

Pilot Plant Testing of Elemental Mercury Re-emission from Wet Scrubbers

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ABSTRACT

A pilot-scale wet lime/limestone flue gas desulfurization (FGD) scrubber system (0.01 MW) was designed, constructed, and debugged to conduct mercury emission control research. The first series of pilot plant tests focused on investigating the phenomenon of Hg^0 re-emission from wet scrubbers with a specific objective of developing a Hg^0 re-emission model that can be used to predict the transient and steady-state Hg^0 concentration increases across a scrubber.

Pilot plant tests were conducted with flue gas generated from a natural gas furnace doped with 2,000 ppm sulfur dioxide (SO_2). Mercuric chloride (HgCl_2) solution was pumped to the scrubber at a controlled rate to simulate the absorption of Hg^{2+} . It was found that the pilot-scale scrubber system can be used to simulate Hg^0 re-emissions. Elevated Hg^0 concentrations were detected both in the scrubber effluent flue gas and the hold tank air reflecting Hg^0 re-emissions in both places. The Hg^0 re-emission rate and pattern can be simulated by a first-order reaction model. When the HgCl_2 feed was terminated, Hg^0 release in the scrubber continued for more than 2 h as the model predicted. In addition, significant Hg^0 re-emission outside of the scrubber was detected.

INTRODUCTION

Wet flue gas desulfurization (FGD) scrubbers can provide the co-benefit of mercury removal by absorbing ionized mercury (Hg^{2+}) in the flue gas generated from coal-fired power plants¹. This co-benefit was included in the newly promulgated Clean Air Mercury Rule (CAMR) by U.S. Environmental Protection Agency (EPA) to reduce mercury emissions from new and existing coal-fired electric utility steam generating units². CAMR will be implemented in two phases with a cap-and-trade program. Initially, a national annual cap of 38 tons (t) is to be reached by 2010, with emission reductions coming primarily as a co-benefit of technologies (e.g., wet-FGD scrubbers) that control other air pollutants. The second-phase sets a national annual cap of 15 t by 2018. The co-benefit will also play an important role in achieving the second-phase mercury reduction goal.

However, it is known that a portion of the Hg^{2+} absorbed in the wet scrubbers can be converted back to elemental mercury (Hg^0) and re-emitted^{1,3}. The Hg^0 re-emission results in an increase of flue gas Hg^0 concentration across the scrubber by as much as 40% and significantly reduces the co-benefit of wet scrubber mercury removal⁴. The Hg^0 re-emission can also have adverse financial impact on power plant operation under the CAMR cap-and-trade program.

Chang and Ghorishi⁵ investigated the Hg^0 re-emission using a laboratory-scale wet scrubber simulator and sodium sulfite and bisulfite solutions under worst case conditions (no oxygen in gas and no precipitation in solution). The experimental results indicated that the absorbed Hg^{2+} can be reduced by aqueous S(IV) (sulfite and/or bisulfite) species and results in Hg^0 re-emission under simulated wet scrubber conditions. The S(IV) induced Hg^{2+} reduction and Hg^0 re-emission mechanism was described by a model which assumes that only a fraction of the Hg^{2+} can be reduced, and the rate controlling step of the overall process is a first-order reaction involving $\text{Hg}\bullet\text{S(IV)}$ complexes formed by the absorbed Hg^{2+} and the S(IV) species. The model predicted that as much as 58% of the Hg^{2+} absorbed can be re-emitted as Hg^0 in a wet scrubber system. In addition, the model predicted that the slurry in a wet scrubber may contain significant amount of $\text{Hg}\bullet\text{S(IV)}$ complexes which can function as a precursor to Hg^0 re-emission outside of the scrubber (e.g., in hold tank, clarifier, and vacuum filter). Hg^0 re-emission outside of the scrubber further reduces the co-benefit of wet scrubber mercury removal and may cause an occupational health hazard in coal-fired power plants.

