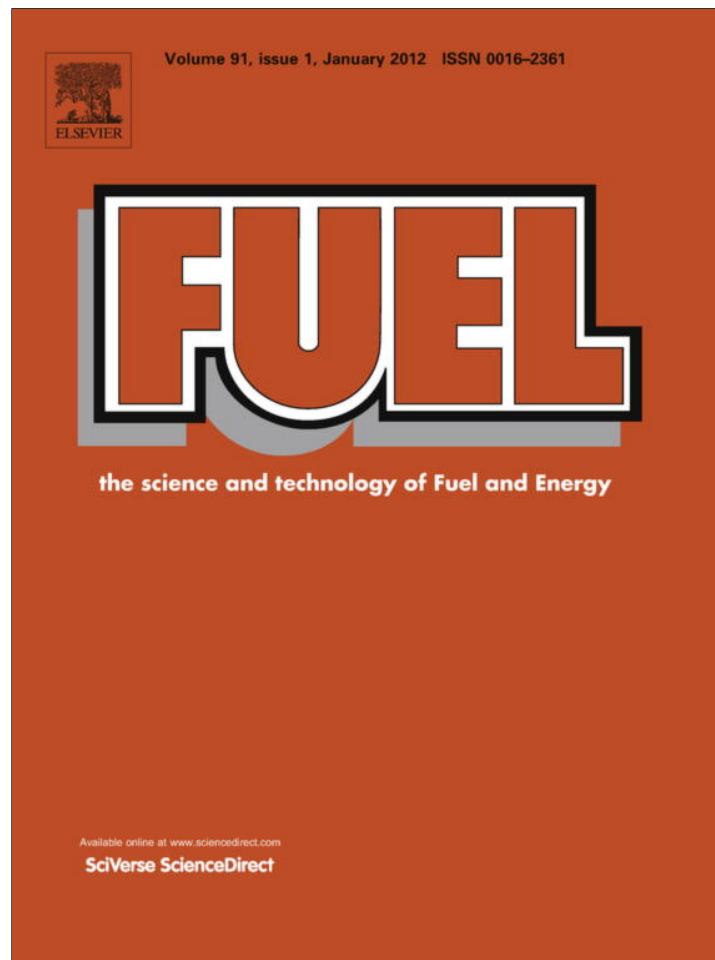


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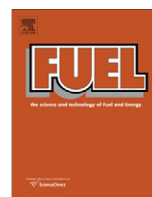


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## Study of elemental mercury re-emission in a simulated wet scrubber

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### ABSTRACT

Mercury is a toxic pollutant that has motivated environmental regulations for emissions reduction from coal-fired power plants. Acid gas wet scrubbers are known to provide the co-benefit of SO<sub>2</sub> control and mercury removal, when mercury is found in the flue gas in the oxidized form. The aqueous ionic chemistry in the scrubbing solution can lead to transformation of the absorbed ionic mercury to the insoluble elemental mercury form, resulting in mercury re-emission and a reduction of the scrubber mercury capture efficiency. Laboratory-scale experiments were performed in a simulated batch scrubber. The experiments were carried out to simulate a forced oxidation limestone reactor. The effect of scrubber temperature and pH, ionic mercury concentration in the liquor, total sulfite, and chloride and bromide ion concentration in solution, and O<sub>2</sub> and CO<sub>2</sub> concentration in the gas on mercury re-emission was investigated. Of particular interest was the investigation of the impact of slurry temperature and CO<sub>2</sub> concentration in the gas, under conditions typical of oxy-fuel combustion condition, on mercury re-emission. The results confirm that oxidized mercury is reduced by aqueous S(IV). Higher concentrations of sulfites, chloride and bromide ions inhibit oxidized mercury transformation to elemental mercury. Higher concentrations of ionic mercury in the liquor and increased scrubber temperature and pH value results in higher re-emission levels of elemental mercury. Additionally, on the impact of oxy-fuel conditions on mercury, it was found that high availability of excess oxygen in the flue gas in contact with the scrubbing solution was found to result in lower conversion of oxidized to elemental mercury. No impact from CO<sub>2</sub> in the flue gas was found on elemental mercury re-emission. However, higher slurry temperatures under oxy-fuel combustion conditions would lead to increased elemental mercury re-emission. For completeness, the effectiveness of sulfide-based additives for abatement of elemental mercury re-emission was also demonstrated in this study. The suppression effectiveness of sodium hydrogen sulfide, sodium sulfide, TMT15<sup>®</sup> and the NaClO-8034 reagent was found at 99%, 97%, 93% and 99%, respectively. These additives promote precipitation of ionic mercury as mercury sulfide.

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### 1. Introduction

The US Environmental Protection Agency (EPA) determined that mercury (Hg) emissions from coal-fired power plants pose significant hazard to public health and must be reduced. Hg is a neurotoxin that can cause acute neurological effects on humans, particularly children. Coal-fired power plants account for approximately 40% of anthropogenic Hg emissions in the US [1]. Although, the future of federal mandated Hg emissions regulation has not been resolved, after court vacating of the EPA proposed Clean Air Mercury Rule (CAMR), several states have enacted stringent Hg limits. Nineteen states have enacted ruling to limit coal-fired power plant Hg emissions. In-place state Hg emissions regulations require Hg removal in excess of 90%, making implementation of Hg

control technology to achieve low Hg emissions levels, a priority for coal-fired plant operators.

