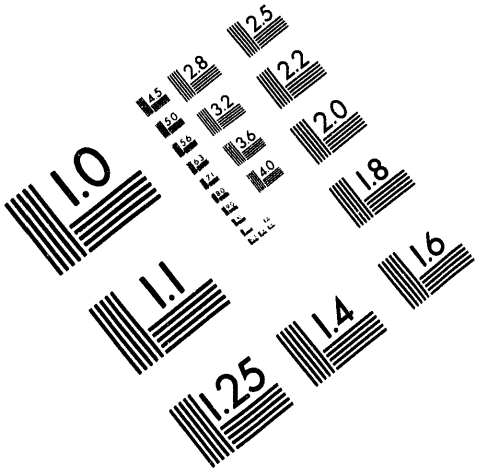

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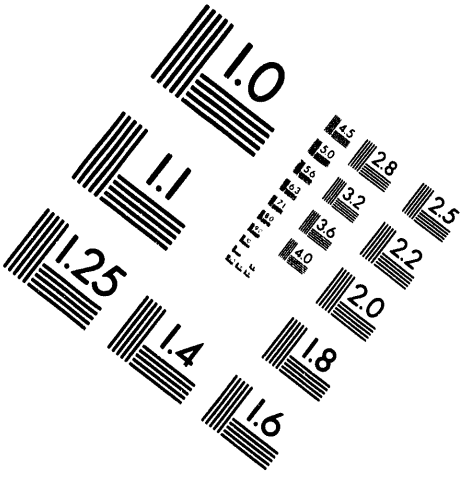

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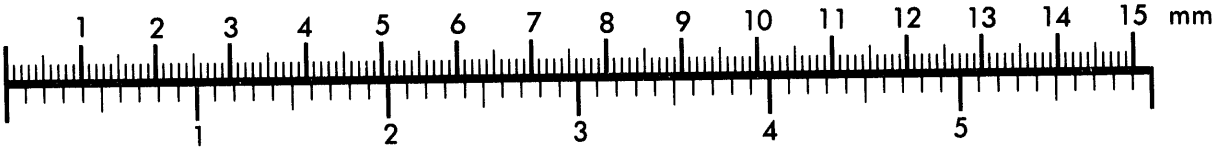

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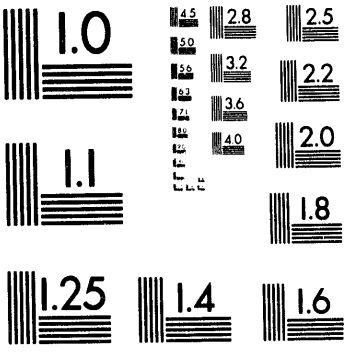

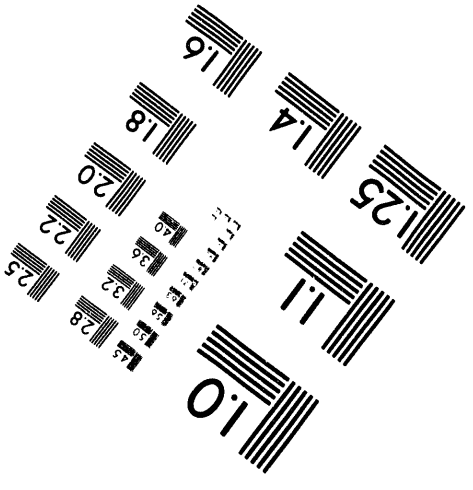

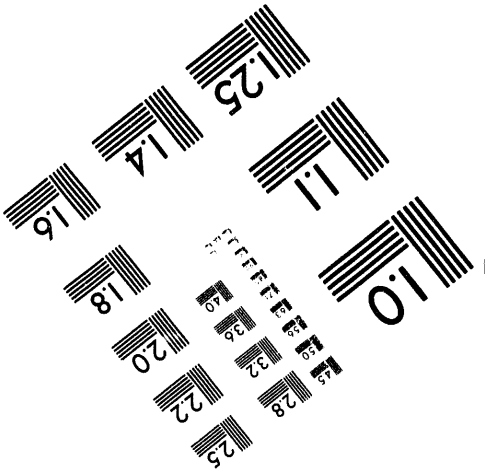

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Experimental Evaluation of Sorbents for the Capture of Mercury in Flue Gases

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INTRODUCTION

Concerns over emissions of hazardous air pollutants (air toxics) have emerged as a major environmental issue. The authority of the U.S. Environmental Protection Agency (EPA) 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 possible 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 elemental mercury, and enhancements or supplemental technologies need to be developed.

