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ABSTRACT

This paper presents results of research being conducted at Argonne National Laboratory on the capture of elemental mercury in simulated flue gases by using dry sorbents. Experimental results from investigation of various sorbents and chemical additives for mercury control are reported. Of the sorbents investigated thus far, an activated-carbon-based sorbent impregnated with about 15% (by weight) of sulfur compound provided the best results. The key parameters affecting mercury control efficiency in a fixed-bed reactor, such as reactor loading, reactor temperature, sorbent size distribution, etc., were also studied, and the results are presented. In addition to activated-carbon-based sorbents, a non-carbon-based sorbent that uses an inactive substrate treated with active chemicals is being developed. Preliminary experimental results for mercury removal by this newly developed sorbent are presented.

INTRODUCTION

Mercury has long been identified as a potential health and environmental hazard. Its emissions, transport, fate, and public health risks are being extensively studied by the U.S. Environmental Protection Agency (EPA), as required by the 1990 Clean Air Act Amendments, as well as by other researchers. In addition to emissions from natural sources, such as volcanoes, municipal waste combustors (MWCs) and coal-fired utility boilers have been identified as two of the major anthropogenic mercury emissions sources. Nriagu (1989) has estimated global anthropogenic mercury emissions at about $910\text{--}6200 \times 10^3$ kg/yr compared with $100\text{--}4,900 \times 10^3$ kg/yr from natural sources (1). Chang and Offen (1995) estimate total anthropogenic mercury emissions in the United States to be about 250 ton/yr, with coal-fired utility boilers contributing about 59 ton/yr (2). Research results have also indicated that most of the flue gas from utility boilers is typically lower in chlorides and higher in sulfur dioxide (SO_2) than MWC exhaust gas. The mercury in utility-boiler flue gas tends to be present primarily as elemental mercury and

oxidized mercury. Therefore, higher ratios of elemental mercury would be expected in the flue gas from coal-fired utility boilers than from MWC. The high volatility of elemental mercury causes it to be present in the vapor form in flue-gas emissions from utility boilers.

The mercury-removal effectiveness of conventional flue-gas cleanup (FGC) technologies depends strongly on the species or compound forms of the mercury in the flue gas. Data collected by the U.S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI) on the operation of electric-power plants show that although conventional FGC technologies are moderately effective in controlling mercury emissions in the chloride form, they perform poorly in controlling emissions of elemental mercury vapor. (3,4) A significant fraction of the total mercury emissions at many coal-burning combustors is in the elemental form, so enhancement or supplemental control technologies need to be developed.

This paper presents results of research being conducted at Argonne National Laboratory (ANL) by dry sorbents on the capture of elemental mercury in flue gas from coal-combustion systems. Parallel research is also being conducted at ANL on the removal of mercury by wet scrubbers. The emphasis is on development of a better understanding of the key factors that control mercury capture. Future work is expected to utilize this information for the development of new or modified process concepts featuring enhanced mercury capture capabilities.

EXPERIMENTAL METHODS

Figure 1 shows a schematic flow diagram of the experimental system. The experiments were conducted using a fixed-bed glass reactor 4 cm in diameter and 14 cm in height. A glass frit is positioned in the lower section of the reactor to support the materials placed inside the reactor. During experiments, the reactor was immersed in a heated sand bath (model no. SBL-2D, Techne, Inc., Princeton, N.Y.) to maintain the desired operating temperature.

The feed gas used for the experiments was supplied by nitrogen cylinders. If desired for later work, however, the system can be integrated with another feed-gas preparation system to provide gas with a composition representative of coal-combustion flue gases. Before entering the reactor, the incoming feed gas was preheated to a preselected operating temperature equal to that maintained in the fixed-bed reactor.

The design capacity of the system is 20 L/min of carrier gas with mercury concentrations of up to 100 mg/m³. The elemental mercury is supplied by means of a mercury permeation tube placed inside a U-shaped glass tube that is immersed in a constant-temperature (about 70°C) water bath. The amount of mercury released from the tube is governed by the permeability of the materials used for the tube, the length of the tube, and the temperature at which the tube is maintained. Permeation tubes were used because this method not only provides precise control of the amount of mercury vapor emitted into the gas stream flowing over the permeation tube, but it is also safer to operate than other techniques.

In a typical experiment, a total of 120 g of either silica sand or a mixture of silica sand and hydrated lime (Ca(OH)₂) in a weight ratio of 40:1 is prepared and placed in the glass reactor.