Power plant data have shown that the percentage of uncontrolled Hg emitted from different plants varies widely, from approximately 10% to 90% of the Hg in the coal. Mercury speciation, adsorption and removal in the boiler is affected by the type of fuel fired at the unit, boiler flue gas and fly ash characteristics and the configuration of pollution control equipment used at the plant. At combustion temperatures, Hg is present as elemental vapor (Hg<sup>0</sup>). As the flue gas cools down in the boiler convective pass, complex homogeneous and heterogeneous reactions take place, resulting in oxidized gaseous forms of Hg, primarily mercuric chloride (HgCl<sub>2</sub>), and particulate-bound Hg (Hg<sub>p</sub>). Elemental mercury is insoluble and is extremely volatile at the operating temperatures of typical air pollution control devices (APCDs), making it difficult to capture in the boiler. On the other hand, oxidized mercury has a tendency to associate with particulate

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matter and it is water-soluble, making it a preferred species that can be removed in electrostatic precipitators and fabric filters for particulate control, and desulphurization scrubbers. Wet flue gas desulphurization (WFGD) is the technology of choice by US coal-fired power plants for high-sulfur applications for sulfur dioxide ( $\text{SO}_2$ ) control. Full-scale data, including EPA's Information Collection Request (ICR) information, have indicated the co-benefit of Hg emissions reduction across WFGDs, ranging from less than 50% for subbituminous and lignite coals to more than 70% for bituminous coals [2,3]. This is mainly due to the inability of wet scrubbers to absorb the insoluble  $\text{Hg}^0$  and the documented transformation of the absorbed ionic form of Hg ( $\text{Hg}^{2+}$ ) to  $\text{Hg}^0$ , and its subsequent desorption into the flue gas [4–6].

The ionic chemistry of Hg in aqueous solutions containing sulfur species has been studied in systems in the atmospheric cycle [7,8]. More recently, and given the relevance  $\text{Hg}^0$  re-emission has in decreasing the overall Hg removal efficiency across WFGDs, the Hg reactions that are characteristic of wet limestone scrubbers have been studied. However, the entire detailed reaction mechanism and the specific conditions under which this process takes place are not fully understood. Studies have identified intermediate S(IV) species, i.e.,  $\text{SO}_3^{2-}$  and  $\text{HSO}_3^-$ , as the main parameter affecting the  $\text{Hg}^{2+}$  reduction and subsequent  $\text{Hg}^0$  re-emission in WFGDs [9,10]. Other parameters have also been found to play a role in the  $\text{Hg}^0$  re-emission chemistry in WFGD reactors. These include the scrubber liquor pH value and temperature, and the availability of chloride ions and oxygen in the aqueous and gaseous phase [9,11,4].

This paper reports experiments performed in a simplified bench-scale simulated wet scrubber, containing a typical limestone-based WFGD liquid solution. The objective of this study was to investigate the reduction of  $\text{Hg}^{2+}$  and subsequent emission of  $\text{Hg}^0$  under a range of WFGD scrubber operating conditions including oxy-fuel combustion condition for constrained  $\text{CO}_2$  emissions. Higher slurry temperatures and  $\text{CO}_2$  concentrations in the gas than those typical of air combustion conditions were used to simulate conditions representative of under oxy-fuel combustion conditions in WFGD's. Different concentrations of  $\text{HgCl}_2$ , and aqueous sulfite, and chloride and bromide ions were added to the simulated scrubber. Emissions of  $\text{Hg}^0$  from the batch reactor were continuously monitored using an Hg analyzer. The reactor temperature and pH level were varied in the range from 20 to 75 °C and from 5 to 6, respectively. Tests were also conducted under variable oxidative and carbon dioxide ( $\text{CO}_2$ ) concentrations of the simulated gas bubbled through the batch WFGD scrubber. Abatement of  $\text{Hg}^0$  re-emission was also investigated using four types of reagents. The four reagents included two commercially available products, and two sulfide-based additives. Utilization of the commercial products and the sulfide compounds with the scrubbing solution demonstrated the effectiveness of additives to suppress the re-emission of  $\text{Hg}^0$  in a bench-scale batch limestone scrubber.

## 2. Experimental

A batch reactor was assembled to perform experiments under simulated WFGD conditions (see Fig. 1). A glass flask was used as the reactor vessel. A gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) slurry solution was prepared, together with limestone ( $\text{CaCO}_3$ ). Experiments were performed using the specified solution as the scrubbing liquor. Different flue gas compositions were prepared using gas bottles containing oxygen ( $\text{O}_2$ ),  $\text{CO}_2$ , and nitrogen ( $\text{N}_2$ ) as a carrier gas. The addition of  $\text{O}_2$  was intended to simulate a forced oxidation process and increase the scrubber solution oxygen availability. Addition of high concentrations of  $\text{CO}_2$  was intended to simulate forecasted new oxy-fuel combustion plants under a  $\text{CO}_2$ -con-

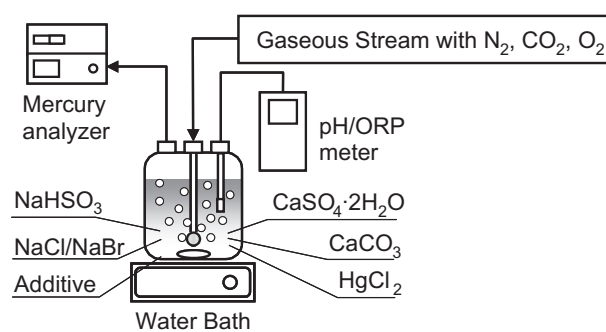


Fig. 1. Schematic of batch WFGD used in the experiments.

strained scenario. The gas flow rate and composition was kept constant by the use of mass flow controllers (MFCs). The synthetic flue gas stream was bubbled into the reactor vessel. A 50  $\mu\text{m}$  frit was attached at the end of the gas supply line in the vessel to generate bubbles and increase gas and liquid mixing. The flue gas path temperature was held at approximately 20 °C by the use of auxiliary heat tapes.  $\text{HgCl}_2$  liquid was added to the slurry solution in the reactor to simulate an ionic Hg concentration corresponding to conditions representative of Eastern US bituminous coal applications in WFGDs, with an Hg concentration in the coal of 100  $\mu\text{g}/\text{kg}$ . The reaction vessel was heated in a water bath to control the slurry temperature. A Teflon stir-bar was introduced into the reaction vessel to continuously stir the content of the solution in the batch vessel. The pH and the redox potential values of the liquid solution were measured using a portable Hanna pH/ORP/temperature meter, Model HI991002. The pH of the solution was controlled through the combined addition of  $\text{CaCO}_3$  and  $\text{H}_2\text{SO}_4$  to the reactor. The S(IV) concentration level in the slurry was controlled by the addition of  $\text{NaHSO}_3$ . Measurement of sulfite concentration in solution was made by an iodometry titration method that involved the use of iodine, HCl and sodium thiosulfate. NaCl and NaBr were used to investigate the impact of Cl and Br ions on  $\text{Hg}^0$  re-emission. All lines were made of Teflon and heat traced to prevent material condensation and absorption on the conveying lines.