The *Development of Advanced Environmental Control Technology* project at Argonne National Laboratory is designed to investigate new concepts leading to advanced control technologies for fossil-energy systems. Within that project, specific research tasks have focused on the development of combined NO_x/SO_2 control technologies, evaluation of waste/by-product materials from advanced FGC systems, and development of new or improved control measures for the abatement of air toxics emissions from fossil-fuel combustion. The last task, upon which this paper is based, also includes the evaluation of any possible effects of captured species on waste disposal, as well as the evaluation of measuring techniques and instruments.

This paper gives a brief overview of potential mercury emissions from coal combustion, the research strategy being followed at Argonne, and results from the experiments carried out thus far on sorbents for mercury capture. Future work is expected to emphasize development of fundamental information on the factors governing the control of mercury, new or modified FGC process concepts, and preliminary economic estimates.

BACKGROUND

The potential for mercury emissions from coal combustion varies considerably from site to site due to differences in coal composition and combustors. It is well known that the chemical composition of coal is highly variable, even within a given seam. The measured concentrations of mercury are no exception, displaying variations that span several orders of magnitude. Bituminous and anthracite coals have the highest mean mercury concentrations, 0.21 and 0.23 ppm, respectively. However, a range in concentrations of 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 concentrations also vary according to geographic region, with coals from the Appalachian and Gulf states having the highest mean

concentrations (0.24 ppm) and those from the Rocky Mountain states and Alaska having the lowest mean values (0.09 and 0.08 ppm, respectively).

The fate of trace elements in the combustion process is influenced by the type of boiler, the operating conditions, and the FGC system, as well as by the concentration of the elements in the coal. 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 $\mu g/Nm^3$.

Few reliable data have been available on the performance of FGC technologies for mercury control. 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 in the gas stream or is converted to another chemical form that can be collected. 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, the chloride form being much more easily captured than the elemental form.

Better data are expected to be available soon for various coals, combustors, and FGC systems as a result of extensive sampling efforts carried out by the U.S. Department of Energy and the Electric Power Research Institute (among others). However, it is likely that large variations will continue to be the norm and that some form of control enhancement or 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. As a result of that 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 the initial laboratory investigations. 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 improved mercury removals are possible. Finally, it was felt that development and validation of experimental procedures on relatively simple dry systems would expedite the acquisition of both useful data and needed laboratory expertise.

Experimental Facility

In order to be able to screen a variety of chemical additives/sorbents and a range of process variations in a rapid and economical manner, a laboratory-scale fixed-bed reactor facility has been designed and constructed at Argonne. A schematic flow diagram of the facility is shown in Figure 1. It is functionally divided into three separate sections: the feed-gas preparation system, the fixed-bed reactor system, and the gas-analysis system. 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 laboratory personnel.

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 $\mu g/m^3$. 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 than 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 is diverted to and flows through the mercury-generation device and is then recombined with the other portion of the feed gas downstream. 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) for calibration purposes. 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 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, made of glass, is 4 cm in diameter and 14 cm in height. To facilitate tubing connection and disconnection, threaded glass fittings are used at both the inlet and outlet ends of the reactor. A glass frit is positioned in the lower section to support the materials placed inside the reactor. 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 $Ca(OH)_2$ 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. For additive/sorbent testing, small amounts of chemicals are being added to the sand/$Ca(OH)_2$ bed material.

To preheat the incoming feed gas to a preselected operating temperature equal to that maintained in the fixed-bed reactor, the gas-transfer line is wrapped with heating tapes. A thermocouple is placed at the end of the preheating section, and its reading is fed back to a temperature controller (Omega CN9000), which regulates the power input to the heating tapes. To avoid fluidization of the bed materials, the preheated feed gas enters the reactor from the top and exits at the bottom. The reactor effluent gas is

then piped in Teflon® tubing to the gas-analysis section. At the beginning of each experiment, the mercury concentration in the feed gas is determined by directing the untreated feed gas into the gas-analysis section. After each experiment is completed, the mercury concentration in the feed gas is checked again to ensure that the desired mercury concentration has been maintained throughout the experiment. Thus far in the experimental program, the feed system has exhibited excellent stability with respect to the feed concentration.

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 bath liner is a cylindrical stainless-steel vessel of welded construction, with an inside diameter of 23 cm and a useable depth of 35 cm. This vessel is suspended in, but thermally insulated from, an outer mild-steel cylindrical container. To support the alundum bed material, a porous plate, made of sintered mesh stainless steel, is mounted across the vessel between compression flanges. Heating is provided by four 1-kW, inconel-sheathed electric heating elements mounted just above the porous plate. A control valve for the fluidization air is provided at the side of the bath. The normal operating-temperature range for the unit is from 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.

