THE IMPACT OF OXY FUEL CONDITIONS ON ELEMENTAL MERCURY RE-EMISSION IN WFGD SYSTEMS

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Abstract

This study evaluates some of the variables that may influence mercury retention in wet flue gas desulfurization plants (WFGD), focusing on oxy-coal combustion processes and differences when compared with atmospheres enriched in N_2. The main drawback of using WFGD for mercury capture is the possibility of unwanted reduction of dissolved Hg^{2+}, leading to the re-emission of insoluble elemental mercury (Hg^0) which decreases efficiency. To acquire a better understanding of the mercury re-emission reactions in WFGD systems, this work analyses different variables that influence the behaviour of mercury in slurries obtained from two limestones, under an oxy-combustion atmosphere. The O_2 supplied to the reactor, the influence of the pH, the concentration of mercury in gas phase and the enhancement of mercury in the slurry were the variables considered. The study was performed at laboratory scale where possible reactions between the components in the scrubber can be individually evaluated. It was found that in an oxy-combustion atmosphere (mostly CO_2), the re-emission of Hg^0 is lower than under N_2-enriched atmosphere and the mercury is mainly retained as Hg^{2+} in the liquid phase.

Keywords: mercury; oxy-combustion; gypsum; limestone

1. Introduction

According to the European Environment Agency, energy production in 2013 contributed more than 55% of the SO_x emissions to the environment.[1] Control of SO_x emissions in coal-fired power plants is carried out mostly by wet flue gas desulfurization systems (WFGD)[2] in which a variety of alkaline chemicals, though generally limestone, are used to capture the SO_2.[3] In most WFGD scrubbing facilities, flue gas containing SO_2 is brought into contact with a limestone-water slurry to form insoluble calcium sulfite hemihydrate and gypsum.

Worth noting is that such facilities also serve as the media whereby other reactions may occur. These reactions depend on a wide variety of solid, liquid and gaseous components reaching these systems, and can be controlled and exploited to capture other undesirable constituents from the gas. The retention of oxidized species of mercury (Hg^{2+}) in the WFGD facilities[4,5] is the one that has created most interest because coal-fired power plants are the main source of toxic mercury emissions.[6,7] A major limitation of this process is the reduction of dissolved Hg^{2+}, leading to the re-emission of insoluble elemental mercury (Hg^0) into the atmosphere and decreasing efficiency of mercury capture. To evaluate this effect, studies of mercury behavior in scrubbers have been carried out at industrial scale and conclusions have been drawn mainly by means of mass balances.[3-5,8,9] However, the results at industrial scale are difficult to generalize because the variables involved may not be subject to modification. This drawback can be overcome by assessing these variables in laboratory scale simulations, as possible reactions between the components in the scrubber can be individually evaluated.[10,11] The behavior of gaseous Hg^{2+} when it comes into contact with a gypsum slurry has already been evaluated using a series of simple atmospheres at

68 laboratory scale,[11,12] the present study was carried out in typical oxy-combustion gas
69 conditions.

70 The attraction on oxy-coal combustion is its potential to reduce CO_2 emissions.[13,14]
71 In oxy-combustions plants, coal is burned in a mixture of O_2 and recirculated flue gas,
72 resulting in a gas stream with a high concentration of CO_2 suitable for capture and
73 storage (CCS). However, this technology may also produce a significant rise in SO_2[15]
74 and mercury[16] concentrations (with respect to conventional air firing) as a result of the
75 recirculation of flue gas. In oxy-combustion processes mercury species in the gas are
76 undesirable not only because of their toxicity but also because Hg^0 can cause
77 technological problems by corroding the Al-alloys in the CO_2 compression units.[17]

78 The present study is based on previous research that has demonstrated the
79 dependence of mercury behaviour on the characteristics and composition of the
80 limestones in WFGD conditions.[2] This is a consequence of the reduction of Hg^{2+} to Hg^0
81 in the slurry caused by metals originating from the limestone impurities. In fact, a
82 significant re-emission of Hg^0 in slurries obtained from limestone with a high content in
83 Fe has been observed independently of the presence of sulphites, which may also lead to
84 Hg^0 re-emission.[12] These findings that were obtained in an inert atmosphere represent
85 the basic knowledge for predicting and understanding mercury behaviour in WFGD
86 systems. However, it still needs to be confirmed in more real atmospheres.

87 As a further contribution to the interpretation and prediction of mercury behaviour
88 in WFGD systems, the present work analyses the effect of different variables on the
89 behaviour of mercury in slurries from two limestones under oxy-combustion conditions.
90 The supply of O_2 to the reactor, the influence of the pH, the mercury concentration in

the gas phase and the enhancement of mercury in the slurry with time were the variables evaluated.

2. Experimental

2.1. Limestone and slurry characterization

Two limestone samples, labelled CaC and CaP, previously characterized both chemically and physically[12] were used to simulate SO_2 capture. Calcium, magnesium, aluminium, silicon, phosphorus, sodium and potassium contents were determined using a Bruker SRS3000 fluorescence spectrometer. Trace metals were analyzed by ICP-MS in a 7700X Agilent device after the samples had been digested with HNO_3 in a microwave oven. The species dissolved in the reactor under the experimental conditions were also determined by ICP-MS. Sulphide content in dissolution was estimated by a colorimetric method.