The experimental process consisted of preparation of the aqueous solution and addition of the  $\text{CaCO}_3$  for pH control. For some experiments, NaBr was added to the solution. The simulated gas stream was then passed through the slurry, while adjusting its temperature. Continuous  $\text{Hg}^0$  concentration detection at the outlet of the simulated WFGD reactor was started at this point, using a PS Analytical (PSA) 10.525 Sir Galahad Hg monitor. The PSA Hg analyzer uses a wet chemistry system to pre-treat the flue gas and convert all forms of Hg to  $\text{Hg}^0$ . The PSA analyzer works based on the principle of atomic fluorescence spectrometry. It was expected that all re-entrained  $\text{Hg}^0$  would be in the outlet gas stream, since that  $\text{Hg}^0$  has a very low solubility in water ( $6 \times 10^{-6}$  g/100 g at 25 °C).  $\text{HgCl}_2$  addition followed, with the wet PSA's chemical reduction unit, with  $\text{SnCl}_2$  used to convert the  $\text{Hg}^{2+}$  to  $\text{Hg}^0$  and determine the ionic Hg concentration in solution. Since that the main focus of these experiments was to investigate the re-emission of  $\text{Hg}^0$  under a range of WFGD scrubber operating conditions, emphasis was put on the continuous monitoring of  $\text{Hg}^0$  at the reactor outlet. Mercury chloride was assumed to be retained in the limestone/gypsum suspension.  $\text{NaHSO}_3$  was added to the slurry and measurement of sulfite concentration performed by the iodine titration method.

Taking into account the operational conditions of actual WFGD systems and the limitations of the experimental setup, a 1 L absorbent volume was used, with a gas flow rate of 2 L/min. The range of experimental conditions used for the scrubber slurry and the

**Table 1**  
Experimental Conditions.

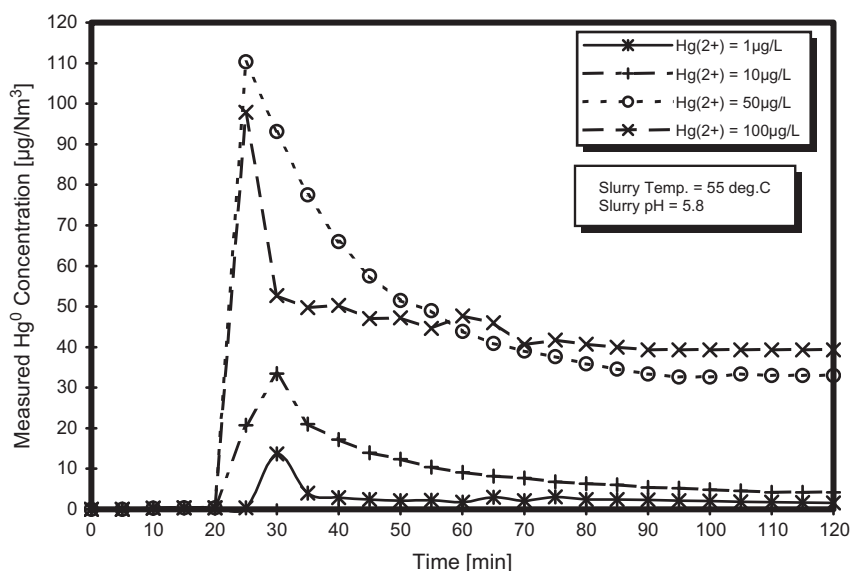
Parameter	Scrubber slurry	Simulated gas
pH (-)	5–6	–
Temperature (°C)	20–75	20
ORP (mV)	40–60	–
O <sub>2</sub> (vol.%)	–	2–20
CO <sub>2</sub> (vol.%)	–	15–90
N <sub>2</sub> (vol.%)	–	Balance
Hg <sup>2+</sup> (μg/L)	1–100	–
CaSO <sub>4</sub> ·2H <sub>2</sub> O (wt.%)	5	–
CaCO <sub>3</sub> (mM)	10	–
S(IV) (mM)	0–10	–

simulated flue gas are included in Table 1. Parametric experiments were performed for a set of conditions of the following individual parameters: Hg<sup>2+</sup> concentration in the slurry, scrubber pH and temperature, O<sub>2</sub> and CO<sub>2</sub> concentration in the gas, and S(IV), Cl<sup>-</sup> and Br<sup>-</sup> concentration in solution. Each experiment was run for a total of 120 min. The Hg<sup>0</sup> re-emission level was continuously monitored at the scrubber outlet, with the reported re-emission level

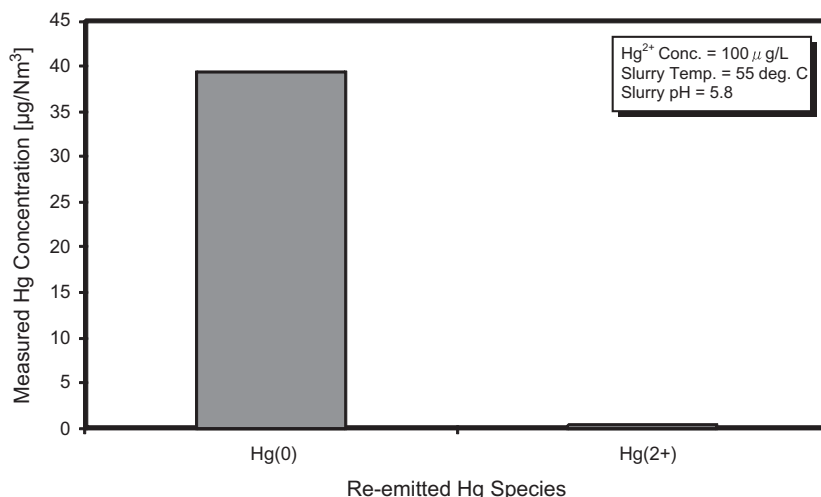
corresponding to the Hg<sup>0</sup> concentration once steady state was achieved. The parametric experiments were followed by tests of additives for Hg<sup>0</sup> re-emission mitigation. The following additives were tested: sodium sulfide (Na<sub>2</sub>S), sodium hydrogen sulfide (NaHS), and the commercially available products, TMT15<sup>®</sup> and Nalco-8034. Na<sub>2</sub>S was obtained from Sigma Aldrich, Inc. (Product No. 243973), NaHS was obtained from Fisher Scientific (Product No. S426-212). Samples of TMT15<sup>®</sup> and Nalco-8034 were provided by Evonik Industries and the Nalco Company, respectively.

