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The capture of oxidized mercury from simulated

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desulphurization aqueous solutions

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Abstract

Elemental mercury in flue gases from coal combustion is difficult to control. However, oxidised mercury species are soluble in water and can be removed with a high degree of efficiency in wet flue gas desulphurization (WFGD) systems operating in coal combustion plants, provided that no re-emissions occur. In this article the mechanisms affecting the re-emission of oxidised mercury species in WFGD conditions via sulphite ions are discussed. The parameters studied include the operating temperature, the pH, the redox potential, the concentrations of mercury and oxygen in the flue gas and the concentration of reductive ions in the solution. The results show that temperature, pH and the concentration of mercury at the inlet of the WFGD systems are the most important factors affecting oxidized mercury removal. The results indicate that sulphite ions, not only contribute to the reduction of Hg^{2+} , but that they may also stabilize the mercury in the liquid fraction of the WFGD limestone slurry. Consequently, factors that increase the sulphite content in the slurry such as a low oxygen concentration promote the co-capture of mercury with sulphur.

Keywords. Re-emission of mercury, mercury speciation, wet flue gas desulphurization

1. Introduction

Inorganic species of mercury are the precursors of more toxic forms, such as methylmercury which accumulates in human organs and has severe effects on the neurological system (Sondreal et al., 2004; Bose-O'Reilly et al., 2010). Coal-fired power plants are the largest source of mercury emissions. Therefore in March 2005 the US Environmental Protection Agency (USEPA) issued the Clean Air Mercury Rule to reduce mercury emissions. Although in February 2008, the Washington DC Circuit vacated the rule, on December 16, 2011, the USEPA finalized the first ever national norms for reducing mercury emissions from coal-fired power plants, preventing about 90% of the mercury being emitted to the air. The Mercury and Air Toxics Standards sets standards for all Hazardous Air Pollutants emitted by coal- and oil-fired steam generation units with a capacity of 25 MW or greater. These standards need to be complied up to 4 years.

The EU (2005) also drew up the community strategy concerning mercury based on specific measures aimed at reducing the circulation of mercury within the EU and the world and at limiting human exposure to this substance. A recent Directive on industrial emissions (EU, 2010) establishes a general framework for reducing pollution from industrial activities in compliance with the principle of pollution prevention and the "polluter pays" principle.

In coal-fired power plants, the mercury present in coal turns into Hg^0 . When the gas cools, Hg^0 is partially converted through different mechanisms into oxidized mercury (Hg^{2+}), which is the predominant species in the flue gas. In most cases, a small proportion of mercury is retained in fly ash particles, which are captured in particle control devices such as electrostatic precipitators or fabric filters. However, most of the mercury escapes from these devices as $\text{Hg}^0(\text{g})$ or $\text{Hg}^{2+}(\text{g})$ species. Due to the solubility

of Hg^{2+} , Wet Flue Gas Desulphurization (WFGD) systems or scrubbers may be considered as a sink for oxidized mercury species. Nevertheless, once Hg^{2+} dissolves in the scrubber slurry, it may react with sulphur compounds (Chang, 2008). Although most of mercury mass balances in WFGD systems indicate that oxidized mercury is efficiently captured and retained in some of these units (Pavlish et al., 2003), high mercury concentrations have been detected at the outlet of the scrubber (Constaniou et al., 1995). This process, which is commonly known as re-emission, occurs via the reduction of Hg^{2+} by sulphite or bisulphite species (Chang and Ghorishi, 2003). Thus, Hg^0 re-emission reduces the efficiency of mercury capture in plants equipped with WFGD.

