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Mercury Capture in Bench-Scale Absorbers

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MERCURY CAPTURE IN BENCH-SCALE ABSORBERS

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INTRODUCTION

Concerns regarding emissions of hazardous air pollutants (air toxics) have emerged as a major environmental issue. The authority of the U.S. Environmental Protection Agency to regulate such pollutants was greatly expanded through the Clean Air Act Amendments of 1990. Mercury emissions have been singled out for particular attention because of concerns over possibly significant effects on human health. Some of those emissions originate in the combustion of coal, which contains trace amounts of mercury. Conventional flue-gas cleanup (FGC) technologies are not very effective in controlling emissions of mercury, and enhancements or supplemental technologies need to be developed.

This paper gives a brief overview of research being conducted at Argonne National Laboratory on the capture of mercury by both dry sorbents and wet scrubbers. The emphasis in the research is on development of a better understanding of the key factors that control the capture of mercury. Future work is expected to utilize that information for the development of new or modified process concepts featuring enhanced mercury capture capabilities.

BACKGROUND

Mercury emissions from coal combustion have been shown to vary considerably from site to site. It is well known that the chemical composition of coal is highly variable, even within a given seam. The concentration of mercury is no exception, as it exhibits variations that span several orders of magnitude. A range in concentration from less than 0.01 ppm up to 3.3 ppm has been reported for bituminous coal, and values as high as 8.0 ppm have been reported for subbituminous coal.¹

The fate of trace elements in the combustion process is influenced by the type of boiler, the operating conditions, and the FGC system. Mercury belongs to a group of elements/compounds denoted as Class III, which remain primarily in the vapor phase within the boiler and subsequent FGC system. However, that state can be influenced by reactions with other elements, such as chlorine, and by fly-ash characteristics that affect adsorption processes. The concentration of mercury in the flue gas from typical coal combustors falls within a range of 10 to 70 $\mu\text{g}/\text{Nm}^3$.

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Few reliable data have been available on the performance of FGC technologies for mercury control on coal-fired systems. Large variations in reported removals have been typical, due both to differences in coal and operating characteristics and to inaccuracies in sampling/analytical procedures. Particulate-matter collectors, such as electrostatic precipitators (ESPs) and baghouses, can be effective for mercury control to the extent that mercury is adsorbed on the fine particulate matter (fly ash) in the gas stream or is converted to another chemical form that can be collected as particulate matter. Reported mercury removals for "cold" ESPs range from 20 to 90%, although the high-end numbers may be due to sampling/analytical problems, since some data sets show maxima of less than 50%. Fewer data are available for baghouses, but removals ranging from 50% to as much as 90% have been reported. Mercury removal in flue-gas desulfurization (FGD) systems shows even more variation, with values ranging from 10% to over 90%. Much of that variation may be caused by differences in the chemical form of the mercury, inasmuch as the chloride form is much more easily captured than the elemental form.

Better data are becoming available as a result of extensive sampling efforts carried out by the U.S. Department of Energy, the Electric Power Research Institute, the Environmental Protection Agency, and others. However, it is likely that large variations will continue to be the norm and that some form of control technology for mercury will ultimately be required for many systems. To support development of those measures, better information on the factors that control mercury capture is needed, as are consistent comparative evaluations of different sorbents and process modifications.

RESEARCH PROGRAM

Argonne's research on the control of mercury emissions began with a critical evaluation of published information on the mercury content of various coals, emission rates for different types of combustors, the efficacy of existing control technologies for capturing mercury, and the status of control techniques in various stages of research and development. The results of that evaluation are given in Reference 1.

Based on the initial study, a number of chemical additives and sorbents with the potential for enhancing the capture of elemental mercury in dry or wet/dry FGC systems were selected for laboratory investigation. The study of dry sorbents was chosen for several reasons. Many existing coal-fired plants have only particulate-matter control, usually in the form of ESPs, and these could be well suited to duct- or furnace-injection of mercury sorbents. Also, European experience with the addition of sorbents/chemicals to spray-dryer systems on municipal waste incinerators has indicated that greatly enhanced mercury removals are possible. A more extensive discussion of this research can be found in Reference 2.

Recently, the research program has been expanded to include investigation of mercury removal in wet scrubbing. The initial study found very little information regarding potential performance enhancements for scrubbers operating on coal-fired systems, although some work has been done for applications in other industries.³ To date, the research has focused on physical modifications designed to improve the absorption of mercury by the scrubber liquid, and on the testing of two chemical agents selected for their potential to react with mercury.