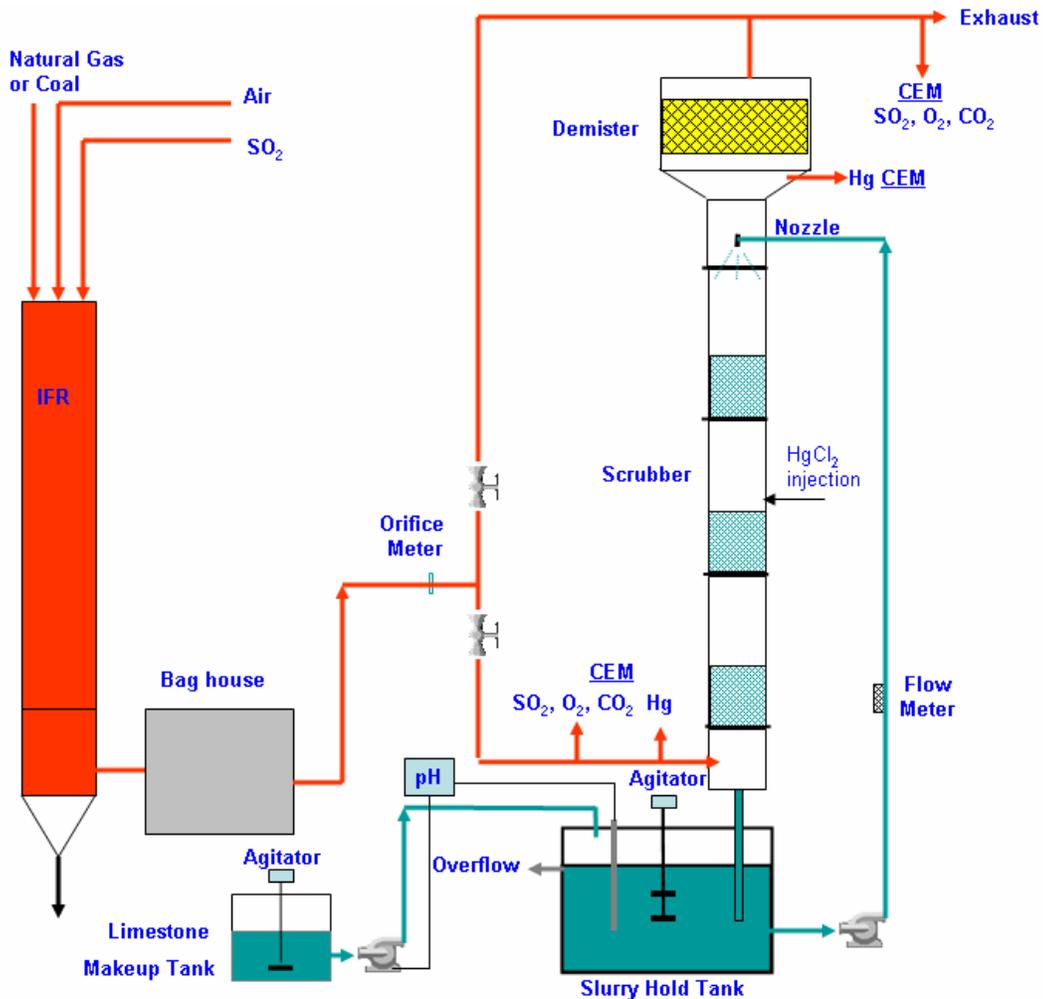
The objective of this research was to conduct pilot plant tests to investigate wet scrubber Hg^0 re-emission under realistic conditions to validate the laboratory test results and to evaluate the potential Hg^0 re-emission outside a wet scrubber.

EXPERIMENTAL PROCEDURE

A wet scrubber pilot plant was used to simulate the operating conditions of FGD systems in coal-fired power plants. Figure 1 shows the schematic of this pilot scrubber system which mainly consists of a wet scrubber, a slurry hold tank, a slurry makeup tank and a

slurry pump. The flue gas is generated from a down-fired cylindrical furnace also known as the innovative furnace reactor (IFR). The IFR is usually fired with natural gas and has a combustion capacity of 150,000 Btu/hr. The fuel is introduced to the top of furnace and combusted with air from axial and tangential directions. The IFR is equipped with a complete continuous emission monitoring (CEM) system for O₂, SO₂, and CO₂ measurements. The IFR is also equipped with a bag house to remove particulate matter from the flue gas. After particulate matter is removed, the flue gas passes through an orifice flow meter before entering the bottom of the scrubber.

Figure 1. The schematic of the pilot-scale wet scrubber system



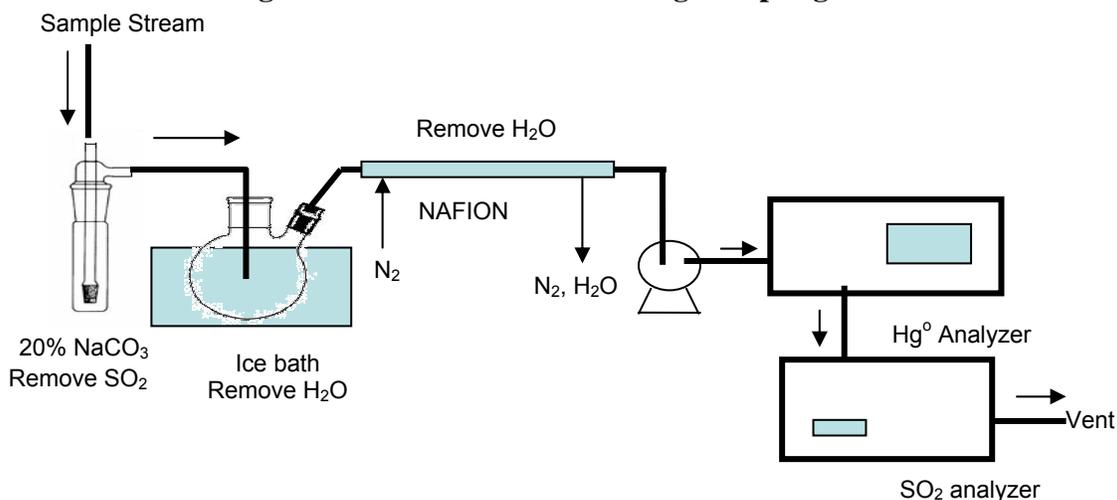
The scrubber is in fact a 3-stage turbulent contact absorber (TCA). The stainless steel TCA is 10 cm in diameter and consists of three 92-cm long sections. Each section contains 20-cm deep hollow plastic balls (2 cm in diameter) supported by a grid at the bottom of the section. The hollow balls, fluidized by the up-flowing flue gas, provide turbulence and promote intimate contact between flue gas and scrubbing slurry so as to improve the SO₂ and Hg²⁺ removal efficiencies. The scrubbing slurry is delivered by a