The $\text{Ca}(\text{OH})_2$ is employed because it is a common sorbent for SO_2 in FGC systems. The large amount of sand is used to avoid channeling caused by lime agglomeration. Except for initial system tests and baseline experiments (as mentioned below), small amounts of selected additives/sorbents were added to the sand/ $\text{Ca}(\text{OH})_2$ bed material. The feed gas flowing through the reactor was maintained at about 10 L/min throughout the experiments. A portion (about 3 L/min) of the feed gas is diverted to the mercury-generation device (the U-shaped glass tube), in order to add the desired amount of mercury vapor, and is then recombined with the other portion of the feed gas downstream. The feed gas, which contains the mercury contaminant, then flows through the preheating tubes and the glass reactor, where physical/chemical reactions between the additive/sorbent and the mercury contaminant occur.

A cooler/condenser is used to lower the temperature of the gas from the reactor and to maintain a consistent gas temperature for analysis. The mercury concentration is measured by using a gold-film mercury vapor analyzer (Jerome 431X) procured from the Arizona Instrument Corp. of Tempe, Arizona. For elemental mercury, the range of the instrument is 0 to 999 mg/m^3 , with a sensitivity of 3 mg/m^3 and an accuracy of $\pm 5\%$ at 100 mg/m^3 . Only a small amount of the treated gas (about 1 L/min) is directed to the gas analyzer, with the balance flowing into the laboratory exhaust system. After analysis, the analyzed gas also flows into the exhaust system.

RESULTS AND DISCUSSION

Following construction and shakedown of the fixed-bed reactor facility, a series of tests was performed to check for background levels of mercury in the apparatus and the laboratory environment. The tests were performed using only purified nitrogen as the carrier gas, without the mercury permeation tube in place, and only sand/ $\text{Ca}(\text{OH})_2$ as the bed material. The gas flow rate was maintained at 10 L/min, and operating temperatures ranged from 50 to 100°C. The results indicated that the entire experimental apparatus functioned well, and no trace amounts of mercury were detected.

Before conducting the additive/sorbent experiments, baseline experiments were carried out under experimental conditions identical with those in the subsequent additive/sorbent experiments, but without addition of any additive/sorbent in the reactor. The purpose of conducting the baseline experiments was to establish a baseline against which to compare the results of additive/sorbent experiments. No measurable mercury removal occurred under any of the experimental conditions studied. A commercial lime hydrate with a very high surface area (sucrose lime hydrate from the Dravo Lime Company) was also tested for mercury removal. Again, no significant mercury removal was observed. The baseline experiments are performed periodically to ensure the reliability and repeatability of the experimental results (such as no residual mercury being accumulated and no additive/sorbent being trapped in the system).

The initial additive/sorbent experiments at ANL were designed to evaluate commercially available activated-carbon sorbents. A total of four activated carbons from different manufacturers were evaluated. The physical characteristics of these sorbents are shown in Table 1. Results from the experiments with activated carbon AC displayed very little mercury removal, as shown in Figure 2. Mercury removal for this sorbent was found to remain low, even when

the amount of carbon in the bed material was increased to 3 g. Mercury removal of greater than 90% was indeed observed when 20 g of this carbon was added to the bed material. However, the breakthrough time (defined as the time from the start of this experiment to when the amount of mercury observed in the effluent stream is 10% of the starting level) was still short (less than 1 min). These results suggest that activated carbon AC would not be a cost-effective sorbent for mercury control under the conditions studied.

The other activated carbon materials performed considerably better, with essentially 100% removal for periods of time ranging from about 5 min to nearly 40 min, as shown in Figure 2. The best removal results were obtained with activated carbon CB-II, which was commercially treated with about 15 wt% sulfur. The addition of active chemicals (such as sulfur compounds) significantly improved the mercury removal capacity of the sorbent. Mercury sorption capacities up to the breakthrough point at two operating temperatures for each activated carbon are compared in Figure 3; the improved performance of CB-II is again evident. Also shown in the figure is the strong effect of temperature on capacity, with a gain of an order of magnitude for a decrease in temperature from 90 to 55°C. The relative superiority of CB-II with respect to other carbons also appears to be enhanced by the lower temperature. These results revealed that both physical adsorption and chemical reactions may be significant factors behind mercury removal mechanisms.

The effects of both temperature and mercury concentration are explored in Figure 4 for sorbent CB-II. Again, the capacity is seen to increase with decreasing temperature, with a particularly strong increase between 90 and 70°C. The capacity of the carbon also increases with the concentration of mercury in the gas, indicating better utilization of the carbon with the greater driving force provided by the higher concentration.

