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INTERPRETING THE RE-EMISSION OF ELEMENTAL MERCURY DURING WET FGD SCRUBBING

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ABSTRACT

Whereas the conventional FGD analysis works well in relating gross FGD operating conditions to SO_2 absorption efficiencies, it is unsuitable for trace metal transformations, especially for Hg re-emission. The reason is that conventional formulations implicitly assume that all oxygen is consumed in sulfite oxidation at the liquid interface on a slurry droplet, and evaluate the rate of sulfite oxidation as an average based on bulk liquid concentrations. The requisite analysis for Hg^{2+} chemistry must automatically shift the redox potential of bulk liquid in the spray from oxidizing to reducing through a balance among the finite-rate reagent fluxes that participate in sulfite oxidation. Our SO_2 capture analysis allows oxygen to penetrate through the liquid film and accumulate in the bulk liquid if its concentration exceeds the stoichiometric requirement for bisulfate oxidation. We also propose a finite-rate reaction for Hg(II) reduction that depends on temperature, pH, and S(IV) species which, in the absence of sufficient oxygen, promote Hg(II) reduction to Hg^0 vapor. This approach predicts reasonable extents of Hg removals and Hg re-emission under realistic FGD operating conditions, without any parameter adjustments. Hg re-emission can occur along the entire absorber at a rate that accelerates slightly along the upper elevations. Smaller slurry droplets re-emit more Hg because they sustain faster absorption of all the reagent gases involved in Hg(II) reduction. The total S(IV) species concentration in the slurry solution promotes re-emission; conversely, the analysis correctly predicts less re-emission for greater Cl ion concentrations in the slurry, in accord with a well-established tendency. Simulations with added S(II) species, as released from commercial additives to suppress Hg re-emission, correctly gave complete precipitation of Hg(II) as HgS(s). These predictions are consistent with full-scale field tests where the addition of NaHS almost completely suppressed Hg re-emission at even the lowest additive levels.

INTRODUCTION

The Hg field-testing literature shows that wet FGDs typically capture at least 90 % of the oxidized Hg (Hg^{2+}) in flue gas, but virtually none of the elemental Hg vapor (Hg^0), because Hg^0 is insoluble in aqueous solutions. However, several full- and bench-scale tests have documented Hg re-emission whereby the Hg^0 concentration at the FGD exit is greater than that at the inlet, suggesting that some of the absorbed Hg^{2+} must be reduced in the solution and re-emitted as Hg^0 vapor. Hg re-emissions have also been observed in natural waters and atmospheric cloud and rain-water cycles1-3, where S(IV) species promote the reduction of Hg^{2+}. Bench-scale studies under well controlled scrubbing conditions showed that Cl^- and O_2 suppress re-emission, whereas Ca^{2+} and Mg^{2+} species promote it.

Our goal is to develop a quantitative analysis that identifies and rank-orders the factors involved in Hg re-emission during wet FGD scrubbing, and can support efforts to mitigate Hg re-emission from full-scale, commercial wet FGDs.

FGD ANALYSIS

To simulate Hg transformations in wet FGD scrubbers, one must first model SO_2 absorption to describe the major solution species (S, Ca, Cl) and their variations with FGD operating conditions (L/G, droplet diameter, T). Given the absorber temperature and the inlet compositions of flue gas and slurry, a conventional FGD analysis predicts the correct pH and reasonable SO_2 absorption rates along the absorber.

It also depicts realistic tendencies for variations in the inlet SO_2 level, and identifies distinctive conditions where elevated HCl levels will reduce SO_2 removal efficiencies by 5 to 10 %, and greater SO_2 removal for smaller slurry droplets, all else the same.

Whereas the conventional FGD analysis relates gross FGD operating conditions to SO_2 absorption efficiencies, it is unsuitable for trace metal transformations, especially for Hg re-emission. The reason is that conventional formulations implicitly assume that all oxygen is consumed in sulfite oxidation at the liquid interface on a slurry droplet, and evaluate the rate of sulfite oxidation as an average based on bulk liquid concentrations. The requisite analysis for Hg^{2+} chemistry and, presumably, other trace metal transformations must automatically shift the redox potential of bulk liquid in the spray from oxidizing to reducing through a balance among the finite-rate reagent fluxes that participate in sulfite oxidation. Our SO_2 capture analysis allows oxygen to penetrate through the liquid film and accumulate in the bulk liquid if its concentration exceeds the stoichiometric requirement for bisulfate oxidation. We also propose a finite-rate reaction for Hg(II) reduction that depends on temperature, pH, and S(IV) species which, in the absence of sufficient oxygen, promote Hg(II) reduction to Hg^0 vapor.

