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Study of elemental mercury re-emission through a lab-scale simulated scrubber

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ABSTRACT

This paper describes a lab-scale simulated scrubber that was designed and built in the laboratory at Western Kentucky University's Institute for Combustion Science and Environmental Technology. A series of tests on slurries of CaO, $CaSO_3$, $CaSO_4/CaSO_3$ and Na_2SO_3 were carried out to simulate recirculating slurries in different oxidation modes. Elemental mercury (Hg^0) re-emission was replicated through the simulated scrubber. The relationship between the oxidation–reduction potential (ORP) of the slurries and the Hg^0 re-emissions was evaluated. Elemental mercury re-emission occurred when Hg^{2+} that was absorbed in the simulated scrubber was converted to Hg^0; then, Hg^0 was emitted from the slurry together with the carrier gas. The effects of both the reagents and the operational conditions (including the temperature, pH, and oxygen concentrations in the carrier gas) on the Hg^0 re-emission rates in the simulated scrubber were investigated. The results indicated that as the operational temperature of the scrubber and the pH value of the slurry increased, the Hg^0 concentrations that were emitted from the simulated scrubber increased. The Hg^0 re-emission rates decreased as the O_2 concentration in the carrier gas increased. In addition, the effects of additives to suppress Hg^0 re-emission were evaluated in this paper. Sodium tetrasulfide, TMT 15, NaHS and HI were added to the slurry, while Hg^{2+}, which was absorbed in the slurry, was retained in the slurry as mercury precipitates. Therefore, there was a significant capacity for the additives to suppress Hg^0 re-emission.

1. Introduction

Mercury is a neurotoxin pollutant that can cause brain defects in fetuses and impede intellectual development in children. Acute and chronic exposure to mercury and methyl mercury in humans results in central nervous system damage, kidney damage, and even death. Coal-fired power plants are the largest man-made source of mercury emissions, and account for 40% of emissions in the US [1–3]. Under the regulation of the Clean Air Interstate Rule (CAIR) and the Clean Air Mercury Rule (CAMR) instituted in March 2005, a number of states and the EPA have proposed regulating air pollutants and mercury emissions from coal-fired power plants [4]. Federal level mercury emission regulations are currently in an unknown state because the US Court of Appeals for the District of Columbia recently vacated the CAMR. To ensure compliance with these and future federal regulations, coal-fired power plants need to know their current mercury emission level [10]. Mercury appears in coal combustion flue gases in the solid and vapor phases (particulate mercury Hg_p in the solid phase and elemental mercury and oxidized mercury Hg^{2+} in the vapor phase). Extensive measurements of mercury emissions from coal-fired power plants were performed. Particulate-bound mercury is typically captured in a particulate-control device, while oxidized mercury is soluble in water and can be captured in certain control equipment, such as wet flue gas desulfurization (FGD) systems; however, elemental mercury is insoluble and difficult to be removed through APCDs, which are consequently emitted at the stack [5].

Wet FGD systems remove sulfur dioxide (SO_2) by scrubbing the flue gas with either a limestone or magnesium-enhanced lime slurry. The wet FGD process is considered a commercially mature technology, and many wet FGD systems are found in coal-fired power plants. The oxidation modes of wet FGD systems mainly include forced oxidation, natural oxidation, and inhibited oxidation. The forced oxidation mode that pumps air to oxidize calcium sulfite is widely used. These wet FGD systems can provide a co-beneficial, effective mercury removal technology to many power plants with wet FGD systems. However, during field tests that are aimed at enhancing the mercury removal performance of wet FGD systems, some of the oxidized mercury initially absorbed in the wet FGD system was re-emitted into the environment. Hg^0 re-emission through wet FGD was monitored at some representative coal-fired units. Over the years, there have been occasional reports of low capture efficiencies of the total mercury, which are often coupled

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with the observation that the elemental mercury concentration exiting the scrubber is higher than that entering [11]. For example, mercury measurements were performed at a unit with a limestone-forced oxidation FGD system, and the results showed that the elemental mercury concentrations were 2.48 and 8.85 μg/dscm at the FGD inlet and stack, respectively. In addition, there was a higher elemental re-emission rate of 257% across the wet FGD systems. The chemical reduction of oxidized mercury back to the elemental form in the FGD slurry is a main explanation for Hg re-emission. The Hg^0 re-emission adversely affected the overall mercury removal efficiency. Many coal-fired power plants focus on controlling Hg^0 re-emission through wet FGD. Hg^0 re-emission results in a decrease in the overall mercury removal efficiency and has an adverse financial impact on power plant operations under the CAMR cap-and-trade program [4,8].

Studies on elemental mercury re-emission in lab- and pilot-scale wet FGD systems were reported in recent years. Chang and Ghorish studied elemental mercury re-emissions by using a Hg^0 UV analyzer, as well as a sodium sulfite and bisulfite solution as a scrubber liquor in the lab-scale scrubber simulator. The experimental data indicated that oxidized mercury can be reduced by aqueous S(IV) (sulfite and bisulfite) species, which results in elemental mercury re-emission. In addition, a prediction model was developed [6]. Chang and Zhao have designed a pilot-scale wet lime/limestone FGD scrubber system (0.01 MW), where the Hg^0 re-emission results from lab-scale findings were validated [7]. The Hg^0 re-emission rates can be simulated by a modified first-order reaction model. Therefore, Hg^0 re-emission was needed to simulate and suppress the lab-scale simulated scrubber. Based on the research data, mercury control technology was performed on pilot- and full-scale wet FGD systems. Niksa and Fujiwara also predicted Hg^0 re-emission through an analysis of equilibrium calculations. Mercury retention is most sensitive to $HgCl_2$, NO, the Ca/S ratio, and the slurry dilution levels in limestone FGDs [9].

