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Study on Reduction Behaviour of Oxidized Mercury to Elemental Mercury through Lab-Scale Wet Simulator†

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The re-emission of elemental mercury was simulated in the lab-scale wet scrubber. Absorbing and dissolving of vapour Hg^{2+} were simulated in the slurry as $HgCl_2$ standard solution was continuously injected into the slurry. Some factors such as oxidation models of wet flue gas desulphurization system, ratio of oxygen to sulphur and a trimercapto-*s*-trazine trisodium salt additive on elemental mercury re-emissions were investigated. Trends of oxidation-reduction potential and pH values of testing slurries with different SO_2 concentrations and testing time were studied. Elemental mercury re-emissions occurred in reduction atmosphere when oxidation-reduction potential of the slurries were negative.

Keywords: Mercury re-emission, Wet simulator, Trimercapto-*s*-trazine trisodium salt additive, Oxidation-reduction potential.

INTRODUCTION

In the recent years, the emission of mercury from coal-fired power plant started to be controlled. The removal and speciation of mercury occurred through a serial of air pollutant control devices (APCDs) such as ESPs, fiber filters, baghouses and flue gas desulphurization (FGD) (dry FGD and wet FGD)[1]. During mercury analysis through air pollutant control devices at full-scale coal-fired power plants, mercury reemission across wet FGDs was tested. Wet FGD systems can provide a co-benefit and effective mercury removal technology and many field tests were performed and some enhanced control methods were employed at many power plants with wet FGD system[2]. Oxidized mercury (Hg^{2+}) is water-soluble and it can be absorbed through wet FGD. However, the field tests aimed at enhancing the mercury removal performance of wet FGD systems were performed and a portion of oxidized mercury initially absorbed in a wet FGD system was reduced to elemental mercury (Hg^0), then insoluble Hg^0 re-emitted into the environment[3]. Hg^0 re-emissions results in decreases of the overall mercury removal efficiencies and have adverse financial impacts on power plant operations. A lab-scale wet FGD simulator was set up to investigate mercury re-emission and suppress it.

EXPERIMENTAL

The re-emissions of elemental mercury were simulated in the lab-scale wet scrubber. Hg^{2+} was introduced into the slurry with injection of $HgCl_2$ standard solutions[4]. Fig. 1 shows a schematic diagram of the lab-scale simulated scrubber and the lime system includes natural oxidation and forced oxidation modes. Lime slurry can absorb sulphur dioxide in the flue gas in wet FGD and calcium sulphite was produced. The calcium sulphite product became calcium sulfate through forced oxidation in oxidation vessel. There was mainly calcium sulphite in the vessel through natural oxidation. Therefore, calcium oxide and calcium sulphite were chosen in the absorber through natural oxidation and forced oxidation, respectively.