Various studies have been conducted in order to determine the factors that may affect the conversion of Hg^{2+} to Hg^0 , using laboratory-scale wet scrubber simulators (Chang and Ghorishi, 2003; Wu et al., 2010b). The results indicate that oxygen concentration in the flue gas seems to have a strong influence on mercury capture. Although some studies show that the reduction of mercury may be enhanced by the presence of air in the gas stream (Chang, 2008), others indicate the opposite effect (Wu et al., 2010b). In most studies high WFGD operating temperatures increase the rate of reduction of Hg^{2+} (Díaz-Somoano et al., 2007; Wang et al., 2010). However, according to Chang (2008), the absorbed Hg^{2+} may be reduced by aqueous S(IV) (sulphite and/or bisulphite) species resulting in Hg^0 re-emission. Hg^{2+} -S(IV) complexes may act as precursors to Hg^0 re-emission both inside and outside the scrubber (e.g., clarifier, vacuum filter). In addition, sulfur species and the kinetics of reactions in the scrubber are affected by the pH of the scrubber slurry (Niksa and Fujiwara, 2005). Various studies have demonstrated that an increase in the pH favors mercury capture (Wo et al., 2009), while in others an increase in mercury re-emission has been detected (Wu et al., 2010b). Hg^0 re-emission has also

been directly related to decreasing concentrations of sulphite and sulphate ions (Chen and Zhang, 2011; Wo et al., 2009). However, the results of Omine et al. (2012) confirm that sulphite ions play also an important role in the capture of Hg^{2+} species in the scrubbing liquor. Thus, this process seems to depend on the concentrations of S(IV) ions in the WFGD systems.

In line with above concerns, this study aims to determine the mechanisms that affect the re-emission of oxidised mercury species in WFGD by the action of sulphite ions. The effect of the operating temperature, pH, redox potential, the mercury and oxygen concentrations in the flue gas, and the concentration of reductive ions in solution, on the re-emission of mercury was assessed.

2. Materials and methods

To investigate the absorption of oxidized mercury and its reduction by sulphite ions, a lab-scale device described in a previous work (Ochoa González et al., 2012) was employed (Fig. 1). A commercial evaporator (HovaCAL) was used to generate mercury species in the flue gas. In this device, an aqueous mercury nitrate solution, which was stabilized in a medium of hydrochloric acid, was evaporated continuously at 200 °C. The addition of chlorhydric acid to the mercury nitrate solution led to the formation of mercury chloride complexes such as HgCl_2 . Consequently, Hg^0 , HgCl_2 are the mercury species that could form in a N_2 atmosphere. In an atmosphere of N_2 and O_2 , HgO may also be present. The reaction flask containing a limestone slurry or a solution with different S(IV) species was stirred and kept at constant temperature (40 °C) during the tests. The pH of the solution was measured continuously by using a Mettler Toledo DL53 Titrator and the redox potential was recorded with an Orion Meter (Model 720A+). The speciation of mercury in the synthetic flue gas was determined following

the Ontario-Hydro method in ASTM D6784-02(2008). Hg^{2+} was trapped in three impingers containing potassium chloride solutions, while Hg^0 was collected in subsequent impingers containing a solution of 5% HNO_3 in 10% H_2O_2 and 4% KMnO_4 in 10% H_2SO_4 .

Preliminary tests indicated that the volume of the liquid or slurry in the reactor does not significantly affect the reduction of Hg^{2+} , and that the quantity of sodium sulphite will remain constant. For each test, 100 mL of slurry or aqueous solution containing 1 mM of sodium sulphite was placed in the reactor. The total flow rate of the flue gas entering the reactor was kept at 3 L min^{-1} by balancing it with nitrogen. The atmosphere of nitrogen or nitrogen plus oxygen, containing $130 \mu\text{g m}^{-3}$ of mercury, was kept in contact with the liquid.

HSC Chemistry 6.1 software was used to calculate the equilibrium constants of the reactions involved in the processes taking place in the scrubber simulator.

