ANL/ES/CP-- 84609

CONF-950647--1

Development of Dry Control Technology for Emissions of Mercury in Flue Gas

HANN S. HUANG, JIANN M. WU, and C. DAVID LIVENGOOD

Energy Systems Division
Argonne National Laboratory
9700 South Cass Avenue
Argonne, Illinois 60439

RECEIVED
JUN 19 1995
OSTI

The Fourth International Congress
on Toxic Combustion Byproducts

Berkeley, California

June 5-7, 1995

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

Work supported by the U.S. Department of Energy, Assistant Secretary for Fossil Energy, under contract W-31-109-Eng-38.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

ABSTRACT

In flue gases from coal-combustion systems, mercury in either the elemental state or its chloride form ($HgCl_2$) can be predominant among all the possible mercury species present; this predominance largely depends on the chlorine-to-mercury ratio in the coal feeds. Conventional flue-gas cleanup technologies are moderately effective in controlling $HgCl_2$ but are very poor at controlling elemental mercury. Experiments were conducted on the removal of elemental mercury vapor by means of a number of different types of sorbents, using a fixed-bed adsorption system. Of the four commercial activated carbons evaluated, the sulfur-treated carbon sample gives the best removal performance, with good mercury-sorption capacities. Promising removal results also have been obtained with low-cost minerals after chemical treatments. These inorganic sorbents could potentially be developed into a cost-effective alternative to activated carbons for mercury removal.

INTRODUCTION

The emission of hazardous air pollutants (air toxics) from various industrial processes, singled out for particular attention in the Clean Air Act Amendments of 1990, has emerged as a major environmental issue. In particular, mercury emissions are the subject of several current studies by the U.S. Environmental Protection Agency (EPA) because of concerns over possible serious effects on human health. Some of those emissions originate in the combustion of coal, which contains trace amounts of mercury, and are likely to be the subject of control requirements in the relatively near future. Data collected by the U.S. Department of Energy (DOE) and the Electric Power Research Institute (EPRI) at operating electric-power plants have shown that although conventional flue-gas cleanup (FGC) technologies are moderately effective in controlling emissions of mercury in the chloride form, they are very poor at controlling emissions of elemental mercury vapor. Since a significant fraction of the total mercury emissions at many sites is in the elemental form, enhancements or supplemental control technologies need to be developed. Coal preparation techniques may be able to remove some of the mercury before combustion, but postcombustion technologies are likely to be needed as well.

This paper presents results from the research being conducted at Argonne National Laboratory (ANL) on the capture of mercury in flue gas from coal-combustion systems by dry sorbents. Parallel research is also being conducted at ANL on the removal of mercury by 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 reported 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; it exhibits variations that span several orders of magnitude. For example, 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) Physical coal cleaning techniques can remove a significant fraction of the mercury before combustion, but the reductions are quite coal-specific and dependent upon the particular cleaning techniques chosen.(2)

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 ranges from less than 10 to more than 50 $\mu g/Nm^3$.

Few reliable data on mercury control have been available for FGC technologies used on coal-fired systems. Large variations in reported removals have been typical, due both to differences in coals and operating characteristics and to inaccuracies in sampling/analytical procedures.(1) 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. Recent data on mercury removals for ESPs range from about 15 to 75%, while very limited removal data for baghouses range from 10 up to 70%. Mercury removal in wet flue-gas desulfurization (FGD) systems is also quite variable, with values ranging from near zero to about 50%.(3,4) Much of that variation may be caused by differences in the chemical form of the mercury, inasmuch as the chloride is much more easily captured than the elemental form.

The DOE- and EPRI-supported utility boiler air-toxics emission studies devoted significant effort to investigating the speciation of mercury forms, as well as other trace-metal forms, in the flue gases from a wide variety of utility plants. Results from these and other, prior studies have revealed that, for mercury, either the elemental mercury or the mercury dichloride ($HgCl_2$) can be the predominant species in the flue gas, depending primarily upon the chlorine content in the coal burned.(5,6) These observations can be largely explained by the results from equilibrium calculations for coal-combustion systems. As shown in Figures 1 and 2, elemental mercury is the predominant form at high temperatures, whereas its chloride form becomes predominant at low temperatures. When the relative amount of chlorine content versus mercury content in coal is high (Figure 1), the transformation of mercury into its chloride form starts to occur at about 750°C. The crossover temperature for the amounts of Hg and $HgCl_2$ in the flue gas being equal is estimated to be about 610°C. At this high temperature, the reported reaction rate is also high.(7,8) Hence, under this condition mercury chloride would be the major form of all the potential mercury species present in the gas. In contrast, when the chlorine-to-mercury ratio in coal substantially decreases (Figure 2), both the incipient and crossover temperatures for mercury chloride formation also significantly decrease. Since the rate for chemical reactions is exponentially slower with decreasing temperature, the amount of mercury chloride formed must be correspondingly less. Consequently, for typical utility boilers or other combustion devices with relatively short flue-gas residence time (on the order