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

After extensive evaluation, a gold-film mercury-vapor analyzer (Jerome 431X) was procured from the Arizona Instrument Corp. of Tempe, Arizona. This analyzer uses a patented gold-film sensor for the detection and accurate measurement of mercury vapor in gas streams. The gold-film sensor is said to be inherently stable and selective to mercury, hence eliminating potential interferences by other compounds (water vapor, SO_2, CO_2, etc.) commonly present in flue gas. The range of the instrument is stated to be from 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 offgas stream from regeneration is also piped to the exhaust system. The operating temperature range for this analyzer is stated to be from 0 to 40 °C. Therefore, a simple glass cold trap is installed upstream of the analyzer.

The project also evaluated a mercury-vapor monitor that has recently been offered by EPM Environmental, Inc., of Mt. Prospect, Illinois. This monitor is based on a dual-beam ultraviolet (UV) photometer and advanced electronics that are reported to give it an accuracy and sensitivity 10 times better than commercial mercury monitors that use single-beam UV photometers. Preliminary experiments indicated that the sensitivity of this unit is comparable with that of the gold-film analyzer, but it is somewhat more stable than the gold-film unit. The performance of UV-based units, however, is known to be interfered with by some of the constituents present in coal-combustion gas. The impact of these gaseous constituents on the performance of these two types of mercury analyzers will be evaluated in future research.

Experiments

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 $Ca(OH)_2$ (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 $\mu g/Nm^3$). Results from these experiments indicated that 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 in the baseline experiments. Again, no significant mercury removal was observed.

Experiments with Chemical Additives. Various chemical additives for mercury removal have been reported in the literature. They 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 have been 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/$Ca(OH)_2$ 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 $\mu g/m^3$ was used, and the feed-gas flow rate was fixed at 10 L/min.

Results from the experiments with activated carbon AC displayed very little mercury removal, as shown in Figure 2. Since mercury removal capacity for this material was reported by the supplier, additional experiments with greater amounts of carbon were also conducted. Mercury removal was found to remain very low even as the amount of carbon was increased to 3 g (no $Ca(OH)_2$ in the bed material). Mercury removal of greater than 90% was indeed observed when 20 g or more of this activated carbon was added to the bed material. However, the breakthrough time (defined as the time when measurable amounts of mercury were observed in the effluent stream) was relatively short, at about 30 min. These results suggest that this activated carbon would not be a cost-effective sorbent for mercury control under the conditions studied in this project.

The other carbon 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 improved performance of this treated carbon is also illustrated in Figure 3, which compares the cumulative mercury

removal for each carbon up to the breakthrough point. Note the strong effect of temperature on capacity, with a gain of an order of magnitude with a reduction in temperature from 90 to 55 °C. The relative superiority of CB-II with respect to the other carbons also appears to be enhanced by the lower temperature.

The effects of both temperature and mercury concentration are explored further in Figure 4 for sample 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 absorption driving force provided by the higher concentration.

In Figure 5, the effects of different particle sizes are illustrated for sample CB-II. In general, smaller sizes give better removal capacity. The effect seems to be particularly strong for particle sizes of 20 μm and below, giving initial removals of essentially 100% versus removals of about 50% or less for particles larger than about 40 μm.

Increasing the loading of carbon in the reactor should also improve removal capacity, and this is borne out in Figure 6, which gives results for carbon loadings ranging from about 1% to nearly 10% of the $Ca(OH)_2$ by weight. It should be noted that with the reactor design being used, very low sorbent loadings not only reduce the total material available for adsorption, but also make it more likely that the gas can pass through the reactor without encountering any sorbent ("bypassing").

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. Figure 7 compares removals for sample AC (essentially no removal), lime combined with calcium chloride ($CaCl_2$) (about 40% removal), and sample AC 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 8 shows that the chloride-treated carbon still gave good removals, but that it did not equal the performance of CB-II. Nevertheless, the potential of this approach to produce inexpensive, effective sorbents is such that further investigations are planned.

CONCLUSIONS

The results and conclusions to date from the Argonne research program on air toxics (mercury) control can be summarized as follows:

- Mercury emissions from coal-fired combustors are generally in the range of 10-70 $\mu g/m^3$ and are highly variable.
- Existing FGC technologies are only partially effective in controlling mercury emissions.
- 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 (with sulfur or $CaCl_2$) can greatly increase the removal capacity of activated carbon.

RESEARCH DIRECTIONS

The investigation of activated carbons in the fixed-bed reactor is continuing, with particular emphasis on various chemical pretreatments. In addition, several candidate noncarbon sorbents have been identified, and test programs have been initiated. 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.

ACKNOWLEDGMENTS

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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 (Sept. 1991).