2. Results and discussion

3.1. Temperature operation

Desulphurization systems typically operate at temperatures between 40 and 60 °C (Díaz-Somoano et al., 2007; Wu et al., 2010a). To study the effect of the variation of this parameter on the reduction rate of Hg^{2+} several tests were performed at temperatures ranging from 30 to 60 °C. Figure 2a represents the Hg^0 continuously monitored at the outlet of the reactor. The results indicate that the rate of reduction of Hg^{2+} diminishes at lower temperatures, which is consistent with the results obtained in previous studies (Chang and Ghorishi, 2003; Wang et al., 2010). At higher temperatures, not only does the time during which the reduction occurs decrease but also the Hg^0 concentration during the first few min of the experiment increases slightly. Higher temperatures

increase the rates of the chemical reactions in which the sulphite and Hg^{2+} species are involved and favor the formation of Hg^0 in accordance to Eq. 1-3:

K_{40 °C}

Since temperature has a strong effect on the re-emission of mercury, lower temperatures are desirable for optimum mercury capture. A temperature of 40 °C was selected as the operating temperature in the lab-scale reactor because at this temperature the total capture of mercury in solution is ensured over a period of time acceptable from an experimental point of view.

3.2. pH and redox potential

The presence of reductive species in the solution depends on the pH value and, as a consequence, the reduction process of Hg^{2+} may occur through different mechanisms. As the mercury solution evaporated in the HovaCAL containing acid, some of the species in gas phase reaching the reactor such as HCl cause a continuous decrease in the pH of the solution. Mercury speciation in the gases obtained from the evaporator showed that the proportion of Hg^{2+} was 96±4%. As Figure 2b shows, the Hg^0 concentration remains constant at 7 µg m⁻³ during the first 120 min of the experiment, which is consistent with the level of Hg^0 detected in the gas from the evaporator. In other words, during the first 120 min of the experiment the Hg^{2+} is completely retained in the reactor and re-emission does not occur. However, the rate of Hg^0 re-emission increases sharply after 120 min, whereas the initial pH value of the solution containing the sulphite ions (8.0) gradually decreases during the experiment (Fig. 2b). pH values

higher than 6.0 stabilize the aqueous Hg^{2+} due to the formation of mercury sulphite complexes such as $\text{Hg}(\text{SO}_3)_2^{2-}$ as follows:

At a pH lower than 6.0 sulphite ions are not stable and, as a consequence, HSO_3^- may form according to Eq. 5.

HgS(IV) complexes, such as HgHSO_3^+ , are not stable in these conditions and decompose into Hg^0 . At 120 min the redox potential increases until it reaches nearly 400 mV by the end of the test (Figure 2c), which indicates that S(IV) species reacted with the Hg^{2+} species, generating sulphate ions in the solution in accordance with Eq. 1. These results suggest that a decrease in the pH and high redox potential values increase the re-emission of mercury in WFGD systems.

3.3. Mercury concentration

The recirculation of water in desulphurization systems for long periods of time generates wastewater with possibly high contents of mercury (Córdoba et al., 2011). This may favor the reaction of oxidised mercury species with sulphite ions and lead to an increase of the concentration of Hg^0 at the flue gas outlet of the scrubber.

The mercury content of wastewater depends on the quantity of mercury in the flue gas. Therefore in order to assess the influence of the concentration of mercury on its re-emission, different concentrations of Hg^{2+} ranging from 50 to 150 $\mu\text{g m}^{-3}$ were tested. Figure 3 illustrates the correlation observed between the mercury concentration in the flue gas and the time needed to start the reduction of Hg^{2+} . The stability of mercury in the solution is higher at low concentrations of mercury. In other words, the higher mercury concentrations, the sooner re-emission starts. These results indicate that the

concentration of mercury in the liquid fraction of these systems influences mercury removal. Therefore, although the bleed stream maintains uniform concentrations of the mayor species such as chloride and sulphates, power plants generating high concentrations of mercury are more likely to increase the amount of mercury re-emitted to the atmosphere with time.

3.4. Oxygen concentration

Forced oxidation WFGD systems typically operate with air injection to ensure a fully oxidized gypsum product. The influence of oxygen concentration on the re-emission of mercury in the scrubber was evaluated at lab-scale when sulphite ions were present in the reactor. The behavior of mercury was studied when the oxygen concentration in the gas stream inlet ranged from 4 to 21%. As Fig. 4a shows, when the sulphite concentration was 1 mM, oxidized mercury is more stable in the scrubbing solution under a carrier gas containing nitrogen. In these conditions no correlation between Hg^0 re-emission and oxygen concentrations was found. However, when the sulphite concentration in the solution was increased to 10 mM (Fig. 4b) a relation between mercury retention and the percentage of oxygen was established. It appears that mercury retention depends on the concentration of sulphite ions in the solution since oxygen promotes the oxidation of such ions in accordance with Eq. 6.

