

SCREENING OF CARBON-BASED SORBENTS FOR THE REMOVAL OF ELEMENTAL MERCURY FROM SIMULATED COMBUSTION FLUE GAS

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ABSTRACT

A fixed-bed reactor system with continuous Hg⁰ analysis capabilities was used to evaluate commercial carbon sorbents for the removal of elemental mercury from simulated flue gas. The objectives of the program were to compare the sorbent effectiveness under identical test conditions and to identify the effects of various flue gas components on elemental mercury sorption.

Sorbents tested included steam-activated lignite, chemically activated hardwood, chemically activated bituminous coal, iodated steam-activated coconut shell, and sulfur-impregnated steam-activated bituminous coal. The iodated carbon was the most effective sorbent, showing over 99% mercury removal according to U.S. Environmental Protection Agency (EPA) Method 101A. Data indicate that adding O₂ at 4 vol% reduced the effectiveness of the steam-activated lignite, chemically activated hardwood, and sulfur-impregnated steam-activated bituminous coal. Adding SO₂ at 500 ppm improved the mercury removal of the sulfur-impregnated carbon. Further, the presence of HCl gas (at 50 ppm) produced an order of magnitude increase in mercury removal with the chemically activated and sulfur-impregnated bituminous coal-based carbons.

INTRODUCTION

Coal combustion and gasification processes together with industrial and commercial operations, such as waste incineration, emit significant quantities of trace elements to the atmosphere each year (1). The 1990 Clean Air Act Amendments have identified eleven trace elements (beryllium, chromium, manganese, cobalt, nickel, arsenic, selenium, cadmium, antimony, lead, and mercury) for control because of their potential harmful effects to the ecosystem. Mercury (along with arsenic and selenium) is of particular concern because it can occur in vapor or submicron fume form, and as such conventional collection devices (precipitators and baghouses) are marginally effective for its removal (2).

Trace element control strategies have recently focused on disposable or regenerable sorbents (activated carbons, coke, limestone) that can be injected as powders directly into flue gas streams or utilized in fluid-bed or fixed-bed reactors. However, homogeneous or heterogeneous reactions with other flue gas constituents (HCl, O₂) can occur. Identifying and controlling these reactions are important in determining the effectiveness of sorbents to capture particular species, e.g., metallic mercury, mercuric chloride, or mercuric oxide. Further, other gases such as carbon monoxide, nitrogen dioxide, and sulfur dioxide have the potential to interfere with the effective sorption of mercury species.

The overall objective of the ongoing project is to identify the conditions (temperature and flow rates) and the controlling processes (mercury species and concentration, flue gas components) for the most effective capture of trace elements by carbon sorbents in combustion and gasification systems.

EXPERIMENTAL

Apparatus and Procedure

The mercury sorbent test apparatus consists of four main subsystems: 1) flue gas generation, 2) mercury injection, 3) sorbent-flue gas contactor, and 4) effluent gas mercury analysis (with data logging). A diagram of the test apparatus is presented in Figure 1.

The simulated flue gas, which can contain N₂, O₂, CO₂, SO₂, HCl, and NO₂, is generated in a manifold system; rotameters provide volume flow control. Elemental mercury vapors are generated with a permeation tube(s). The permeation tube mercury desorption rate, and consequently, the simulated flue gas mercury concentration, is a function of the permeation tube's N₂ sweep gas equilibrium temperature. Permeation tube temperature control, to within 0.1°C of setpoint, is provided by a condenser heated with circulating heat-transfer fluid.

A U.S. Environmental Protection Agency (EPA) Method 5 in-stack particulate sampling filter is used as a sorbent bed containment device. The interior of the filter assembly, including filter support grid, and all other components in contact with the mercury-laden gas are Teflon-coated. The filter assembly and influent tubing are electrically heated to maintain the desired temperature and prevent condensation. A downflow configuration is used to minimize entrainment of powdered sorbents. The filter static and

differential pressures are monitored using pressure gauges. The filter assembly can be equipped with a thermocouple to measure the flowing gas temperature.