recirculation pump from the slurry hold tank to the spray nozzle located at the top of the TCA and travels downward through the TCA back to the slurry hold tank. Prior to discharging into the exhaust duct, the flue gas passes through a chevron-type demister at the top of scrubber to remove the carryover of mist.

The slurry hold tank, located below the TCA, is about 200 liters in volume. A heating pad, wrapped around the outside wall of the slurry hold tank, is used to bring the slurry into desired temperature before each test. The slurry in the hold tank is agitated by a motor to keep the solids uniformly suspended. The pH of the slurry in the hold tank is controlled by the addition of calcium carbonate slurry from the limestone makeup tank. A feedback control loop is used to regulate the calcium carbonate feed rate to maintain pH in the hold tank at a desired level.

For each test, a 140-liter batch of slurry with approximately 5% solids (calcium sulfite hemi-hydrate crystals) was used. Since the flue gas generated from natural gas contains no SO₂ and mercury, pure SO₂ from a gas cylinder was injected into the duct to achieve the desired flue gas SO₂ concentration. HgCl₂ solution (i.e., a dilute aqueous solution of HgCl₂) was used as the source of Hg²⁺. A peristaltic pump was used to deliver the HgCl₂ solution to the middle stage of TCA at a constant rate (e.g, 5 cc/min) through each test.

Figure 2. The schematic of the Hg⁰ sampling train



The concentrations of SO₂, O₂, and CO₂ etc. were continuously monitored by a CEM system. Continuous online measurement of elemental mercury was performed with a UV spectrometer. Since the analyzer responds to Hg⁰ as well as SO₂, 20% NaCO₃ solution was used to remove SO₂ from the sampling stream as shown in Figure 2. After the SO₂ is removed, the gas flowed through an ice bath to knock out the majority of the moisture. Prior to entering the mercury analyzer, a NAFION gas dryer (Perma Pure Inc.) that can selectively remove water vapor from the sampling stream was used to ensure the gas stream was ready and dry for the mercury analyzer. A SO₂ analyzer was used to monitor the SO₂ concentration in the gas stream after the mercury analyzer to confirm that adequate removal of SO₂ by the 20% Na₂CO₃ solution is achieved. Repeated quality

checks have shown that this dryer system has no affinity toward adsorption of elemental mercury present in the gas stream.