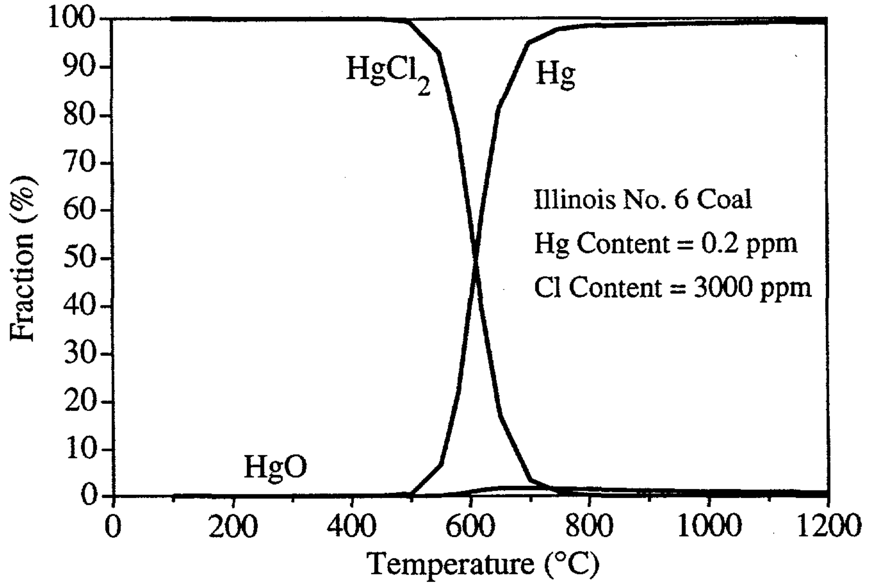

Figure 1. Equilibrium distribution of Hg species in coal combustion, Cl/Hg=15,000

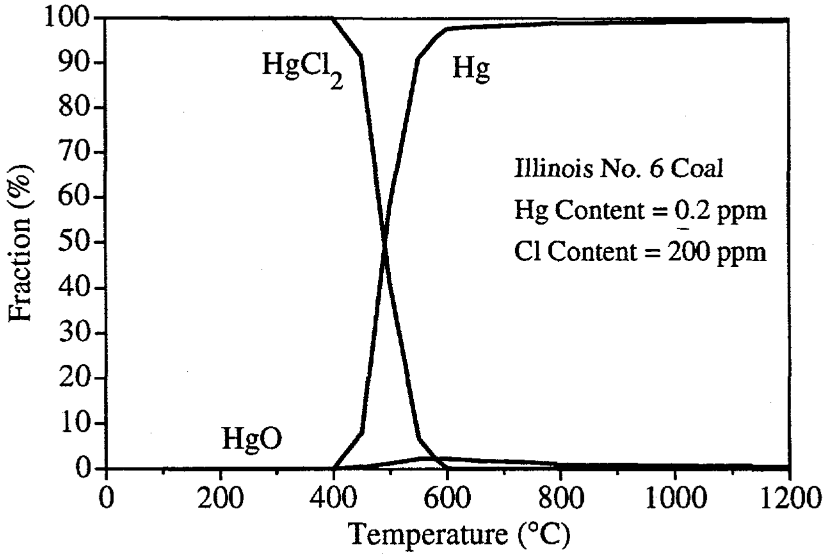

Figure 2. Equilibrium distribution of Hg species in coal combustion, Cl/Hg=1,000

of seconds) through the heat-transfer sections, elemental mercury is expected to remain as the major species so long as the chlorine-to-mercury ratio is low.

Most available information on mercury control technologies for combustion sources has originated in work with waste incinerators.(1) In such cases, activated carbon has been shown in field tests to be an effective sorbent for overall mercury removal, probably because the starting mercury levels in flue gases are high and mercury chloride is predominant because of high chlorine content in the waste materials. However, very few laboratory studies using simulated flue gas representative of compositions encountered in coal-combustion systems, and on sorbents other than activated carbon, have been reported. Since flue-gas conditions at coal-fired utility boilers are much different with respect to temperature and composition than those found at waste incinerators, the performance/economics of activated carbon and other potential sorbents can be expected to vary.