The effects of particle size and sorbent loading are illustrated in Figures 5 and 6 for sorbent CB-II. In general, smaller particle sizes give better removal performance. The effect seems to be particularly strong for particle sizes of 20 mm and smaller, giving initial removals of essentially 100% versus removals of about 50% or less for particles larger than about 40 mm. As expected, increasing the loading of the sorbent in the reactor also improves removal performance (Figure 6). At the specified operating temperature and particle size, 100% mercury removals were obtained as the loading was increased over 0.06 g.

The success of the sulfur-treated activated carbon (CB-II) is thought to be based on a combination of physical adsorption and chemical reactions that produce mercury sulfide. This suggests that chemical additives producing other compounds, such as mercury chloride, might also be beneficial for removals. To explore this possibility, the activated carbon AC, which previously gave essentially no removal, was treated with calcium chloride (CaCl_2) in the ratio of about 6:1 by weight. The treated carbon gave excellent removals with about 33% carbon in the carbon/lime mixture. In order to obtain a meaningful comparison of the sulfur- and CaCl_2 -impregnated carbons, the total sorbent was reduced to about 2%. Figure 7 shows that the chloride-treated carbon still gave good removals and actually performed better than carbon CB-II.

In addition to the activated-carbon-based sorbents, several high-surface-area or low-cost mineral substrates have been identified and used as sorbents in the experiments. Results from

initial tests with three of these materials (Table 1) indicated only moderate mercury removal performance with the molecular sieve sorbent, and negligible removals for the pumice and vermiculite. The samples are being treated with chemical additives shown to be effective with activated carbon, and tests are being run at various additive loadings, mercury concentrations, and flue-gas temperatures. Figure 8 gives the results of experiments with volcanic pumice treated with CaCl_2 , potassium iodide (KI), and elemental sulfur. Although the untreated pumice was ineffective for mercury removal, all of the treatments produced significant mercury removals. At 70°C , the sulfur-treated sorbent gave 100% removal for over an hour; the iodide-impregnated sorbent gave 100% removal for a few minutes, followed by a decrease in removal that appeared to level out at about 30%. The chloride-impregnated sorbent behaved somewhat differently, with the removal gradually increasing to a final value of about 30%. The results suggest that the use of lower-cost mineral substrates treated with active chemicals (such as sulfur and iodide compounds) may provide an alternative to relatively costly activated carbon for mercury removal.

CONCLUSIONS

The results and conclusions from the research being conducted at Argonne on the capture of elemental mercury in simulated flue gas by using dry sorbents can be summarized as follows:

- Lime hydrates, either regular or high-surface-area, are not effective in removing mercury.
- Mercury removal is enhanced by the addition of activated carbon; the removal capacity of activated carbon increases with decreasing temperature, decreasing particle size, increasing sorbent loading, and increasing mercury concentration.
- Both physical adsorption and chemical reactions may be significant factors behind mercury removal mechanisms.
- Chemical pretreatment (e.g., with sulfur or CaCl_2) can significantly increase the removal capacity of activated carbon.
- Under the current experimental conditions, the tested mineral substrates have moderate to negligible mercury removals.
- Chemically treated mineral substrates have the potential to be developed into effective and economical mercury sorbents.

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Table 1
Characteristics of Candidate Sorbents

Sorbent	Cost ^a (\$/lb)	Surface Area (m ² /g)	Bulk Density (g/cm ³)	Median Particle Size (μm)
AC ^b	0.50	1000	0.54	2000-2500 ^c
WPL ^b	0.50	894	0.57	2000-2500 ^c
PC-100 ^b	0.50	965	0.52	2000-2500 ^c
CB-II ^b (sulfur-treated)	3.90	1050	0.56	2000-2500 ^c
Molecular Sieve	8.00	645	0.52	3.8
Vermiculite	0.13	12.9	0.18	580
Pumice	0.10	8.2	1.23	21

^aApproximate - variable lot size

^bActivated carbon

^cCommercial specifications - samples ground to less than 100 μm for tests

Figure 1. Fixed-bed reactor facility.

Reactor Loading - Silica Sand/ $\text{Ca}(\text{OH})_2$ /Carbon = 120g/2.97g/0.03g,

Flow Rate = 10 L/min, Reactor Temperature = 55°C

Figure 2. Mercury breakthrough curves for activated carbons.

Figure 3. Comparison of adsorption capacities at two different temperatures.

Figure 4. Effects of Temperature and Concentration on Adsorption Capacity

Figure 5. Effect of carbon particle size on mercury removal.

Figure 6 Effect of reactor loading on mercury removal.

Figure 7. Comparison of mercury removals by carbons treated with sulfur or CaCl_2 .

Figure 8 Effects of Chemical Pretreatment on an Inert Substrate at 70°C.