

**New Mercury Control Technology for the Ft. Dix Waste-to-Energy Plant**

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## INTRODUCTION

Mercury emissions from waste-to-energy plants, municipal solid waste incinerators, and other industrial processes have come under increased regulatory scrutiny. National Emission Guidelines were recently promulgated for municipal incinerators eventually requiring either 85% mercury removal or compliance with an  $80 \mu\text{g}/\text{Nm}^3$  emission standard.<sup>1</sup>

The ability of air pollution control equipment to remove mercury from a gas stream has been found to be largely a function of the particular mercury species present, their concentrations, and the gas temperature. Mercury chloride ( $\text{HgCl}_2$ ) tends to be found in incinerator flue gases and this species may be well-removed by activated carbon injection,<sup>2</sup> wet scrubbing,<sup>3</sup> or even hydrated-lime injection at low temperatures.<sup>4</sup> When the gas streams are relatively small, as with incinerators, fixed beds of mercury sorbents are also feasible. Beds of granular activated carbon have long been used to remove mercury vapors from small gas volumes in chloro-alkali plants and from other industrial processes.<sup>5</sup> The co-absorption of water and  $\text{SO}_2$ , leading to bed-soaking and corrosive sulfuric acid production, however, can limit this method of control. And activated carbon beds can spontaneously combust. However, very thick carbon beds have been applied in Europe in recent years on incinerator streams for the adsorption of mercury and other toxic species.<sup>6</sup>

Finer activated carbons can also be injected into the gas stream and removed in a particulate removal device.<sup>6,7</sup> Activated carbons can do a good job capturing high concentrations of mercury chloride, particularly when injected at relatively low temperatures. However, once the carbons are injected, they are lost; they become mixed in with large masses of acid gas sorbents and/or fly ash, which goes to disposal. Any sorbed mercury is not recovered.

The elemental form of mercury, unfortunately, has proven to be much more difficult to control. Elemental mercury is not soluble in water, and even iodine-impregnated activated carbons<sup>8</sup> and lime at extremely-high injection rates<sup>4</sup> may do little to remove it at temperatures above 300 F.

The operators of some incinerators need to be concerned about elemental mercury capture. While the mercury in most incinerator streams is predominantly  $\text{HgCl}_2$ , this is not always the case. Prior compliance measurements from the Ft. Dix municipal waste-to-energy plant in New Jersey, for example, indicate a high degree of elemental mercury.<sup>9</sup> And some sites, like that at Ft. Dix, do not have a cool-side baghouse for activated carbon injection. Moreover, to meet the new 85% mercury removal requirements, some sites will have to remove a significant amount of elemental mercury. For example, if 90% of the mercury in a gas is in the form of  $\text{HgCl}_2$  and activated carbon injection removes 90% of that, the 81% net removal is less than the 85% minimum.

After promising early experiments, the U.S. EPA and Air Force awarded Sorbent Technologies Corporation contracts to develop and demonstrate granular elemental mercury sorbents for incinerator use. The target was a recoverable-mercury sorbent that would last for from six-months to two years on a concentrated incinerator stream in a thin, simple, panel-bed arrangement. Two sorbent materials have been developed in this effort: a low-temperature version from which the mercury can be recovered, and a high-temperature version for upstream applications. This paper describes some of the work that has been done on these sorbents. Sorbent Technologies is scheduled to demonstrate the new mercury sorbent technology at the Fort Dix incinerator later in 1997.

## PANEL-BED SORBENT PELLETS

### Laboratory Screening

A laboratory test stand was constructed to evaluate the elemental mercury capture performance of various sorbent chemistries and a large number of screening runs were conducted. While the majority of treatments gave little evidence of any mercury sorption, two chemical combinations showed excellent potential.

The test stand used in the screening program included bottled gases, mass flow controllers, a constant-temperature oil bath, laboratory oven, mercury analyzers, and a computer data acquisition system. Elemental mercury was introduced into the simulation gas from permeation tubes. These tubes emit highly-constant elemental mercury vapor at rates strictly dependent on their temperature. A certified permeation tube, traceable to NIST standards, was used to calibrate the analyzer. During testing, the permeation tubes were placed inside a glass container that was maintained at a constant temperature using a constant-temperature oil bath. The permeation rate of mercury was varied by using multiple permeation tubes or by changing the temperature of the bath.

To test the various materials, a small fixed-bed of the candidate sorbent material was held in a custom-fabricated glass chamber which was heated in a laboratory oven to the simulation temperature. To prevent the absorption of mercury by the test apparatus, all components exposed to the mercury-laden gas stream were constructed of Teflon or glass and heated. The mercury-laden gas was pre-heated in an inert, glass-bead-loaded preheater before it entered the sorbent bed.