### 3. Results and discussion

Elemental Hg emission data from the simulated WFGD reactor were obtained for a range of HgCl<sub>2</sub> concentrations in the slurry, as well as for a range of reactor pH and temperature conditions. Fig. 2 shows Hg<sup>0</sup> emission curves plotted as Hg<sup>0</sup> concentrations measured at the outlet of the reactor as a function of time for different concentrations of Hg<sup>2+</sup> in solution. HgCl<sub>2</sub> was injected at the minute 20 into the experiments. The exhaust Hg<sup>0</sup> concentration increased initially as each experiment proceeded, and the



**Fig. 2.** Effect of Hg<sup>2+</sup> concentration in the slurry on Hg<sup>0</sup> re-emission.



**Fig. 3.** Separation measurement of re-emitted Hg species.

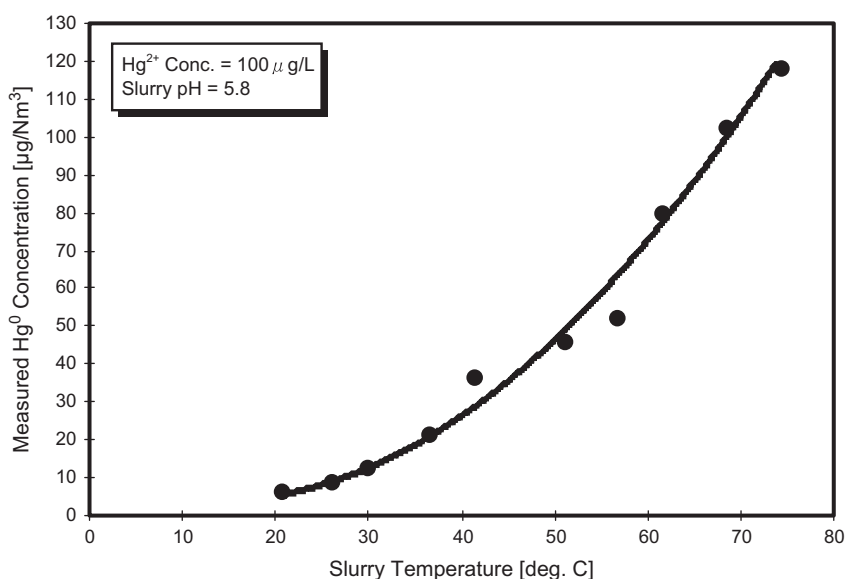


Fig. 4. Effect of slurry temperature on  $\text{Hg}^0$  re-emission.

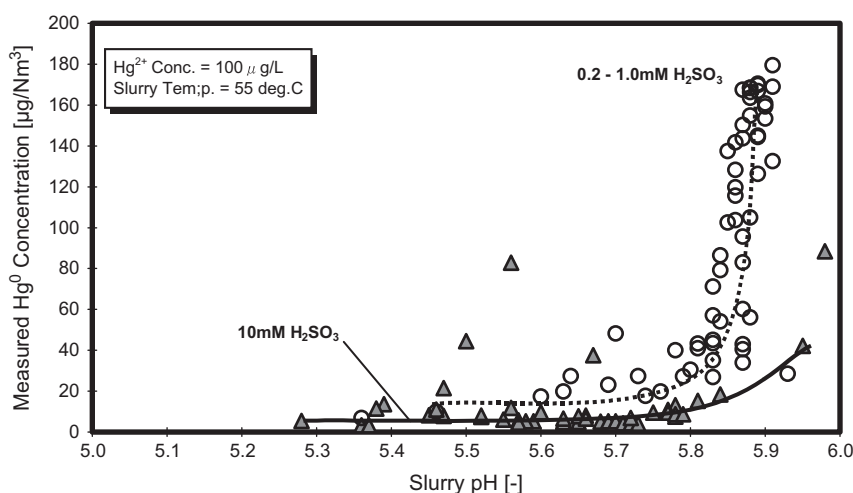


Fig. 5. Increase in  $\text{Hg}^0$  as a function of slurry pH value and sulfite concentration.

$\text{Hg}^0$  concentration approached a plateau after approximately 90 min. Reported  $\text{Hg}^0$  re-emission levels correspond to these steady-state values. No carry-over of  $\text{Hg}^{2+}$  was observed in the reactor effluent stream during this experiment performed in this study (see Fig. 3). Tests reported in Fig. 2 were performed at a pH level, slurry temperature and ORP value of approximately 5.8, 55 °C and 47 mV, respectively. The simulated flue gas consisted of 5%  $\text{O}_2$ , 15%  $\text{CO}_2$  and 80%  $\text{N}_2$ . The impact of the  $\text{Hg}^{2+}$  concentration in the slurry reported in Fig. 2 is consistent with ICR data reported by Ref. [4], which show a direct relationship between the amount of Hg removed across wet lime or limestone scrubbers and the concentration of oxidized Hg that enters the WFGD. The maximum  $\text{HgCl}_2$  value of 100  $\mu\text{g/L}$  used in these tests is typical of  $\text{Hg}^{2+}$  concentration in scrubber liquor corresponding to a Hg concentration in the coal of 100  $\mu\text{g/kg}$ , 95/5% breakdown between  $\text{Hg}^{2+}/\text{Hg}^0$  entering the scrubber, and a  $\text{HgCl}_2$  removal across the WFGD of 95%. It was found that the impact of mercuric ion concentration on Hg reduction to  $\text{Hg}^0$  is of first order.