RESULTS AND DISCUSSIONS

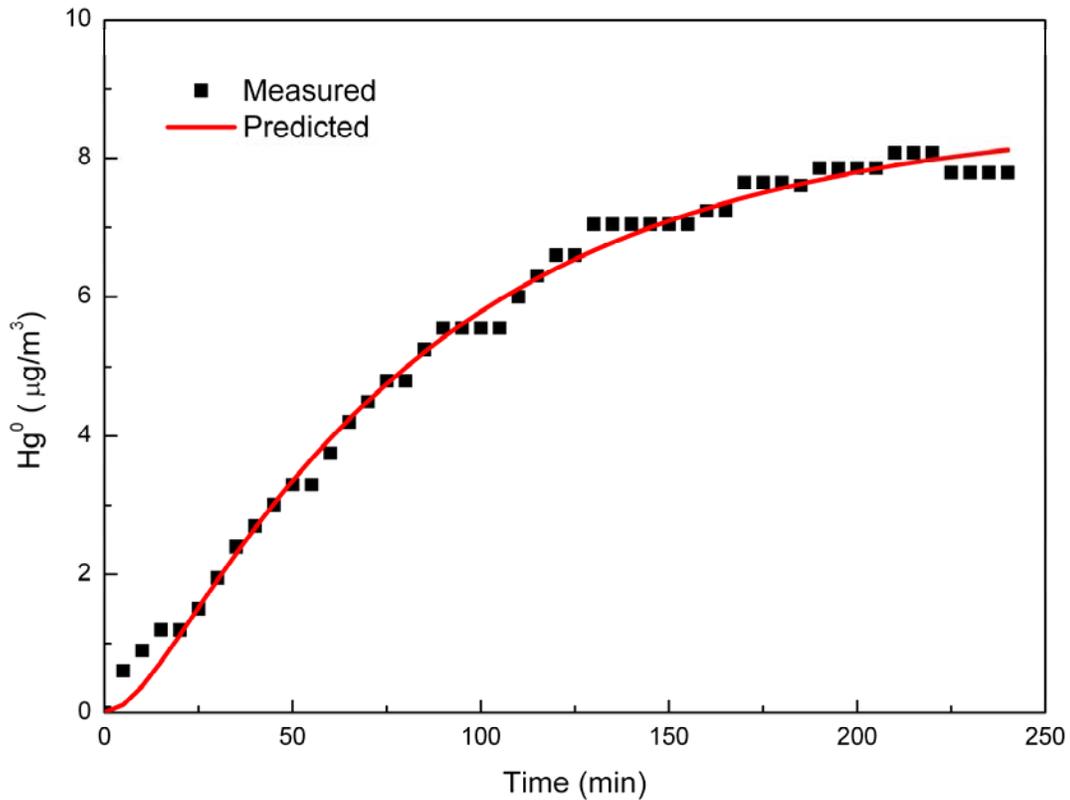
Wet Scrubber Hg⁰ Re-emission

The typical pilot plant operating conditions are listed in Table 1. Initially, no HgCl₂ was injected into the scrubber. Flue gas Hg⁰ concentration at the scrubber inlet was usually less than 0.5 μg/m³ as natural gas was burned in the furnace and no Hg⁰ concentration change across the scrubber was measured. The HgCl₂ feed to the middle stage of the scrubber was initiated (time 0) after the major operating conditions were stabilized. Within a few minutes after time 0, flue gas Hg⁰ concentration across the scrubber began to increase. The increase reflected the reduction of Hg²⁺ added to the slurry and the re-emission of the product as Hg⁰. Figure 3 shows the Hg⁰ emission curve plotted as measured flue gas Hg⁰ concentrations at the scrubber exit vs. time for a typical test. As shown in Figure 3, the scrubber exit Hg⁰ concentration continued to increase as the experiment proceeded, but the rate of increase gradually slowed, and the flue gas Hg⁰ concentration seemed to approach a plateau after approximately 3 h.

Table 1. Typical test conditions

Flue gas flow rate (<i>G</i>), l/min	850
Inlet flue gas SO ₂ concentration, ppm	2000
Flue gas O ₂ concentration, %	7-8
Flue gas CO ₂ concentration, %	7-8
Hold tank slurry volume (<i>V</i>), l	140
Hold tank pH	6.0
Slurry recirculation rate (<i>L</i>), l/min	11.4
Hold tank slurry temperature, °C	55
Hg ²⁺ feed rate (<i>F</i>), μg/min	25

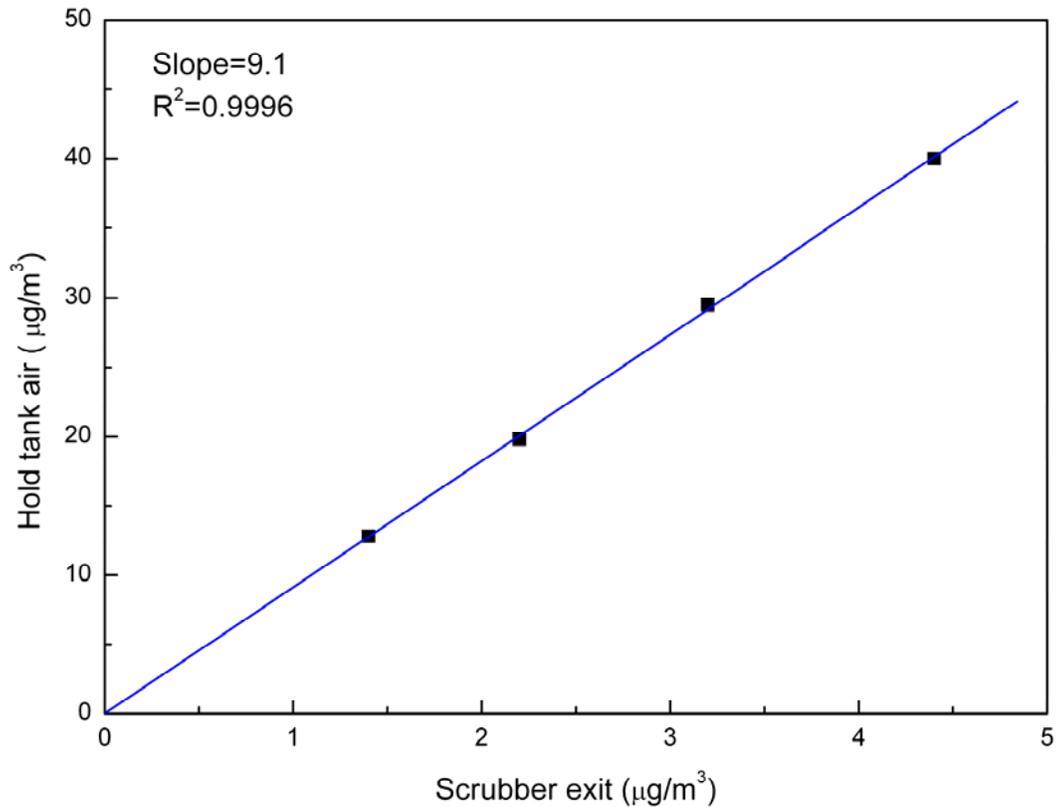
Figure 3. Comparison of measured scrubber exit flue gas Hg^0 concentrations with model predictions



