aq) \qquad - \qquad (Eq. 3)$$

$$Hg^{2+}(aq) + OH^-(aq) \leftrightarrow Hg(OH)^+(aq) \qquad 2.39 \cdot 10^{10} \qquad (Eq. 4)$$

$$Hg^{2+}(aq) + 2OH^-(aq) \leftrightarrow Hg(OH)_2(aq) \qquad 3.42 \cdot 10^{20} \qquad (Eq. 5)$$

As Figure 2b shows, the sharp increase in the Hg^0 concentration at 120 min was due to a decrease in the pH of the scrubbing solution at values lower than 6 which was a result of the evaporation of the acidic mercury solution in the HovaCAL (Figure 2b). The most generally accepted mechanism of mercury re-emission through sulphite and bisulphite ions in scrubber solutions is summarized in Eq. 6 and 7. These reactions indicate that Hg^{2+} is reduced by S(IV) species to Hg^0, Eq. 6 being the most thermodynamically probable mechanism for the reduction of Hg^{2+}.

$$K_{40°C}$$

$$Hg^{2+}(aq) + SO_3^{2-}(aq) + H_2O \leftrightarrow Hg^0(g) + SO_4^{2-}(aq) + 2H^+(aq) \qquad 1.19 \cdot 10^{26} \qquad (Eq. 6)$$

$$Hg^{2+}(aq) + HSO_3^-(aq) + H_2O \leftrightarrow Hg^0(g) + SO_4^{2-}(aq) + 3H^+(aq) \qquad 6.12 \cdot 10^{18} \qquad (Eq. 7)$$

The stability of $Hg(SO_3)_2^{2-}$ is higher than that of $HgSO_3$ and only $HgSO_3$ decomposes to produce Hg^0.[7,13] In an excess of sulphite ions, the formation of stable complexes such as $Hg(SO_3)_2^{2-}$ or $Hg(OH)_2$ could have prevented Hg^0 re-emission during the first 120 minutes through Eq. 2 and 5. During this time the redox potential remained relatively constant at 270 mV (Figure 2b). After two hours, the re-emission of mercury increased sharply due to the decomposition of $HgSO_3$ (Eq. 6) while the pH decreased abruptly at values lower than 6, suggesting that protons were generated in the scrubbing solution. The redox potential increased until it reached nearly 400 mV by the end of the test, which indicates that S(IV) species reacted with the Hg^{2+} species, generating sulphate

ions in the solution in accordance with Eq. 6. The re-emission of mercury was tested under these conditions in the presence of other ions such as halide, nitrate, sulphate and carbonate ions.
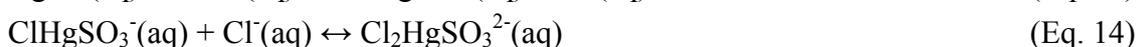
3.1. Halide ions

A set of tests was performed to compare the effect of chloride at different initial pH values by increasing the concentration of hydrochloric acid. As Figure 2.a illustrates, Hg^0 re-emission decreased at concentrations of chloride ions higher than 2 mM of HCl. For lower HCl concentrations (0.1, 0.5 and 2 mM) the reduction started at 100, 20 and 10 min, respectively. As shown in Figure 2b, the decrease in the initial pH value for these solutions at 7.5, 5.0 and 4.5 correspondingly may promote the formation of other mercury complexes with a lower stability, such as $HgHSO_3^+$. HCl absorbing solutions whose concentrations were 0.5 and 2 mM reduced the initial pH values until about 3.0 and increased the initial redox potential until 400 mV (Figure 2.b). As a consequence, the sulphite species may have become unstable and in turn the mercury-sulphite complexes. In addition, the formation of $Hg(OH)_2$ and $Hg(OH)^+$ was limited by the low pH values. Conversely, for concentrations of chloride higher than 2 mM, pH values lower than 4.5 and redox potential values higher than 400 mV mercury reduction did not occur for 200 min. This may have been the result of the increasing stability of the different chloride mercury species in the scrubbing solution. These results point to the formation of different mercury chloride complexes ($HgCl^-$, $HgCl_2$, $HgCl_3^-$ or $HgCl_4^{2-}$) in accordance with reactions of Eq. 8-11 which were thermodynamically favoured at the temperature at which the tests were carried out.