The computerized implementation covers the process chemistry occurring in both a counterflow absorber and slurry holding tank. The tank analysis determines the required limestone feedrate for a given tank RTD and the solids PSD into the spray nozzles within the absorber. It also determines how much liquid must be extracted to maintain a target Cl concentration in the tank. Among these results, only the limestone PSD affects the behavior in the absorber. The absorber analysis determines the SO_2 capture and the compositions of liquid and solids that return into the holding tank. Given the absorber temperature and the inlet compositions of flue gas and slurry, the analysis predicts the SO_2 capture efficiency; complete slurry composition and flue gas composition; slurry pH; the quantitative enhancement of mass transfer by acid dissociations in the slurry; and the relative contributions of liquid and gas resistances to the overall mass transfer rate. All quantities are resolved as functions of distance along the absorber axis.

RESULTS AND DISCUSSION

The base test case process parameters in the simulations correspond to NYSEG's Kintigh station, which was tested under a U.S DoE program to evaluate additives for high SO_2 removal[4]. In the simulations we assume that a single spray header delivered the entire liquid flow into an absorber section of 10 m height with a diameter of approximately 12 m. The calculated value of the liquid pH is 5.65, in good agreement with the measured value of 5.67.

All rate constants in the analysis were assigned values from the characterization literature and were not adjusted further in the course of this work. The rate constant for Hg^{2+} reduction was based on a reported value for conditions that mimicked Hg transformations in cloud water[3], in spite of the fact that $HgSO_3$ is unstable under FGD operating conditions.

The % Hg re-emission (based on Hg^{2+} at the FGD inlet) and total Hg removal (% Hg-T) for the base case are presented in Fig. 1 along with the SO_2 removal. In this and all succeeding figures, the absorber inlet is on the right and the slurry spray manifold at the absorber exit is on the left. The Hg^{2+} absorption approached 99 % at the exit of the absorber and is not shown. Whereas SO_2 was continuously removed along the length of the absorber, most of the Hg was removed in the lower section of the countercurrent FGD at a much greater efficiency than SO_2 removal. We attribute this high level of Hg capture near the entrance to the high aqueous solubility of $HgCl_2$. As the flue gas moves towards the top of the absorber, there is a slight decrease in the Hg-T removal. This is because at the higher Hg^{2+} concentrations in solution, the rate of reduction and re-emission increase, as seen in Fig. 1. For the baseline case with 20% Hg^0, the re-emission gradually increases to approximately 20 % and the Hg-T removal reaches 65 %.

The effect of variations in inlet SO_2 partial pressures was examined by altering the bulk liquid S(IV) concentrations. Since the baseline case S(IV) concentration corresponds to an SO_2 partial pressure of 3275 ppm, a lower partial pressure must result in a lower S(IV) concentration in a closed loop absorber. A change in inlet SO_2 partial pressure alone is not sufficient to alter the liquid phase chemistry because the aqueous S(IV) concentrations are high relative to SO_2 absorption in a single absorber flow cycle. To examine the model response to variations in the inlet SO_2 partial pressures, four bulk liquid S(IV) concentrations between 3.5 and 6.5 mM were examined. All other simulation conditions were kept the same as the base case and only the alkalinity was adjusted for each S(IV) concentration to maintain the solution pH. The Hg-T removal and Hg re-emission for the different S(IV) concentrations are shown in Fig. 2. As expected, the SO_2 removal was unaffected by the change in liquid S(IV) concentration. In all