The chemical reactivity of the limestones was calculated by neutralization of a blend of 1.0 g of limestone and 1.0 g of $CaSO_4 \cdot 2H_2O$ with a solution of 0.5 N H_2SO_4 at 50 ºC for 6 hours. The pH was kept at values of 5.0±0.1 using a Mettler Toledo DL53 titrator. The limestone conversion was established as the stoichiometric ratio of sulphuric acid consumed.

2.2. Lab-scale device

The mechanisms of retention and re-emission of elemental mercury in scrubbers were simulated using the lab-scale device[18] described in Figure 1. The equipment consisted of i) a flue gas generation unit for obtaining oxidized mercury, ii) a glass reactor where the slurry was prepared and checked and iii) a continuous mercury

114 analyser (VM-3000) that recorded the Hg^0 (mercury re-emitted) at the outlet of the
115 reactor.

116 **Figure 1.** Experimental device used at lab scale.
117

118 A commercial gas generator system (HovaCAL GmbH) coupled to an evaporator
119 was used to generate different concentrations of Hg^{2+} by evaporation, at 200 ºC, of a
120 mercury nitrate solution, stabilized in 10 mM of hydrochloric acid. The carrier gases
121 used consisted of 70% of CO_2 and different concentrations of O_2 (4 and 20%), balanced
122 with N_2, set to a flow rate of 3 $L \cdot min^{-1}$. Sulphur dioxide (1000 ppm) was also included in
123 the flow gas in specific experiments. The gas was conducted to the reactor through PFA
124 pipes kept at temperature of 120 ºC to avoid the condensation of moisture and mercury.

125 The reactor consisted of a 500 mL, three-necked, round-bottomed glass flask fitted
126 with an inlet and an outlet for the flue gas, and an additional connection for the pH
127 electrode and a titrator. A thermostat system supplied with a stirring unit ensured a
128 constant temperature (40 ºC) and the right mixture of mercury and slurry. The gypsum
129 slurry was prepared by adding sulphuric acid to a limestone slurry with a 1% solid
130 content. The pH was continuously recorded on an Orion Meter (Model 720A+) fitted
131 with an Orion electrode 9678BNWP. When necessary, the pH was adjusted by adding
132 1N of NaOH using a Mettler Toledo DL53 titrator.

133 **2.3. Mercury analysis**

134 The mercury concentration in the solid and liquid products was analysed using a
135 LECO Automatic Mercury Analyser, AMA 254. The mercury species in the gypsum
136 were identified by a thermal programmed desorption procedure (HgTPD)[19] using a
137 continuous mercury analyzer (RA-915) coupled to a furnace (PYRO-915), both from

Lumex. The furnace consisted of two chambers in series, the first chamber serving to pyrolyze the solid samples and the second chamber to reduce the mercury compounds to elemental mercury. The mercury species were characterized according to the temperature range in which they were released from the sample.[19]

3. Results and discussion

The study was performed at laboratory scale using two limestone samples to react with SO_2 in two gas compositions: i) 70% CO_2 + 20 O_2% + 10% H_2O and ii) 70% CO_2 + 4% O_2 + 10% H_2O + 16% N_2. In each case, the distribution of mercury in the by-products produced in the reactor was compared under three different conditions:

(a) Precipitating the gypsum at the beginning of the experiment with sulfuric acid resulting in a pH of 5.5. Henceforth this will be referred to as conditions A (with 20% O_2) and A*(with 4% O_2).

(b) Bubbling SO_2 in the solution while the pH was adjusted to 5.5 by adding NaOH. Henceforth this will be referred to as conditions B (with 20% O_2).

(c) Bubbling SO_2 in the slurry, which caused a decrease in the pH of the slurry during the experiments. Henceforth this will be referred to as conditions C (with 20% O_2).

3.1. Characterization of the limestones and aqueous phase

The most important characteristics of limestones CaC and CaP[12] and the aqueous phases of the gypsum slurries designated as CaC(aq) and CaP(aq) are shown in Table 1. The average particle size and apparent porosity are of the same order in both cases, 32 and 26 μm and 38 and 41% for CaC and CaP, respectively. The Ca content was ~ 39% in both limestone samples, although minor components were present in different concentrations, the most noticeable differences between CaC and CaP are the Fe (877

162 μg·g^{-1}), Mn (177 μg·g^{-1}), Mg (0.27%) and Si (0.94%) contents which were higher in
163 CaC, whereas Sr content (1958 μg·g^{-1}) was higher in CaP.

164 **Table 1.** Chemical composition of the liquid fraction of the slurries from CaC and CaP
165 limestone samples.
166

167 The chemical composition of CaC(aq) and CaP(aq) (Table 1) indicates that the
168 dissolution of elements may depend on the gas composition entering the reactor, which
169 in turn might modify the pH of the slurry. Three main significant remarks need to be
170 made concerning the data in Table 1:

171 i) There is no correlation between the concentration of impurities dissolved and its
172 content in the limestone.

173 ii) The composition of the inlet flue gas affects the dissolution of some impurities,
174 especially in the slurry from CaP. When O_2 increased from 4% to 20% the dissolution
175 of elements such as Mg, Mn, Ni, Fe and Zn slightly decreased probably as consequence
176 of pH and Eh variations. While the pH remains nearly constant at conditions A with
177 CaC slurry, in the case of CaP is more acid at the beginning of the experiments.