Consequently, sulphite ions may contribute to mercury retention in the scrubbing solution, whereas oxygen promotes the re-emission of Hg^0 since it reduces the amount of sulphite ions. Hence, the stability of the complexes formed between Hg^{2+} and SO_3^{2-} , such as HgSO_3 or $\text{Hg}(\text{SO}_3)_2^{2-}$, is diminished. In these experimental conditions the

formation of HgSO_4 according to Eq. 6-7 seems unlikely since there is no retention of mercury in the presence of sulphate ions formed via sulphite oxidation (Eq. 6). Although some authors found that oxygen favors the capture of the mercury (Wu et al., 2010b) in this paper it is demonstrated that stable complexes such as HgSO_3 or $\text{Hg}(\text{SO}_3)_2^{2-}$ may be formed at high $\text{SO}_3^{2-}/\text{Hg}^{2+}$ ratios in the scrubber systems.

3.5. S (IV) species

Because the presence of S(IV) species may influence mercury reduction, the level of re-emission of Hg^0 when both sulphite and bisulphite ions are present in solution was evaluated. Nitrogen was used as carrier gas to release the Hg^0 generated in the reactor and also to stabilize the mercury in solution. The equilibrium constants for the reduction reactions predicted with HSC Chemistry software at 40 °C are shown in Eq. 1 and 8:

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

These data show that, regardless of kinetic factors, the reduction of Hg^{2+} by sulphite and bisulphite ions is possible, since the equilibrium constant of the reaction in which sulphite ions are involved is higher than that of the bisulphite anions. The re-emission of Hg^0 for different proportions of sulphite and bisulphite ions was monitored keeping the total concentration of S(IV) constant. Figure 5 shows the re-emission of Hg^0 for different proportions of sulphite and bisulphite ions ranging from 0 to 100%. When both types of ion are present in the solution, as the sulphite concentration increases the re-emission of mercury decreases. Thermodynamic predictions indicate that the reduction reaction involving sulphite ions is slightly faster (Eq. 1), but the experimental data obtained suggest that sulphite ions could stabilize Hg^{2+} over a period of time, converting

the Hg^{2+} in solution into $\text{Hg}(\text{SO}_3)_2^{2-}$ or HgSO_3 . Of these complexes HgSO_3 is the less stable according to the rate constants described according to data from Constaninou et al. (1995) for both complexes:

3.6. Sulphite ion concentration

As already mentioned, the presence of sulphite ions at high concentrations may stabilize the dissolved mercury species in the scrubber. The mercury re-emission curves obtained for different initial sulphite concentrations are shown in Fig. 6a. The data represented in this Figure indicate that the reduction of the dissolved mercury starts after a period of time which is proportional to the concentration of sulphite ions. More mercury is retained, as concentration of sulphite ion increases. The reduction of mercury was detected when the pH value of the scrubbing solution dropped to below 6.0. Low concentrations of sulphite, which are consistent with forced oxidation conditions, produced high levels of mercury re-emissions. This finding confirms that sulphite ions are not the only species involved in the reduction of Hg^{2+} (Eq. 1). Sulphite ions also allow the formation of relatively stable mercury species such as HgSO_3 and $\text{Hg}(\text{SO}_3)_2^{2-}$ in agreement with Eq. 11-12. According to thermodynamic data taken from the literature, mercury sulphite complexes are thermodynamically stable at 25 °C according to Constaninou et al. (1995):