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.

On the basis of 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 used with municipal waste incinerators has indicated that greatly enhanced mercury removals are possible. A more extensive discussion of this research can be found in Reference 9.

EXPERIMENTAL SYSTEM

A schematic flow diagram of the experimental system is shown in Figure 3. It is functionally divided into three separate sections: the feed-gas preparation section, the fixed-bed reactor section, and the gas-analysis section. The entire experimental apparatus, with the exception of the carrier-gas supply and the mercury vapor analyzer, is housed inside a glass-paneled vented hood to minimize the risk of any exposure to mercury vapor by the laboratory personnel. A description of the individual sections is provided below.

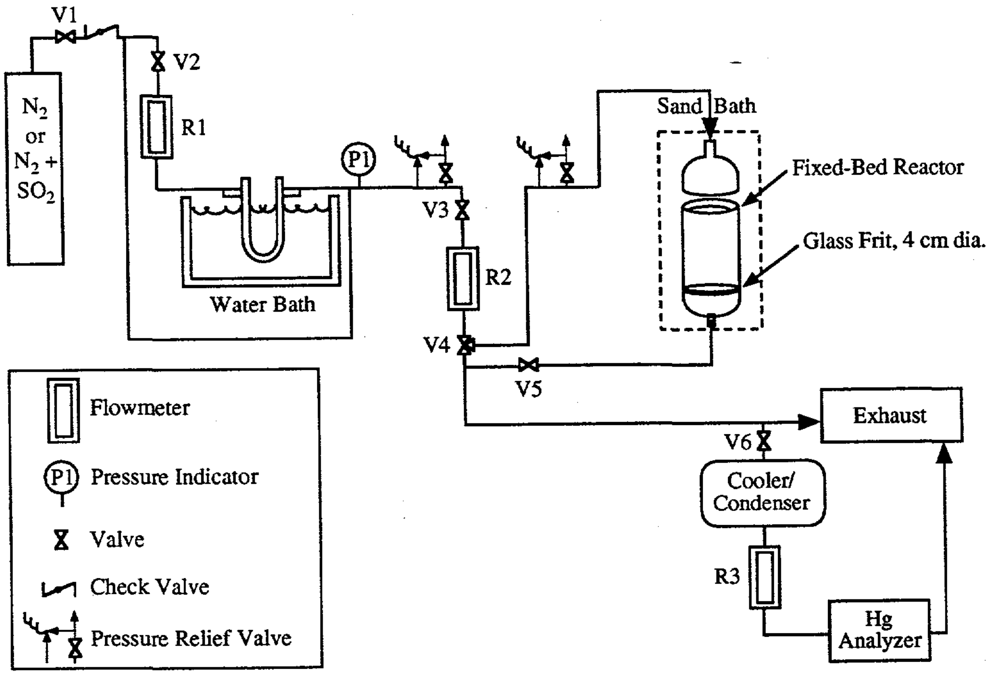

Figure 3. Schematic diagram of fixed-bed reactor facility

Feed-Gas Preparation Section

The feed-gas preparation section 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 μg/m^3. The use of permeation tubes was selected 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 compared with other techniques. 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. After recombination, the mercury-containing feed gas is directed to the fixed-bed reactor section.

Five mercury-containing permeation tubes in various lengths have been procured from VICI Metronics of Santa Clara, California. Three of the tubes are certified (NIST-traceable). At the suggested operating temperature of 70°C, the permeation rate for the tubes was determined to be about 70 ng/min per centimeter of length. Nitrogen or nitrogen/sulfur dioxide mixture from cylinders has been used to supply the feed gas. If desired for later work, however, the mercury-vapor generation device can be integrated into another existing feed-gas preparation system that can provide a feed gas with a composition representative of coal-combustion flue gas.

Fixed-Bed Reactor Section

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 ($Ca(OH)_2$) in a weight ratio of 40:1. The $Ca(OH)_2$ has been 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. For additive/sorbent testing, small amounts of material being studied are added to the sand/$Ca(OH)_2$ bed material.

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.