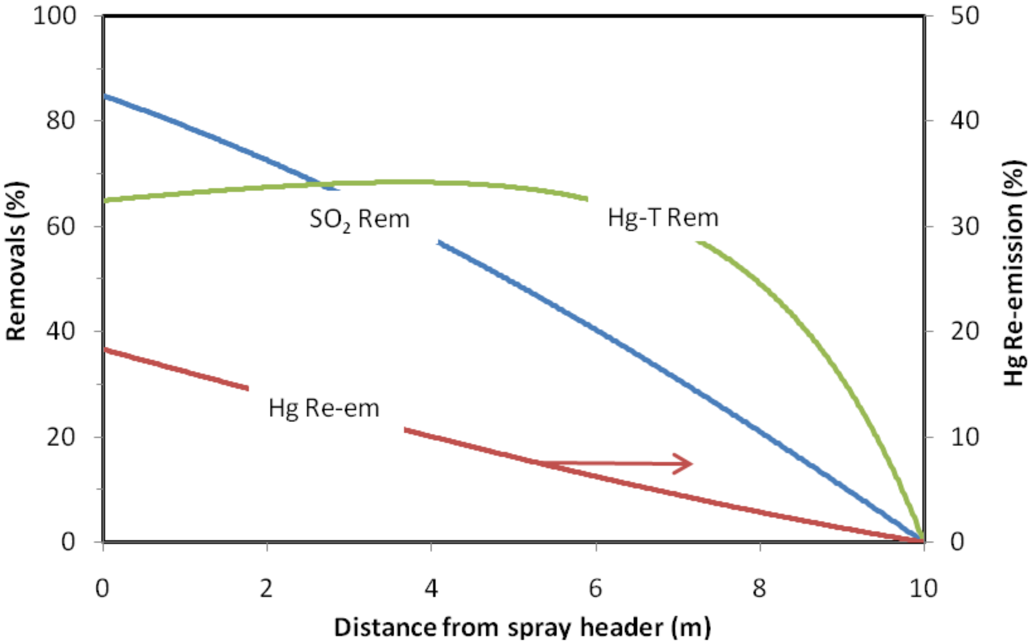

Figure 1. SO_2 and total Hg removals (left y-axis) and percentage Hg re-emission (right y-axis) along the length of the absorber.

cases, the absorption of Hg^{2+} exceeded 99 % and is not shown in the figure. As the S(IV) concentration was increased from approximately 3.5 to 6.5 mM, the Hg-T capture efficiency decreased from 72 to 62 % with an increase in Hg re-emission by a similar percentage. The increase in re-emission is directly related to an increase in S(IV) concentration and the consequent increase in Hg-S(IV) species levels in the bulk liquid. For a two-fold increase in S(IV) concentrations, the Hg-S(IV) fraction in the solution at the absorber exit increased from 14 to 36 % with an associated decrease in Hg-Cl levels. The Hg re-emission therefore appears to linearly track the Hg-S(IV) levels in the solution.

The Cl^- ion plays a crucial role in the capture of Hg in scrubber solutions. In closed loop FGDs, the recirculating slurry quickly becomes concentrated in species like HCl that are absorbed from the flue gas and are not removed by precipitation reactions such as those of calcium sulfite and sulfate. The Cl^- ion concentration is regulated to control corrosion problems by continuously purging a portion of the liquid stream from the reaction tank. The concentrations of Cl-species are therefore much greater than they would be in open-loop systems, as seen in the present case. Similar to examination with varying S(IV) concentration, we varied the slurry Cl^- ion concentration between 0.55 and 0.68 kmol/m^3 and adjusted the alkalinity to maintain the slurry pH. The Hg-T removal and Hg re-emission for the different Cl^- ion concentrations appears in Fig. 2, which clearly shows that for progressively greater Cl^- ion in the solution, the Hg(II) species preferentially partition into Hg-Cl complexes that reduce re-emission, which is consistent with the observations in bench- and pilot-scale experiments reported in the literature. In the present simulations, as the Cl^- ion concentration in the liquid was increased from 0.5 to 0.68 kmol/m^3, the aqueous Hg(II) ions associated with Cl increased from 66 to 84 % with an associated decrease in Hg-S(IV) complexes. The change in Cl^- did not have an effect on Hg^{2+} absorption since it was in excess of 99 % in all cases. The increased partitioning of Hg(II) into Hg-Cl complexes decreased re-emission by 11 %. For the case under simulation with an inlet flue gas Hg^{2+} of 80 %, the Hg-T removal increased from 62 to 72 % as the Cl^- ion concentration in the liquid was increased from 0.50 to 0.68 kmol/m^3.