178 iii) A great increase in acidity in the medium, as occurred in conditions C, where
179 the pH values decreased from 5.5 to 1.8, favors the dissolution of some metals. A
180 portion of sulfur species in solution cannot be ruled out in these conditions.

181

182 **3.2. Effect of oxygen supply on Hg behaviour**

183 WFGD can operate under natural or under forced oxidation conditions where O_2 is
184 injected into the tank to ensure full oxidation of the sulphur by-products.[20] To evaluate

the effect of increasing O_2 on mercury re-emission, inlet flue gases containing 150 $\mu g \cdot m^{-3}$ of Hg^{2+} and different concentrations of O_2 were bubbled into the slurries prepared with CaC and CaP limestones. The percentages of CO_2 and water vapour in the inlet gas stream were kept constant at 70% and 10%, respectively. In these conditions, the pH of the slurries reaches a value of 5.5 during most of the experiment (Conditions A and A*). For both concentrations of O_2 (4 and 20%), the re-emitted Hg^0 was less than 13% of the inlet Hg^{2+}, remaining almost constant during the test (Figure 2). The increase in the O_2 concentration caused a slight drop (approximately 3%), in the re-emission of Hg^0 in the slurries. This is consistent with results of a previous study[21] which concluded that O_2 content in the inlet flue gas higher than 5% stabilizes Hg^{2+} in the slurry.

Figure 2. Partitioning of Hg in the gas, liquid and solid by-products of the scrubber from CaC and CaP limestones. Flue gas composition: 70% CO_2 + 10% H_2O + O_2 (4 or 20%) + N_2 (balance) + 150 $\mu g \cdot m^{-3}$ Hg.

Figure 2 illustrates the partitioning of mercury in the by-products. Apart from the amount of Hg^0 re-emitted, the distribution of mercury between the liquid and solid differed considerably in the two slurries. Most of the mercury was dissolved in the aqueous phase in both slurries, but in the case of CaP slurry the concentration of mercury was higher in the solid fraction. The S^{2-} content in the liquid phase of the CaP slurry was analysed but the detection limit (0.1 mg/L) for this species was not reached. Although the dissolution of soluble sulphides potentially present in CaP limestone could not be proven, the formation of HgS from S^{2-}disolved should not be ruled out. The mercury species present in the solid fraction of CaP were identified by HgTPD (Figure 3).

Figure 3. Mercury thermal decomposition profile of gypsum from CaP limestone. Flue gas composition: 70% CO_2 + 10% H_2O + 4% O_2 + 16% N_2 + 150 $\mu g \cdot m^{-3}$ Hg.

The desorption profiles show two peaks, the main one at around 190±11 ºC and a second one, of less intensity, at 305±12 ºC. According to a previous study carried out using the HgTPD technique[22], these temperatures correspond to desorption of black HgS and red HgS, respectively. Although red HgS is more stable than black HgS, systems with favorable thermodynamic conditions may produce black HgS. In fact, previous studies have identified these species in gypsum samples from scrubbers[22,23]. However, the exact mechanisms involved in the formation of HgS have not yet been established.

Some mechanisms have been suggested in the literature[24,25] to explain the formation of HgS. Although they cannot be ratified from the results of this work, cannot be discarded. When discussing these possible mechanisms, it must be borne in mind that the reaction of SO_2(g) with limestone produces $CaSO_3$ which, in the presence of O_2, forms $CaSO_4$. Although sulfide is not normally present in WFGD slurries and sulfites are not stable at pH values lower than 6, the following mechanism is suggested whereby mercury might catalyze the disproportionation of sulfite[24] to yield sulfate and sulfide (reaction I).

$$4\ SO_3^{-2}\ (aq) \rightarrow SO_4^{-2}\ (aq) + S^{-2}\ (aq) \qquad \Delta G^{40ºC} = -48.608\ kcal \qquad [I]$$

There is some preliminary spectrophotometric evidence[24] to suggest that mercury catalyzes the reduction of sulfites even when this reaction is thermodynamically favored but very slowly under most conditions. This means that sulfide would be close to

mercury at a molecular level and it could then react to form insoluble HgS[24] according to reaction II.

S^{-2} (aq) + Hg^{+2} (aq) → HgS (s) $\Delta G^{40ºC}$ = -72.896 kcal [II]

This interpretation would explain the formation of HgS in the slurries identified by HgTPD (Figure 3). Moreover, the formation of HgS depends on O_2 concentration. As can be observed in Figure 2, the precipitation of HgS was slightly lower in the atmosphere richest in O_2. According to reaction III, an increase of O_2 content would produce less sulfite and consequently less sulphide (reaction I).

$2SO_3^{2-}$ (ac) + O_2 (ac) → $2SO_4^{2-}$ (ac) $\Delta G^{40ºC}$ = -122.848 kcal [III]

To the best of our knowledge, this mechanism has still not been confirmed, but in any case, it is not the only possible mechanism responsible for the formation of HgS. The presence of CO(g) in the gas would act as reducing agent for SO_4^{2-} (reaction IV), as has been previously postulated[25], generating sulfides that would immediately react with Hg^{+2} to precipitate mercury as HgS. However in our particular case we have not identified CO(g) in the gas atmosphere in significant amounts.