Gas-Analysis Section

Mercury measurements are made by using 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 (SO_2), carbon dioxide, etc.) usually present in flue gas. However, some sensitivity to SO_2 (when oxygen is also present) at concentrations commonly found in flue gas has been revealed in our work, and suitable compensation must be made. For mercury, the range of the instrument is 0 to 999 $\mu g/m^3$, with a sensitivity of 3 $\mu g/m^3$ and an accuracy of $\pm$ 5% at 100 $\mu g/m^3$.

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.

Measurements of other flue-gas species, such as SO_2, nitrogen oxides, carbon dioxide, and oxygen, can be made by using a conventional flue-gas analysis package, described in some detail in Reference 10.

RESULTS AND DISCUSSION

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 sorbent/additive experiments, a series of experiments was conducted with the fixed-bed reactor empty, filled with sand (120 g), or filled with sand plus $Ca(OH)_2$ (117 g plus 3 g) as the bed materials. Reagent-grade $Ca(OH)_2$ was used. These experiments were run at two bed temperatures (70 and 90°C) and one mercury concentration level (100 $\mu g/Nm^3$). 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 Sorbents/Additives

Various sorbents and chemical additives for mercury removal have been reported in the literature. These include activated carbon, 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 were 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 has included investigation of the effects of varying process parameters, such as sorbent particle size, sorbent loading in the reactor, reactor/gas temperature, and mercury concentration.[4] For most of the tests, the amounts of sorbent added ranged from 1 to 10 wt% (relative to the lime). Three fixed-bed reactor temperatures were evaluated: 55, 70, and 90°C. Target mercury concentrations in the feed gas of either 44 or 96 $\mu g/m^3$ were used, and the feed-gas flow rate was fixed at 10 L/min.

Initial experiments were directed towards the evaluation of commercially available activated carbon sorbents. Recently, the research has been focused on the development and testing of lower-cost alternatives to activated carbon for mercury control. The physical characteristics of some of the materials that have been investigated are summarized in Table 1.

Table 1. Physical Characteristics of candidate sorbents/substrates

Sorbent/ Substrate	Surface Area (m^2/g)	Bulk Density (g/mL)	Median Particle Size (μm)
AC/AC	1000	0.54	41
AC/WPL	894	0.57	13.4
AC/PC-100	965	0.52	17.6
AC/CB-II	1050	0.56	12
M-SIV	645	0.52	3.8
Vermiculite	12.9	0.18	580
Pumice	8.2	1.23	21

Activated Carbon (AC) Sorbents:

Four activated carbons from different manufacturers have been evaluated. Results from the experiments with activated carbon AC displayed very little mercury removal, as shown in Figure 4. Since mercury removal capacity for this material was reported by the supplier, additional tests with increased amounts of the material were also conducted. Mercury removal 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 when the amounts of mercury observed in the effluent stream were 10% of the starting level) was still short. These results suggest that activated carbon AC would not be a cost-effective sorbent for mercury control under the conditions studied.