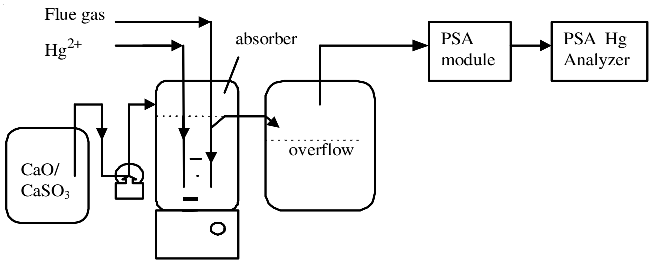

Fig. 1. Schematic diagram of the lab-scale simulated scrubber

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This system consisted in oxidized mercury injection system, carrier gas system, scrubbing system, gas conditioning system and mercury analyzer system. The oxidized mercury injection system included a syringe pump and a syringe. The syringe pump can control 2.04 mL/h injection rate of oxidized mercury solution and the syringe was connected into the bottom of the flask through a 1/16 Teflon tube. The simulated flue gas system included HCl, SO_2, O_2 and N_2 and their flow rates were controlled by calibrated flow meters, respectively. All the materials of tubes must be teflon and stainless steel. The scrubbing system was composed of a round bottom flask with four necks, water bath, magnetic stirring system and temperature controllers. The simulated scrubber was a bubbler type simulated scrubber, the flask had a capacity of 500 mL and four necks were used as inlet of injecting oxidized mercury solution, inlet of lime injection, inlet of simulated flue gas and outlet of overflow, respectively. A coarse frit was attached to the end of simulated flue gas inlet in the flask and fine bubbles were generated, then fine bubbles increased mixing of gas with slurry and residence time of simulated flue gas in the slurry. The water bath was used to keep the slurry at the range of operation temperature of slurry. A magnetic stirring machine and a magnetic bar were used to make the slurry mix well during the course of testing. Temperature control system included some heat tapes and three temperature controllers, which kept the carrier gas tubes heated at 160 ºC in case of transformation of mercury speciation in the tubes between outlet of scrubber and gas conditioning system and the tubes were connected directly with PSA module and analyzer. The wet simulator operation parameters and testing matrix are shown in Tables 1 and 2.

RESULTS AND DISCUSSION

According to TMT lab-scale matrix, 12 runs were performed in the lab-scale devices. During the testing, only the ratios of oxygen to sulphur and reagents of CaO and $CaSO_3$ in the absorber were changed. Elemental mercury concentrations were analyzed through the lab-scale wet FGD simulator with natural and forced oxidation, respectively with change of ratios of oxygen to sulphur.

Elemental mercury re-emission concentrations and their suppressions at wet simulator with natural oxidation system were plotted in Fig. 2. Oxidized mercury was reduced to elemental mercury and emitted form the slurries when SO_2 gas passed through the slurries. With decreasing of O/S, the elemental mercury concentrations were increasing because there were more strong reduction environment. When TMT additives were added to the slurries, TMT prevented oxidized mercury from reducing into elemental mercury because TMT produced a precipitate with Hg^{2+}. Elemental mercury re-emissions and control at wet simulator with forced oxidation system were plotted in Fig. 3. Elemental mercury emitted from the slurries with forced oxidation system, but Hg^0 concentrations insignificantly increased, which were the same as baseline mercury concentrations. When oxidized mercury was injected into the slurries, there was no SO_3^{2-} atmosphere because $CaSO_3$ were oxidized into $CaSO_4$ by oxygen gas in the slurries, therefore there were no elemental mercury re-emissions.

Average elemental mercury concentrations during the testing in the 12 runs were calculated and plotted in Fig. 4. During natural oxidation testing, elemental mercury re-emission without TMT injection is apparent, while it is no noticeable during forced oxidation test without TMT injection. During natural oxidation tests, elemental mercury re-emission rates increased with decreasing of ratios of oxygen to sulphur because oxidized mercury was reduced into elemental mercury in soluble SO_3^{2-} atmosphere in the slurry (eqn. 1). In oxygen existing condition, $CaSO_3$ was oxidized into $CaSO_4$. The higher the oxygen concentrations were, the lower $CaSO_3$ concentrations were in the slurry. Therefore elemental mercury re-emission

TABLE-1
OPERATION PARAMETERS AT LAB-SCALE WET SIMULATOR

Item	Contents	Gas mixture and slurry flow rate
Simulated flue gas (800 mL/min)	SO_2 1000 ppm HCl 200 ppm O/S 3, 6, 12/	(1) 96 mL/min (2900 ppm in N_2 cylinder gas), (2)160 mL/min (1000 ppm in N_2 cylinder gas), (3) 96 mL/min (5 % O_2 in N_2 cylinder gas), O/S = 12
Hg^{2+}	9 µg/m^3	0.034 mL/min (1.06×10^{-6} mol/L standard solution)
Lime slurry (TMT15)	Ca/S = 2 TMT15 1.5m L/m^3 gas	Rate of liquid pump 12mL/min; lime slurry density, 0.727 mg/mL, TMT 15, 1.2 µL/min
Absorber solution	400 mL	pH = 6.5, temperature = 55 ºC

Note: TMT 15 is 15 wt % aqueous solution of trimercapto-s-triazine, tri-sodium salt ($C_3N_3S_3Na_3$) from Degussa.