Many factors, which are relative to the wet FGD's chemistry and operational parameters, have been involved in elemental mercury re-emission chemistry. To better understand the performance of Hg^0 re-emission and its abatement in the wet FGD system, a lab-scale batch-simulated scrubber was designed and installed at Western Kentucky University. Some operational parameters and four kinds of reagents in the absorber were chosen. Mercuric chloride ($HgCl_2$) solution was pumped into the simulated scrubber to simulate the absorption of Hg^{2+} in the scrubber of wet FGD systems. It was a better tool to simulate and suppress Hg^0 re-emission to screen out affecting factors and additives in the simulated scrubber system.

2. Experimental

2.1. Experimental apparatus

Fig. 1 shows a schematic diagram of a lab-scale wet FGD simulated system. The elemental mercury (Hg^0) re-emission and the factors that impact Hg^0 re-emission were investigated by using the simulated scrubber. This system consisted of an oxidized mercury (Hg^{2+}) injection system, carrier gas system, scrubbing system, gas conditioning system and mercury analyzer system. The scrubbing system was composed of a round bottom flask with three necks, a water bath, a magnetic stirring system and temperature controllers. The simulated scrubber was operated under bubbling mode. The flask had a capacity of 500 ml, and three necks were used as inlets for injecting the oxidized mercury solution as well as the inlet and outlet carrier gas. The water bath was used to keep the slurry in the operational temperature range. A magnetic stirring machine and a magnetic bar were used to keep the solids uniformly suspended in the slurry during tests. The Hg^{2+} injection system was a syringe pump system, which can deliver the Hg^{2+} solution as well as control and adjust its injection rates. The Hg^{2+} solution went directly to the bottom of the flask through a Teflon tube with a 1/16-inch diameter. The carrier gas system included cylinder gases, mass flow controllers (MFCs) and delivery piping, which was either made of Teflon or stainless steel tubes. The desired flow rates of the carrier gases were controlled by calibrated MFCs. A coarse frit was attached to the end of the carrier gas inlet in the flask. Then, fine bubbles were generated, which increased the mixing of the gas with the slurry. The temperature control system included heating lines that were heated to about 160 °C to prevent mercury loss prior to the mercury speciation analyzer.

2.2. Experimental materials

With the exception of the compressed air, the carrier gases were ultra high purity cylinder gases. The compressed air had been treated and dried in the laboratory. Calcium Oxide, calcium sulfite, calcium sulfate, sodium sulfite, sodium tetrasulfide (Na_2S_4) and hydroiodic acid (HI) were the chemical reagents from Fisher Scientific; the mercuric chloride standard and the sulfuric acid were trace metal grade reagents. The TMT 15 additive was from Evonic-Degussa Corporation, while the NaHS was from Sigma–Aldrich, Inc. The water was deionized water, which was treated with the ELGA Purelab option in the laboratory. All of the connecting tubes were stainless steel or Teflon tubes in case of penetration, condensation and adsorption of mercury on the wall of the tubes and connecting parts. The impingers and the flask were vitreous and cleaned before every test.

2.3. Experimental procedure

At the beginning of each test, a slurry with the desired concentration (0.5% w/w) was prepared and poured into the flask; the flask was submerged into the water bath at the desired temperature (40, 50, or 60 °C). The magnetic stirring machine started to stir, and the slurry was mixed well. A 1.06×10^{-7} mol/l $HgCl_2$ solution was transferred into a syringe, which was set up on a syringe pump, and the $HgCl_2$ injection rate was set at 10 ml/h. The carrier gas with a flow rate of 800 ml/min was introduced into the scrubber. The carrier gas came in contact with the slurry through the scrubber. Then, the carrier gas arrived at the gas conditioning system and the mercury analyzer, which initiated the test. When the blank testing values of the mercury concentrations in the carrier gas were stable, the $HgCl_2$ solution was injected. Each test was performed for 110–125 min, which depended on the actual conditions. The gas conditioning system included a module, cooler and controller. The sample gas was split in two in the module, and the controlled streams were sent to different impingers. The first section contained tin chloride ($SnCl_2$), which reduced all of the oxidized mercury present in the sample to Hg^0 and the original elemental mercury. Therefore, the mercury became vapor phase total mercury. The second sample stream entered an impinger that contained potassium chloride (KCl), which scrubbed the sample stream of any oxidized mercury and left only a stream of elemental mercury. Moisture in the gas was also removed by using a cooler that enabled us to report the Hg levels on a dry basis. The gases from both lines were then sent to the Hg analyzer system.

The pH value and the oxidation–reduction potential (ORP) were tested before and after each test. A standard mercury solution with the desired volume was diluted with HNO_3 and deionized water. Then, the 1.06×10^{-7} mol/l oxidized mercury solution was prepared. The oxidized mercury (20 ml) was injected into the slurry during the testing period, and the pH value of the slurry was monitored. The pH value slightly decreased during the oxidized