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

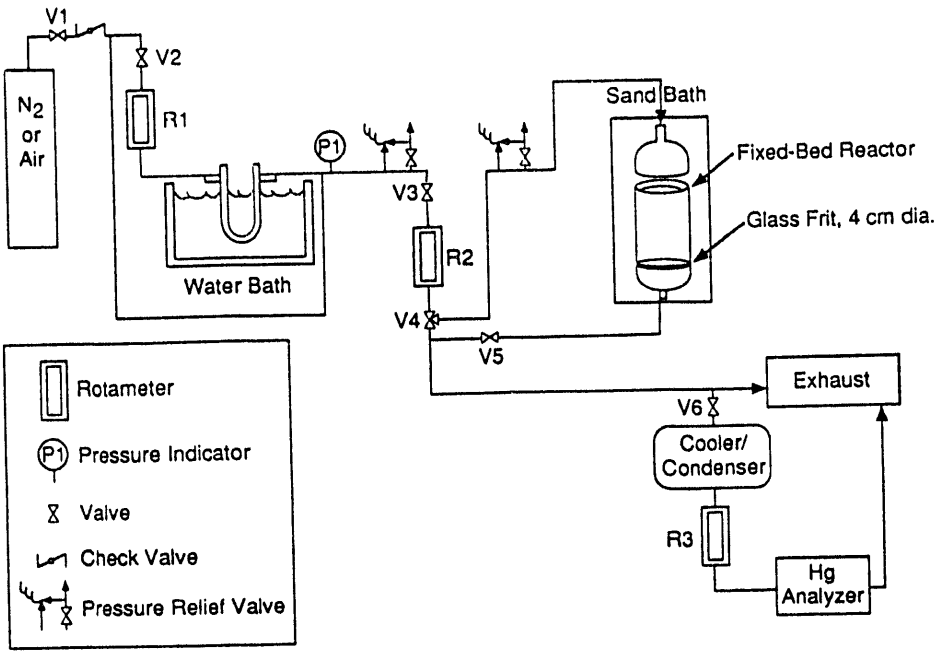

Figure 1. Fixed-bed reactor facility.