TABLE-2
LAB-SCALE MERCURY RE-EMISSION TESTING MATRIX

Test No.	FGD oxidation type	TMT	Flue gas flow rate (mL/min)	HCl (ppm)	SO_2 (ppm)	O/S	Testing time (min)
1	Natural	Without	800	200	1000	12	150
2	Natural	Without	800	200	1000	6	135
3	Natural	Without	800	200	1000	3	145
4	Natural	With	800	200	1000	12	125
5	Natural	With	800	200	1000	6	125
6	Natural	With	800	200	1000	3	125
7	Forced	Without	800	200	1000	12	130
8	Forced	Without	800	200	1000	6	130
9	Forced	Without	800	200	1000	3	130
10	Forced	With	800	200	1000	12	130
11	Forced	With	800	200	1000	6	130
12	Forced	With	800	200	1000	3	130

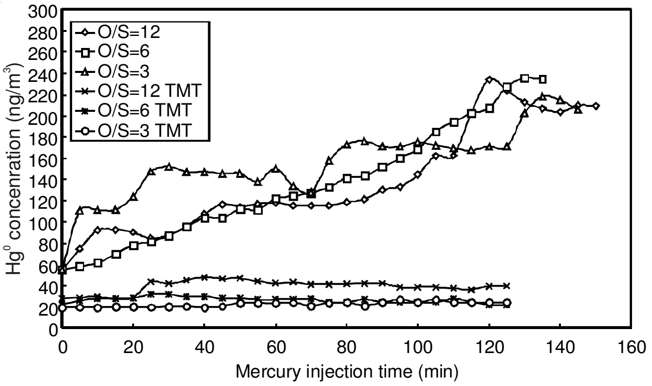

Fig. 2. Hg^0 concentrations with Hg^{2+} injection time at natural oxidation wet simulator

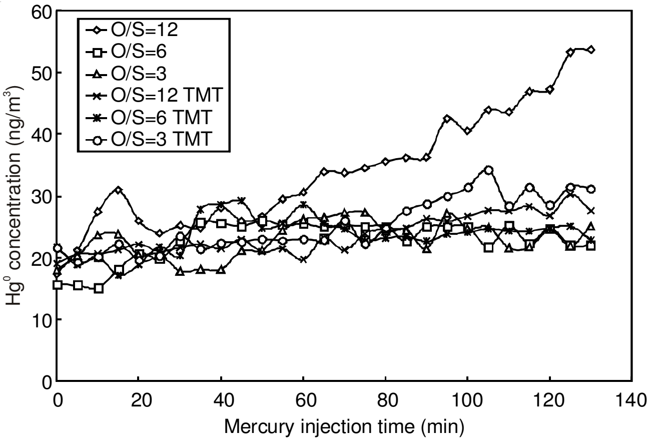

Fig. 3. Hg^0 concentrations with Hg^{2+} injection time at forced oxidation wet simulator

rates increased with decreasing of oxygen concentrations. Elemental mercury re-emission was suppressed by injecting TMT 15 additive. The reaction of oxidized mercury forming insoluble precipitate Hg_3TMT_2 reduced occurrence of reaction from Hg^{2+} to Hg^0 at soluble sulphite environment (eqn. 2). But elemental mercury re-emission rates increased with increasing of the ratios of oxygen to sulphur, oxygen concentration maybe affect Hg^0 re-emission suppressing efficiencies.

$$HSO_3^- + Hg^{2+} + H_2O_{(l)} \rightarrow Hg^0_{(g)} + SO_4^{2} + 3H^+ \quad (1)$$

$$3Hg^{2+} + 2\ TMTNa_3 \rightarrow Hg_3TMT_2 + 6Na^+ \quad (2)$$

During forced oxidation tests, elemental mercury re-emission trends were not noticeable because oxidized mercury can not be reduced into elemental mercury under the condition of $CaSO_4$ slurry. As we know, oxidized mercury was reduced into elemental mercury in sulphite environment. Elemental mercury re-emissions occurred during some field tests at power plants with forced oxidation wet FGD. The re-emission phenomenon can be simulated in the lab-scale wet FGD and mercury re-emissions were abated through chemical additives injection technology. Operation variations including oxygen condition, mercury concentration and mercury speciation at inlet and composition of simulated flue gas should be considered.