$$\textbf{K}_{40°C}$$

$$Hg^{2+}(aq) + Cl^-(aq) \leftrightarrow HgCl^+(aq) \qquad 1.45 \cdot 10^7 \qquad (Eq.\ 8)$$

$$HgCl^+(aq) + Cl^-(aq) \leftrightarrow HgCl_2(aq) \qquad 3.24 \cdot 10^6 \qquad (Eq.\ 9)$$

$$HgCl_2(aq) + Cl^-(aq) \leftrightarrow HgCl_3^-(aq) \qquad\qquad 1.34 \qquad (Eq.\ 10)$$
$$HgCl_3^-(aq) + Cl^-(aq) \leftrightarrow HgCl_4^{2-}(aq) \qquad\qquad 4.19 \qquad (Eq.\ 11)$$

Moreover, as mercury is able to form relative stable compounds with sulphite and chloride ions[13,15], complexes such as $ClHgSO_3^-$ or $Cl_2HgSO_3^{2-}$ (Eq. 12-14) may form in the solution as follows:

$$HgSO_3(aq) + Cl^-(aq) \leftrightarrow ClHgSO_3^-(aq) \qquad\qquad\qquad\qquad (Eq.\ 12)$$
$$HgCl_2(aq) + SO_3^{2-}(aq) \leftrightarrow ClHgSO_3^-(aq) + Cl^-(aq) \qquad\qquad (Eq.\ 13)$$
$$ClHgSO_3^-(aq) + Cl^-(aq) \leftrightarrow Cl_2HgSO_3^{2-}(aq) \qquad\qquad\qquad (Eq.\ 14)$$

When chloride ions were added by dissolution of KCl, the results showed a similar trend (Figure 3a), although the kinetics of the processes were slightly slower since complexes between Hg^{2+}, chloride ions and sulphite ions may have formed in the scrubbing solution. The point in time at which the reduction occurred was similar in each case because the initial pH value of the solutions was similar and reduction of Hg^{2+} only started when the pH value reached values lower than 6. The pH of the solution 50 mM KCl and 1 mM Na_2SO_3 decreased sharply 25 min after the beginning of the test and redox potential values reached about 600 mV at the end of the test. This suggests that the equilibrium of Eq. 3 was modified and $Cl_xHgSO_3^{x-}$ complexes may have been formed in the solution in accordance with Eq. 12-14.

Similar results to those of KCl were obtained in the tests carried out with different concentrations of fluoride or bromide ions (Figures 3b and 3c). The reduction of mercury was delayed by the presence of these halogen ions, no mercury reduction being detected at all during the experiments for 2 mM KBr and 50 mM KF. Whereas HgF_2 decomposed in water to form HgO (Eq. 15), chloride and bromide ions formed stable complexes with Hg^{2+} in accordance with Eq. 8-14 and 16-19, respectively. The
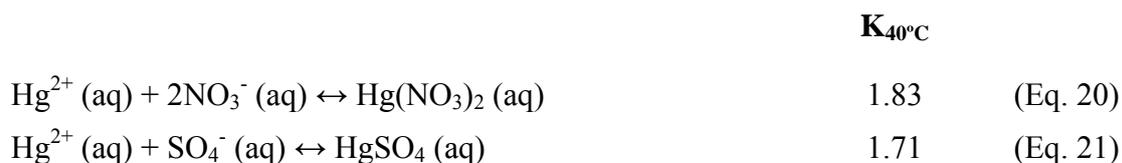
formation of $HgBr_2$ was thermodynamically more favoured than $HgCl_2$ at 40ºC. This suggests that $HgBr_2$ was one of the most stable mercury complexes in the solution as can be seen below:

	$K_{40ºC}$	
$HgF_2(aq) + H_2O \rightarrow HgO(aq) + 2HF(aq)$	-	(Eq. 15)
$Hg^{2+}(aq) + Br^-(aq) \leftrightarrow HgBr^+(aq)$	$5.24 \cdot 10^8$	(Eq. 16)
$HgBr^+(aq) + Br^-(aq) \leftrightarrow HgBr_2(aq)$	$1.51 \cdot 10^8$	(Eq. 17)
$HgBr_2(aq) + Br^-(aq) \leftrightarrow HgBr_3^-(aq)$	$1.17 \cdot 10^2$	(Eq. 18)
$HgBr_3^-(aq) + Br^-(aq) \leftrightarrow HgBr_4^{2-}(aq)$	$1.11 \cdot 10^1$	(Eq. 19)