EXPERIMENTAL FACILITIES

Argonne's FGC-laboratory facilities include a complete wet scrubber system and a spray-dryer/fabric-filter system. Supporting facilities include a gas supply system capable of blending synthetic flue gas from bottled gases, on-line gas-analysis packages, and data loggers.⁴ In order to screen a variety of dry chemical additives/sorbents over a range of process variations in a rapid and economical manner, a laboratory-scale fixed-bed reactor facility has also been designed and constructed. New supporting facilities include a feed-gas preparation system that can provide known concentrations of mercury in a gas stream, and an on-line mercury-analysis system. The following sections briefly describe the new facilities, as well as the wet scrubber system.

Feed-Gas Preparation

The feed-gas preparation system includes a mercury-containing permeation tube, a constant-temperature water bath, and a carrier-gas supply. The design capacity of the section is 20 L/min of gas with mercury concentrations of up to 100 $\mu\text{g}/\text{m}^3$. 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. In operation, the permeation tube is placed inside one leg of a U-shaped glass tube, the other leg of the tube being filled with glass beads to ensure uniform heating of the incoming gas stream. The lower portion of the U-shaped tube is immersed in a constant-temperature bath to maintain the desired temperature. A portion (about 3 L/min) of the feed gas flows through the tube and is then recombined with the balance of the gas. The normal operating temperature for the water bath is about 70 °C, which gives an emission rate of about 70 ng/min/cm for the permeation tubes. The feed-gas stream has consisted of nitrogen for the work conducted thus far, but other gases can be added using the existing blending system.

Gas-Analysis

The gas-analysis system includes a mercury-vapor analyzer and a cooling unit to condition the gas. A small portion (about 1 L/min) of the gas to be analyzed is directed into the mercury analyzer, and the balance of the gas flows into the laboratory exhaust system. After analysis, the analyzed gas also flows into the exhaust system.

The mercury concentration is measured with a gold-film mercury-vapor analyzer (Jerome 431X) that was procured from the Arizona Instrument Corp. of Tempe, Arizona. The gold-film sensor is said to be inherently stable and selective to mercury, thereby eliminating potential interferences by other compounds (water vapor, sulfur dioxide, carbon dioxide, etc.) commonly present in flue gas. The range of the instrument is 0 to 0.999 mg/m^3 mercury, with a sensitivity of 0.003 mg/m^3 and an accuracy of $\pm 5\%$ at 0.100 mg/m^3 . An inconvenient feature of this type of analyzer is that it needs to be regenerated periodically by an internal electric heating element. The operating temperature range for the instrument is 0 to 40 °C. Therefore, a simple glass cold trap is installed upstream of the analyzer.

Fixed-Bed Reactor

The fixed-bed reactor vessel, which is constructed of glass, is 4 cm in diameter and 14 cm in height. A glass frit is positioned in the lower section to support materials placed inside the

reactor. To avoid fluidization of the bed materials, the feed gas enters the reactor from the top and exits at the bottom. During shakedown and baseline tests, the reactor was packed with either silica sand (120 g) or a mixture of silica sand and hydrated lime ($\text{Ca}(\text{OH})_2$) in a weight ratio of 40:1. The $\text{Ca}(\text{OH})_2$ has been employed because it is a common sorbent for sulfur dioxide in FGC systems. The large amount of sand is used to avoid channeling caused by lime agglomeration. For additive/sorbent testing, small amounts of material being studied are added to the sand/ $\text{Ca}(\text{OH})_2$ bed material. A diagram of the reactor with the feed and analyzer systems is shown in Figure 1.

To maintain a uniform temperature during experiments, the fixed-bed reactor is immersed in a fluidized-bed, constant-temperature bath (model No. SBL-2D) manufactured by Techne, Inc., of Princeton, New Jersey. The normal operating-temperature range for the unit is 50 to 600 °C, with temperature fluctuations specified as less than 1 °C at the lower end of the range and about 3 °C at the upper end. To preheat the incoming feed gas to a temperature equal to that maintained in the fixed-bed reactor, the gas-transfer line is wrapped with heating tapes.

Wet Scrubber

Figure 2 shows a flow diagram for the wet scrubber system. All of principal vessels are constructed of glass. The scrubber column has an inside diameter of 7.6 cm and an active height of nearly 53 cm. It is normally operated in a countercurrent mode with the flue gas entering at the bottom. The scrubber is constructed of several interchangeable sections so that it can be configured as a flooded column (no internals), a four-stage disc and donut column, or an intermediate combination. For the experiments described here, the combination mode was used with the lower part of the column flooded with scrubber liquor. The desired level in the scrubber is maintained through a combination of a sieve plate in the bottom of the column (which "holds up" some of the liquid) and adjustment of the recirculation rate between its limits of 330 and 1420 mL/min.

