DOE/MC/30097 -- 5668
(DE97002298)

Task 2.5 - Effectiveness of Sorbents for Trace Elements

Semi-Annual Report
January 1 - June 30, 1995

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Work Performed Under Contract No.: DE-FC21-93MC30097

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ACKNOWLEDGMENT

This semiannual was prepared with the support of the U.S. Department of Energy (DOE), Morgantown Energy Technology Center, Cooperative Agreement No. DE-FC21-93MC30097. However, any opinions, findings, conclusions, or recommendations expressed herein are those of the author(s) and do not necessarily reflect the views of the DOE.

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1.0 INTRODUCTION

Significant quantities of trace elements are emitted to the atmosphere each year as a result of the large volumes of coal used in combustion and gasification processes as well as from other industrial and commercial operations, such as waste incineration and chlorine and alkali production (1). Owing to their potentially harmful effects on the ecosystem, eleven trace elements have been identified for control action under the 1990 Clean Air Act Amendments: beryllium, chromium, manganese, cobalt, nickel, arsenic, selenium, cadmium, antimony, lead, and mercury. Although appearing as trace species, arsenic, selenium, and mercury are of particular concern, since they can occur in gaseous or submicron fume form; consequently, substantial amounts can pass through the conventional collection devices such as precipitators and baghouses.

Current trace element collection strategies focus on sorbents as a collection method. The sorbents generally consist of a large volume of inexpensive, disposable activated coke or char with modest sorption activity. An alternative approach is to use innovative technology to produce a regenerable sorbent material with enhanced sorption characteristics, from which trace metals are recovered.

Following the release of trace metals such as arsenic, selenium, and mercury from coal combustion and gasification, homogeneous and heterogeneous reactions can occur (2). Identifying and controlling these reactions are important in determining the effectiveness of sorbents to capture particular species, for example, metallic mercury and mercuric chloride. Activated carbon, alone and impregnated with sulfur or iodide, has been used as a capture sorbent. However, mercury in the presence of oxygen at elevated temperatures ($<500°C$) may form mercuric oxide, thus lessening the effectiveness of carbon as a capture agent. Other gases, such as carbon monoxide, nitrogen dioxide, and sulfur dioxide, also have the potential to interfere with the effective sorption of mercury species. In addition to activated carbon, fly ash has also been implicated in mercury reactions and mercury sorption (3, 4). Quantitative kinetic data regarding the sorption processes of trace elements in combustion and gasification gas streams are scarce, and the sorption mechanisms not well understood. Hence, a research strategy to develop a basis for air quality control management of trace element emissions is timely.

2.0 OBJECTIVES

The overall objective of the project is to identify the conditions for the most effective capture of trace elements by carbon sorbents and the controlling processes for trace element sorption in combustion and gasification systems. The specific objectives are as follows:

- To identify the parameters, including temperature, mercury species concentration, and flow rate, in controlling the level of mercury sorption by activated carbons in a laminar flow combustion system.
- To identify the effects of various flue gas components, including oxygen, affecting mercury species sorption by carbon sorbents.

- To generate sorption kinetic data to assist in developing a preliminary understanding of the mechanism of mercury sorption by carbon-based materials.

3.0 ACCOMPLISHMENTS

During the previous four-month period, a testing apparatus was operated to evaluate select sorbents for removing elemental mercury from simulated utility or incinerator flue gas streams. Five commercial activated carbons were tested as elemental mercury sorbents. The sorbents were ranked according to mercury removal effectiveness under varied test conditions (e.g., flue gas composition). The effect of various flue gas components (O_2, SO_2, and HCl) on elemental mercury removal was noted.

3.1 Experimental Apparatus

The mercury sorbent test apparatus consisted 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 (1).

The simulated flue gas, which can contain N_2, O_2, CO_2, SO_2, HCl, and NO_2, was generated in a manifold system; rotameters provided volume flow control for each flue gas component. Elemental mercury (Hg^o) vapors were generated with permeation tubes manufactured by VICI

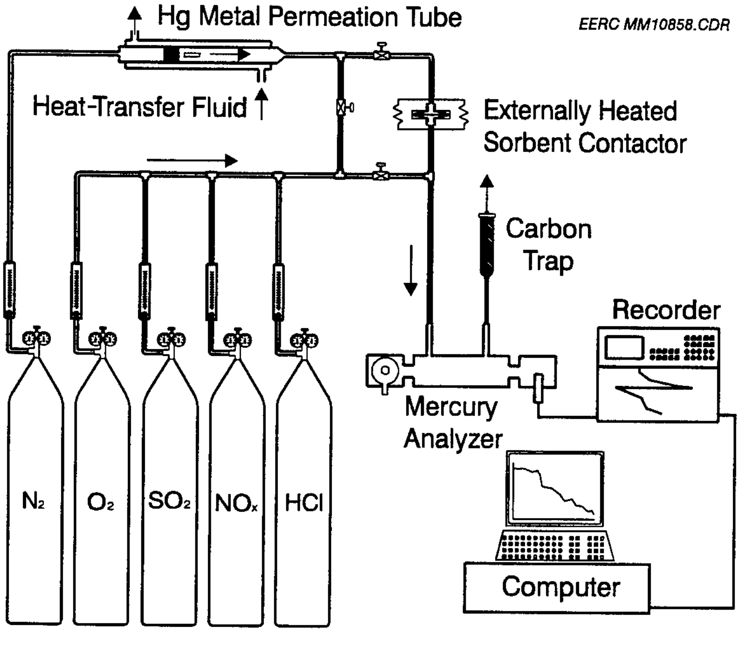

Figure 1. Test apparatus using effluent mercury analysis.