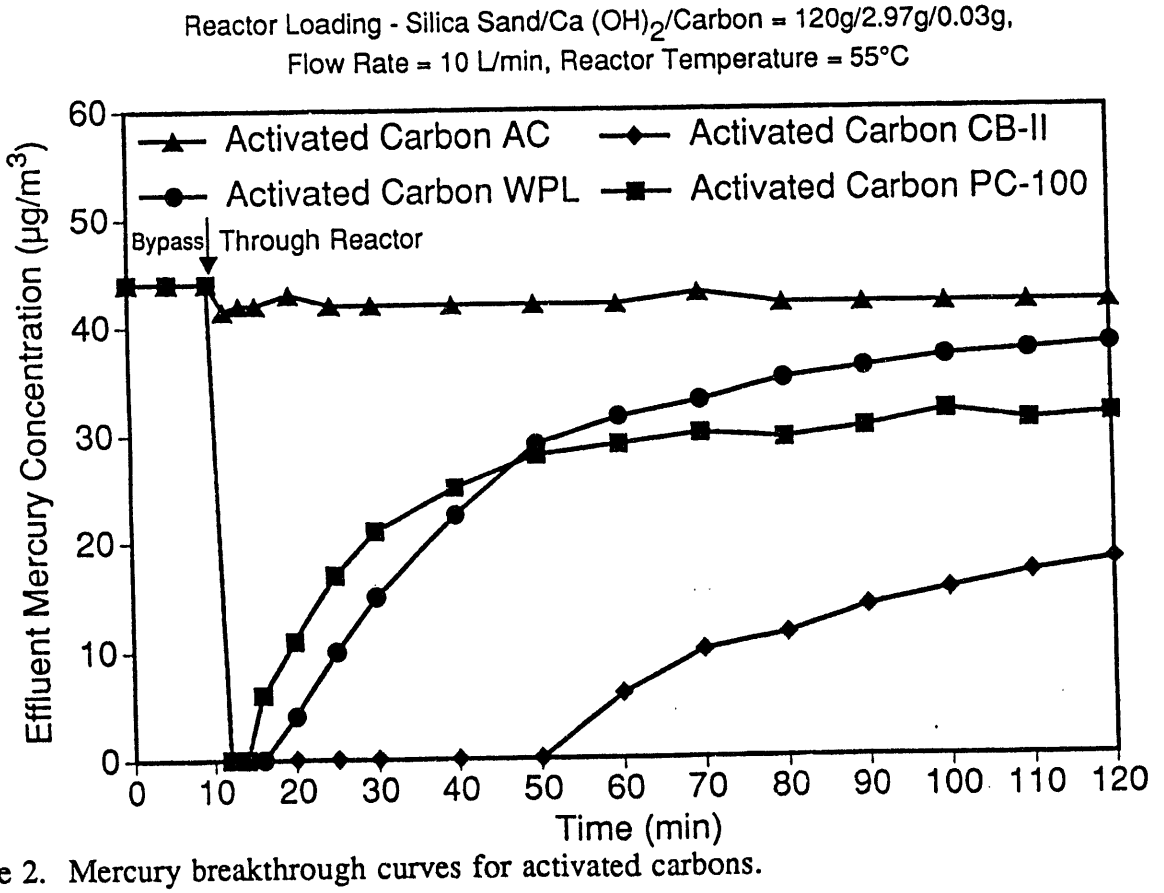

Figure 2. Mercury breakthrough curves for activated carbons.

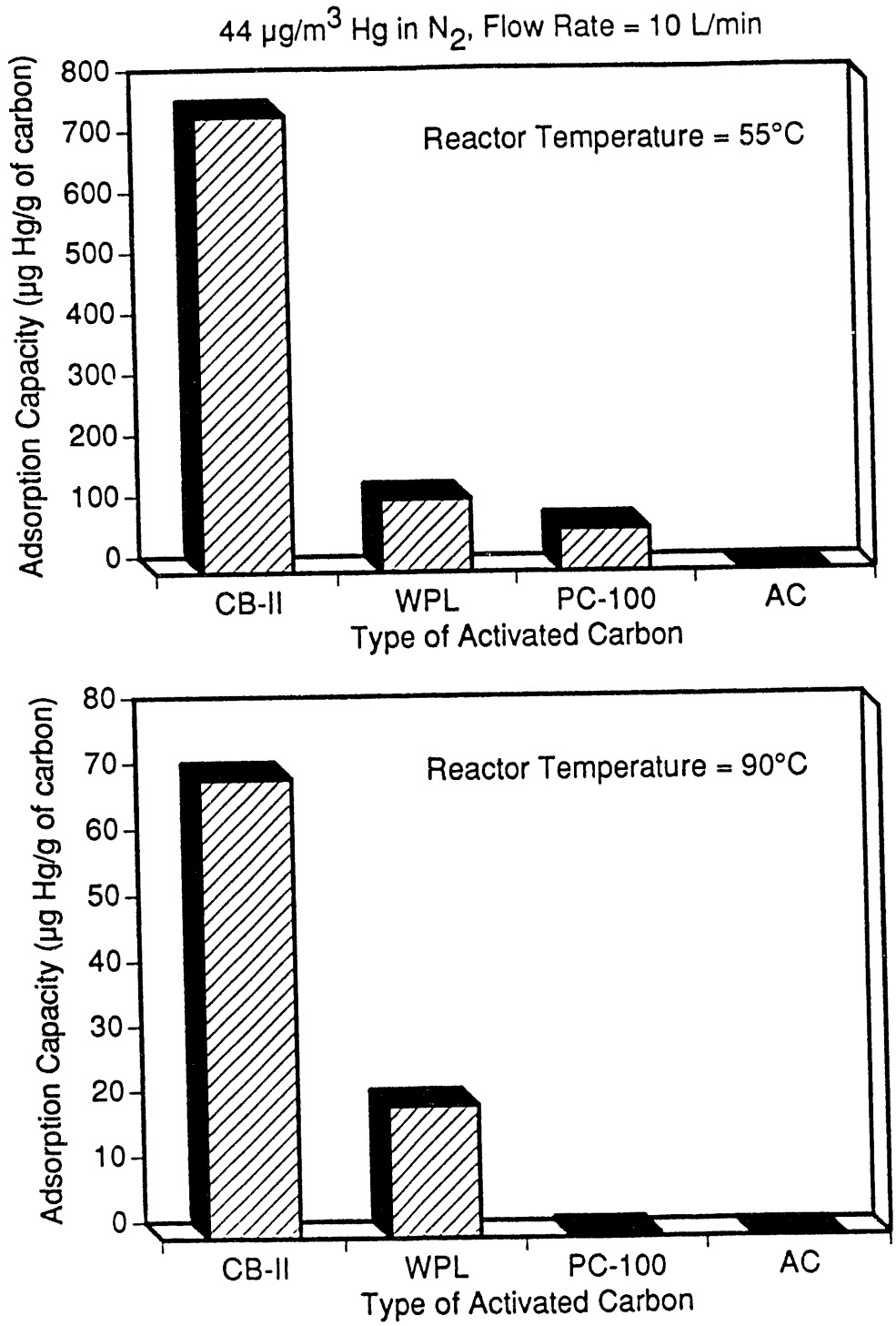

Figure 3. Comparison of adsorption capacities at two different temperatures.