The temperature of the scrubber liquor can be adjusted by heating the holding tank with heat tapes. The pH of the liquid in the holding tank is sampled continuously and can be adjusted either manually or automatically by adding reagent from a chemical feed tank.

EXPERIMENTAL RESULTS

Dry Sorbents

Preliminary Tests. 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 laboratory environment. Those tests were performed at temperatures ranging from 50 to 100 °C, with only sand in the fixed-bed reactor, and without the mercury permeation tube in place. The entire experimental apparatus functioned well, and no trace amounts of mercury were detected.

Baseline Experiments. In order to establish a performance baseline against which to compare the results of additive/sorbent experiments, a series of experiments was conducted with the fixed-bed reactor empty, filled with sand (120 g), or filled with sand plus $\text{Ca}(\text{OH})_2$ (117 g plus 3 g) as the bed materials. Reagent-grade $\text{Ca}(\text{OH})_2$ was used. These experiments were run at two bed temperatures (70 and 90 °C) and one mercury concentration level (100 $\mu\text{g}/\text{Nm}^3$). There was no

measurable mercury removal under these conditions. 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.

Experiments with Chemical Additives. Various chemical additives for mercury removal have been reported in the literature. These include activated carbon impregnated with various chemicals (notably sulfur and iodine), modified zeolites, glass fibers coated with special chemicals, and pure chemicals (such as sulfur, selenium, and ferrous sulfide and sulfate). Of these potential additives, the activated-carbon-based chemicals and alkali-sulfide compounds are being systematically investigated first in this project because of the high mercury removals reported in tests on waste-incineration units. In addition to comparing the performance of different types of sorbents/additives, the research program includes investigation of the effects of varying process parameters, such as sorbent particle size, sorbent loading in the reactor, reactor/gas temperature, and mercury concentration.

Four different activated carbons were used in the initial research. The characteristics of these materials are summarized in Table 1. Each carbon sample was first pulverized and sieved to obtain different size fractions. For each experiment, the candidate material was thoroughly mixed with the sand/ $\text{Ca}(\text{OH})_2$ mixture before the reactor was filled. To provide a consistent comparison of the effectiveness of the additives, the same set of experimental conditions was used for each material. The amounts of carbon added ranged from 1 to 10 wt% (relative to the lime) for most of the tests, although higher values were evaluated in a few cases. Three fixed-bed reactor temperatures were evaluated: 55, 70, and 90 °C. A mercury concentration in the feed gas of either 44 or 96 $\mu\text{g}/\text{m}^3$ was used, and the feed-gas flow rate was fixed at 10 L/min.

Results from the experiments with different carbons are shown in Figure 3. While carbon AC displayed very little mercury removal, the other samples gave considerably better performance, with essentially 100% removal for periods of time ranging from about 5 min up to nearly 40 min. By far the best results were obtained with sample CB-II, which was commercially treated with about 15 wt% sulfur.

The effects of both temperature and mercury concentration are explored in Figure 4 for sample CB-II. The capacity is seen to increase with decreasing temperature, with a particularly strong increase between 89 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 absorption driving force provided by the higher concentration.

The success of the sulfur-treated 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, sample AC (which previously gave essentially no removal) was treated with CaCl_2 in the ratio of about 6:1 by weight. The treated carbon gave excellent removals, with no breakthrough observed even at the one-hour point of the experiment. However, these results were obtained 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 loading was reduced to about 2%. Figure 5 shows that the chloride-treated carbon still gave good removals and actually performed better than the sulfur-treated

carbon CB-II. The potential of this approach to produce inexpensive, effective sorbents is such that further investigations are planned.

Recently, several proprietary sorbents have been tested under the same conditions as used for the activated carbons. Excellent results were obtained for several of the samples and tests are continuing. In addition, samples of activated carbons prepared specifically for mercury control have been received from several manufacturers and will soon be incorporated into the research program.

Wet Scrubbing

Preliminary data from various field-sampling campaigns indicate that elemental mercury is not appreciably removed in typical wet scrubber systems. This is not surprising given the very low solubility of mercury, even as compared to nitric oxide (NO), which is notably difficult to remove in a wet scrubber without some form of chemical enhancement (such as ferrous-EDTA addition). In previous research, Argonne's wet scrubber has demonstrated baseline removals of about 90% for sulfur dioxide and only 1-2% for NO. Therefore, very little if any removal of mercury was anticipated.