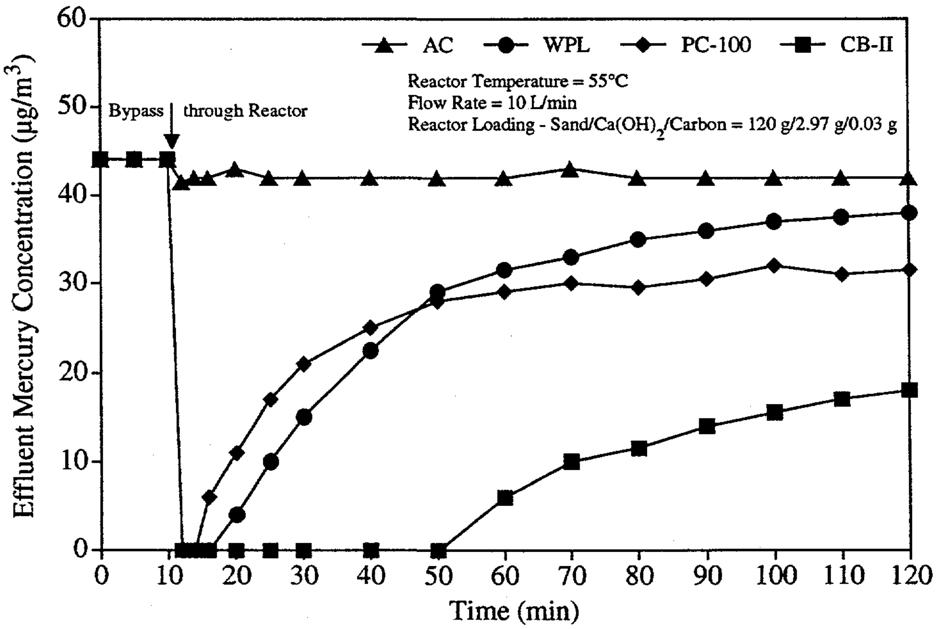

Figure 4. Mercury breakthrough curves for different activated carbons

The other activated carbon materials gave considerably better performance, with essentially 100% removal for periods of time ranging from about 5 min up to nearly 40 min. The best removal results were obtained with activated carbon CB-II, which was commercially treated with about 15 wt% sulfur. Mercury sorption capacities at two operating temperatures for each activated carbon up to the breakthrough point are compared in Figure 5; the improved performance of CB-II is also evident. Also shown in the figure is the strong effect of temperature on capacity, with a gain of an order of magnitude with 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.

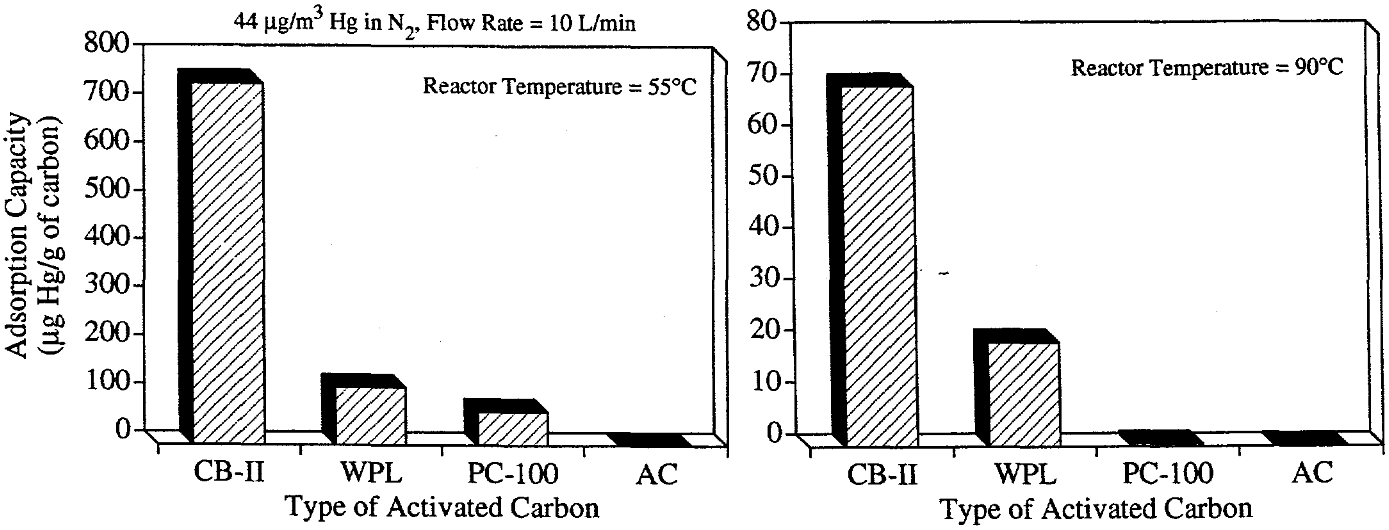

Figure 5. Comparison of adsorption capacities at two different temperatures

The effects of both temperature and mercury concentration are explored in Figure 6 for sorbent CB-II. Again, 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 driving force provided by the higher concentration.