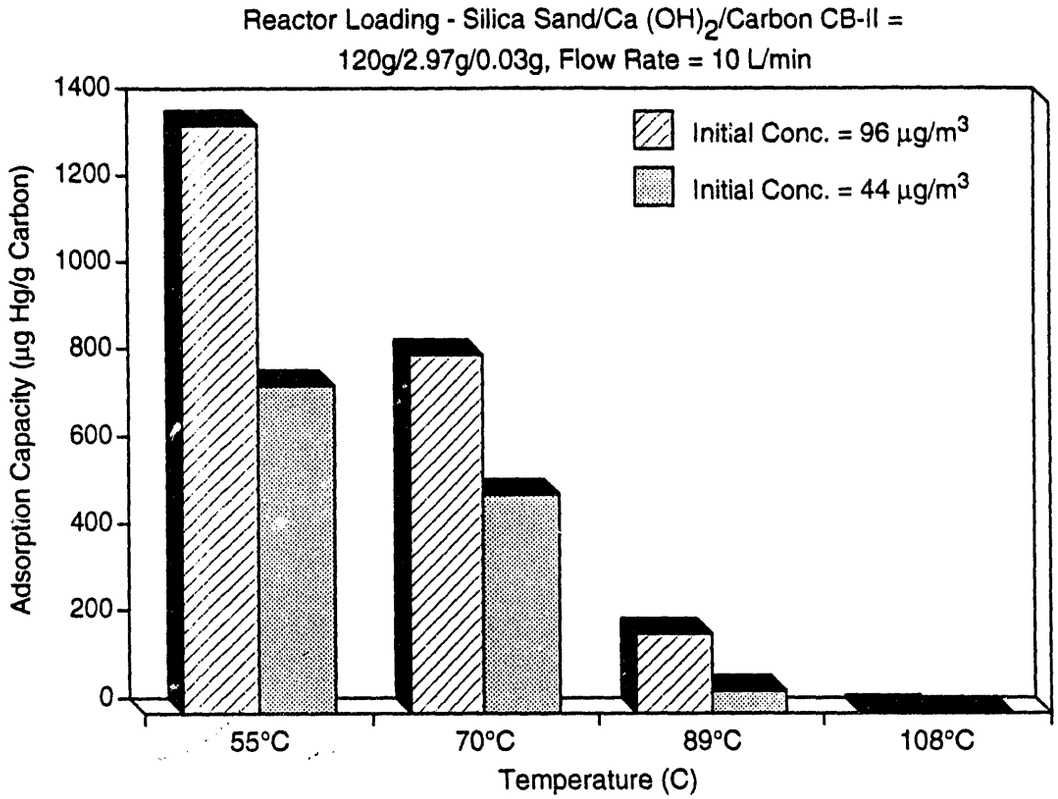

Figure 4. Effects of temperature and mercury concentration on adsorption capacity.