Most additives to control Hg re-emission from scrubbers, such as Na_2S_4, TMT-15™ and NaHS, release S(II) ions in the slurry and precipitate Hg as HgS (s). We examined the addition of small amounts of S(II) into the base case scrubber solution and simulated Hg capture. Even at 1 μM concentrations of the additive, all the Hg(II) precipitated as HgS(s), which establishes the maximum Hg^{2+} concentration in the solution. For 1 μM of S(II) added to the solution, the maximum total dissolved Hg(II) was only 10^{-33}. The Hg-T removal with and without S(II) addition is shown in Fig. 3. With 80 % $HgCl_2$ in the flue gas, essentially all Hg^{2+} was retained in the solid phase. These predictions are consistent with the B&W tests at Endicott

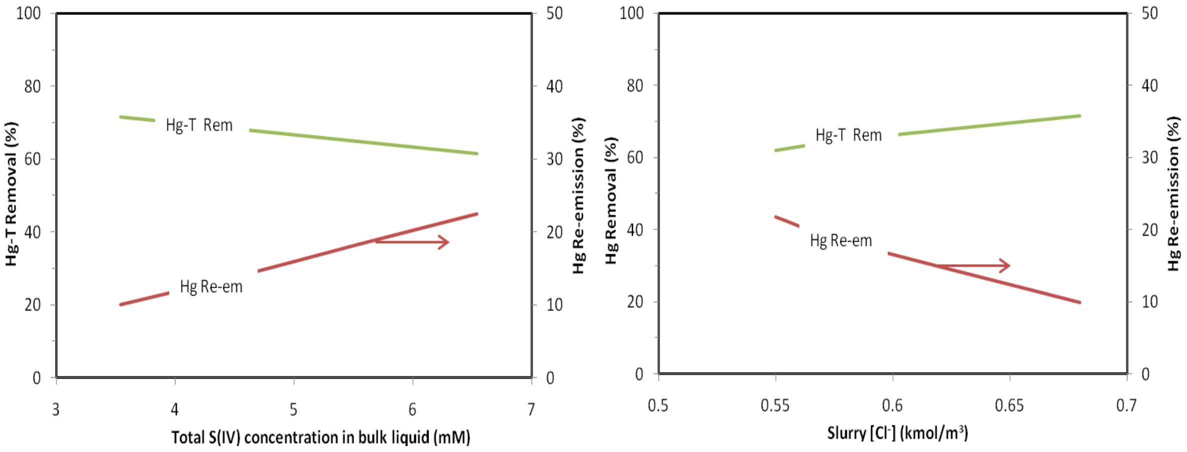

Figure 2. (Left Panel) Effect of bulk liquid S(IV) concentration on total Hg removal (left y-axis) and percentage Hg re-emission (right y-axis); (Right Panel) Effect of slurry Cl^- concentration on total Hg removal (left y-axis) and Hg re-emission (right y-axis).