The impact of slurry temperature on  $\text{Hg}^0$  re-emission from the simulated WFGD is shown in Fig. 4. The experiments reported in

Fig. 4 were performed at a pH of 5.8 and with a gas composition of 5%  $\text{O}_2$ , 15%  $\text{CO}_2$  and 80%  $\text{N}_2$ . The experimental range of temperature used in these experiments was from 20 to 75 °C. While the temperature of the scrubbing liquor in WFGD scrubbers is usually between 50 and 60 °C, under air combustion condition, it is about 70 °C under oxy-fuel combustion conditions. The results reported in Fig. 4 are in line with results reported in Ref. [9]. As the temperature in the slurry is raised, the  $\text{Hg}^{2+}$  reduction to  $\text{Hg}^0$  increases. Additionally, these results indicate that at higher WFGD slurry temperatures, typical of oxy-fuel combustion systems, the potential for re-emission of  $\text{Hg}^0$  is increased. For these experiments, the  $\text{HgCl}_2$  concentration in the reactor was approximately constant. Figs. 5 and 6 show results of variations in solution pH and sulfite concentration in the slurry. The reactor temperature for these experiments was set at 55 °C. Re-emission of  $\text{Hg}^0$  increases at higher pH values and with decreased S(IV) concentration (see Fig. 5). Limestone scrubbers in power plant applications work in the 5–6 pH range. Fig. 6 shows the behavior of  $\text{Hg}^0$  and sulfite during sulfite oxidation. The re-emission of  $\text{Hg}^0$  starts to increase significantly when the sulfite concentration approaches the

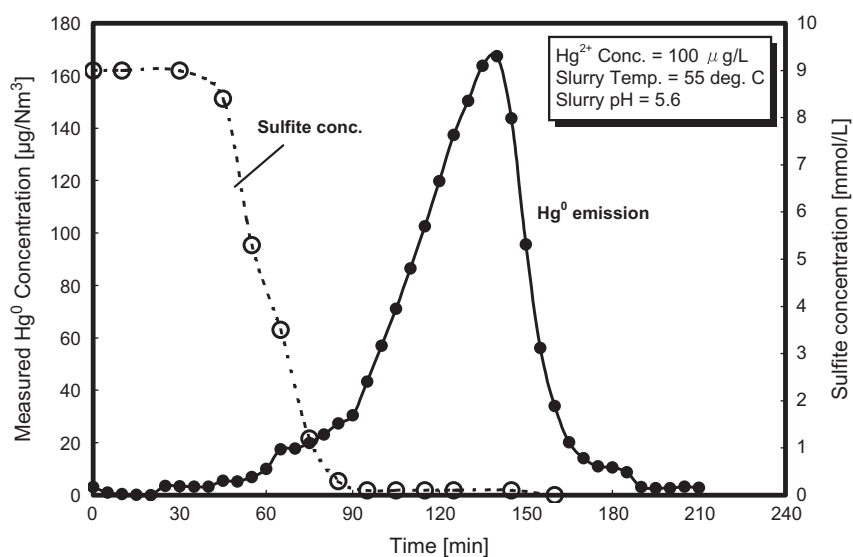


Fig. 6. Hg<sup>0</sup> re-emission and sulfite concentration in the process of sulfite oxidation.

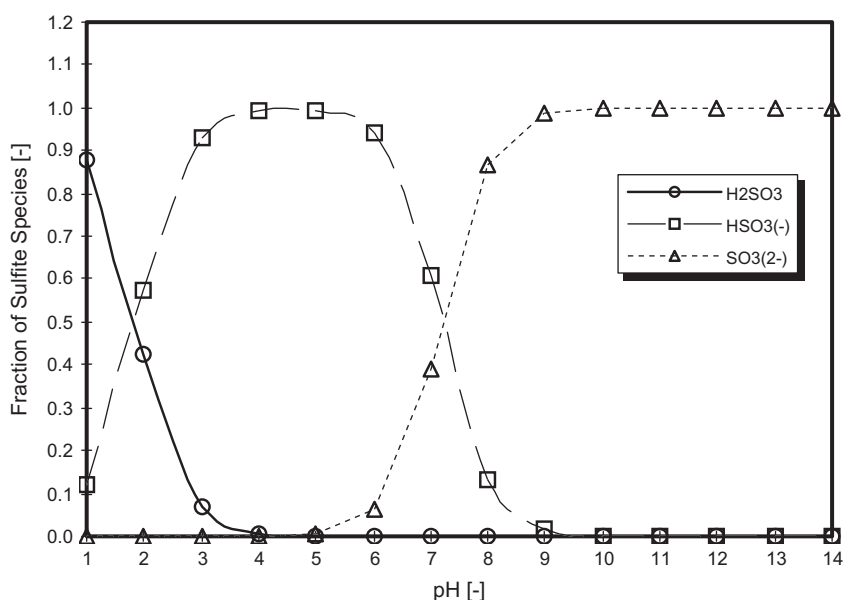
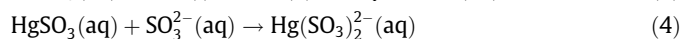
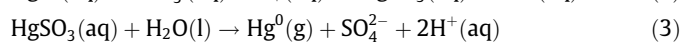
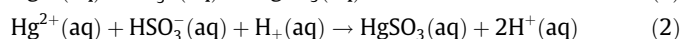
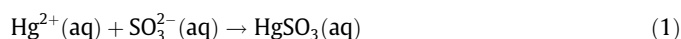


Fig. 7. Equilibrium results for sulfite species in the liquid.

0 mmol/L level. These results are consistent with observations made in other studies that noted that the sulfite-Hg<sup>2+</sup> reduction mechanism in WFGD scrubbers begins to act at pH values greater than 5 [12,13]. The current understanding of Hg ionic chemistry in WFGD scrubber solutions can be summarized by the following reaction set [9,4,14]:



The overall path for this reaction mechanism indicates that Hg<sup>2+</sup> dissolved in the solution is reduced by sulfite ions (SO<sub>3</sub><sup>2-</sup> and HSO<sub>3</sub><sup>-</sup>) to form Hg<sup>0</sup> (Reactions (1)–(3)). However, excess concentrations of SO<sub>3</sub><sup>2-</sup> would promote formation of mercuric-sulfite complex that would prevent re-emission of Hg<sup>0</sup> (Reaction (4)). This was

observed in this study and reported in Fig. 6. The trend of the Hg<sup>0</sup> emission curve vs. sulfite concentration in the slurry in Fig. 6 exhibits the behavior outlined by Reactions (1)–(4). This curve was obtained at a pH value of 5.6. The rate of dissociation of HgSO<sub>3</sub> appears to limit the re-emission of Hg<sup>0</sup>, with high concentrations of sulfite inhibiting the Hg reduction. Fig. 7 shows calculated equilibrium fractions of sulfite species in the liquid as a function of the slurry pH. Although, the majority of the sulfite species is HSO<sub>3</sub><sup>-</sup> in the actual WFGD system, operating in the 5–6 pH range, the concentration of SO<sub>3</sub><sup>2-</sup> is of the order of five times larger than that of Hg (for the case of 100 µg/L Hg concentration and 0.1 mM sulfite concentration). This results in ionic Hg concentrations as indicated in Fig. 8 (at a pH of 5.0). Furthermore, the equilibrium calculation results of Fig. 8 confirm that sulfite influences the reduction Hg<sup>2+</sup> to Hg<sup>0</sup> [15]. In Fig. 8, Hg(SO<sub>3</sub>)<sub>2</sub><sup>2-</sup> increases, as the sulfite concentration in the slurry is raised. The proceeding discussion validates the results of Fig. 5 in that high concentrations of sulfite inhibit Hg reduction in WFGD's.

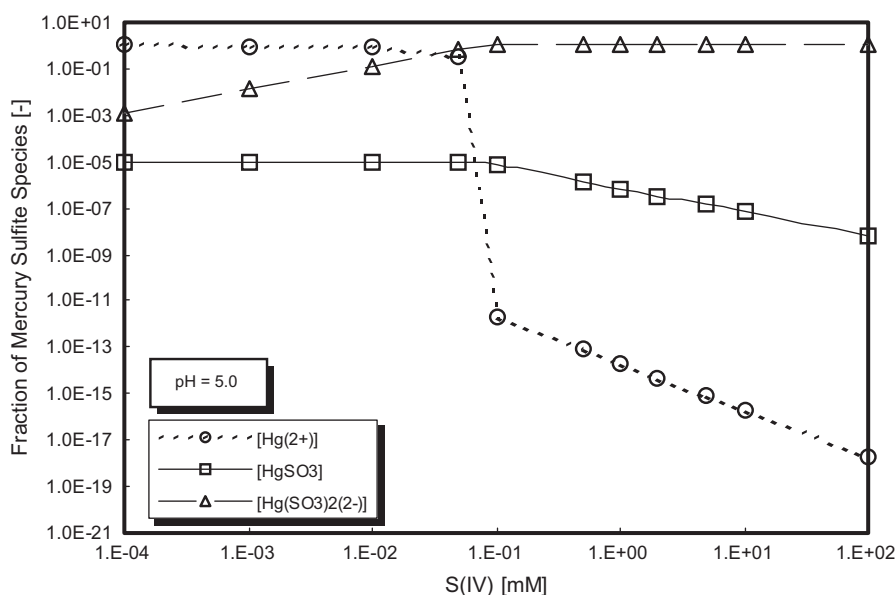


Fig. 8. Equilibrium results for mercury sulfite species in the liquid.

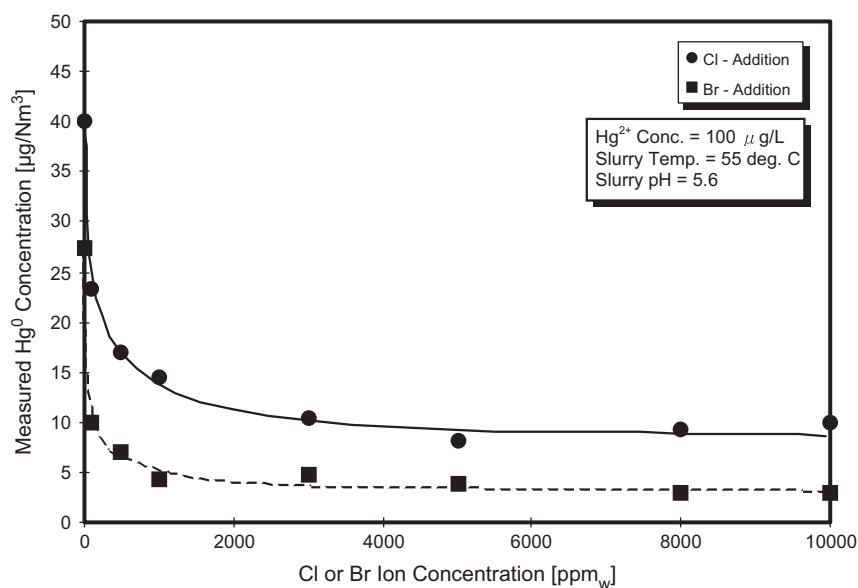
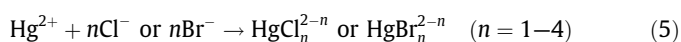


Fig. 9. Effect of halogen ion concentration in the slurry on Hg<sup>0</sup> re-emission.

The impact of halogen concentration in solution on Hg<sup>0</sup> re-emissions was also investigated in the WFGD batch reactor. Refs. [13,14] have indicated the sensitivity of the reduction of Hg<sup>2+</sup> by sulfite ions to the concentration of chloride ion in WFGD solutions. It has been established that if Cl<sup>-</sup> is present, Hg<sup>2+</sup> will form mercury chloride complexes, inhibiting the reduction of Hg by sulfite. This effect is illustrated in Fig. 9. Experiments were performed with the same gas concentration used for the experiments reported in Fig. 4. Similar conditions of pH and slurry temperature as reported for Figs. 5 and 6 were used for experiments with added concentrations of Cl and Br ions. The results in Fig. 9 confirm the reaction of Hg<sup>2+</sup> with halogen ions to form more stable mixed Hg-halogenated complexes, due to the excessive chloride and bromide ion concentration in suspension, for example [16]:



Testing was additionally performed to investigate the sensitivity of Hg<sup>0</sup> re-emission from a simulated WFGD reactor to the O<sub>2</sub> and CO<sub>2</sub> concentration in the flue gas. The interest was to investigate the impact future oxy-fuel conditions would have on Hg transformations in WFGD's. Figs. 10 and 11 show Hg<sup>0</sup> outlet concentration results obtained using O<sub>2</sub> concentrations of 5%, 10% and 20%, and CO<sub>2</sub> concentrations of 15%, 65% and 90%, respectively, with N<sub>2</sub> balancing the mixture. For both sets of experiments the Hg<sup>2+</sup> concentration in the slurry was 100 µg/L and the reactor temperature was 55 °C. The slurry pH values are indicated in Figs. 10 and 11. Fig. 10 shows that as the O<sub>2</sub> availability is increased in the range from 2% to 20%, Hg<sup>0</sup> re-emission is reduced by approximately 20% for the entire O<sub>2</sub> range from the Hg<sup>0</sup> concentration obtained at 2% O<sub>2</sub>. The redox potential measurements ranged from 46 to 56 mV, not a significant change. Given that the experiments with different concentrations of O<sub>2</sub> in the gas were performed in

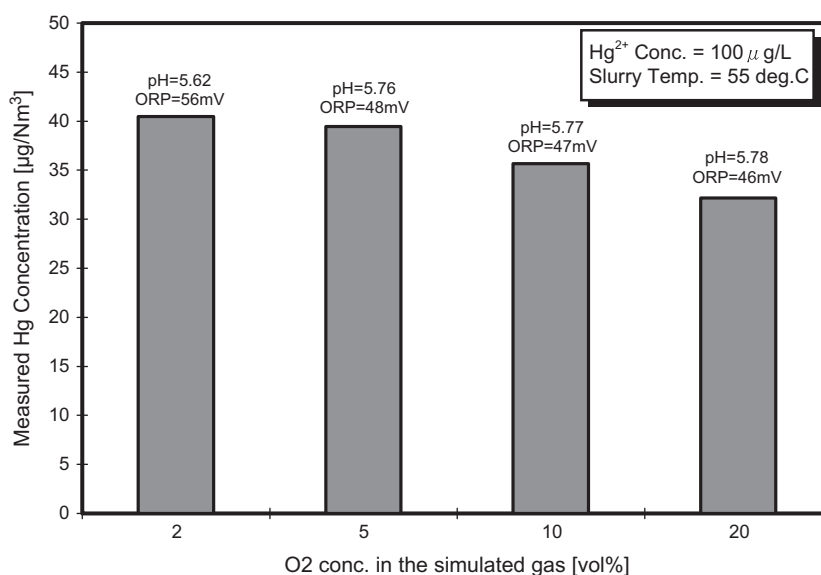


Fig. 10. Influence of oxygen availability on Hg<sup>0</sup> re-emission.

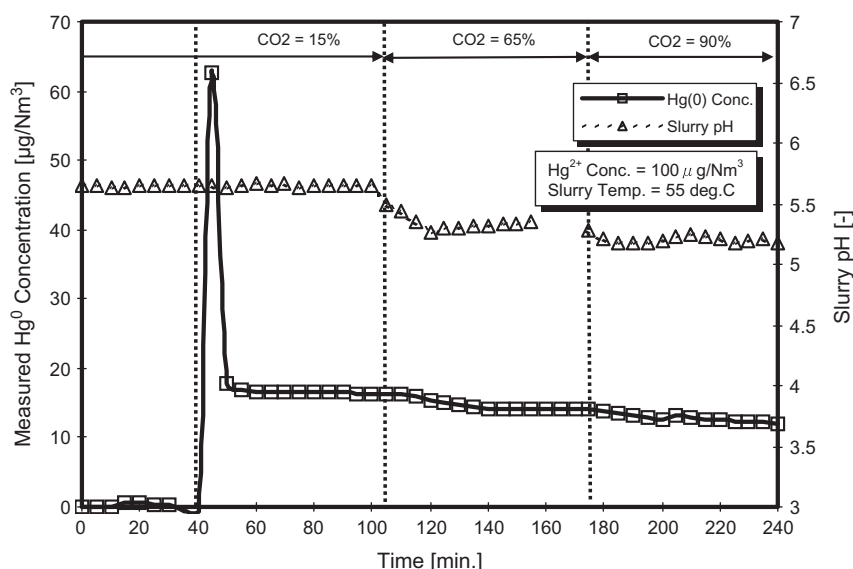
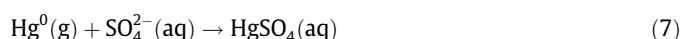
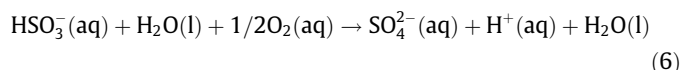


Fig. 11. Influence of carbon dioxide availability on Hg<sup>0</sup> re-emission.

the absence of chlorides, precluding oxidation of Hg<sup>0</sup> back to HgCl<sub>2</sub><sup>2+</sup> and HgCl<sub>3</sub><sup>-</sup>, it would be expected that the excess O<sub>2</sub> would have reacted with sulfite ions to form sulfates (and bisulfates). These sulfur ions will react with any reduced Hg<sup>0</sup> to form mercuric sulfate (HgSO<sub>4</sub>). The proposed reaction mechanism is:



HgSO<sub>4</sub> in water would be hydrolyzed, precipitating to the basic sulfate, Hg<sub>3</sub>O<sub>2</sub>(SO<sub>4</sub>) [11]. Another contributing aspect of the Hg<sup>0</sup> re-emission inhibition by excess O<sub>2</sub> is discussed in Ref. [17]. This reference notes the increase in Hg<sup>0</sup> solubility at higher temperatures and under addition of air to aqueous solutions by about 700 times.

Fig. 11 shows the effect of increased CO<sub>2</sub> concentration in the simulated flue gas on Hg<sup>0</sup> emissions at the outlet of the batch

WFGD reactor. It was expected that the excess CO<sub>2</sub> gas concentration would have increased concentration of HCO<sub>3</sub><sup>-</sup> or CO<sub>3</sub><sup>2-</sup> in solution, which would reduce Hg<sup>2+</sup> to Hg<sup>0</sup> through formation of the Hg(HCO<sub>3</sub>)<sub>2</sub> or HgCO<sub>3</sub> complex. However, it was found that the elevated CO<sub>2</sub> volume content in the gas from 15% to 90% had a negligible effect on Hg<sup>0</sup> re-emission. There is a slight decreasing trend in the Hg<sup>0</sup> concentration in Fig. 11; however, this could be explained by the decrease in the pH level of the slurry, which helps to mitigate Hg<sup>0</sup> re-emission, as confirmed in this study.