Hold Tank Hg^0 Re-emission

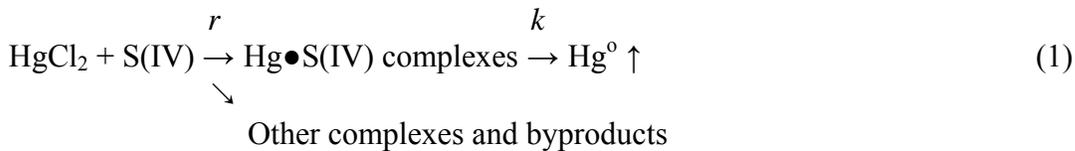
In addition to scrubber exit, the air space Hg^0 concentration in the slurry hold tank was also measured. Figure 4 shows the measured Hg^0 concentration in the hold tank top air space above the slurry and the corresponding Hg^0 concentration in the scrubber exit flue gas. Figure 4 indicates that there is a linear relationship between the hold tank air and the scrubber exit flue gas Hg^0 concentrations. In other words, the hold tank Hg^0 emission rate was proportional to that in the scrubber. Figure 4 shows that the average ratio between hold tank air and scrubber exit flue gas Hg^0 concentration was about 9.1. The hold tank was covered but not sealed and ambient air can leak in and out of it through various openings. Using a tracer gas technique, the hold tank air exchange rate was estimated to be 24 l/min. Compared with the 850 l/min flue gas flow rate, the Hg^0 re-emission in the hold tank should be approximately 25.7% of that in the wet scrubber. Therefore, significant amount of Hg^0 re-emission occurred in the hold tank.

Figure 4. The linear relationship of Hg⁰ concentrations between scrubber exit flue gas and hold tank air



Hg⁰ Re-emission Model

The pilot plant Hg²⁺ reduction and Hg⁰ re-emission pattern is very similar to that reported by Chang and Ghorishi⁵. It was also found that the model suggested by Chang and Ghorishi⁵, as shown by equation (1), can be used to simulate the pilot plant data with minor modifications.



The modified model was established on the basis of the following assumptions: (1) due to its high solubility, all the HgCl₂ fed to the scrubber was absorbed by the scrubbing slurry; (2) in the presence of S(IV) species, the absorbed HgCl₂ reacted with S(IV) to instantly form a number of complexes and byproducts; (3) only a fraction, *r*, of the HgCl₂ fed in to the scrubber formed Hg•S(IV) complexes, which underwent a series of chain reactions to generate Hg⁰; (4) the rate controlling step of the chain reactions can be represented by a first-order reaction with respect to Hg•S(IV) complexes and a global

rate constant , k ; (5) because of the insoluble nature, all the Hg^0 in the recirculation slurry was either released in the hold tank or stripped off and exited the scrubber with the effluent gas; (6) the hold tank Hg^0 emission rate can be simulated by a mass transfer across a phase boundary model assuming the emission rate is proportional to the liquid phase Hg^0 concentration in the hold tank slurry.

When the hold tank slurry is well-mixed, the following material balance equation can be established to represent the mercury absorption and reduction in the pilot plant:

$$V \frac{d[Hg \bullet S(IV)]}{dt} = rF - kV[Hg \bullet S(IV)] \quad (2)$$

Where:

V = the volume of the slurry in the hold tank, l

$[Hg \bullet S(IV)]$ = the concentration of $Hg \bullet S(IV)$ complexes in the slurry, $\mu g/l$

r = the fraction of the Hg^{2+} that forms the $Hg \bullet S(IV)$ complexes

F = the Hg^{2+} feed rate to the scrubber, $\mu g/min$

k = the first-order reaction rate constant, min^{-1}

The solution of equation (2) with initial conditions of $[Hg \bullet S(IV)]=0$ at $t=0$ is:

$$[Hg \bullet S(IV)] = \frac{rF}{Vk} (1 - e^{-kt}) \quad (3)$$

On the basis of assumptions (5) and (6), the Hg^0 re-emission can be modeled as:

$$V \frac{d[Hg^0]}{dt} = kV[Hg \bullet S(IV)] - L[Hg^0] - k_H A_H [Hg^0] \quad (4)$$

