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# REMOVAL OF MERCURY FROM COAL-COMBUSTION FLUE GAS

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## ABSTRACT

Combustion sources, including those using coal for fuel, contribute a significant fraction of total anthropogenic mercury emissions. Recent field studies have shown that current flue-gas cleanup (FGC) systems are relatively ineffective in controlling elemental mercury, which is a major component of the mercury emissions for many systems. Research at Argonne National Laboratory has been focused on techniques to enhance the capture of elemental mercury in existing FGC systems. For dry processes, these studies have included evaluation of activated carbons and investigation of sorbents based upon chemical pretreatment of low-cost mineral substrates. To enhance the ability of wet scrubbers to capture mercury, the studies have looked at the effects of improved mass transfer through both mechanical and chemical means, as well as the conversion of elemental mercury into more soluble species that can be easily absorbed.

## INTRODUCTION

Title III of the Clean Air Act Amendments of 1990 focused attention on controlling emissions of hazardous air pollutants (HAPs). Among the listed HAPs, mercury emissions have been singled out for particular attention. Some of those emissions originate in the combustion of coal, which contains trace amounts of mercury. Mercury emissions from coal combustion have been shown to vary considerably from site to site. Those emissions depend not only on the composition of the coal, but also on the type of boiler, the operating conditions, and the FGC system. Mercury belongs to a group of elements and compounds denoted as Class III, which remains 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 (e.g., unburned carbon) that affect adsorption processes. The concentration of mercury in the flue gas from typical coal combustors ranges from less than 10 to more than 50  $\mu\text{g}/\text{Nm}^3$ .

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Significant variations in the performance of FGC systems were observed in recent tests by the Department of Energy and the Electric Power Research Institute at a variety of operating power plants. Mercury removals in electrostatic precipitators (ESPs) ranged from about 15 to 75%, while very limited data gave a range of removals for baghouses from 10 up to 70%. Mercury removal measurements for wet flue-gas desulfurization (FGD) systems were also quite variable, with values ranging from near zero to about 50% [1]. Much of the variation in removal performance may be caused by differences in the chemical form of the mercury in the flue gas. The presence of chlorine in coal means that mercury can be found in both the elemental (Hg) and chloride ( $HgCl_2$ ) species, with the relative amounts depending on such factors as the ratio of chlorine to mercury, the gas temperature, and the gas residence time at various temperatures [2]. The huge difference in solubility between the two species is particularly important in wet scrubbing applications.

## RESEARCH PROGRAM

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 dry 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. Therefore, initial phases of this research focused on the performance of various activated carbons [3], while more recent work has investigated the potential of low-cost mineral substrates pretreated with several different chemical compounds.

The presence of wet FGD systems at many power plants and industrial facilities has provided an impetus for investigation of mercury removal in wet scrubbing. The research has included physical modifications designed to improve the absorption of mercury by the scrubber liquid, testing of chemical agents selected for their potential to react with mercury, and investigation of oxidizing agents that can convert Hg into  $HgCl_2$  or another soluble species. Recent work has focused on a commercial oxidant formulation that appears to take advantage of a synergism between the removal reactions for different gas species.

The research employed Argonne's FGC-laboratory facilities that include a fixed-bed reactor system for studying dry sorbents, a complete wet scrubber system, and a spray-dryer/fabric-filter system. Supporting facilities include a system that can provide known concentrations of elemental mercury in a gas stream, a gas-supply system capable of blending synthetic flue gas from bottled gases, on-line gas-analyzers, and data loggers. Detailed descriptions of all of the systems can be found in References 4 and 5.

## EXPERIMENTAL RESULTS

### Dry Sorbents

Following initial shakedown tests that verified that neither the sand nor the lime used as diluents in the fixed bed gave any measurable mercury removal, a variety of dry sorbents were studied. Parameters studied included sorbent particle size, sorbent loading in the reactor, reactor/gas temperature, and mercury concentration [3,4]. Three fixed-bed reactor temperatures were evaluated: 55, 70, and 90°C. Target mercury concentrations in the nitrogen feed gas of either 44 or 96  $\mu\text{g}/\text{m}^3$  were used, and the feed-gas flow rate was fixed at 10 L/min.