These results showed that bromide was the most efficient anion for retaining Hg^{2+} in solution because a small concentration of KBr was necessary to stabilize the mercury in the simulated WFGD solution which achieved a mercury concentration of 0.7 $\mu g \cdot mL^{-1}$ at the end of the experiment. The pH for a concentration 50 mM KF in the 120-150 min range decreased at a slower rate than those of the blank and the 50 mM KCl and 10 mM KBr scrubbing solutions (Figure 3c). Consequently, the redox potential of the solution containing fluoride ions was lower than that of the sulphite solution. Fluoride exhibited the strongest basic character and maintained an efficient control of the basic pH throughout the experiment. Fluoride may have reacted with Hg^{2+} and sulphite like chloride through Eq. 12-14. Instead of forming complexes between Hg^{2+}, fluoride and sulphite ions, HgO may have generated. Conversely, the pH of the solution containing 10 mM KBr and sulphite ions decreased faster than the pH of the sulphite solution whereas the redox potential increased slightly, which suggests that complexes between Hg^{2+}, bromide and S(IV) ions were formed.

3.2. Nitrate and sulphate ions

Analysis of the Hg^0 curves (Figures 4a and 4b) shows that the presence of nitrate and sulphate ions did not modify the chemistry of the mercury in solution and did not have any significant effect on the stabilization of the mercury. No differences in the re-emission of mercury were detected as the concentration of these ions increased up to 20 mM. Although the thermodynamic equilibrium data indicate that the formation of $Hg(NO_3)_2$ and $HgSO_4$ was slightly favoured (Eq. 20 and 21), the experimental results suggest that the reduction of Hg^{2+} was the dominant process. No variations in the pH data throughout the experiments were found and the redox potential values increased only slightly when the re-emission of mercury started after 120 min (Figure 4c). These results prove that mercury was stable in WFGD liquids containing an excess of S(IV) species due to the formation of stable complexes such as $Hg(SO_3)_2^{2-}$ or $Hg(OH)_2$.

$$\mathbf{K_{40^\circ C}}$$

Hg^{2+} (aq) + $2NO_3^-$ (aq) $\leftrightarrow$ $Hg(NO_3)_2$ (aq)	1.83	(Eq. 20)
Hg^{2+} (aq) + SO_4^- (aq) $\leftrightarrow$ $HgSO_4$ (aq)	1.71	(Eq. 21)

In WFGD systems, mercury sulphate may form.[24] Although $HgSO_4$ decomposes into HgO(s) in water, the capture of mercury was not affected during the tests. This indicates that the formation of $HgSO_4$ through Eq. 21 may be limited in scrubber systems since the reduction of Hg^{2+} by sulphite ions is more favoured thermodynamically and/or kinetically.

3.3. Carbonate ions

A batch of tests was carried out in the presence of carbonate ions generated from the dissolution of limestone and also from sodium carbonate which provided a higher alkalinity than that of limestone (Figure 5). Mercury was observed to be more stable at higher sodium carbonate concentrations. 30 mg·L^{-1} stabilized the mercury in solution

for at least 400 min (Figure 5a). Similar results were obtained for calcium carbonate (Figure 5b) but significant differences were found in the stability of the mercury in the slurries. The re-emission of mercury was suppressed for 400 min by 60 mg·L^{-1} of carbonate when sodium carbonate was used, while higher concentrations were necessary in the case of calcium carbonate. Sodium carbonate provided a significantly higher alkalinity than calcium carbonate which suggests that the sodium salt caused the delay in the reduction of the mercury. The effect of the carbonate was to increase the pH causing the sulphite ions to stabilize. This suggests that stable complexes may have been formed between sulphite, hydroxide and Hg^{2+} ions, such as $HgSO_3$, $Hg(SO_3)_2^{2-}$ and $Hg(OH)_2$. The formation of such complexes is thermodynamically favoured in these conditions according to the equilibrium constants in the literature (Eq. 1 and 2).[11] In these experiments, the re-emission of mercury was only detected when the pH values of the slurries were lower than 6.0 for both the limestone and sodium carbonate (Figure 5c). At a pH higher than 7.0, the species $HgHCO_3^+$, $HgCO_3$ and $Hg(CO_3)_2^{2-}$ may also have been present in the scrubber solutions. These results corroborate that the pH is a key parameter for achieving a highly efficient WFGD mercury retention system. As the operating pH depends on the concentration of $SO_2(g)$ and the type of limestone, the alkalinity provided by the sorbent used in the scrubber may play an important role in mercury capture in such systems. The redox potential values shown in Figure 5c again demonstrate the strong relationship between the re-emission of mercury and the oxidation-reduction character of the suspensions.