The elemental mercury concentration in the simulated flue gas stream is continuously monitored using a DuPont Model 400 ultraviolet (253.7 nanometer) photometric analyzer. A Buck Scientific Model 400 cold-vapor ultraviolet analyzer has also been used to monitor the filter inlet mercury concentration. Mercury concentration values from the analyzers are continuously logged to a chart recorder; a data acquisition unit coupled with a lap-top computer has been used to log mercury analyzer output data and select system temperatures. Diaphragm-type and bubble-type gas meters have been used to measure the total gas rate.

Sorbents

The following five commercial activated carbons were evaluated as elemental mercury sorbents: 1) chemical-activated hardwood (AC1), 2) steam-activated lignite (AC2), 3) 5% sulfur-impregnated steam-activated bituminous coal (AC3), 4) chemically activated bituminous coal (AC4), and 5) 10% iodine-impregnated steam-activated coconut shell (AC5). The activated carbons were tested as powders; the sulfur and iodine impregnated carbons were obtained in granular form and then comminuted to a nominal 200-mesh (75-micron) top size.

Tests Performed

Twenty-seven tests were performed using the five sorbents. Test variables included sorbent type, O₂ concentration (0 or 4 vol%), SO₂ concentration (0 or 500 ppm), and HCl concentration (0 or 50 ppm). Common test parameters were as follows: a nominal mercury concentration of 100 µg/m³, gas rate of 26 scfh, filter assembly gas temperature of 150°C (300°F), and sorbent mass of 0.20 g. The tests are summarized below.

- Six tests, one each with AC1 and AC2 and two each with AC3 and AC5, used 100 vol% N₂ as the simulated flue gas
- Five tests, one each with AC1, AC2, AC3, AC4, and AC5, used 4 vol% O₂, 96 vol% N₂ as the simulated flue gas
- Thirteen tests, two each with AC1 and AC2 and three each with AC3, AC4, and AC5, used a simulated flue gas composed of 4 vol% O₂, 96 vol% N₂, plus 500 ppm SO₂
- Three tests, two with AC3 and one with AC4, used 4 vol% O₂, 96 vol% N₂, plus 500 ppm SO₂ and 50 ppm HCl as the simulated flue gas

EPA Method 101A (3) was applied to the filter assembly influent and effluent simulated gas streams during one test with the AC5 (iodated carbon) in the presence of O₂ + SO₂. This test was performed to quantify total mercury removal by the carbon and to compare the result against the general trend of the ultraviolet analyzer output. Further, the test was applied to assess if elemental mercury was being converted to an oxidized form in the presence of AC5, and thus not adsorbed by the carbon or detected by the ultraviolet analyzer, but collected by the permanganate solution of EPA Method 101A.

Similarly, EPA draft Method 29 (4) was applied to the filter effluent stream in the single test with the AC4 (chemically activated bituminous coal) in the presence of O₂ + SO₂ + HCl. Similarly to the test with AC5, this test was applied to assess if elemental mercury was being converted to oxidized and/or chloride forms in the presence of AC4. With this test, chloride forms of mercury would be collected in the peroxide solution.

The test duration for each EPA method was one half-hour. The EPA Method 101A permanganate solution and draft Method 29 peroxide and permanganate solutions were analyzed by cold-vapor atomic adsorption using a Leeman Labs PS200 automated mercury analyzer.

RESULTS AND DISCUSSION

The effluent gas from the filter assembly was monitored for <100% mercury capture and 0% mercury capture (breakthrough). Adsorption curves, which show the mercury removal efficiency as a function of gas-sorbent contact time, are presented in Figures 2 and 3 for tests conducted with 0 and 4 vol% O₂, respectively.

Tests at 0 vol% O₂ indicated that AC1 and AC3 each exhibited an instantaneous lowering of Hg⁰ removal efficiency to 46% and 10%, respectively. Breakthrough with these respective carbons was achieved in approximately 4 and 24 minutes. The AC2 exhibited a slower loss of mercury removal efficacy, achieving breakthrough in approximately 30 minutes. Tests with 4 vol% O₂ indicated that AC1, AC2, and AC3 showed similar instantaneous losses of mercury removal efficiency but with more rapid attainment of breakthrough, 0.5, 18, and 10.5 minutes, respectively, than tests without oxygen. The AC4, first used in tests with O₂, exhibited superior mercury removal efficiency relative to the AC1, AC2, and AC3 sorbents, achieving breakthrough after 94 minutes.