SO_4^{2-} (aq) + Hg^{2+} (aq) + 4CO (g) → HgS (s) + $4CO_2$ (g) $\Delta G^{40ºC}$ = -120.438 kcal [IV]

In any case, the concentration of HgS is considerably higher in the gypsum obtained from CaP than in the gypsum from CaC (Figure 2). This could be a consequence of the presence of a higher content of Fe impurities in CaC (Table 1) that would favor the formation of FeS instead of HgS due to the competitive reaction V.

S^{2-} (aq) + Fe^{2+} (aq) → FeS $\Delta G^{40ºC}$ = -23.711 kcal [V]

Furthermore, the lower reactivity observed in CaP than CaC would involve a higher concentration of available SO_3^{2-} and HSO_3^{2-} species which could be reduced to form HgS, as previously explained (reactions I and II).

3.3. Influence of the pH on mercury re-emission under oxy-fuel conditions.

Figure 4 shows the distribution of mercury when tests were performed by precipitating the limestones under conditions A, B and C. In the experiments where SO_2 was bubbled through the slurries (condition C), Hg^0 re-emission was maximum ~30% for CaC and ~50% for CaP, as a consequence of the fall in pH. If, as is widely accepted, variations in the pH of the scrubber liqueur determine the presence of reductive species, thereby modifying Hg^0 re-emission[26,27], the mechanisms that might explain this behaviour are summarized in reactions VI and VII.

$$Hg^{2+}(aq) + SO_3^{2-}(aq) + H_2O \rightarrow Hg^0(g) + SO_4^{2-} + H^+(aq) \quad \Delta G^{40ºC} = -44.626 kcal \text{ [VI]}$$

$$Hg^{2+} + HSO_3^-(aq) + H_2O \rightarrow Hg^0(g) + SO_4^{2-}(aq) + 3H^+(aq) \Delta G^{40ºC} = -34.181 kcal \text{[VII]}$$

Figure 4. Partitioning of Hg in the gas, liquid and solid by-products of the scrubber from CaC and CaP limestones under conditions A, B and C.

The role of sulfites has been questioned in some conditions. Some studies have demonstrated that when sulfites are present in high concentrations they may form complexes with Hg^{2+}, stabilizing these species in the liquid[10,11]. Moreover, some studies have reported that at least in conditions A and B no sulfites were present[21]. If sulfites were not the factor responsible for Hg^{2+} reduction, other species in the slurry may have reduced Hg^{2+} to Hg^0. The mechanisms proposed involve reactions with specific metals, especially Fe, according to reaction VIII.

277 $2Fe^{2+}$ (aq) + Hg^{2+} (aq) → Hg^{0} (g) + $2Fe^{3+}$ (aq) $\Delta G^{40ºC}$ = -2.994 kcal [VIII]

278 In fact, when different concentrations of Mn ($^{2+}$ and $^{4+}$), Ni ($^{2+}$ and $^{3+}$), and Fe ($^{2+}$
279 and $^{3+}$) were introduced to the slurry from CaC limestone, only in the case of Fe^{2+} the
280 re-emission of Hg^{0} was observed.

281 When the re-emission of Hg^{0} under conditions A, B and C is compared (Figure 4),
282 differences are observed. It must be remembered that B and C were performed by
283 bubbling SO_2 into the limestone slurry, but B maintaining a constant pH (5.5), and C
284 varying as consequence of the dissolution of SO_2. It is observed that Hg^{0} re-emission
285 decreased at pH 5,5. This re-emission is nearby to the obtained in condition A, where
286 gypsum was precipitated before that mercury species had reached the reactor. Figure 4
287 also shows that the formation of HgS was higher in the gypsum produced under
288 conditions B, following reactions I, II, or IV ,

289

290 **3.4. Effect of mercury concentration in gas phase**

291 As already mentioned, the partial recirculation of flue gases in an oxy-combustion
292 power plant enhances the concentration of mercury in the gas entering the WFGD over
293 time[18]. This is apart from the fact that the proportion of Hg^{2+} and Hg^{0} in the scrubber
294 may vary in each power plant, because mercury in the flue gas not only depends on coal
295 characteristics but also on the performance of the SCR (Selective Catalytic Reduction)
296 in the NOx reduction[28] and the particle capture systems. [29]

297 Experiments designed to determine the influence of Hg concentration in the gas
298 were performed using slurries prepared with the gypsum precipitated with H_2SO_4
299 (condition A). The gas streams contained 25, 50 and 150 $\mu g \cdot m^{-3}$ of Hg^{2+}. In all cases the
300 re-emission of Hg^{0} was lower than 13%. In contrast to previous results performed in

other atmospheres[10], the re-emission of Hg^0 was not a function of the mercury concentration in the inlet gas, probably due to the high O_2 content (20%) present in the oxy-combustion atmosphere used in this study (section 2.2). However, the partitioning of mercury in the by-products differed significantly. Figure 5 shows the different mercury contents in gypsum and water and re-emitted in the gas from the slurries CaC and CaP when the experiment was performed under conditions A (pH 5.5). Three important conclusions can be drawn:

i) In both gypsum slurries the re-emission of Hg^0 is low and of the same order, regardless of the concentration of Hg^{2+} reaching the slurry.

ii) The quantity of Hg^{2+} retained in the water increases with the increase in the concentration of mercury entering the slurry.

iii) As previously observed (Figure 4), the quantity of Hg^{2+} retained in the gypsum depends on the characteristics of the slurry. When CaC limestone was used to precipitate gypsum, Hg^{2+} was preferentially retained in the water, whereas when CaP limestone was used a significant amount of Hg^{2+} remained in the gypsum as HgS. Moreover, as the Hg^{2+} concentration in the gas increased, the mercury content in the gypsum obtained from CaP increased while it remained constant in the gypsum formed from CaC (Figure 5).