To assess the relationship between mercury emission and the pH, the flue gas containing mercury, nitrogen and oxygen was used to simulate forced oxidation conditions. A small amount of limestone was added to the reactor as sorbent and diluted sulphuric acid was used to reduce the pH value. As can be seen in Figure 6, the

concentration of Hg^0 increased, as the pH decreased and the redox potential increased. At a pH lower than 6.0 the sulphite ions were not as stable which indicates that $HgHSO_3^+$ may have formed according to the potential redox-pH diagram illustrated in Figure 7. $HgHSO_3^+$ is less stable than other sulphite -mercury complexes so the rate of reduction may have increased significantly. Thus, sulphite ions may also have favored the retention of mercury through the formation of stable complexes such as $Hg(SO_3)_2^{2-}$. These results are not consistent with the data obtained by Omine and Wu et al. indicating that the ratio of $Hg^{2+}:SO_3^{2-}$ influences the equilibriums of Eq. 1 and 2 and, as a consequence, the re-emission of the mercury is modified. These data are in good agreement with those of fluoride, chloride, bromide, nitrate and sulfate tests, confirming that the pH is an important parameter that must be controlled if the re-emission of dissolved mercury in wet scrubber systems is to be avoided.

4. Conclusions

The influence of halide, nitrate, sulphate and carbonate ions, which are the most abundant ions in the liquid fraction of the byproducts of wet flue gas desulphurization systems, has been evaluated. The anions present in a solution containing sulphite ions may influence mercury stability in solution depending on the type of anion, its concentration and the pH. Fluoride, chloride and bromide ions contribute to mercury stabilization, bromide being the most efficient anion for retaining mercury in aqueous solutions. High carbonate concentrations prevent the reduction of mercury by sulphite ions, probably due to the formation of complexes between Hg^{2+}, sulphite, hydroxide or carbonate. However, nitrate and sulphate ions do not influence the equilibrium between mercury and sulphite ions and, as a consequence, mercury is not stabilized in the presence of these anions. In short, the results of this study indicate that the pH is one of

the most important parameters for achieving efficient control of mercury pollution in desulphurization systems.

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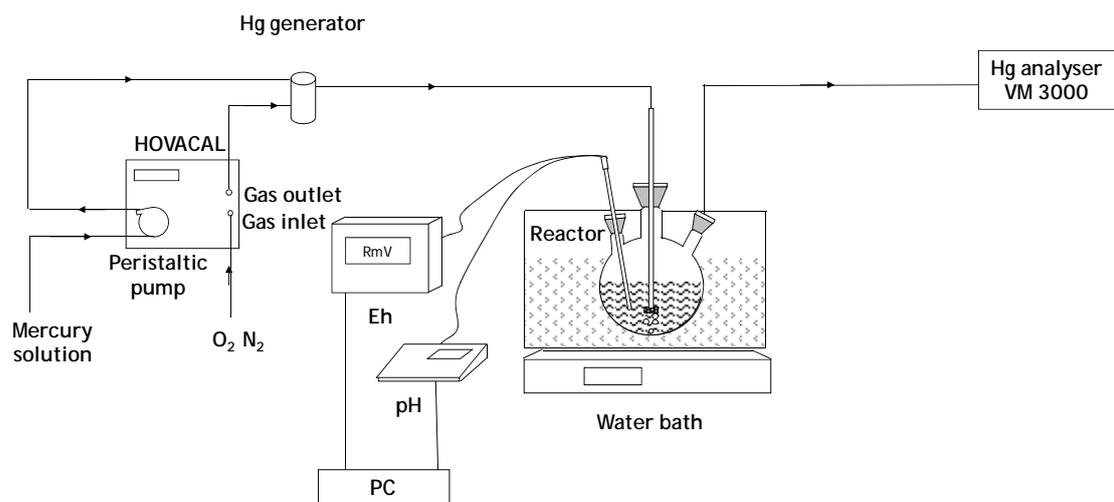
Figure captions

Figure 1. Lab-scale apparatus used to evaluate elemental mercury re-emission.

Figure 2. Re-emission of mercury using different scrubbing solutions in typical wet scrubber conditions: (a) re-emission of mercury and (b) pH and redox potential as a function of time.

Figure 3. Re-emission of mercury using different scrubbing solutions in typical wet scrubber conditions: (a) influence of chloride, (b) fluoride, (c) bromide ions and (d) pH and redox potential.