A data acquisition system allowed long-term, unattended system operation. The elemental mercury measurements were made using a Jerome 431-X gold-film mercury analyzer, manufactured by Arizona Instruments, and/or a Jupiter cold vapor atomic adsorption (CVAA) analyzer. The Jerome analyzer uses a gold-film sensor to measure elemental mercury vapor. The gold-film sensor is inherently stable, selective to elemental mercury, and has a detection range from 0 to 999  $\mu\text{g}/\text{Nm}^3$ . The sensor is periodically regenerated. The Jupiter CVAA instrument has a dual-beam design that decreases zero-drift and improves the way in which the sample gas is refreshed in the sample cell. By altering the feed line configuration, this CVAA instrument is capable of providing continuous elemental mercury measurement with no interference from acidic gases, such as  $\text{SO}_2$ .

### Low-Temperature Sorbents

After screening many potential chemistries, a good low-temperature elemental mercury sorbent was found. We call this material low-temperature "Merksorbent." The new material can be pelletized for low-pressure-drop application in panel-beds and shows good potential for long-term mercury capture at temperatures from about 130 F to 220 F. Importantly, once the Merksorbent is saturated, the captured mercury is easily recovered with simple thermal treatment.

The new sorbent's potential for long-term elemental mercury-capture is suggested in Figure 1. With a mercury inlet concentration of 150  $\mu\text{g}/\text{Nm}^3$ , a space velocity of 2400  $\text{hr}^{-1}$ , and a 7.6-cm deep sorbent bed, a removal rate of over 95% was obtained with no diminution in performance in a 70-hour run. The ultimate capacity of the sorbents has not yet been determined.

## Mercury Desorption Tests

Effectively sorbing the mercury from the exhaust gas is not enough; it must be assured that it no longer threatens human health or the environment. Consequently, leachability and thermal desorption tests were conducted to explore the safety and mercury recovery potential of the new sorbent. Saturated sorbent containing approximately 0.12 wt% of mercury from a long-term utilization test run was used in these studies.

If a waste material like the saturated sorbents is easily leachable, heightened precautions are necessary in its storage and transport, and disposal can be expensive. Two 5-gram samples of the partially-saturated sorbent, containing approximately 6.000 mg of mercury, were sent to an independent testing laboratory, Electro-Analytical Laboratories of Mentor, Ohio, for standard Toxic Characteristic Leaching Procedure (TCLP) extraction analysis. Two identical samples were subjected to an 18-hour extraction with a 20:1 solution-to-solids ratio using an acetic acid solution with a pH of 2.9. The detection limit of the process was 0.010 mg Hg/liter. The first sample had a TCLP extraction test result of 0.082 mg Hg/liter; the second sample had a result of 0.080 mg Hg/liter. The TCLP mercury leachate level to qualify as hazardous wastes is 0.200 mg Hg/liter. Thus, these saturated sorbent samples would not be classified as a hazardous waste.

It is not ultimately helpful to remove mercury from the gas phase if it is simply transferred to another medium. Mercury captured by activated carbon injection, for example, becomes mixed in with other fly ash that is ultimately sent out for land disposal. The mercury is not recovered, but left to become a potential groundwater pollutant. The sorbents examined in this research, however, present the possibility of mercury recovery.

A growing secondary source of mercury supply is its recovery from mercury-containing wastes, which are roasted in retort furnaces to recycle their mercury. Today there are five secondary mercury recovery facilities around the country, supplying about half of the U.S. needs for mercury by retorting mercury wastes and condensing out and purifying the mercury for sale.<sup>10</sup> Nine U.S. gold smelting and refining operations, which supply about 60 tons of by-product mercury per year, could also be used for this purpose.

Experiments were performed to examine the new sorbent's thermal recovery potential. A 0.50 g sample of partially-saturated sorbent, with a known quantity of sorbed mercury, was heated under a flowing gas stream and the elemental mercury content of the off-gas was continuously measured. In order to accurately measure the mercury, a low desorption temperature of 450 F and was selected. Integrating under the desorption curve revealed that after six hours fully 85% of the mercury had evolved from the sorbent.

Mercury recovery retort furnaces and ore roasters operate at a temperature of about 1100 F. A desorption test was carried out at this temperature also. Under these conditions, however, the mercury desorbed from the materials so quickly and in such quantities that the initial exit mercury concentration was far over the upper detection limit of the analyzer, even with 80:1 dilution sampling. The mercury concentration of the off-gas rapidly dropped to zero after a period of two minutes, indicated a very fast desorption process at this temperature. Thus, the mercury captured by the new sorbents should be desorbed very quickly and completely by the furnaces of mercury recovery facilities.