Figure 5. Hg content in the gas, liquid and solid by-products of the scrubber from CaC and CaP limestones at different Hg concentrations in gas phase. Flue gas composition: 70% CO_2 + 10% H_2O + 20% O_2.

3.5. Effect of mercury accumulation in the reactor

The water used in most WFGD systems is a blend of fresh and recycled water, a portion of which has gone through a filtration process for the separation of gypsum. Consequently, the water blend employed in industrial scrubbers to prepare the limestone slurry is being continuously enriched with the dissolved species in the scrubber.[30] Since the Hg^{2+} content in the water increases, the chemical and physical interactions responsible for the re-emission of Hg^0 and the partitioning of mercury between the solid and liquid phases may change. To evaluate this effect experiments were performed under conditions A (using H_2SO_4 as precipitating agent) and C (bubbling SO_2). They were performed for CaC and CaP slurries to which 1, 2 and 5 $mg \cdot L^{-1}$ of Hg^{2+}, were added to simulate recycled water.

Figure 6. Partitioning of Hg and pH values in the slurry from CaC limestone under a) condition C (bubbling SO_2) and b) condition A (precipitating gypsum with H_2SO_4). Flue gas composition: 70% CO_2 + 10% H_2O + 20% O_2 + 150 $\mu g \cdot m^{-3}$ Hg.

The partitioning of mercury in both slurries exhibited the same trend. Figure 6 shows the results for the slurry from CaC limestone. The results showed that in both conditions, A and C, the re-emission of Hg^0 was higher than when fresh water was used to prepare the slurry. Moreover, the re-emission increased as the Hg^{2+} concentration in the recycled water increased.

The behavior of mercury in experiments performed under conditions C was more noticeable (Figure 6). As was previously explained (section 3.3) a decrease in the pH values produces an increase of mercury re-emission.

4. Final remarks: the influence of CO_2 and O_2 on mercury re-emission

Since the final objective of this study was to determine the effect of oxy-combustion conditions on the behavior of mercury in a scrubber at laboratory scale, the results obtained in the atmospheres with 150 $\mu g \cdot m^{-3}$ Hg, 70% CO_2, 10% H_2O and (4-20%) O_2, will now be compared with those obtained previously under N_2-enriched atmospheres using the same limestones.[11,12, 18]

In the N_2 atmosphere (pH 7),[12] the re-emission of Hg^0 was nearly 100% according to the evaluation of the slurry from CaC limestone, whereas in the case of CaP slurry almost 100% of the Hg^{2+} was retained in the gypsum. Stabilization of the pH in the CO_2 atmosphere (pH 5.5) with different concentrations of O_2 prevented the reduction reactions. The lower mercury re-emission observed in oxy-combustion atmosphere confirms previous observations[21] and the same effect ought to occur in all limestones of similar characteristics to CaC.

If the pH decreases (< 5.5), as occurred in experiments performed under conditions C, the re-emission will increase regardless of O_2 concentration. However, if the pH is stable (condition A), an increase in the O_2 concentration will cause a drop in the re-emission of Hg^0 in the slurries because O_2 is involved in the reduction reactions.

There is a parallel behavior between re-emission and characteristics of the slurry whatever the atmosphere. Under oxy-combustion and N_2 conditions,[12] the mercury captured in the solid phase as HgS was always higher in CaP slurry than in CaC slurry.

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Figure captions

Figure 1. Experimental device used at lab scale.

Figure 2. Partitioning of Hg in the gas, liquid and solid by-products of the scrubber from CaC and CaP limestones. Flue gas composition: 70% CO_2 + 10% H_2O + O_2 (4 or 20%) + N_2 (balance) + 150 $\mu g \cdot m^{-3}$ Hg.

Figure 3. Mercury thermal decomposition profile of gypsum from CaP limestone. Flue gas composition: 70% CO_2 + 10% H_2O + 4% O_2 + 16% N_2 + 150 $\mu g \cdot m^{-3}$ Hg.

Figure 4. Partitioning of Hg in the gas, liquid and solid by-products of the scrubber from CaC and CaP limestones under conditions A, B and C.

Figure 5. Hg content in the gas, liquid and solid by-products of the scrubber from CaC and CaP limestones at different Hg concentrations in gas phase. Flue gas composition: 70% CO_2 + 10% H_2O + 20% O_2.

Figure 6. Partitioning of Hg and pH values in the slurry from CaC limestone under a) condition C (bubbling SO_2) and b) condition A (precipitating gypsum with H_2SO_4). Flue gas composition: 70% CO_2 + 10% H_2O + 20% O_2 + 150 $\mu g \cdot m^{-3}$ Hg.

Table 1. Chemical composition of the liquid fraction of the slurries from CaC and CaP limestone samples.