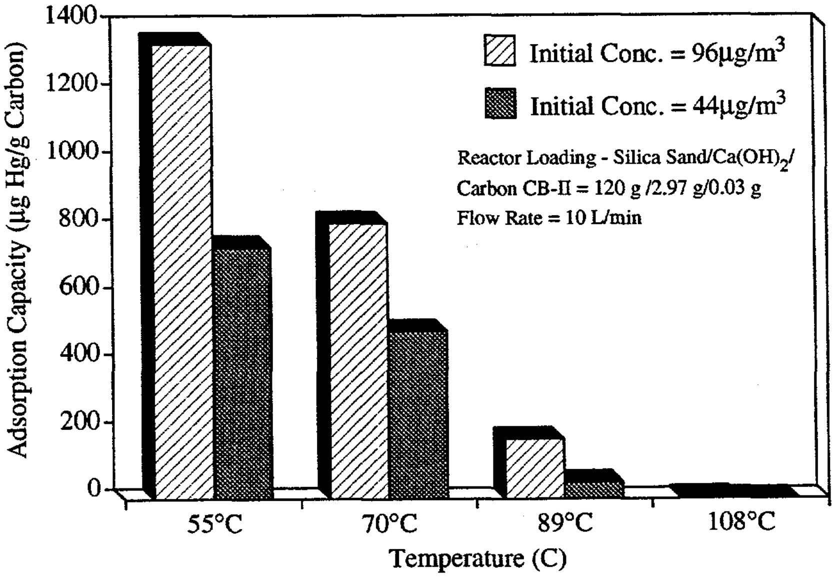

Figure 6. Effects of temperature and concentration on adsorption capacity

The effects of particle size and sorbent loading are illustrated in Figures 7 and 8 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 µm and smaller, giving initial removals of essentially 100% versus removals of about 50% or less for particles larger than about 40 µm. As expected, increasing the loading of the sorbent in the reactor also improves removal performance (Figure 8). At the specified operating temperature and particle size, 100% mercury removals were obtained as the loading was increased over 0.06 g.

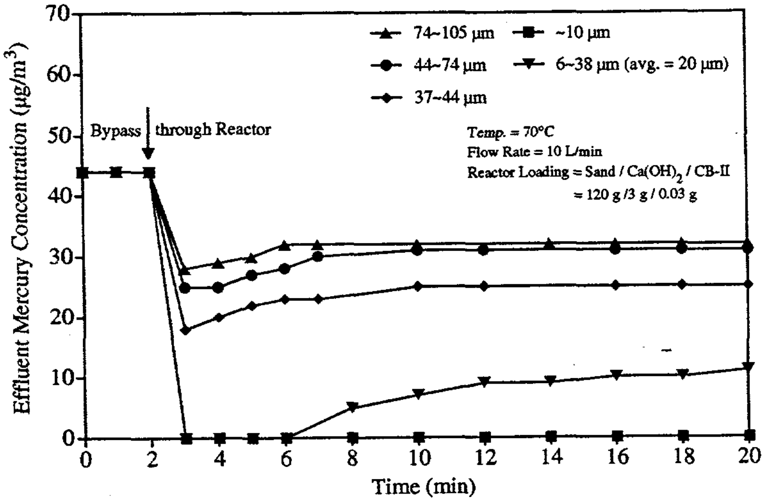

Figure 7. Effect of carbon particle size on mercury removal

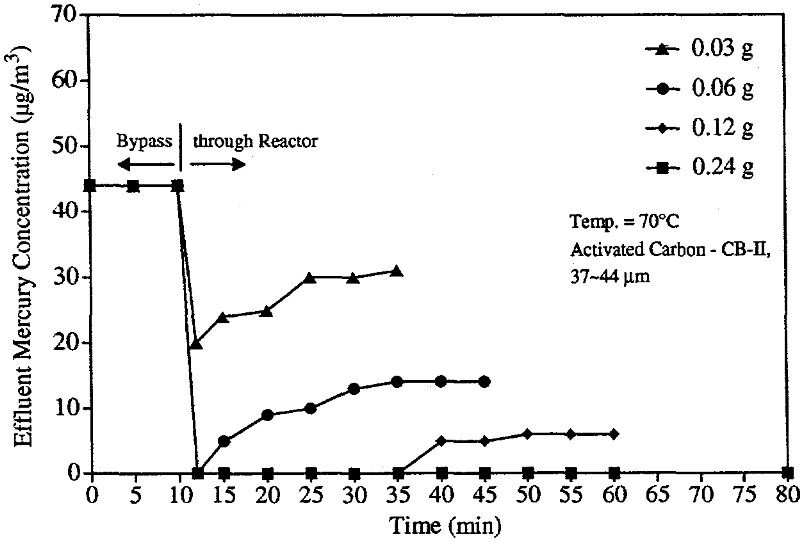

Figure 8. Effect of sorbent loading on mercury removal

The coal-combustion flue gas normally contains a significant amount of sulfur dioxide (SO_2). A series of experiments was performed to evaluate whether the presence of SO_2 in the feed gas may affect the CB-II sorbent performance. At a SO_2 concentration level of 1000 ppm in the feed gas, the results indicated that there was no significant effect on the sorbent performance.