## High-Temperature Sorbents

A second elemental mercury sorption chemistry was also discovered which operates at higher temperatures, from 220 F to over 450 F. This composition can also be easily pelletized into granular, low-pressure-drop, panel-bed sorbents. However, while this sorbent material is capable of operating under more extreme conditions, unlike the low-temperature version, its mercury is not thermally recoverable.

At higher temperatures, elemental mercury is difficult to capture. For example, the performance of an activated carbon at higher temperatures is plotted in Figure 2. One gram of a granular activated carbon (Calgon CPG; 12x40 mesh) was tested over the range of 280 F to 400 F with gas containing 40  $\mu\text{g}/\text{Nm}^3$  mercury. The test was run with air also spiked with  $\text{SO}_2$  and moisture. Measurements were simultaneously taken on both the Jupiter and Jerome instruments.

With dry air, 1.0 g of this carbon in a 2.5 cm bed was capable of sorbing about 45% of the mercury at 400 F. However, when 0.06 lb-of-moisture-per-pound-of-dry-air was added to the gas stream, the mercury removal level dropped to zero. Apparently with carbon, water molecules compete for the same sites as the mercury. After the gas temperature was lowered to 300 F, a small amount of mercury sorption began to occur, perhaps to 10% removal. At high temperatures, this carbon does not appear to be a good candidate for elemental mercury capture.

In contrast, a run with a 3.8 cm bed of the new high-temperature Mercsorbent pellets is shown in Figure 3. Here the gas flow and face velocity were the same as the previous test, but the mercury concentration was twice as high. This gas was spiked with 200 ppm each of  $\text{SO}_2$  and HCl. For over 65 hours at 230 F, the Mercsorbent removed over 95% of the elemental mercury in the gas stream. When the temperature was raised to 300 F for the last three hours of the experiment, the removal rate increased to nearly 100%.

These Mercsorbents can work well at even higher temperatures. Figure 4 contains a plot of a short-term test of a 2.5 cm bed of pelletized sorbent as a function of temperature. The data from this test indicate the potential for 90+% elemental mercury removal up to 700 F.

## Bench-Scale Testing

Based on the earlier laboratory runs, sorption testing of the low-temperature sorbents was then scaled up to a large 150  $\text{m}^3/\text{hr}$  (90 acfm) simulation system. This bench-scale system included a propane burner, elemental mercury spiking system, dilution air intake for temperature control, 24 m of ducting, an orifice plate for flow measurement, three heated sample lines for gas analysis at various points, and a variable speed ID fan. The spiking system was capable of adding 50  $\mu\text{g}/\text{Nm}^3$  of elemental mercury to the hot gas stream.

A thin filter of the new sorbent was inserted into the end of the ducting. Sitting in a drum, the conically-shaped, flat filter was 1 m high, 0.5 m at its maximum diameter, and 7.5 cm thick. It held 15 kg of the new sorbent. See Figure 5. At a gas flow rate of 150 m<sup>3</sup>/hr, with a space velocity of 2700 hr<sup>-1</sup>, the pressure drop across the filter was only 0.5 cm of water column. When operated in multi-hour tests, the sorbents removed from 80% to 100% of the mercury passing through them, depending on the operating conditions.

## POWER PLANT SLIP-STREAM TESTING

The low-temperature Mercsorbents were also tested in the field on actual flue gas from the Ohio Edison Company's R.E. Burger station near Shadyside, Ohio. A test rig was constructed that drew off a slipstream of the plant flue gas after the electrostatic precipitator and divided it between six small test beds. Approximately 550 lpm of gas with approximately 3.5 µg/Nm<sup>3</sup> of elemental mercury was drawn through each of the sorbent test beds, 13-cm in diameter and 15-cm deep, for nine days. A blower returned the gas to the ductwork.

Each sampling train consisted of a particulate pre-filter, ice bath, two acid-gas filters in series, two gold-coil dosimeters, a mass flow controller, and a pump operating at 90 cc/min. The acid-gas filters were to eliminate any hydrogen sulfide or other acidic gases. The gold-film dosimeters are made to sorb very low concentrations of elemental mercury, concentrating it for more accurate measurement. Two dosimeters in series were used to insure that all of the elemental mercury was collected. They are designed not to sorb any mercury chloride that may be in the gas. After 90 minutes, the dosimeters were removed and analyzed using the Jerome instrument. The elemental mercury concentrations of the gas is the mass of mercury collected divided by the total gas volume sampled. To save time, three sampling lines, with a total of six dosimeters, were run simultaneously.