	CaC[12]	CaC(aq)			CaP[12]	CaP(aq)		
		Conditions A* (4%O_2+ H_2SO_4)	Conditions A (20%O_2+ H_2SO_4)	Conditions C (20%O_2+ SO_2)		Conditions A* (4%O_2+ H_2SO_4)	Conditions A (20%O_2+ H_2SO_4)	Conditions C (20%O_2+ SO_2)
Ca (ppm)	39.1	406	407	391	39.2	420	384	279
K (ppm)	<100	75	308	315	<100	100	174	131
Mg (ppm)	2700	13	14	21	1800	9.0	6,8	8,7
Na (ppm)	<100	1,7	2,2	5.2	<100	2,7	2,6	4,3
Mn (ppm)	177	0.7	0.7	1.0	53	2.8	2.2	2.2
Sr (ppm)	211	0.6	0.6	1.0	1958	2.1	1.8	1.9
Fe (ppm)	877	0.17	0.23	1,6	90	0.5	0.11	2,5
P (ppm)	<100	0.003	N.D.	1.2	<100	0.002	N.D.	1.0
S (ppm)	N.D	N.D.	0.01	126	300	N.D.	N.D.	80
Si (ppb)	9400	5	N.D.	253	7300	4	N.D.	760
Zn (ppb)	7.0	2	3	24	6.4	11	3	67
Al (ppb)	900	N.D.	N.D.	38	900	8	N.D.	149
Cr (ppb)	<100	N.D.	N.D.	3	<100	N.D.	N.D.	
Co (ppb)	500	N.D.	N.D.	N.D.	300	18	14	15
Ni (ppb)	<100	2	2	6	<100	11	8	16
Cu (ppb)	1200	N.D.	N.D.	16	1100	N.D.	N.D.	45
Pb (ppb)	400	<1	<1	17	500	<1	<1	30
As (ppb)	600	N.D.	N.D.	2	500	N.D.	N.D.	4
Sn (ppb)	<100	N.D.	N.D.	5	<100	N.D.	N.D.	3
Sb (ppb)	<100	3	N.D.	6	<100	N.D.	N.D.	2