Characteristics of some of the sorbents investigated thus far are given in Table 1. By far the best removal results for the activated carbons were obtained with sample CB-II, which was

commercially treated with about 15 wt% sulfur. The success of the sulfur-treated carbon 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 removal. To explore this possibility, another carbon sample (AC), which previously gave essentially no removal, was treated with calcium chloride in the ratio of about 6:1 by weight. The treated carbon gave excellent removals and actually performed better than the sulfur-treated carbon.

Recent research has focused on development of lower-cost alternatives to activated carbon. Tests of the last three materials in Table 1 in the as-received condition gave moderate mercury removals for the molecular sieve sample and essentially no removals for pumice and vermiculite. While the untreated pumice was ineffective for mercury removal, pretreatment with calcium chloride, potassium iodide, and sulfur produced significant removals. At 70°C, the sulfur-treated sorbent gave 100% removal for over an hour, while 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%. In order to explore the effects of temperature on the treated sorbents, additional tests were run at a temperature of 150°C. Figure 1 gives a comparison of the results at the two temperatures for the iodide- and sulfur-impregnated sorbents. The iodide-impregnated sample behaved very similarly at the two temperatures. However, the sulfur treatment that was so effective at the lower temperature was found to be totally ineffective at the higher temperature. This may be due to a change in the form of the sulfur, but this issue has not yet been resolved.

### Wet Scrubbing

Preliminary data from field-sampling campaigns have indicated that elemental mercury is not appreciably removed in typical wet-scrubber systems. This is not surprising given the very low solubility of mercury in the elemental form. Initial experiments were conducted with no packing in the scrubber and with various degrees of "flooding" in the lower part of the column to promote gas-liquid contact. The scrubbing liquors tested were distilled water, a saturated  $\text{Ca}(\text{OH})_2$  solution, and a  $\text{Ca}(\text{OH})_2$  solution with 1000 ppm of potassium polysulfide. The polysulfide has been claimed to promote mercury removal in other research [6]. The mercury inlet concentration was about 40  $\mu\text{g}/\text{m}^3$ , the liquid height in the column 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.

Addition of ceramic-saddle packing produced removals of 3 to 5% with distilled water at 22°C, and removals of 6 to 7% were obtained when the temperature was raised to 55°C. Stainless-steel packing 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%. Since the polysulfide gave no measurable removals in water alone, it appears that there is a positive synergistic effect on removal involving the combination of polysulfide and stainless steel.

In an effort to promote greater mercury capture through changing its chemical form, tests were conducted with several additives that combine strong oxidizing properties with relatively high vapor pressures. Tests with minimal gas-liquid contacting yielded mercury removals as high as 100%, and indicated that the removal reactions were occurring in the gas phase above the scrubber liquor. However, tests with the addition of  $\text{SO}_2$  to the gas stream showed the

additives to be very reactive with that species as well, which could result in excessively high additive consumption in order to realize effective mercury control.

Recently, tests have been conducted with a new combination of oxidizing chemicals, NOXSORB™, which is a product of the Olin Corporation. Typical feed-gas compositions have included 1000 ppm SO<sub>2</sub>, 200 ppm nitric oxide (NO), 15% carbon dioxide (CO<sub>2</sub>), and 33 µg/m<sup>3</sup> Hg. Figure 3 shows removal data for Hg, SO<sub>2</sub>, and NO from a batch test with a dilute (4%) solution of the as-received NOXSORB™ concentrate. An outlet reading of zero was obtained for Hg over a period of about 24 min. During that period, the NO outlet concentration decreased rapidly to near zero and then rose gradually to where it was almost equal to the inlet value. The breakthrough in the Hg concentration (the point at which the concentration rises above zero) appeared to coincide with the point at which the NO concentration leveled off. The apparent correlation between NO and Hg removals from this and other tests may imply that the mercury is reacting with a product or intermediate of the NO removal process. A moderate degree of SO<sub>2</sub> removal was also observed during the time the NOXSORB™ solution was circulating.