The mercury content of gas from power plants is about two orders of magnitude lower than that of waste incinerators and some measurement difficulties were experienced. An interferant gas appeared to affect our measurements at these levels. By using a plain vermiculite dummy bed, however, a method was developed to correct the readings. Using the dummy-bed correction, the elemental mercury removal rates measured after nine days varied from between about 75% and 97%, similar to what was seen in the laboratory. These numbers are approximate because the mercury sampling at the power plant was episodic and the inlet mercury would be expected to vary over the nine days.

To do a mass balance, a sample from one of the Burger beds was thermally desorbed at a low temperature of 400 F. A plot of the results appears in Figure 6. Integrating under this curve provides a value for the amount of mercury sorbed. The consistent mercury removal efficiencies for this sorbent observed in a laboratory test, field slipstream test, and calculated based on the desorption test, are shown in Figure 7. Combining the desorption result with measurements of mercury in the Burger plant gas stream suggests an average mercury removal rate of about 80 to 90% for the new sorbent under the actual flue gas conditions.



## FABRIC FILTER BAGS

Research is also underway to examine other possible ways of applying the Mercisorbent chemistries to flue-gas applications. For example, many municipal waste incinerators have spray dryers and fabric filters in their air pollution control trains. At these facilities an additional strategy is available. First, activated carbon injection would remove the majority of the oxidized mercury species, such as mercury chloride. Then, the large surface area in the baghouse would be exploited by treating the fabrics with the mercury-reactive substances to create a polishing filter for elemental mercury.

### Low-Temperature Fabrics

Initial laboratory tests of the mercury-sorbing baghouse fabrics have been promising. So far, the treatments have been successfully applied to samples of commercial baghouse fabrics of acrylic, polyester, and Ryton, and to both felts and weaves.

In one example, a 5.4-cm diameter polyester fabric filter sample was treated with the new low-temperature chemistry and dried. A simulated flue gas at 1 lpm, spiked with elemental mercury to about  $170 \mu\text{g}/\text{Nm}^3$ , was then passed through the fabric. The gas temperature was held at 160 F, a temperature representative of spray dryer baghouses.

Over 95% mercury removal was achieved for nearly 24 hours under these conditions. This sample was then further saturated at higher gas flow rates for 108 more hours, in 5 additional tests examining changes in various conditions. Although still not saturated and removing most of the mercury passing through it, the testing was stopped with the sample having sorbed 4.1 mg of mercury, or almost 2 g  $\text{Hg}/\text{m}^2$  of fabric. A photograph of the fabric, with its captured mercury coating very evident, appears in Figure 8. Like the low-temperature Mercisorbent pellets, the baghouse application allows for simple recovery of the sorbed mercury. When the fabric filter bags have met their useful life, the mercury-laden fabrics could be shipped to a mercury recovery facility.

When operating on a pulse-jet baghouse, the mercury-laden stream would pass through the fabric at a high rate. To examine such conditions, a treated fabric was tested at a very high air-to-cloth ratio of 8 ft/min. The results of this run appears in Figure 9. The elemental mercury concentration into the fabric was  $150 \mu\text{g}/\text{Nm}^3$  and the gas temperature was 160 F. Even at this high gas-flow rate, mercury removal averaged about 90% in this 50 hour test.

### High-Temperature Fabrics

The high-temperature sorbent composition can also be applied to baghouse fabrics. In the next example, a high-temperature Teflon® baghouse fabric (Pyro-Tex®) was treated with the high-temperature Mercisorbent. The fabric was then was then tested in the laboratory test stand with a  $200 \mu\text{g}/\text{Nm}^3$  mercury simulation gas at 375 F and an air-to-cloth ratio of 4.0 ft/min. The performance of this material leveled off at about 70% elemental mercury removal at about 40 hours. See Figure 10.

Of course, much more development and testing of this concept is required, with much longer run times, lower concentration mercury streams, and frequent bag pulsing. Disposal of the mercury-containing bags must also be addressed. However, the sorption capacities of the samples has been high and no breakthroughs have yet been achieved. The concept deserves further work.

## FUTURE PLANS

Laboratory and bench-scale testing and optimization of the sorbents at Sorbent Technologies Corporation is an ongoing activity.

Like many incinerator facilities around the country, the refuse incinerator at Fort Dix in New Jersey has a mercury emission problem. Prior compliance sampling at this unit suggests that a significant amount of its mercury is in the elemental form. While it complies with other emission regulations, this Army incinerator has been unable to meet its operating permit mercury limit (0.00093 lb/hr) or the new statewide mercury standards (65  $\mu\text{g}/\text{dscm}$  now and 28  $\mu\text{g}/\text{dscm}$  later) on a regular basis. The facility has been fined by the State of New Jersey for its mercury emissions. Sorbent Technologies Corp. is scheduled to demonstrate the new recoverable-mercury sorbent technology at this Fort Dix incinerator in later 1997.