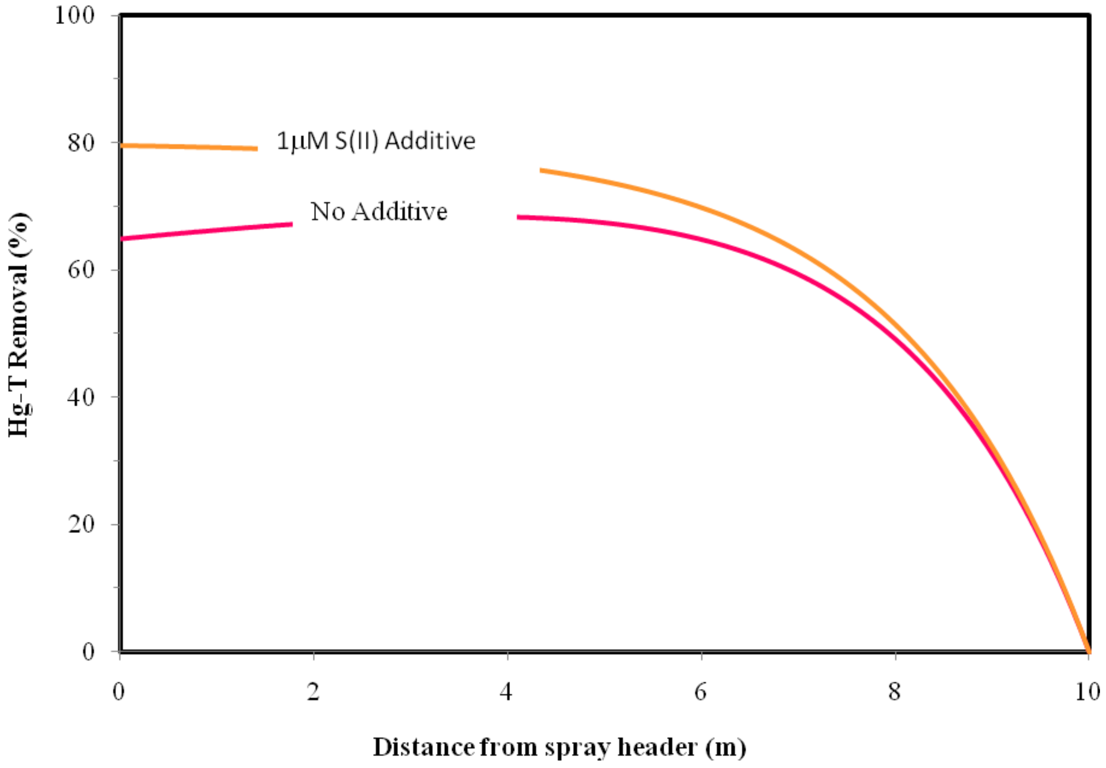

Figure 3. Hg-T removal along the length of the absorber with and without an S(II) concentration of 1 µM.

station[5] where the addition of NaHS almost completely suppressed Hg re-emission and the extent of re-emission did not bear any relation to the additive feed rate.

We also simulated the addition of S(II) under oxidizing conditions where we increased the pH to 6.5 and reduced the S(IV) species concentration such that oxygen was in excess. Such conditions arise in lime-based FGDs that operate at a higher pH and partition most of the S(IV) species into SO_3^{2-} and other forms instead of HSO_3^-, under a positive redox potential due to excess O_2. Under such conditions, equilibrium shifts the added S(II) species to their oxidized forms which prevents any precipitation of HgS solids. This is consistent with B&W tests at the Mg/lime FGD at Zimmer station[5] where an NaHS additive did not improve the baseline Hg-T capture efficiency even at high additive feed rates. Our model does not predict any re-emission under excess O_2 conditions, so the Hg capture profile is similar to the one shown in Fig. 3 depicting almost complete capture of Hg^{2+}. For lower S(IV) concentrations and excess O_2, our analysis explains the ineffectiveness of S(II)-based additives, although it also gives no re-emission for such conditions. It is conceivable that both the oxidation of S(II) and the precipitation of HgS(s) may be kinetically limited, in which case the relative rates will determine whether any HgS solids would be precipitated before the oxidation of S(II) is complete.

CONCLUSIONS

Our FGD scrubbing analysis predicts reasonable extents of Hg removals and Hg re-emission under realistic FGD operating conditions, without any parameter adjustments. Whereas most Hg^{2+} in flue gas is captured near the flue gas inlet, at the bottom of the absorber, Hg re-emission can occur along the entire absorber at a rate that accelerates slightly along the upper elevations. Whereas predicted Hg removals are insensitive to droplet diameter, smaller slurry droplets re-emit more Hg because they sustain faster absorption of all the reagent gases involved in Hg(II) reduction. The total S(IV) species concentration in the slurry solution promotes re-emission; conversely, the analysis correctly predicts less re-emission for greater Cl ion concentrations in the slurry, in accord with a well-established tendency. Simulations with added S(II) species, as released from commercial additives to suppress Hg re-emission, correctly gave complete precipitation of Hg(II) as HgS(s). These predictions are consistent with full-scale field tests where the addition of NaHS almost completely suppressed Hg re-emission and the extent of re-emission did not bear any relation to the additive feed rate.

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