Where:

$[Hg^0]$ = the Hg^0 concentration in the hold tank slurry, $\mu g/l$

L = the slurry recirculation rate through the scrubber, l/min

k_H = the inter-phase mass transfer coefficient in the hold tank, dm/min

A_H = the hold tank liquid-gas inter-phase surface area, dm^2

The solution of equation (4) with initial condition of $[Hg^0]=0$ at $t=0$ is:

$$[Hg^0] = \frac{rF}{L^*} \left[1 - \frac{L^*(e^{-kt}) - Vk(e^{-\frac{L^*}{V}t})}{(L^* - Vk)} \right] \quad (5)$$

Where:

L^* = the sum of L and $k_H A_H$

The flue gas Hg^0 concentration at the scrubber exit can be estimated by:

$$C_{Hg^0} = \frac{L}{G} [Hg^0] = \frac{LrF}{L^*G} \left[1 - \frac{L^*(e^{-kt}) - Vk(e^{-\frac{L^*}{V}t})}{(L^* - Vk)} \right] \quad (6)$$

Where:

C_{Hg^0} = the scrubber exit flue gas Hg^0 concentration, $\mu g/m^3$

G = the flue gas flow rate through the scrubber, m^3/min

As discussed in previous Section, the pilot plant hold tank Hg^0 emission rate was estimated to be 25.7% of that in the scrubber, thus; $L^* = 1.257L$. When the values of L , G , F , and V are known (see table 1), there are only two adjustable parameters, r and k , in equation (6). Using a nonlinear regression curve routine, implemented on a microcomputer, values of r and k can be obtained by fitting equation (6) to the pilot plant scrubber exit flue gas Hg^0 concentration data as shown in Figure 3. The estimated value of r and k are 0.368 and 0.0124 min^{-1} , respectively.

Residue Mercury Emissions

The $HgCl_2$ feed to the scrubber was terminated at the end of 240 min of the test. A residual mercury emission test was conducted by continuing SO_2 scrubbing operation at the same conditions without $HgCl_2$ feed for additional 160 min. The model predicts that, after initial 240 min operation, the slurry should contain $Hg \bullet S(IV)$ complexes equivalent to $5.0 \mu g/l$ of Hg . In addition, there should also be $0.60 \mu g/l$ of Hg^0 in the slurry. Based on the model assumptions, the residual mercury (i.e., $Hg \bullet S(IV)$ complexes) should continue to form Hg^0 and result in a long-lasting Hg^0 emission even without any Hg^{2+} supply. The Hg^0 emission without $HgCl_2$ feed can be simulated by equations (2) and (4) with F set at 0. According to the model, the residual mercury emission reflected as the measured flue gas Hg^0 concentration at the scrubber exit, C_d , can be represented by the following equation:

$$C_d = \frac{Lk[Hg \bullet S(IV)]_o (e^{-\frac{L^*}{V}t} - e^{-kt})}{G(k - \frac{L^*}{V})} + \frac{L[Hg^0]_o e^{-\frac{L^*}{V}t}}{G} \quad (7)$$

Where:

C_d = the scrubber exit flue gas Hg^0 concentration, $\mu g/m^3$

$[Hg \bullet S(IV)]_o$ = the slurry $Hg \bullet S(IV)$ complex concentration when the $HgCl_2$ feed was terminated, $\mu g/l$

$[Hg^0]_o$ = the slurry Hg^0 concentration when the $HgCl_2$ feed was terminated, $\mu g/l$