## 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 elemental mercury.
- Mercury removals with activated carbon decrease with increasing temperature, larger particle size, and decreasing mercury concentration in the gas.
- Chemical pretreatment can greatly increase the removal capacity of activated carbon and inert mineral substrates.
- Sorbents treated with different chemicals respond in significantly different ways to changes in flue-gas temperature.

Preliminary results from the wet scrubbing research include:

- No removal of elemental mercury is obtained under normal scrubber operating conditions.
- Mercury removal can be improved by the addition of packing or other techniques to increase the gas-liquid contact area.
- Stainless steel packing appears to have beneficial properties for mercury removal. A synergism between stainless steel and polysulfide solutions has been observed.
- Oxidizing additives may be used in conjunction with wet scrubbing to greatly enhance removals. Synergisms between the removals of different flue-gas species may yield the selectivity required to avoid excessive additive consumption.

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## REFERENCES

1. Schmidt, C.E., and T.D. Brown, 1994, *Results from the Department of Energy's Assessment of Air Toxics Emissions from Coal-Fired Power Plants*, presentation at Illinois Coal Development Board Program Committee Meeting, Nov. 15.
2. Huang, H.S., J.M. Wu, and C.D. Livengood, 1995, *Development of Dry Control Technology for Emissions of Mercury in Flue Gas*, Proc. The Fourth International Congress on Toxic Combustion Byproducts, Berkeley, Calif. June 5-7.
3. Livengood, C.D., H.S. Huang, and J. M. Wu, 1994, *Experimental Evaluation of Sorbents for the Capture of Mercury in Flue Gases*, Proc. 87th Annual Meeting & Exhibition of the Air & Waste Management Association, Cincinnati, Ohio, June 19-24.
4. Livengood, C.D., M.H. Mendelsohn, H.S. Huang, and J.M. Wu, 1995, *Development of Mercury Control Techniques for Utility Boilers*, Proc. 88th Annual Meeting & Exhibition of the Air & Waste Management Association, San Antonio, Texas, June 18-23.
5. Mendelsohn, M.H., and J.B.L. Harkness, 1991, *Enhanced Flue-Gas Denitrification Using Ferrous-EDTA and a Polyphenolic Compound in an Aqueous Scrubber System*, Energy & Fuels, 5(2):244-247.
6. Yan, T.Y., 1991, *Reaction of Trace Mercury in Natural Gas with Dilute Polysulfide Solutions in a Packed Column*, Industrial & Engineering Chemistry Research, 30(12):2592-2595.

Table 1  
Characteristics of Candidate Sorbents

Sorbent	Cost <sup>a</sup> (\$/lb)	Surface Area (m <sup>2</sup> /g)	Bulk Density (g/cm <sup>3</sup> )	Median Particle Size (μm)
AC <sup>b</sup>	0.50	1000	0.54	2000-2500 <sup>c</sup>
WPL <sup>b</sup>	0.50	894	0.57	2000-2500 <sup>c</sup>
PC-100 <sup>b</sup>	0.50	965	0.52	2000-2500 <sup>c</sup>
CB-II <sup>b</sup> (sulfur-treated)	3.90	1050	0.56	2000-2500 <sup>c</sup>
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

<sup>a</sup>Approximate - variable lot size

<sup>b</sup>Activated carbon

<sup>c</sup>Commercial specifications - samples ground to less than 100 μm for tests