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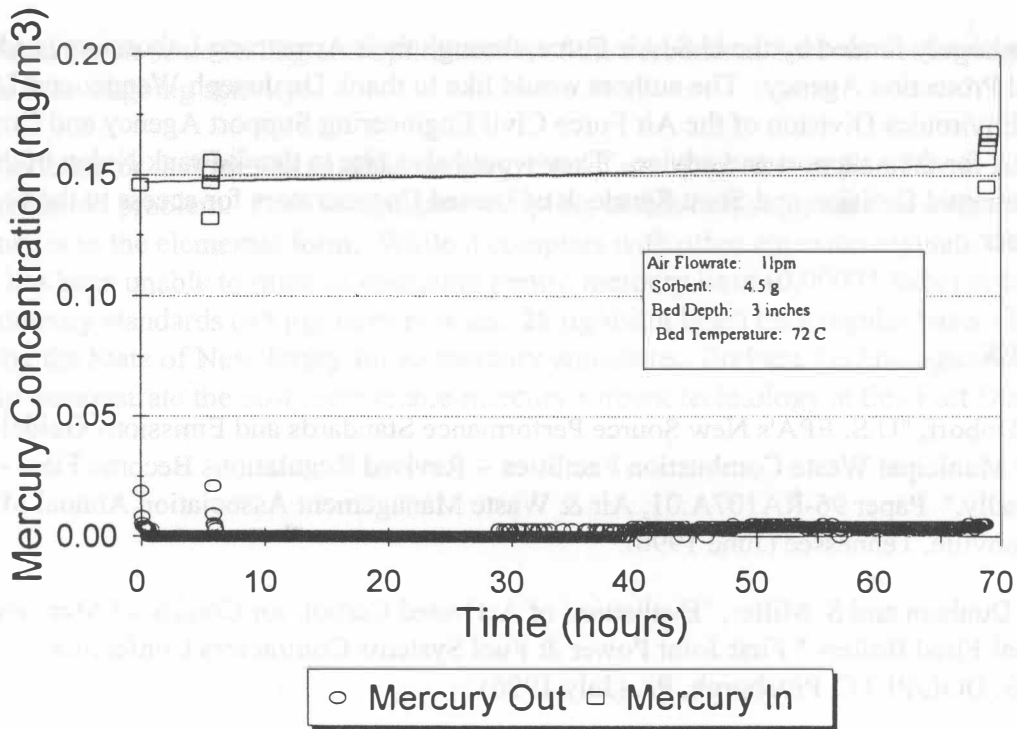


Figure 1. Elemental mercury removal of low-temperature Mercisorbent.

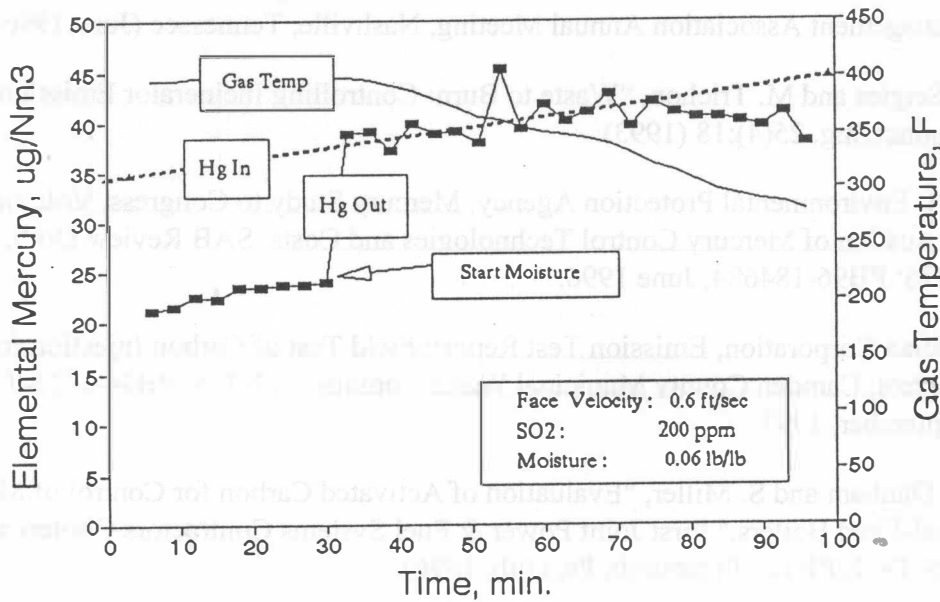


Figure 2. Elemental mercury removal of an activated carbon at high temperatures.