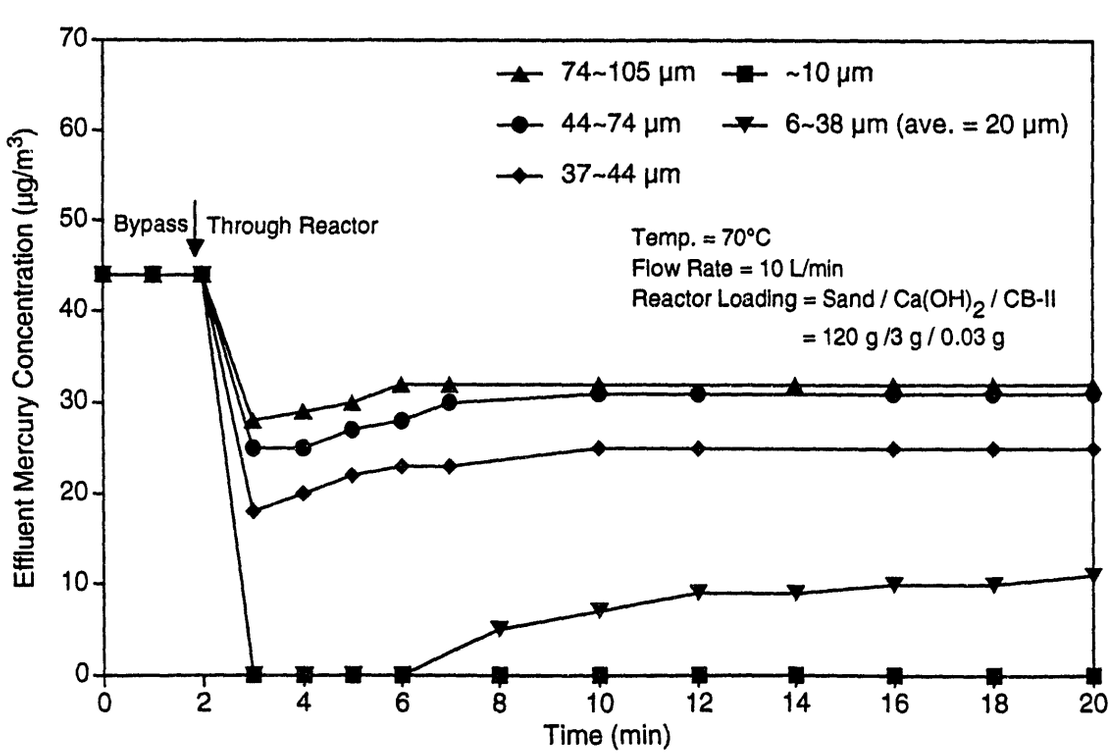

Figure 5. Effect of carbon particle size on mercury removal.

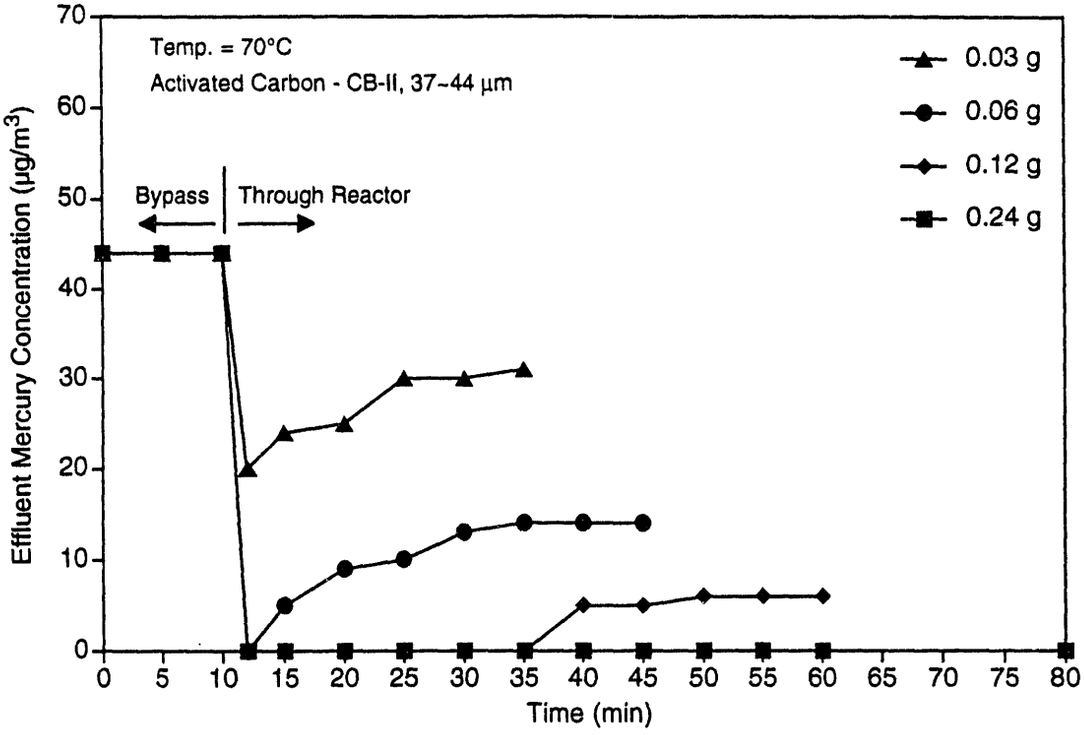

Figure 6. Effect of reactor loading on mercury removal.