The AC5 iodated carbon appeared to be vastly superior to the other carbons in tests with and without O₂. The baseline analyzer output indicates that elemental mercury was 100% adsorbed when using 0 vol% oxygen after over 20 hours; a replicate test produced identical results. As was observed with AC5 in tests without O₂, elemental mercury was 100% adsorbed even after 112 minutes, a test duration almost 20 minutes longer than the next most effective sorbent.

The addition of SO₂ appeared to have a selective influence on mercury removal efficiency relative to that of O₂. A plot of the sorbent contactor effluent gas mercury concentration is shown in Figure 4 for tests performed using 4 vol% O₂ and 500 ppm SO₂ combined. Trends are similar to those from tests performed without SO₂ in that AC1 and AC2 are the least effective sorbents, showing an instantaneous loss in removal efficiency and the most rapid attainment of breakthrough. Similarly to tests without SO₂, AC5 (iodated carbon) retained essentially 100% removal efficiency. However, AC3 showed a slower loss of effectiveness relative to AC1 and AC2, with a breakthrough time 50% longer than that with AC2.

The EPA Method 101A test using AC5 indicated that elemental mercury was removed by this carbon at a high level of effectiveness. The mass concentration of mercury in the effluent and influent permanganate solutions, 78 µg and 0.2 µg per one-half liter, respectively, indicated that mercury removal was over 99 wt%, agreeing well with analyzer output data. However, the sorption data or its analyses do not provide evidence of any conversion of mercury to oxidized form.

The results of tests performed with AC3 and AC4 using 50 ppm HCl indicated evidence of interaction or reactions that enhance mercury removal efficiency. A monitoring plot of effluent gas mercury concentration as a function of gas contact time (or total mercury flow) is presented in Figure 5 for a test performed with AC3. The sawtooth curve shows the change in mercury concentration, and presumably mercury removal efficiency, effected by starting and stopping the HCl gas flow. The straight baseline, which indicated nearly 100% mercury removal with flowing HCl, contrasts with the curve for AC3 in Figure 4, generated without HCl. During the periods without HCl injection, the mercury concentration curve exhibited a similar, slow degradation in mercury removal as seen in Figure 4. Upon injection of HCl, the return to essentially 100% mercury removal was immediate.

A replicate test with AC3 and a single test with AC4 using 50 ppm HCl produced similar results. The EPA (draft) Method 29 with AC4 showed that elemental mercury was removed at a high level of effectiveness. The mass concentration of mercury in the effluent peroxide and permanganate solutions, 0.3 and 1.9 µg per one-half liter, indicated that mercury removal was over 97 wt%, agreeing with the analyzer output. The quantitation of mercury in the peroxide trap further suggests that chloride forms of mercury were produced, and, as such, were removed by the AC4.

CONCLUSIONS

The AC5 (iodated) activated carbon appeared to be the consistently superior sorbent regardless of the simulated flue gas atmosphere; AC1 (chemically activated hardwood) was consistently the least effective. Adding O₂ at 4 vol% apparently reduced the effectiveness of all carbons except the iodated carbon. The effect of adding SO₂, however, appeared to more selective, increasing the effectiveness of the sulfur-impregnated carbon relative to the other carbons. Adding HCl at 50 ppm had the apparent effect of enhancing the mercury removal efficiency of the sulfur-impregnated and chemically activated bituminous coals to a level comparable to the iodated carbon.

REFERENCES

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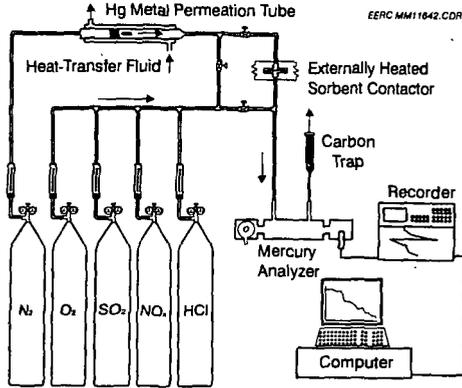


Figure 1. Mercury sorbent test apparatus.