Figure 5. Comparison of measured and model predicted residue mercury reemissions

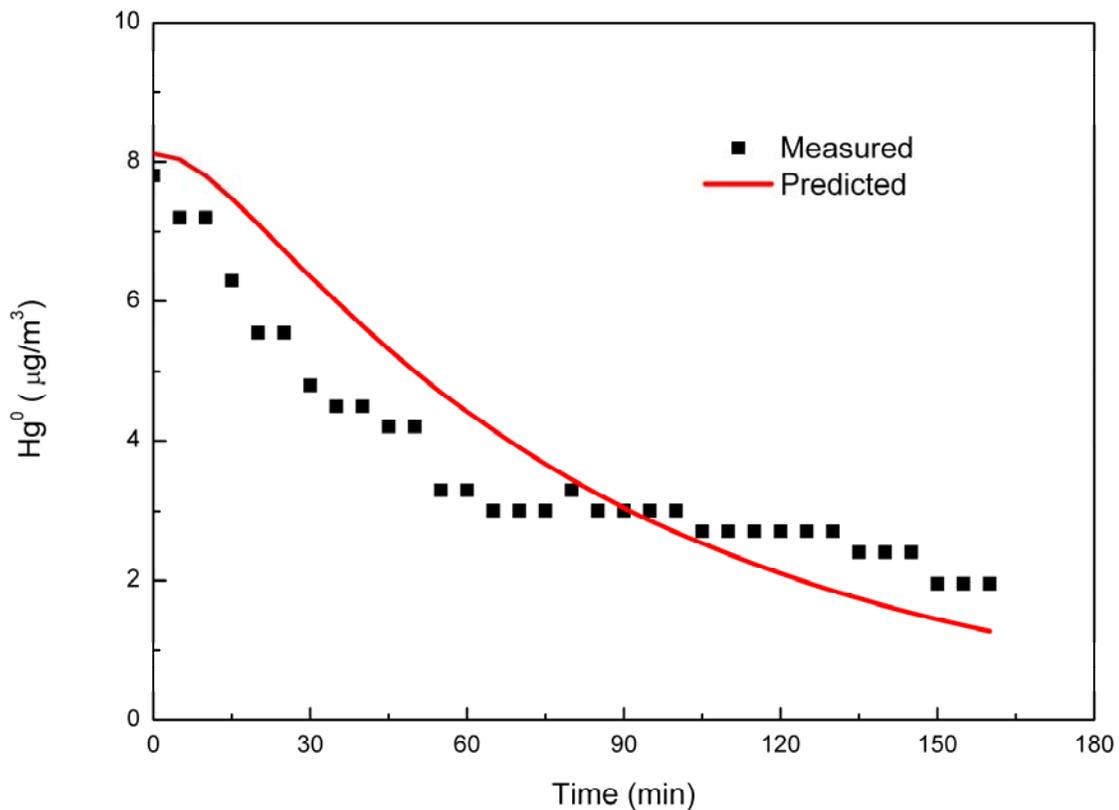


Figure 5 shows a comparison between the measured residual mercury emissions and the model predictions using the values of $k=0.0124 \text{ min}^{-1}$, $[Hg \bullet S(IV)]_o=5.0 \text{ } \mu g/l$, and $[Hg^0]_o=0.60 \text{ } \mu g/l$ as estimated by the first 240 min baseline data with $HgCl_2$ feed. Figure 5 shows that, as predicted by equation (7), the residual mercury emissions lasted for several h with a gradual decay. However, pilot plant data shows that the decay rate slowed down considerably after about 100 min and the residual mercury emissions may last longer than the model predicted.