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 sample 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

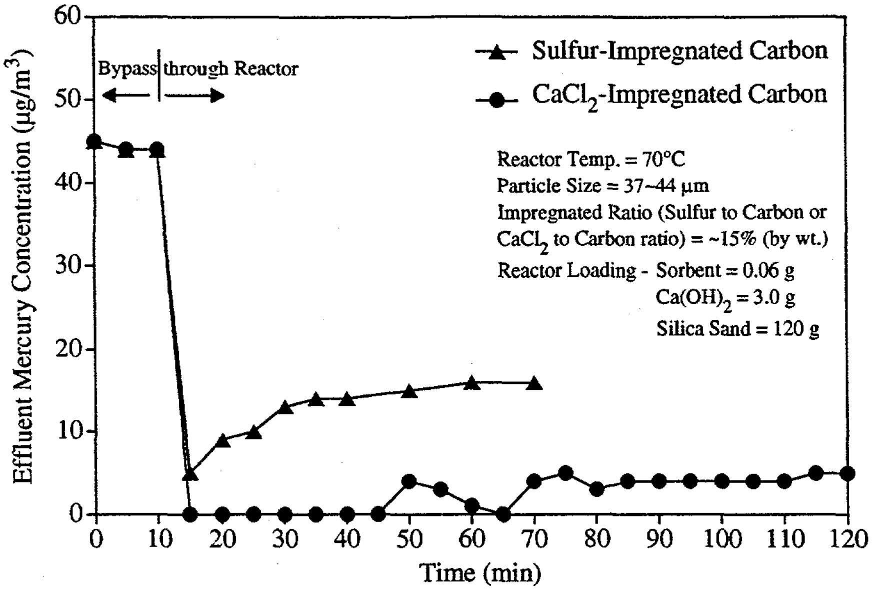

Figure 9. Comparison of mercury removals by carbon treated with sulfur or $CaCl_2$

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 9 shows that the chloride-treated carbon still gave good removals and actually performed better than carbon CB-II.

Inorganic Materials

Several high-surface-area or low-cost mineral substrates have been identified, and samples have been obtained. 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 concentrations, mercury concentrations, and flue-gas temperatures. Figure 10 gives the results of experiments with volcanic pumice treated with $CaCl_2$, potassium iodide (KI), and 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%.

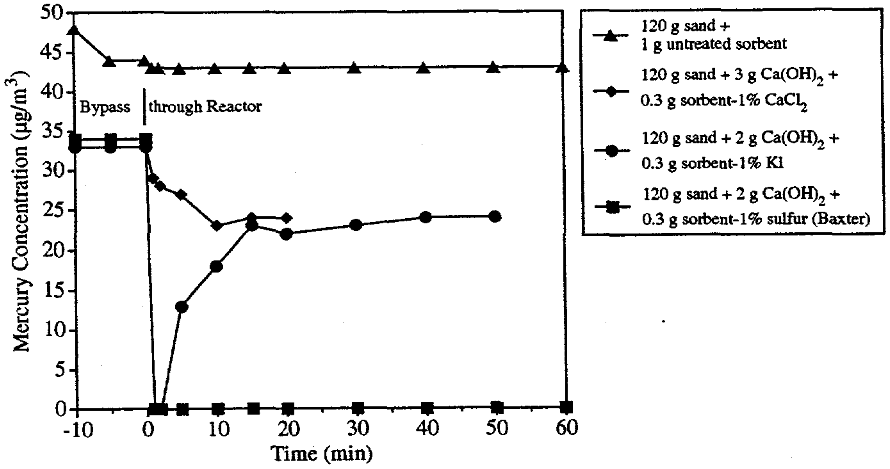

Figure 10. Effects of chemical pretreatment on an inert substrate at 70°C

As noted previously, flue-gas temperature has been shown to be a particularly important variable in mercury capture. In order to explore the effects of temperature on the treated sorbents, additional tests were run at a temperature of 150°C. Figure 11 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 is still under study and has not yet been resolved.