Preliminary experiments were conducted using the scrubber as described above with distilled water, a saturated Ca(OH)_2 solution, and a Ca(OH)_2 solution with 1000 ppm of potassium polysulfide. The polysulfide has been claimed to promote mercury removal in other research.³ The mercury inlet concentration was about $40 \mu\text{g}/\text{m}^3$, the liquid column height was varied up to 43 cm, and the temperature was varied between 22 and 50 °C. No mercury removal was detected under any of these conditions.

Next, 0.95-cm ceramic-saddle packing was added to the column and the inlet mercury concentration was increased to approximately $100 \mu\text{g}/\text{m}^3$. Sodium hydroxide (NaOH) addition was used to control pH over a range of 5 to 12. Removals of 3 to 5% were observed with distilled water over that range of pH values and removals of 6 to 7% were obtained when the temperature was raised from 22 to 55 °C. However, tests involving polysulfide addition had to be terminated when reactions with the ceramic saddles produced hydrogen sulfide (H_2S) that interfered with the operation of the mercury analyzer.

Stainless-steel packing (0.61 cm) was tried next and gave the rather unexpected result of 11% removal with no liquid in the column. Removals with water in the column ranged from 15 to 20%. Addition of polysulfide to the scrubber produced a noticeable increase in removal up to about 40%. It should be noted that this additive requires a very high pH to maintain its stability and this is likely to preclude its use in most FGD systems.

In order to increase the gas-liquid interfacial area, a gas-diffusion stone was installed above the sieve plate and used to introduce the gas into the scrubber. Tests were performed with and without packing (stainless steel), and with and without polysulfide in the liquor. In all cases, the mercury removals were approximately 24%, indicating that the bubble size was by far the dominant factor.

Recently, another chemical additive has been identified which has improved mercury removals (using the diffusion stone mentioned above) to as high as 80%. Ongoing research is focused on quantifying the practical potential of this additive.

CONCLUSIONS

The results and conclusions to date from the Argonne research on dry sorbents can be summarized as follows:

- Lime hydrates, either regular or high-surface-area, are not effective in removing mercury.
- Mercury removals are enhanced by the addition of activated carbon.
- Mercury removals with activated carbon decrease with increasing temperature, larger particle size, and decreasing mercury concentration in the gas.
- Chemical pretreatment (e.g., with sulfur or CaCl_2) can greatly increase the removal capacity of activated carbon.

Preliminary results from the wet scrubbing research include:

- No removal of elemental mercury is obtained under normal scrubber operating conditions.
- Mercury removal is improved by the addition of packing or production of smaller gas bubbles to increase the gas-liquid contact area.
- Polysulfide solutions do not appear promising for enhancing mercury removal in typical FGC systems.
- Stainless steel packing appears to have beneficial properties for mercury removal and should be investigated further.
- Other chemical additives may offer greatly enhanced removals.

RESEARCH DIRECTIONS

The investigation of activated carbons and other sorbents in the fixed-bed reactor is continuing, with particular emphasis on various chemical pretreatments. Process concepts that demonstrate both technical and economic potential for mercury control will be further developed by using an existing laboratory-scale spray-dryer/fabric-filter system that can be configured for a wide range of process variations. In parallel with the dry-sorbent research, the factors that control mercury removal in wet FGD systems are being studied in a laboratory-scale wet scrubbing system. An improved understanding of the removal process is expected to lead to the identification of process modifications and/or additives to enhance mercury control.

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Table 1. Physical characteristics of activated carbons.

Activated Carbon	Source of Material	Surface Area (m ² /g)	Bulk Density (g/mL)	Porosity	Median Particle Size (μm)
AC	Coconut shell	1000	0.54	0.62	41
WPL	Bituminous coal	894	0.57	0.58	13.4
PC-100	Bituminous coal	965	0.52	0.54	17.6
CB-II (sulfur-impregnated)	Bituminous coal	1050	0.56	0.58	10

Figure 1. Fixed-bed reactor facility.

Figure 2. Wet scrubber system.

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 3. Mercury breakthrough curves for activated carbons.

Figure 4. Effects of temperature and mercury concentration on adsorption capacity.

Figure 5. Comparison of mercury removals by carbons treated with sulfur or CaCl_2 .

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