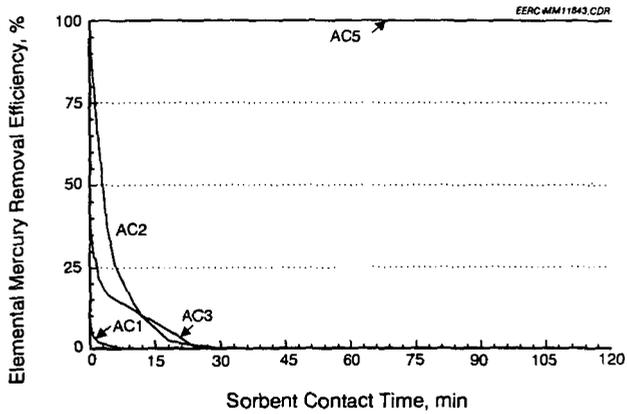


Figure 2. Mercury removal efficiency curve, 0 vol% O₂.

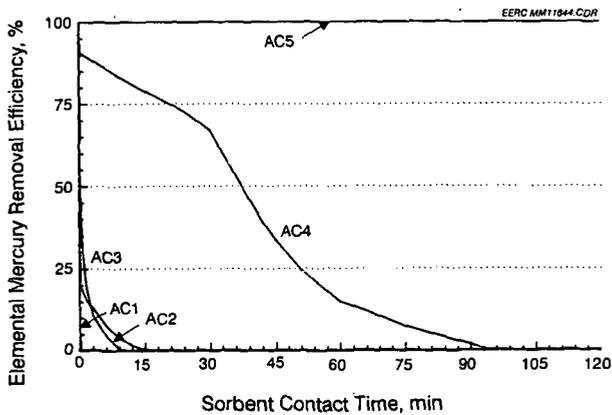


Figure 3. Mercury removal efficiency curve, 4 vol% O₂.

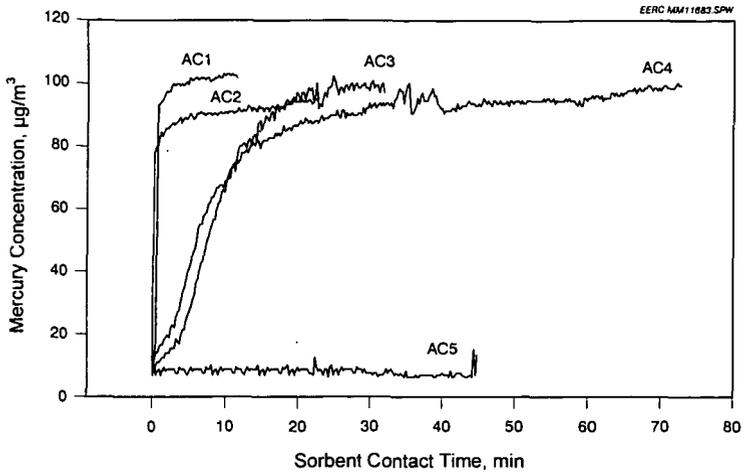


Figure 4. Comparative effectiveness of activated carbons for elemental mercury sorption; 4 vol% O_2 and 500 ppm SO_2 .

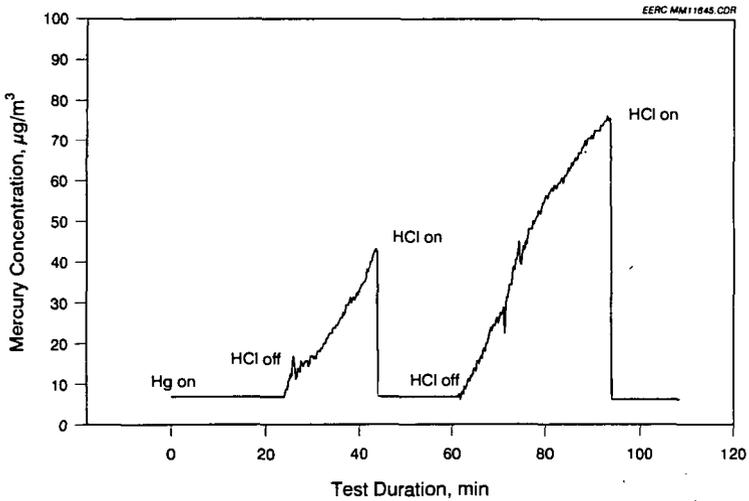


Figure 5. Mercury sorption by sulfur-impregnated steam-activated bituminous coal (AC3); 4 vol% O_2 , 500 ppm SO_2 , 50 ppm HCl.