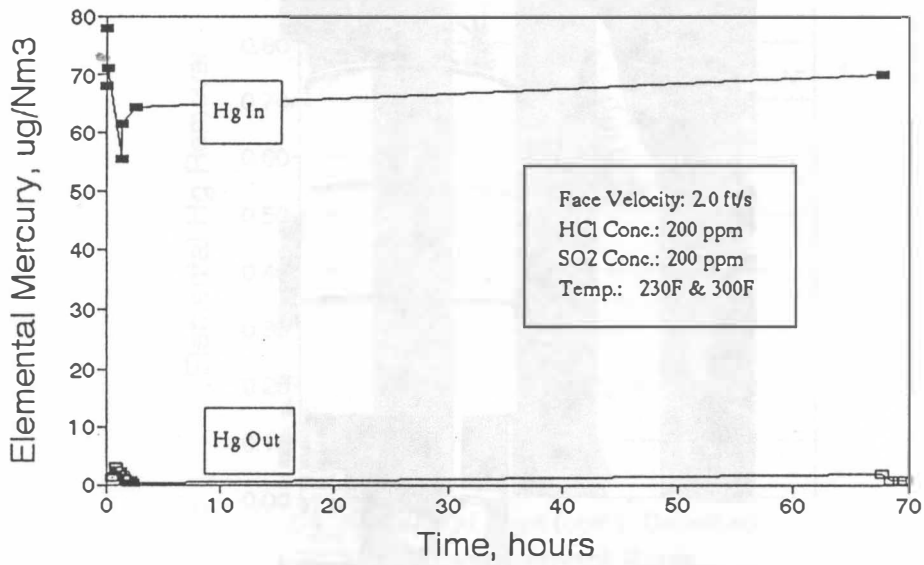


Figure 3. Elemental mercury removal of high-temperature Mercsorbent.

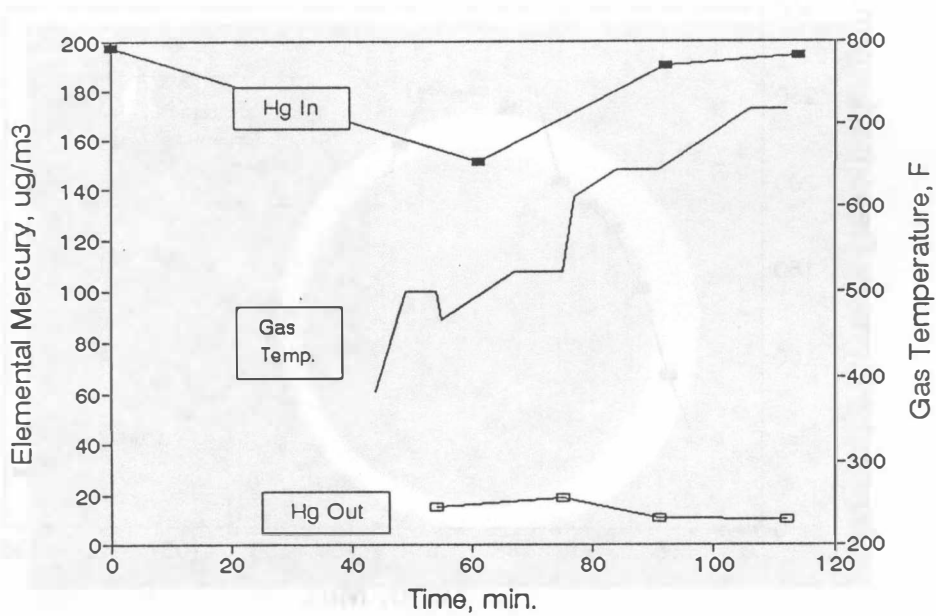
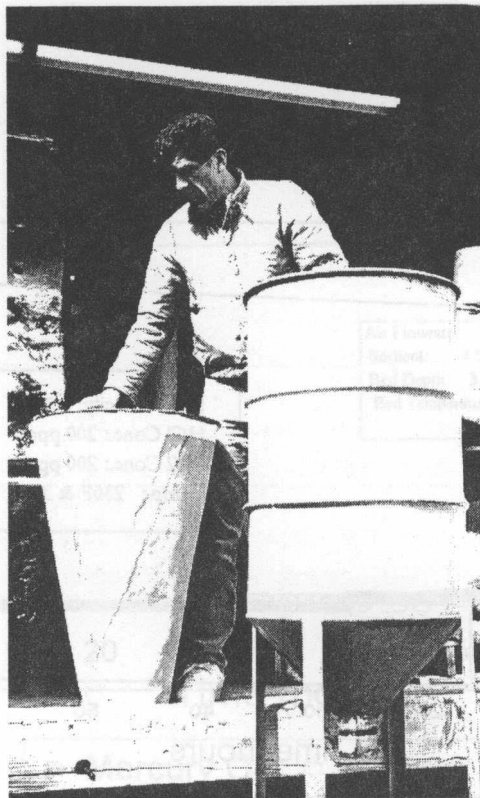
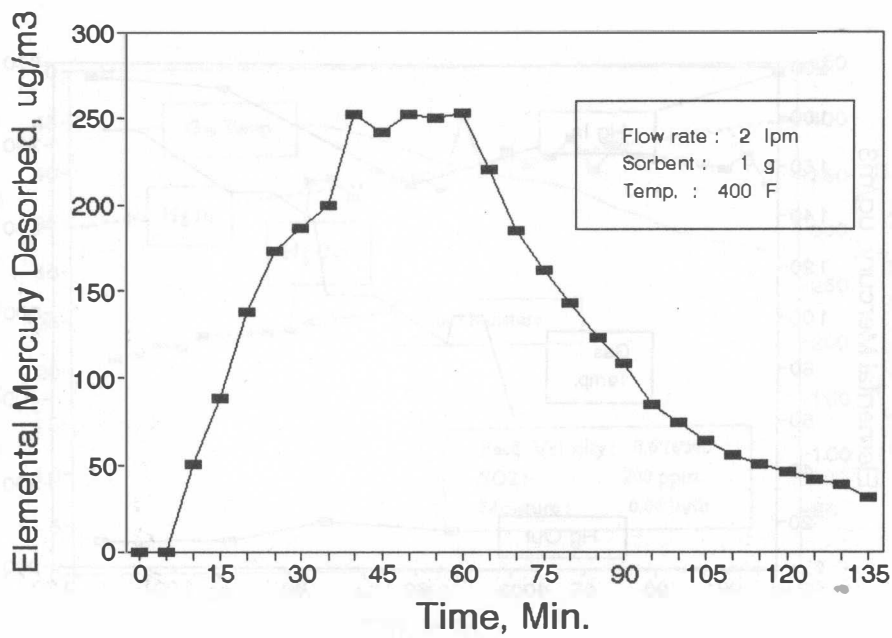