N.D.: not detected

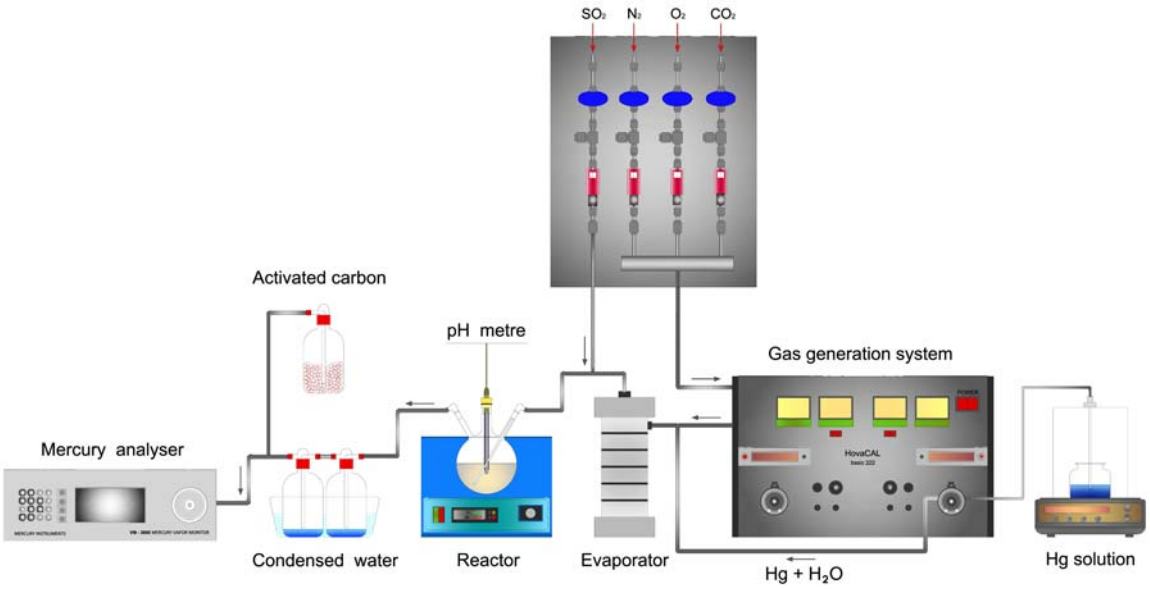


Figure 1

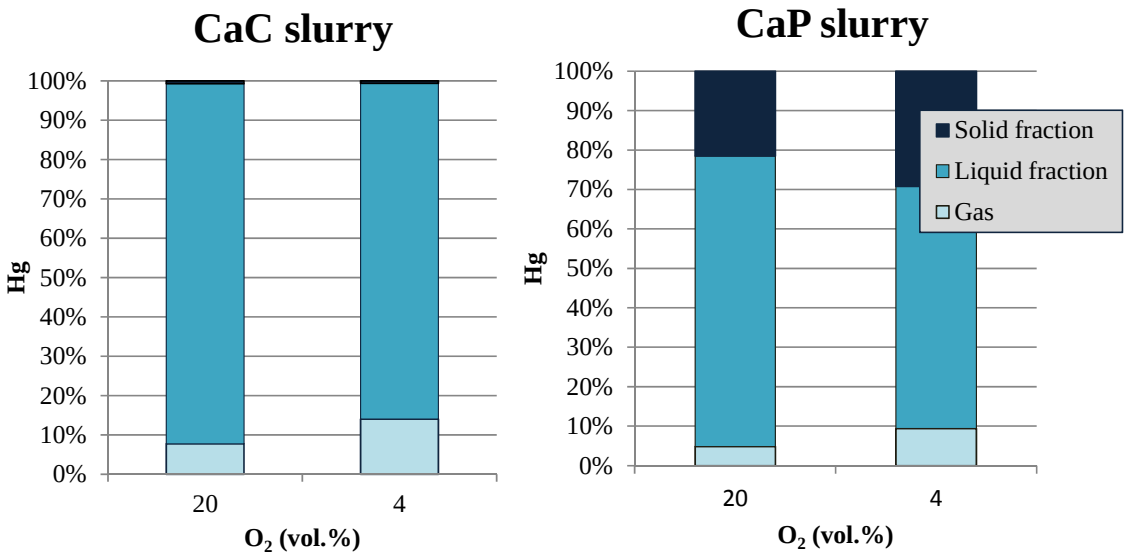
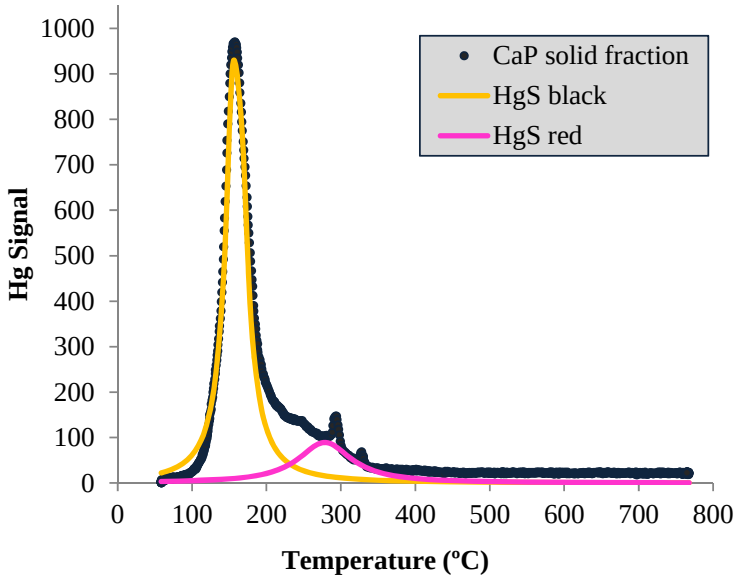


Figure 2



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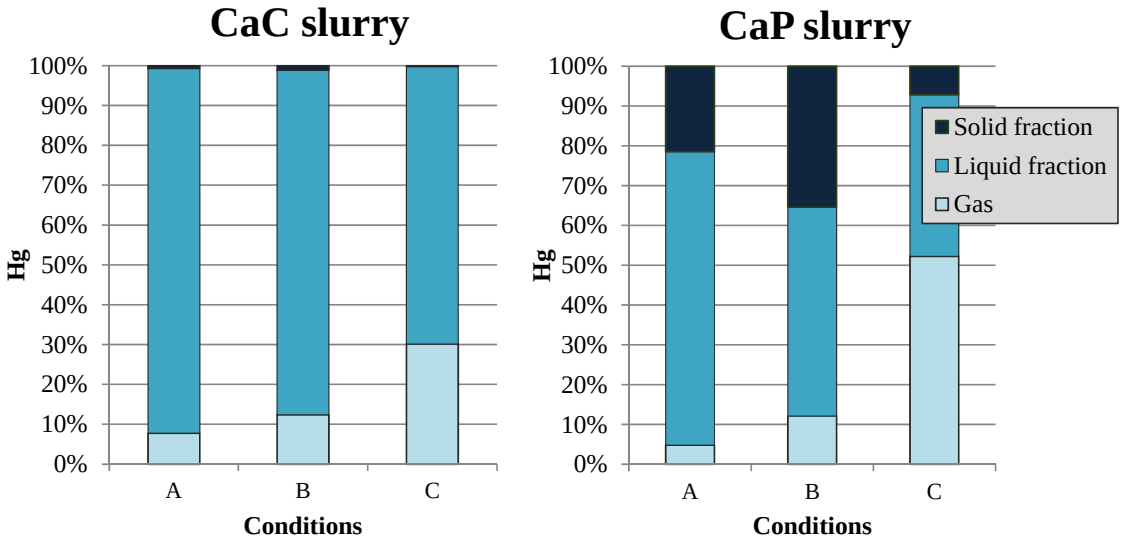