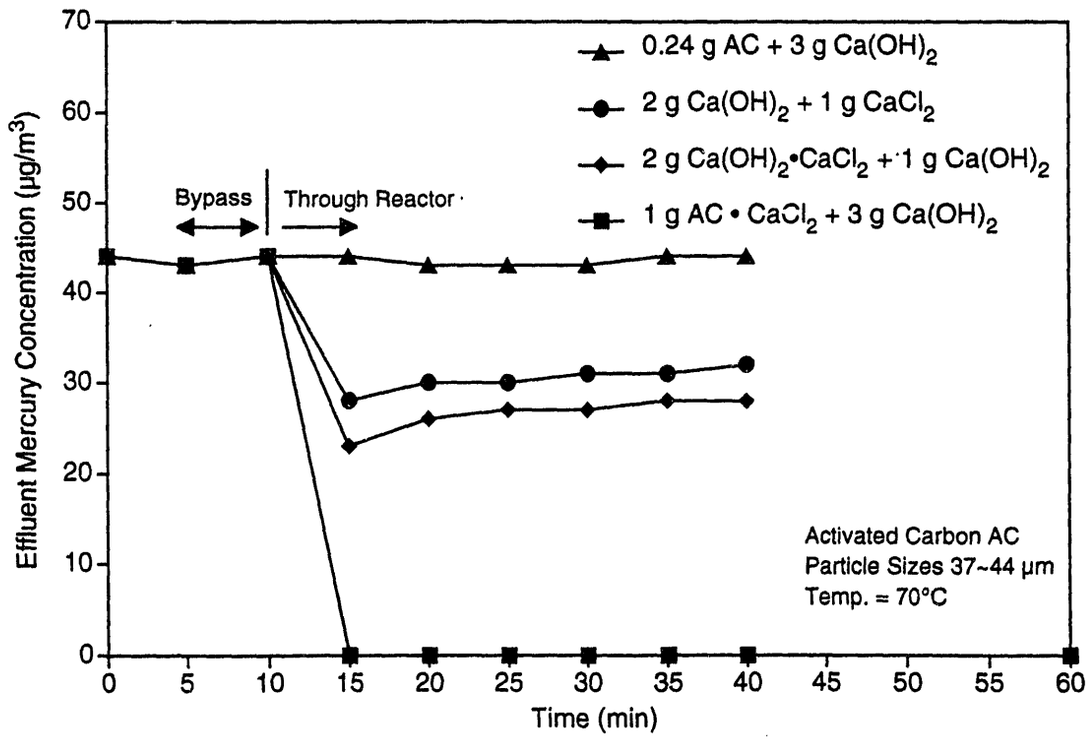

Figure 7. Effect of $CaCl_2$ treatment on mercury removal by carbon and lime.

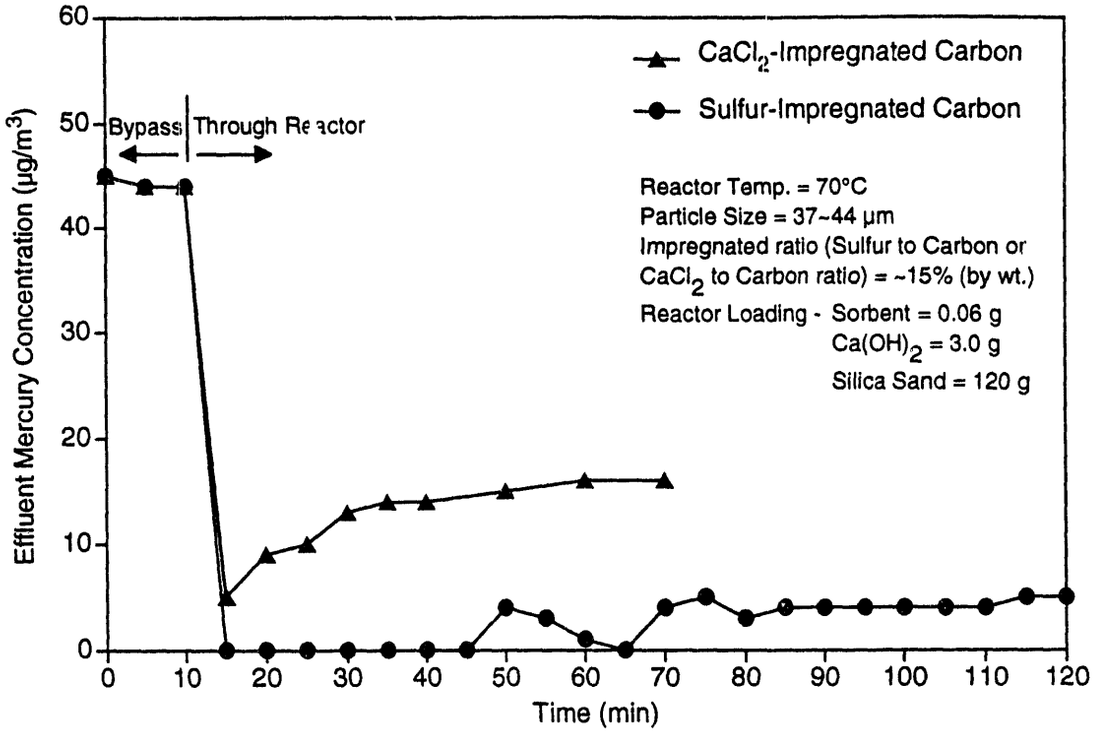

Figure 8. Comparison of mercury removals by carbons treated with sulfur or $CaCl_2$.

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