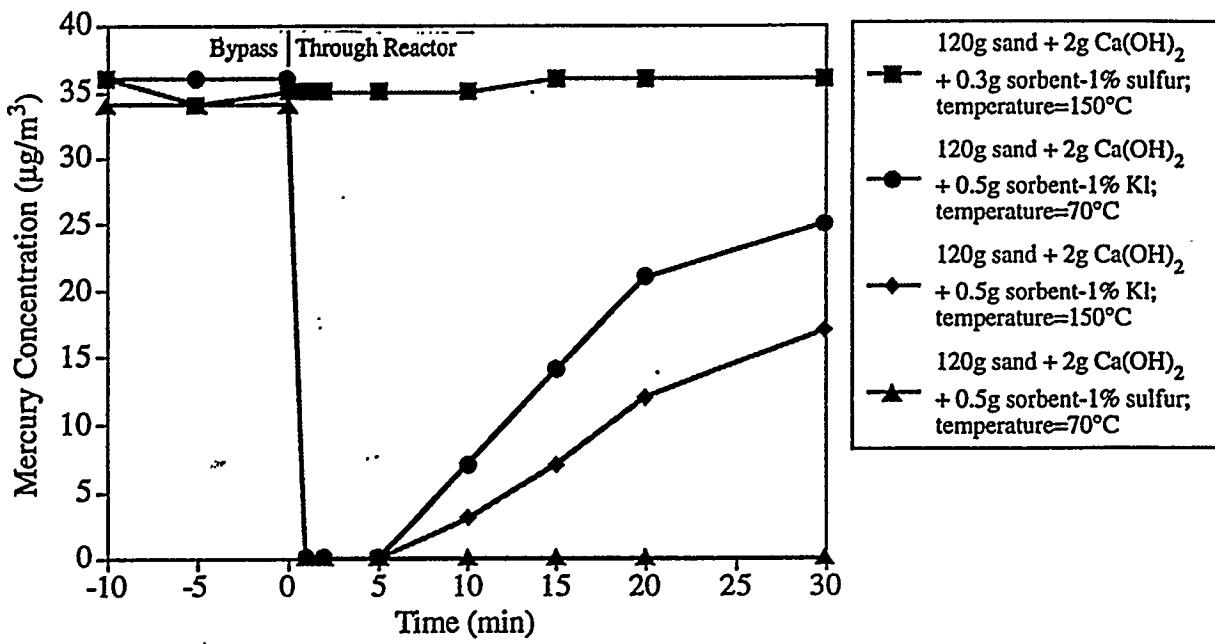


Figure 1. Effects of Different Temperatures on a Chemically Pretreated Inert Substrate

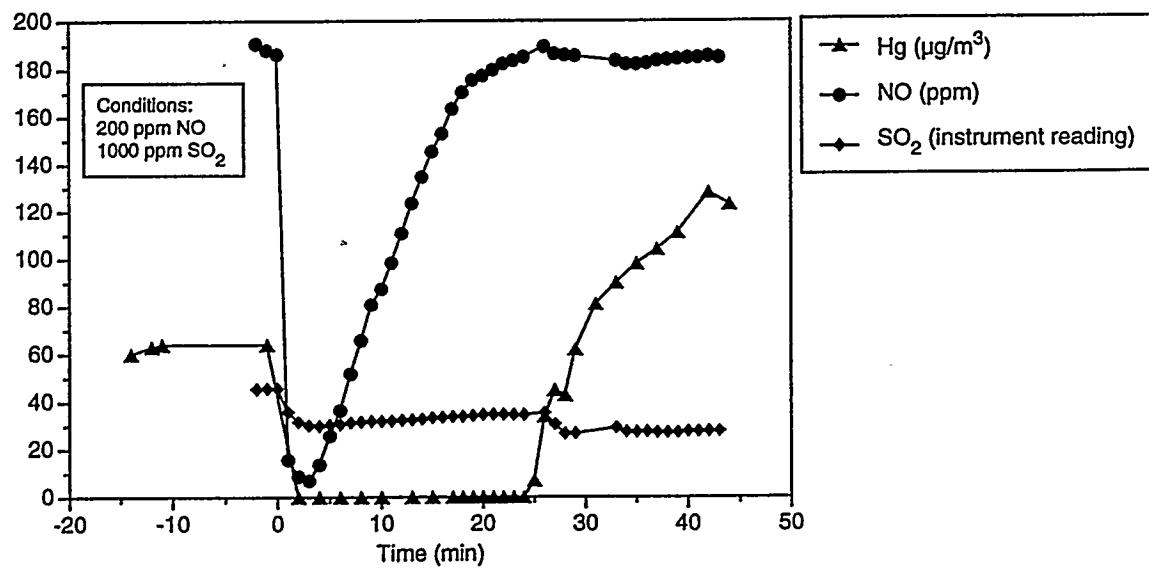


Figure 2. Removals of Hg, NO, and SO<sub>2</sub> in the Wet Scrubber with a 4% NOXSORB™ Solution