To complement this study on Hg<sup>0</sup> re-entrainment in WFGD's, abatement of Hg<sup>0</sup> re-emission was investigated in this study using additives that would counter the Hg<sup>2+</sup> to Hg<sup>0</sup> reduction reactions by formation of solid compounds that would precipitate in the WFGD scrubber by-product. It has been reported that addition of sulfide compounds to the scrubbing solution in WFGDs is effective in suppressing re-emission of Hg<sup>0</sup> (see Refs. [18–20]). The potential chemistry will involve redox reactions of sulfide ions in solution with Hg<sup>2+</sup> to form HgS precipitate. Four reagents were tested,



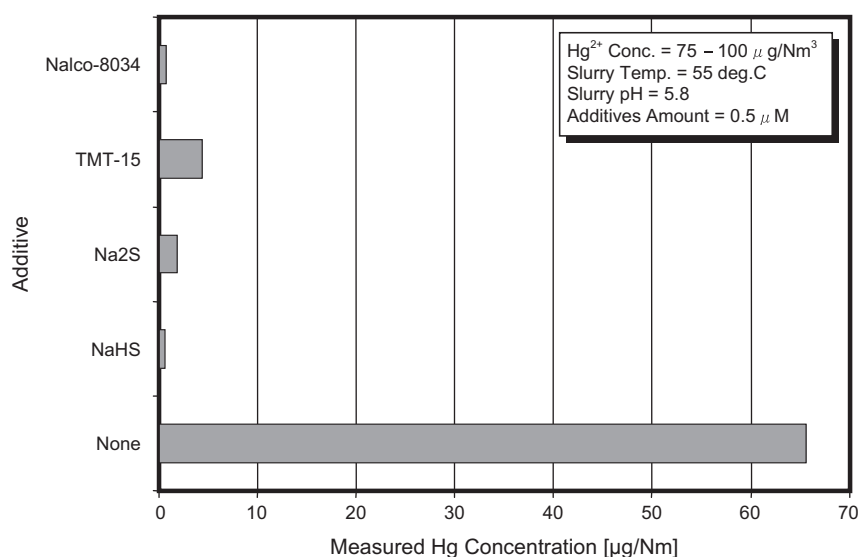


Fig. 12. Performance of sulfide-based additives on Hg<sup>0</sup> re-emission.

which included two commercially available products, and two sodium/sulfur-based additives. The commercial products were Nalco-8034 from the Nalco Company and TMT15<sup>®</sup> from Evonik Industries. The sodium/sulfur additives were Na<sub>2</sub>S and NaHS. Fig. 12 shows the results obtained with addition of 0.5 µM concentration of each additive. The slurry was maintained at 55 °C, with a pH value of 5.8. The gas composition used in these experiments was 5% O<sub>2</sub>, 15% CO<sub>2</sub> and 80% N<sub>2</sub>. The removal efficiency of Hg<sup>0</sup> re-emission from the simulated scrubber gaseous effluent was 98.9%, 93.2%, 97.1% and 99.0% for the Nalco-8042, TMT15<sup>®</sup>, Na<sub>2</sub>S and NaHS, respectively. The resulting slurry was filtered by a 0.45 µm pore size membrane filter. The Hg concentration that resulted in the filtrate of the slurry was 74.3, 0.8, 4.4, 1.9, and 0.6 µg/L for the condition of no additive, and for the Nalco-8042, TMT15<sup>®</sup>, Na<sub>2</sub>S and NaHS, respectively; indicating that the Hg-bound precipitate would be separated with the fine portion of the WFGD system by-product. It was demonstrated that Hg<sup>0</sup> concentrations below 10 µg/Nm<sup>3</sup> can be achieved by injection of less than 0.01 ppm<sub>w</sub> of additive in the scrubber liquor. Results available in literature of studies conducted with injection of the commercial products and sodium/sulfur-based compounds have been inconsistent due to dissimilar test conditions of bench-scale and full-scale applications. The results presented in this paper provide comparative results of different additives under similar simulated WFGD conditions.

#### 4. Conclusions

It is accepted that WFGD systems can efficiently remove oxidized Hg from the flue gas of coal-fired power plants. However, the aqueous ionic chemistry that occurs in calcium-based scrubbers can reduce the absorbed ionic Hg to insoluble elemental Hg, reducing the overall WFGD Hg capture efficiency. Results from a simulated batch forced oxidation limestone reactor confirmed that sulfite ions participate in the reduction of Hg<sup>2+</sup> to Hg<sup>0</sup>, which is re-emitted from the scrubber into the exhaust gas. Higher concentrations of S(IV) ions in the liquor inhibit oxidized Hg transformation to Hg<sup>0</sup>. The results of this study agree with other research results that a strategy that consists of operational and chemistry changes to mitigate re-emission of Hg<sup>0</sup> would include reduction in the ionic Hg concentration in the liquor, decrease in solution pH value and temperature, and increase in chloride ionic strength in the

solution. It was also found that high availability of excess O<sub>2</sub> in the flue gas in contact with the scrubbing solution results in lower conversion of oxidized to elemental Hg. Under potential oxy-fuel combustion conditions expected from future CO<sub>2</sub>-constrained scenarios, the impact of higher concentrations of CO<sub>2</sub> in the flue gas, on Hg<sup>0</sup> re-emission is negligible, with higher slurry temperatures potentially leading to an increase in Hg<sup>0</sup> re-emission. The effectiveness of sulfide-based additives for abatement of Hg<sup>0</sup> re-emission was also confirmed in this study. The suppression effectiveness of sodium hydrogen sulfide, sodium sulfide, TMT15<sup>®</sup> and the Nalco-8034 reagent was found at 99%, 97%, 93% and 99%, respectively. These additives promote precipitation of mercury in WFGD scrubbers, preventing the Hg<sup>2+</sup> to Hg<sup>0</sup> reduction. The Hg-bound precipitate would be separated with the fine portion of the WFGD system by-product.

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