Trends of ORP and pH with SO_2 concentrations and testing time: The ORP (oxidation-reduction potential) can be quantitatively measured with variations in concentrations of oxidizers and reducers. The ORP values can be used to show oxidation and reduction capability in the solutions. When 1000 ppm and 2000 ppm SO_2 flew through the lime slurry, ORP and pH were tested online and their readings were once five minutes (Fig. 5).

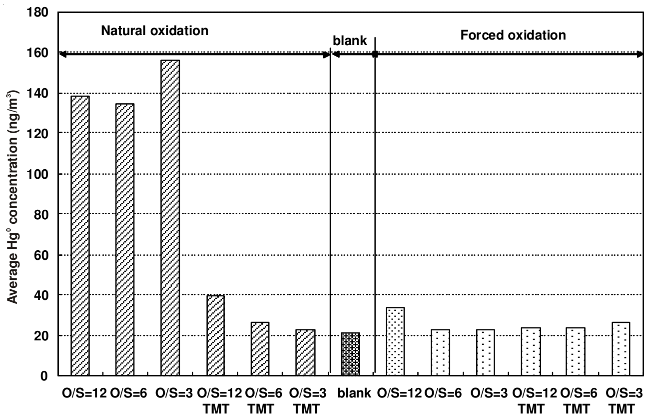

Fig. 4. Comparison of average elemental mercury re-emission concentration

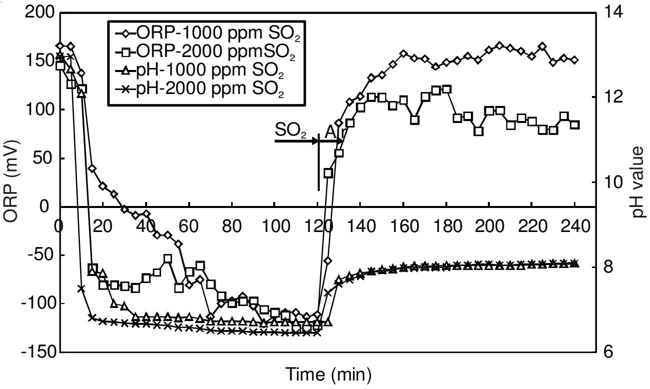

Fig. 5. ORP and pH trends with SO_2 flew through slurry

The ORP values of the lime slurries were positive when the testing began and it started to decrease until those were negative at 0.5 h varying from 165.5 mV to -113.9 mV when SO_2 gas passed through the lime slurry. There existed reduction environment in the slurries and elemental mercury re-emission occurred as shown in Fig. 2. Air was switched to the slurry when injection time was 2 h and the ORP values increased rapidly from -125 mV to be positive. There were no reduction condition in the slurry and the elemental mercury re-emission rates were small as shown in Fig. 3. The pH value of the slurries also varied from 12.97 to 6.83 with SO_2 passing through the lime slurries and it changed from 6.45 to 7.91 when air was switched to the slurry. Elemental mercury re-emission did not occurred in alkaline condition, while Hg^{2+} can be reduced to Hg^0 in the weak acidic condition.

Conclusion

During natural oxidation testing, elemental mercury re-emissions without TMT injection were apparent, while those were no noticeable during forced oxidation tests without TMT injection. The ORP values of the lime slurries varied from 165.5 mV to -113.9 mV when SO_2 gas passed through the lime slurry. There existed reduction environment in the slurries and elemental mercury re-emission occurred. Air was switched to the slurry and the ORP values increased rapidly from -125 mV to be positive. The pH values of the slurries were investigated when gases were switched from SO_2 to air and Hg^{2+} was reduced to Hg^0 in the weak acidic condition.

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