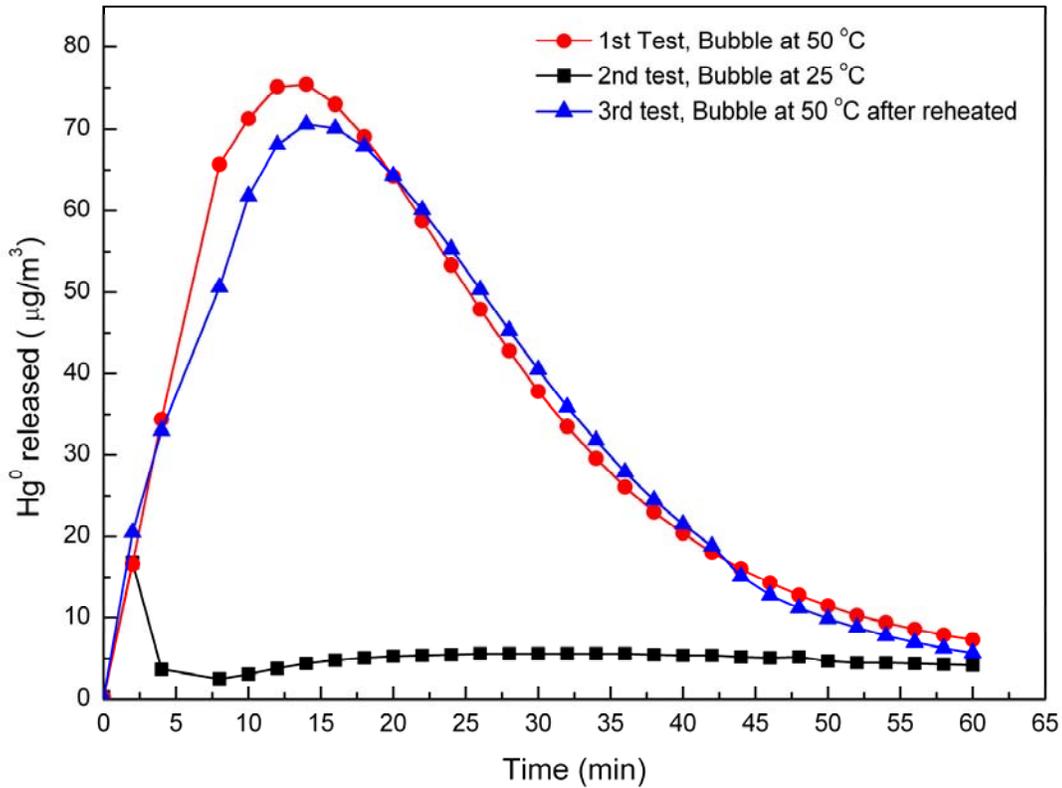
Hg⁰ Re-emission Outside Scrubber Loop

Slurry samples were taken from the hold tank to evaluate the possibility of Hg⁰ re-emission outside the scrubber recirculation loop. Preliminary tests were conducted with 1.1 l/min of air flowing over the surface of 150 g slurry in a glass impinger without any mixing or shaking. Less than 1.0 µg/m³ of Hg⁰ was detected in the the impinger effluent air reflecting an extremely low Hg⁰ re-emission. However, when the air was bubbled through the slurry with a fritted glass sparger as shown in Figure 2, the impinger exit air Hg⁰ concentration increased rapidly.

To further evaluate the Hg⁰ re-emission outside the scrubber loop, a group of three air stripping tests were performed. The first test was carried out by bubbling 1.1 ml/min of air through a glass impinger containing 150 ml slurry maintained at 50 °C. Figure 6 shows that the air Hg⁰ concentrations (represented by solid circles) at the impinger exit increased immediately after the air bubbling started. The Hg⁰ concentration increase continued for about 15 min and reached a peak as high as 75 µg/m³. After the peak, the exit air Hg⁰ concentration gradually decreased. The residue Hg⁰ emission lasted for more than 1 h with about 7.5 µg/m³ Hg⁰ concentration in the impinger effluent air at the end of the test. The total amount of Hg⁰ emitted from the impinger in the first 60 min was estimated to be 2.4 µg which is equivalent to a Hg⁰ re-emission capacity of 16 µg/l in the slurry. The second test was performed at room temperature with the same operating conditions as the first one. Residue Hg⁰ emissions, represented by solid squares in Figure 6, still occurred. However, the emission pattern is different from that of the first test at 50 °C. Instead of a peak, the impinger air effluent Hg⁰ concentration increased to a plateau within 25 min and decreased very slowly for the rest of the test. In addition, the emission rate was also considerably lower than that of the first test. The total amount of Hg⁰ emitted in 60 min was estimated to be only 0.36 µg, equivalent to a Hg⁰ re-emission capacity of 2.4 µg/l in the slurry. The third test was conducted with slurry reheated to 50 °C after cooling to room temperature by sitting quiescently for about 2h. Figure 6 shows that the residue Hg⁰ emission rate and pattern, represented by solid triangles, are very similar to that of the first test. The estimated total amount of 60-min Hg⁰ emission for the third test was 2.3 µg, equivalent to a Hg⁰ re-emission capacity of 15.3 µg/l in the slurry, which was also very close to that of the first test.

The results indicate that the hold tank slurry contained considerable amount of mercury species that can be converted to Hg⁰ and released. The estimated Hg⁰ emission capacity of the first and the third tests was both significantly higher than the model predictions, i.e., 5.0 µg/l of [Hg•S(IV)]_o plus 0.6 µg/l of [Hg⁰]_o. One possibility for this to happen is that some of the “other complexes and byproducts” originally accumulated (see equation 1) might have converted (e.g., via reversible or side reactions) to Hg⁰ when the slurry was bubbled with air at 50 °C. When the slurry was at room temperature and undisturbed, the conversion rate was considerably lower and much less Hg⁰ was released.

Figure 6. The mercury reemission out of the wet scrubber loop



CONCLUSIONS

Pilot plant tests confirmed the previous laboratory experimental results that considerable amount of absorbed Hg^{2+} can be reduced by S(IV) species and cause an increase of flue gas Hg^0 concentration across a wet-FGD scrubber. In addition, elevated Hg^0 concentrations were detected in the hold tank air. The estimated pilot plant hold tank Hg^0 emission rate was as high as 25.7% of that in the scrubber.

The wet scrubber Hg^0 re-emission rate can be simulated by a modified first-order reaction model. Pilot plant data also validated the model predictions of residual mercury emissions outside the scrubber loop. Temperature and disturbance (e.g., by mixing, pumping, bubbling, and vacuuming) can significantly affect the residual mercury emission rate.

The hold tank Hg^0 emission can significantly decrease the effective mercury removal efficiency in a wet-FGD scrubber system. In addition to the residual mercury emissions outside a scrubber loop in coal-fired power plants, Hg^0 emissions can also occur in the waste/byproduct treatment facilities. The hold tank and residual mercury emissions not only reduce the co-benefit mercury removal of a scrubber but also cause health hazard concerns of occupational mercury exposure.

ACKNOWLEDGEMENTS

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