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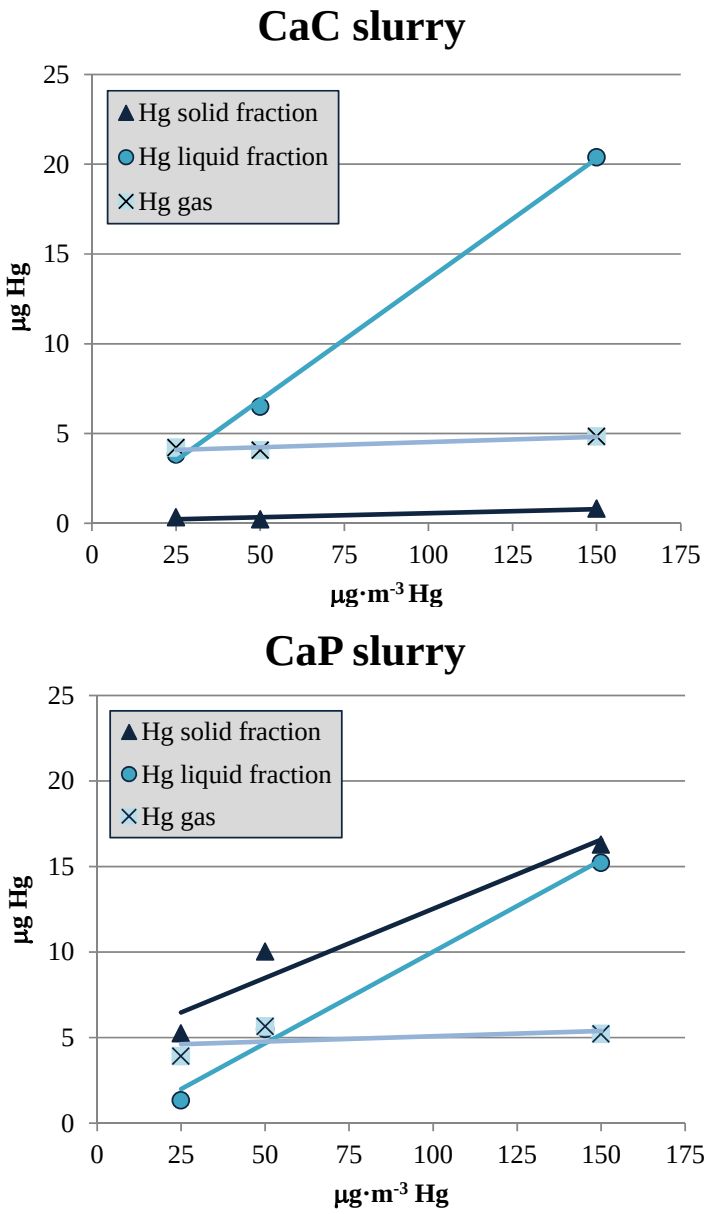
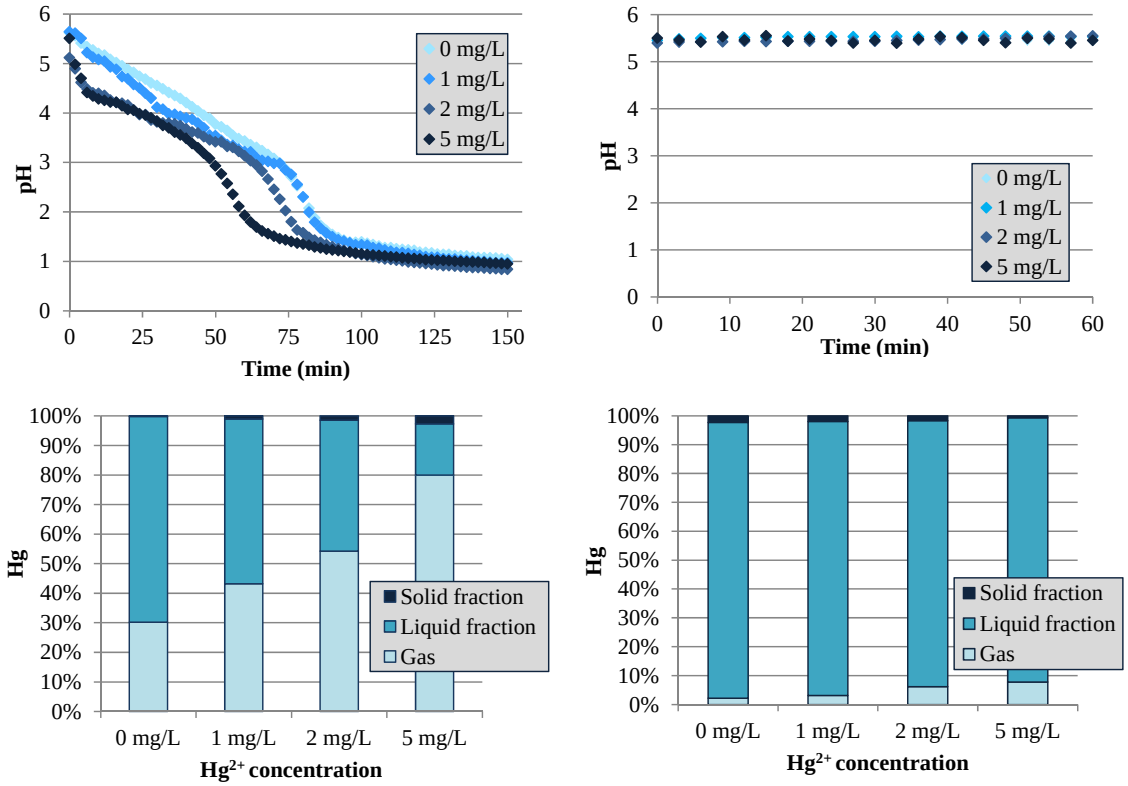

CaC slurry
Hg solid fraction
Hg liquid fraction
Hg gas
µg Hg
µg·m-3 Hg
0
5
10
15
20
25
0
25
50
75
100
125
150
175
CaP slurry
Hg solid fraction
Hg liquid fraction
Hg gas
µg Hg
µg·m-3 Hg

Figure 5


pH
Time (min)
0 mg/L
1 mg/L
2 mg/L
5 mg/L
Hg
Solid fraction
Liquid fraction
Gas
Hg2+ concentration
0 mg/L
1 mg/L
2 mg/L
5 mg/L

(a) (b)

Figure 6