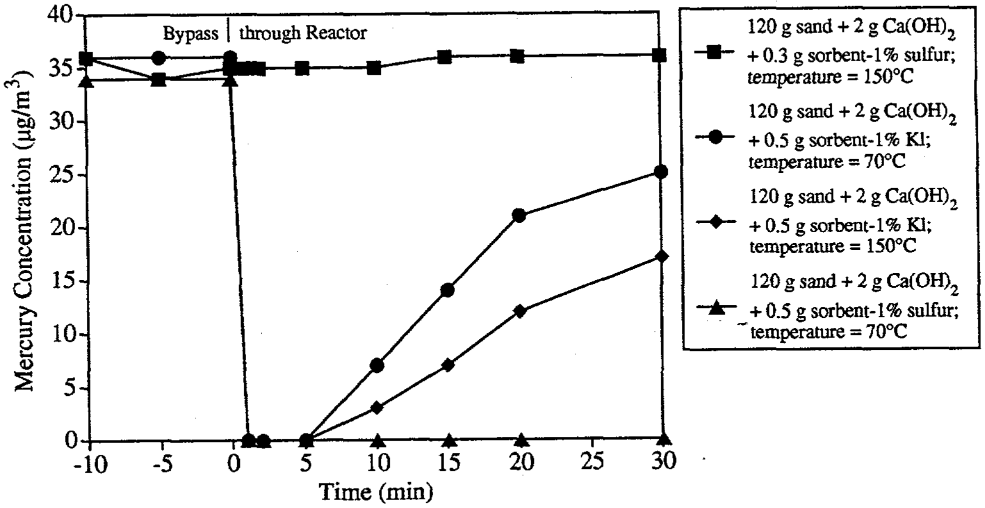

Figure 11. Effects of temperature on chemically treated inert substrate

CONCLUSIONS

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

- Either elemental mercury or its chloride form can be the predominant form in coal-combustion flue gas; very little of the elemental mercury is removed by conventional FGC systems.
- Lime hydrates, either regular or high-surface-area, are not effective in removing elemental mercury.
- Mercury removals are enhanced by the addition of activated carbon.
- Mercury removals with activated carbon increase with decreasing temperature, smaller particle size, increasing sorbent loading, and increasing mercury concentration in the gas.
- Chemical pretreatment (e.g., with sulfur or $CaCl_2$) can greatly increase the removal capacity of activated carbon.
- Chemically treated mineral substrates have the potential to be developed into effective and economical mercury sorbents.
- Sorbents treated with different chemicals respond in significantly different ways to changes in flue-gas temperature.

ACKNOWLEDGMENTS

The work reported here is supported by the U.S. Department of Energy, Assistant Secretary for Fossil Energy, under contract W-31-109-Eng-38. The authors gratefully acknowledge the guidance and support for this research provided by Perry Bergman, Charles Schmidt, and Charles Drummond of the Pittsburgh Energy Technology Center. Appreciation is also extended to Professor Tom C. Ho of Lamar University for providing us with a copy of the software used in the equilibrium calculations for coal-combustion systems and to Sherman Smith for his contributions to the laboratory operations.

REFERENCES

1. Huang, H.S., C.D. Livengood, and S. Zaromb, *Emissions of Airborne Toxics from Coal-Fired Boilers: Mercury*, Argonne National Laboratory report ANL/ESD/TM-35 (1991).

2. Toole-O'Neil, B., and D. Akers, *Precombustion Control of Air Toxics*, presentation at The Economic and Environmental Aspects of Coal Utilization VI, The Engineering Foundation, Santa Barbara, Calif., Jan. 29 - Feb. 3, 1995.

3. Schmidt, C.E., and T.D. Brown, *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, 1994.

4. Schmidt, C.E., M. Baird, and P. Chu, *Hazardous Air Pollutants (HAPs) Emissions Characterization*, presentation at the 1995 SO_2 Control Symposium, Miami, Fla., March 28-31, 1995.

5. Bush, P.V., Southern Research Institute, personal communication, April 19, 1995.

6. Meij, R., *The Fate of Mercury in Coal-Fired Power Plants and the Influence of Wet Flue-Gas Desulfurization*, Water, Air, and Soil Pollution, 56(4):21-33 (1991).

7. Hall, B., O. Lindqvist, and E. Ljungstrom, *Mercury Chemistry in Simulated Flue Gases Related to Waste Incineration Conditions*, Environ. Sci. Technolo., 24(1):108-111 (1990).

8. Hall, B., P. Schager, and O. Lindqvist, *Chemical Reactions of Mercury in Combustion Flue Gases*, Water, Air, and Soil Pollution, 56(4):3-14 (1991).

9. Livengood, C.D., H.S. Huang, and J. M. Wu, *Experimental Evaluation of Sorbents for the Capture of Mercury in Flue Gases*, Proc. 87th Annual Meeting and Exhibition of the Air & Waste Management Assn., Cincinnati, Ohio, June 19-24, 1994.

10. Mendelsohn, M.H., and J.B.L. Harkness, *Enhanced Flue-Gas Denitrification Using Ferrous•EDTA and a Polyphenolic Compound in an Aqueous Scrubber System*, Energy & Fuels, 5(2):244-247 (1991).