Figure 4. Emission of Hg^0 using a scrubbing solution containing nitrate (a) and sulphate ions (b) and pH and redox potential of the solutions (c).

Figure 5. Emission of Hg^0 using a scrubbing solution containing carbonate ions ((a) Na_2CO_3 and (b) $CaCO_3$) and pH and redox potential of the suspensions (c).

Figure 6. Influence of the pH and the redox potential. Absorbent solution: 20 mg $CaCO_3$ + different quantities of sulphuric acid. 1mM S(IV). Flue gas: [Hg]=130 $\mu g \cdot m^{-3}$, $N_2 + O_2$.

Figure 7. Eh-pH diagram for sulphur species at 40ºC (1 mM S).

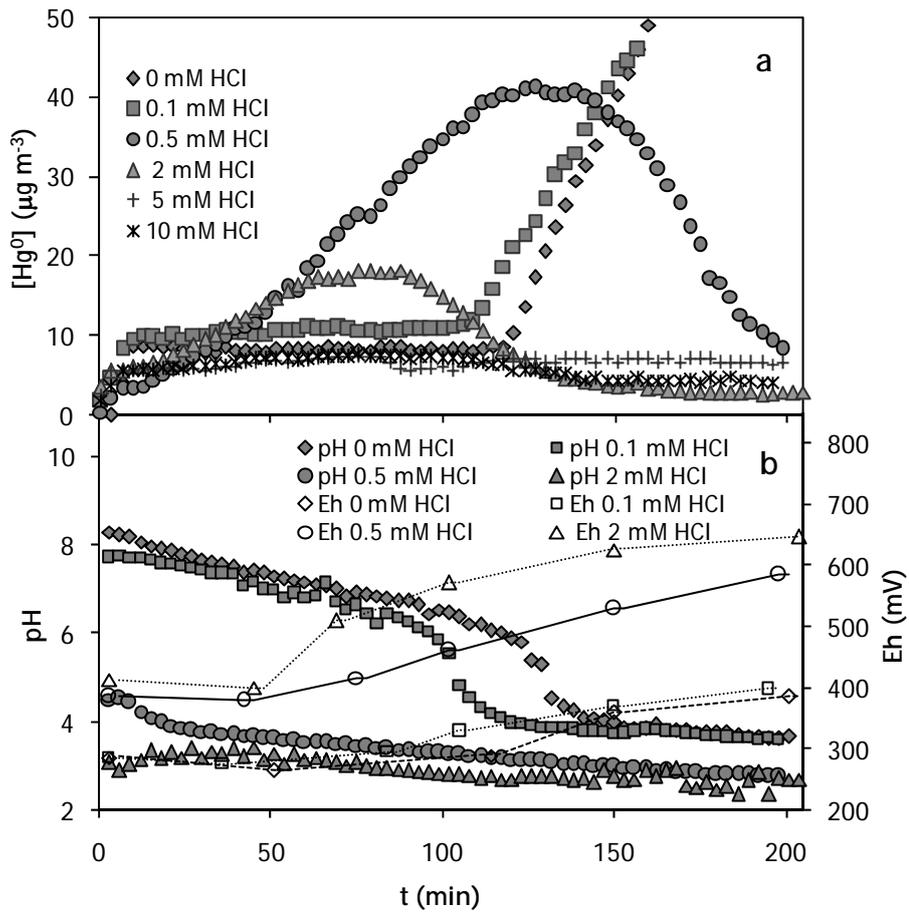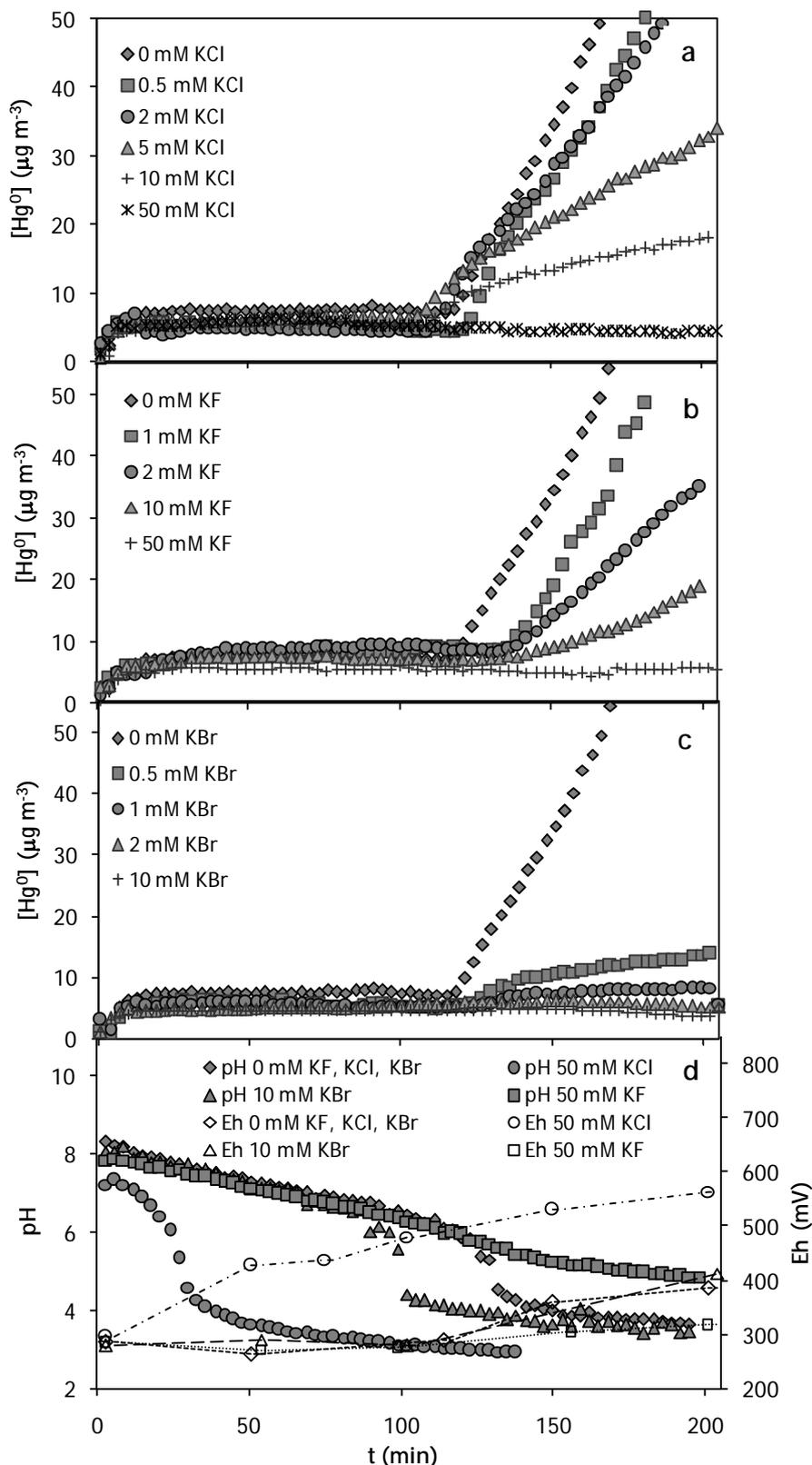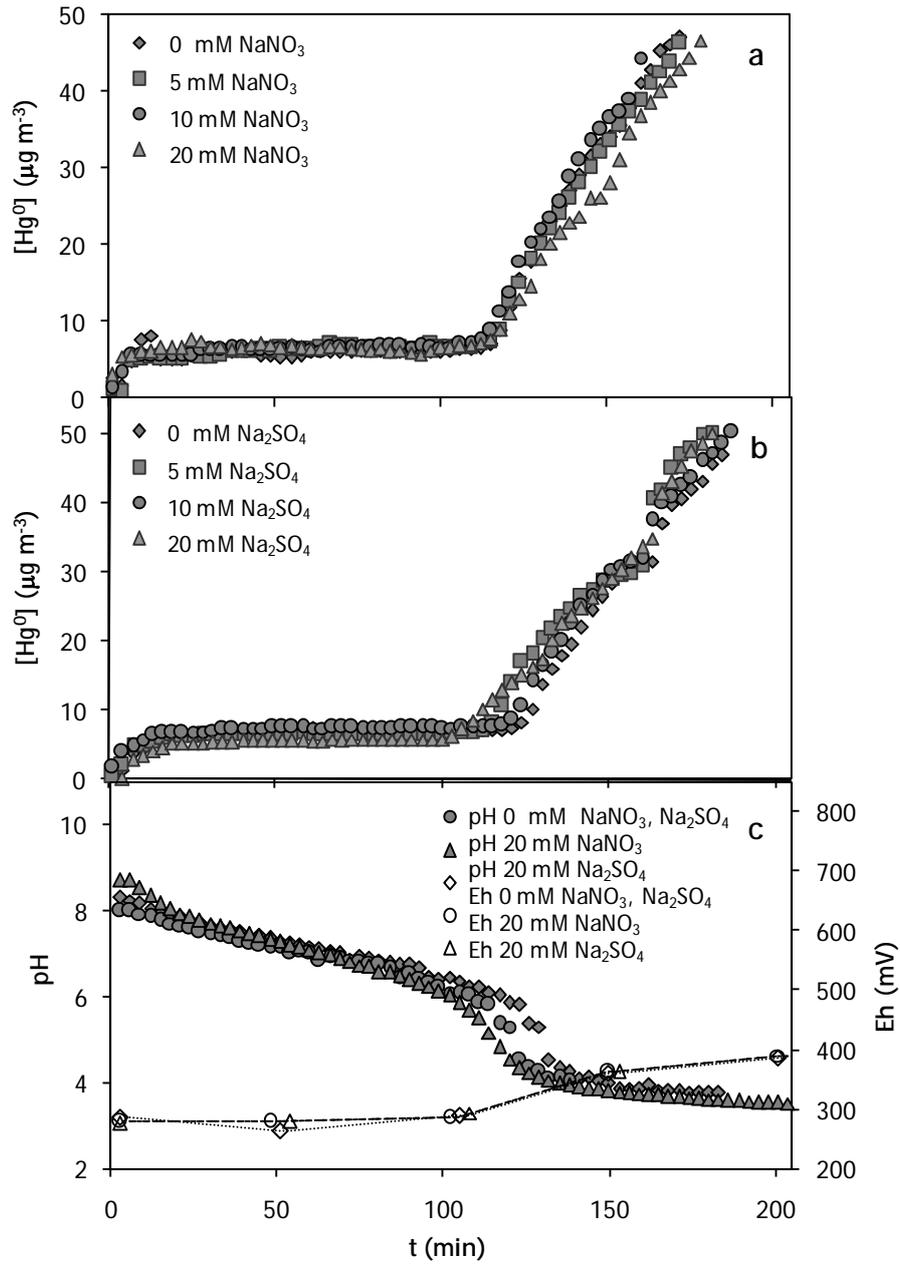**Figure 1.** Lab-scale apparatus used to evaluate elemental mercury re-emission.