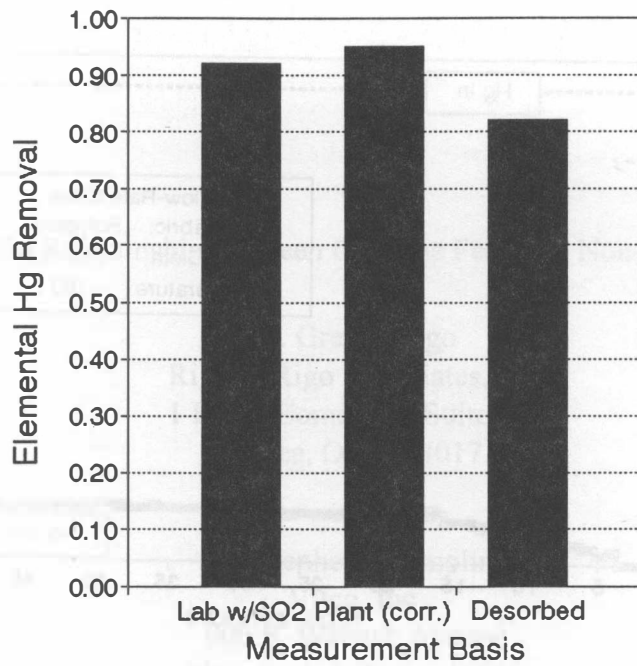
Figure 4. High-temperature range of Mercsorbent.



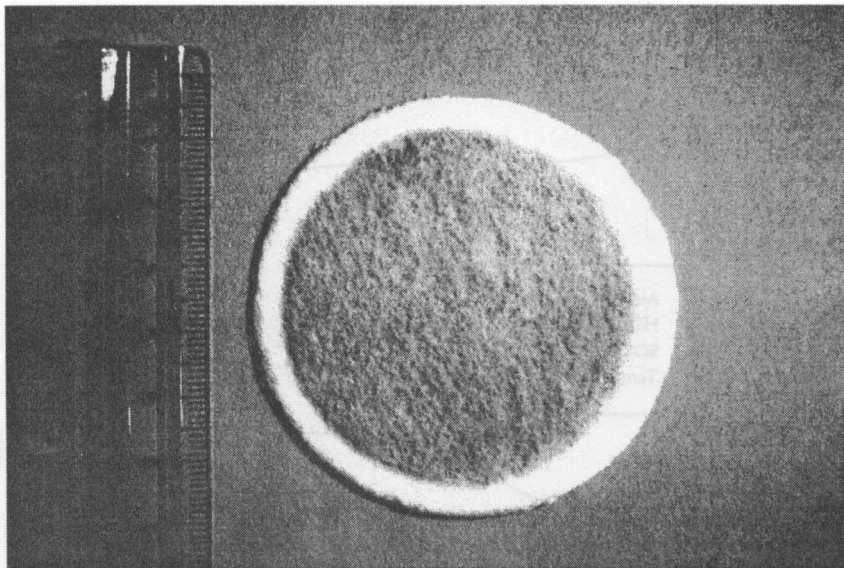
**Figure 5.** Small conical panel-bed filter of mercury sorbents.