The effect of sulphite ion concentration when limestone is used as sorbent for sulphur species was compared in an air and an inert atmosphere. The use of air as carrier gas allows the simulation of forced oxidation conditions in desulphurization systems, which favor the production of calcium sulphate instead of calcium sulphite. In such conditions the improvement observed in the stabilization of mercury may be either due to the formation of a basic carbonate of mercury ($\text{HgCO}_3 \cdot 3\text{HgO}$ or $\text{HgCO}_3 \cdot 2\text{HgO}$) or to the adsorption of Hg^{2+} by the particles of the sorbent (limestone) or by the reaction product (gypsum). The re-emission data for Hg^0 in the experiments with different initial sulphite concentrations and a small amount of limestone (20 mg) are shown in Fig. 6b. The mercury re-emission curves indicate that under forced oxidation conditions, the retention of Hg^{2+} improves, as the sulphite concentration increases, to the point where Hg^{2+} retention in a solution of 10 mM of sulphite is 100%. These results agree with those obtained in an inert atmosphere, where mercury retention diminished for lower concentrations of sulphite ions. The addition of calcium carbonate to the sulphite solution increases the pH and stabilizes aqueous mercury through the formation of Hg^{2+} and SO_3^{2-} complexes.

As mentioned before, despite the impact of the bleed stream in desulphurization systems, the use of coals whose concentration of mercury is high and the slurry circulation increase the amount of dissolved mercury. To simulate this process of accumulation of mercury in solution, oxidized mercury was added to the reactor before the retention test (Fig. 6c). If these data are compared with those of Fig. 6b, it can be seen that the presence of mercury in the reactor favors the reduction of Hg^{2+} . Consequently, water with a high mercury content and low concentration of sulphite ions favors the re-emission of this element to the atmosphere.

4. Conclusions

The effect of different parameters on Hg^{2+} stability in simulated WFGD conditions was studied on a lab-scale device and by continuously monitoring the Hg^0 concentration under various conditions. The reduction of mercury species and the mechanisms involving reactions between Hg^{2+} and sulphite ions can vary considerably. Low temperatures and low concentrations of mercury in the scrubbing solution favor mercury capture in scrubber systems. The sulphite ions, not only contribute to the reduction of Hg^{2+} , but may also stabilize the mercury present in the liquid fraction of the WFGD limestone slurry depending on the conditions. The sulphite ion content is reduced by oxygen present in the flue gas. Consequently forced oxidation conditions in WFGD may result in the destabilization of mercury-sulphite complexes.

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Figure captions

Figure 1. Scheme of the WFGD system to evaluate mercury retention.

Figure 2. Effect of the operating temperature of the reactor on the re-emission of elemental mercury (a) and influence of the pH (b) and redox potential (c) of the scrubbing solution on elemental mercury emission. ($T^a = 40\text{ }^{\circ}\text{C}$) (b). Reactor: $[\text{S(IV)}] = 1\text{ mM}$; flue gas composition: N_2 , $130\text{ }\mu\text{g m}^{-3}\text{ Hg}$.

Figure 3. Effect of oxidized mercury concentration in its reduction. Reactor: 1 mM S(IV) ; $T^a = 40\text{ }^{\circ}\text{C}$; flue gas composition: N_2 .

Figure 4. Elemental mercury emission for different concentrations of O_2 . $T^a = 40\text{ }^{\circ}\text{C}$; flue gas composition: N_2 , O_2 , $130\text{ }\mu\text{g m}^{-3}\text{ Hg}$. Reactor: 1 mM S(IV) (a) and 10 mM (b).

Figure 5. Elemental mercury emissions obtained with scrubbing solutions containing different ratios of sodium sulphite: sodium bisulphite. Reactor: 1 mM S(IV) ; $T^a = 40\text{ }^{\circ}\text{C}$; flue gas composition: N_2 .

Figure 6. Effect of the concentration of Na_2SO_3 on the reduction of mercury. Flue gas composition: N_2 , $130\text{ }\mu\text{g m}^{-3}\text{ Hg}$ (a,b) and air (c). Reactor: solution containing 1 mM S(IV) (a), slurry containing 1 mM S(IV) , 20 mg of limestone (b) and slurry containing 1 mM S(IV) , 20 mg of limestone, 0.4 ppm Hg (c).

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