Figure 2. Influence of hydrogen chloride using different scrubbing solutions in typical wet scrubber conditions: (a) re-emission of mercury and (b) pH and redox potential as a function of time.

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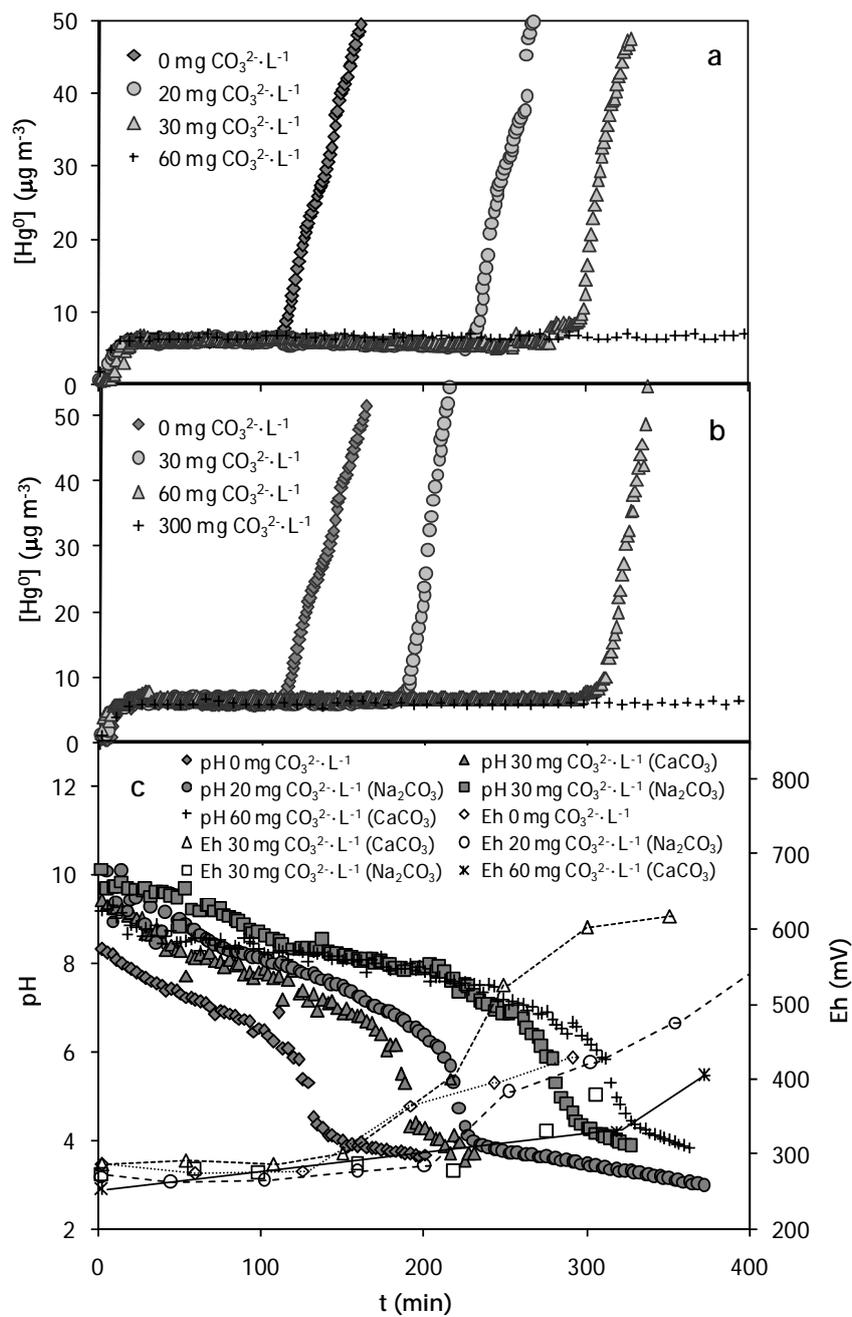
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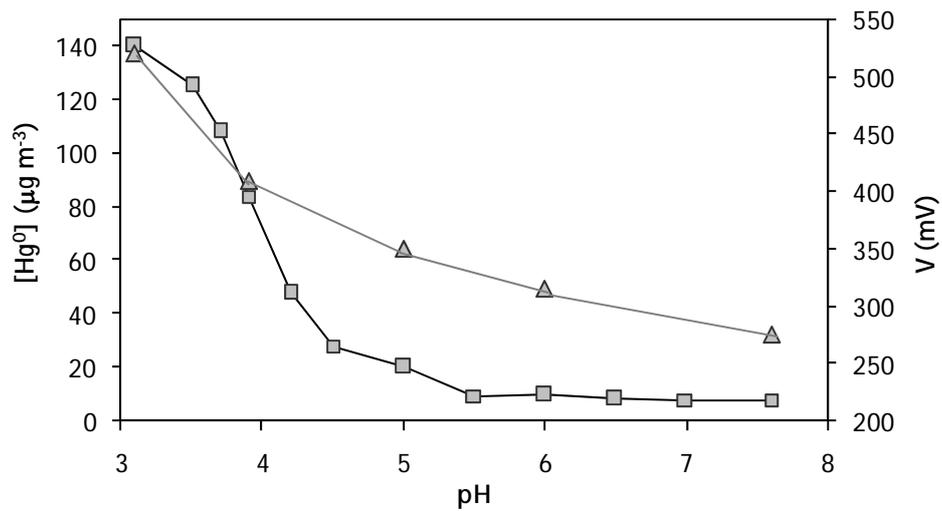
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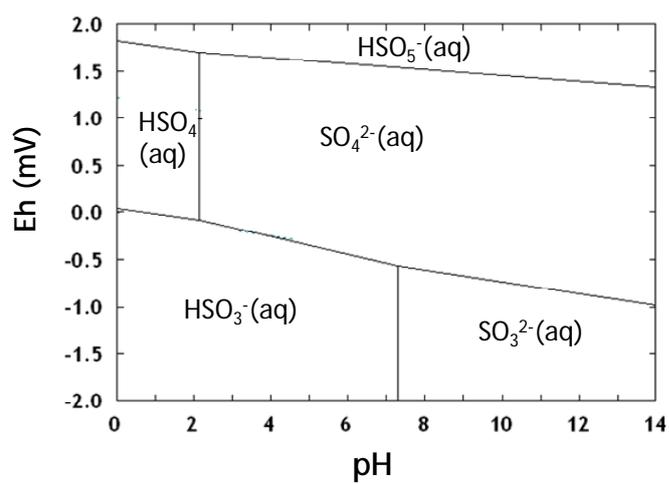
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