**Figure 6.** Desorption of elemental mercury from the Burger station Mercsorbent.



**Figure 7.** Low-temperature performance of Burger plant Mercsorbents.



**Figure 8.** Mercury captured on a low-temperature Mercsorbent baghouse fabric.

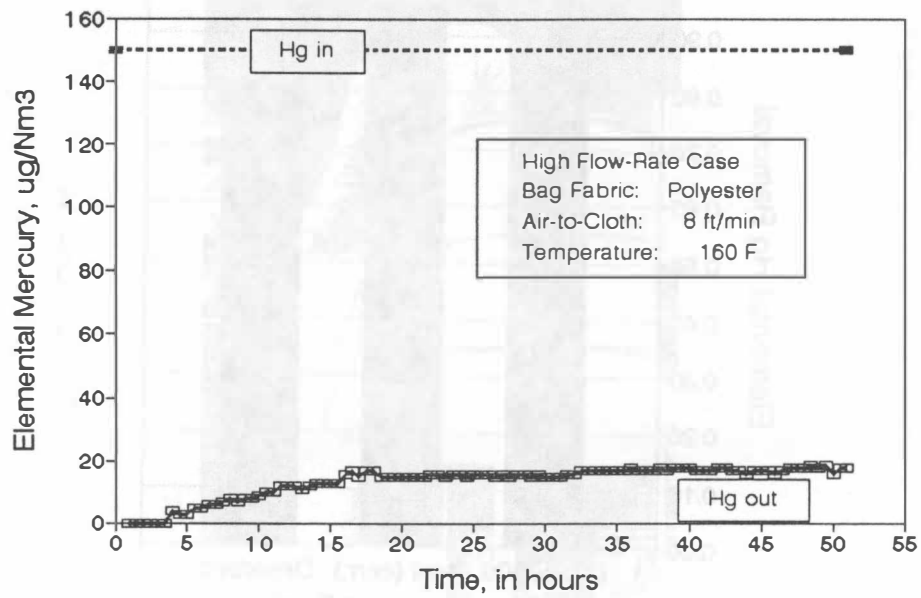


Figure 9. Results of a low-temperature Mercsorbent baghouse fabric test.

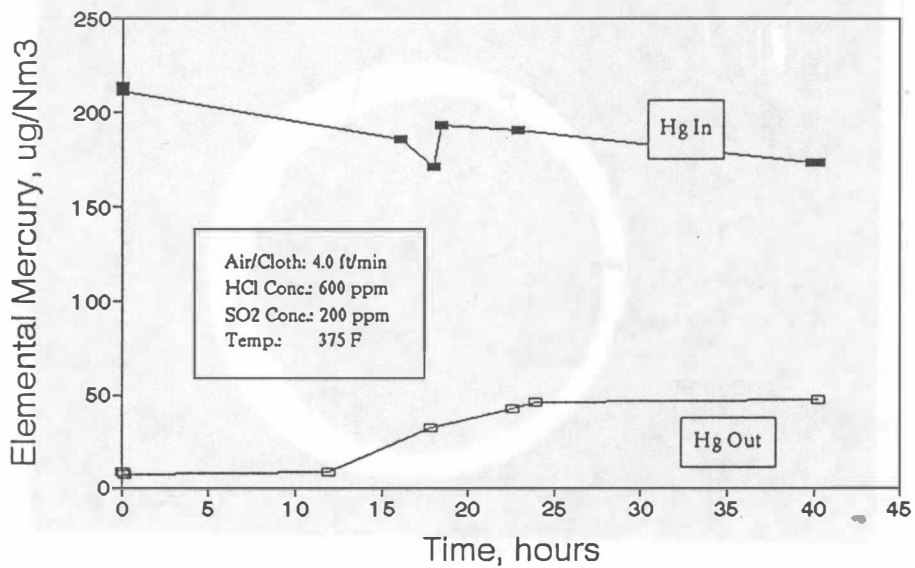


Figure 10. Results of a high-temperature Mercsorbent baghouse fabric test.