Metronics. Components in contact with the mercury-laden gas are primarily made of Teflon® or quartz; an exception is tygon tubing, which is used in small lengths as a connector between components. All components downstream of the mercury injection point were heated to prevent mercury and water condensation.

An externally heated filter assembly, the type typically used for EPA Method 5 (5) in-stack particulate sampling, was used as a sorbent bed containment device. The interior of the filter assembly, including filter support grid, is Teflon®-coated. The filter assembly was oriented perpendicular to the gas stream; a downflow configuration was used to minimize entrainment of the powdered activated carbon sorbents. The filter assembly was equipped with a thermocouple to allow measurement of the flowing gas temperature.

Continuous monitoring of the elemental mercury concentration in the simulated flue gas stream was provided by a cold-vapor ultraviolet (253.7 nanometer) DuPont Model 400 photometric analyzer. Mercury concentration values from the analyzer were continuously logged to a chart recorder; a Fluke Hydra Data Acquisition Unit coupled with a lap-top computer was used to log the mercury analyzer output data as well as select critical system temperatures. A diaphragm-type dry gas meter was used to measure the total gas rate.

3.2 Experimental Procedure

Briefly, the experimental procedure for sorbent testing employed during the past performance period was as follows.

The continuous mercury analyzer was first zeroed and spanned with the simulated flue gas by bypassing the filter assembly. The filter assembly was then charged with the desired mass of sorbent, connected to the influent and effluent tubing, and then wrapped with a muff-type heater. The filter assembly and influent tubing were then heated to the desired temperature while flowing simulated flue gas (without mercury vapor) over the sorbent. The N_2 sweep gas containing the elemental mercury vapor was diverted to the simulated flue gas stream, initiating the test. The effluent gas from the filter assembly was monitored for breakthrough ($<100\%$ mercury capture) and complete sorbent loading (0% mercury capture).

3.3 Activated Carbon Sorbent Properties

The test program assessed five commercial activated carbons as elemental mercury sorbents; the sorbents included 1) American Norit (AN) Darco FGD, a steam-activated lignite carbon; 2) AN Darco KB, a chemical-activated hardwood; 3) AN Darco PC 100, a chemical-activated bituminous coal; 4) Barnebey & Sutcliffe (B&S) Corp. CB, a 10% iodine-impregnated, steam-activated coconut shell; and 5) Alcoa Mersorb LH, a 5% sulfur-impregnated, steam-activated bituminous coal.

3.4 Tests Performed

During the past four-month period, thirteen sorbent tests were performed using the five sorbents. Test variables included sorbent type, sorption temperature, and HCl concentration. Conditions common to all tests were a nominal mercury concentration of 100 $\mu g/m^3$, a nominal gas rate of 23.5 scfh, and 4 vol% O_2 and 500 ppm SO_2 (balance N_2) in the flue gas.

Eight tests (one test each with AN Darco KB and Darco FGD, and two tests each with AN Darco PC 100, B&S CB, and Alcoa Mersorb LH) were performed at 150°C (300°F) to compare carbon effectiveness for elemental mercury removal at identical conditions. Two tests were performed at 120°C (250°F) with the AN Darco PC 100 to observe the effect of temperature on elemental mercury removal. Gaseous hydrochloric acid (HCl) at 50 ppm was added in two tests with Alcoa Mersorb LH and one test with AN Darco PC 100.

EPA Method 101A (6) was applied to the filter assembly influent and effluent simulated gas streams during one test with the Barnebey & Sutcliffe CB (iodine-impregnated carbon) in the presence of $O_2 + SO_2$. 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 whether elemental mercury was being converted to an oxidized form in the presence of Barnebey & Sutcliffe CB 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 (7) was applied to the filter effluent stream in the single test with the Darco PC 100 (chemically activated bituminous coal) in the presence of $O_2 + SO_2 +$ HCl. Similarly to the test with Barnebey & Sutcliffe CB, this test was applied to assess whether elemental mercury was being converted to oxidized forms (e.g., mercuric chloride) in the presence of Darco PC 100. With this test, oxidized 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.

3.5 Results and Discussion

Plots of mercury removal efficiency and sorbent contactor effluent gas mercury concentration are presented in Figures 2 and 3, respectively, for tests performed using 4 vol% O_2 and 500 ppm SO_2 combined. The data presented in Figure 2 are from tests previously described (8). Trends for mercury removal and effluent gas mercury concentration are similar to data from tests performed without O_2 or SO_2 in that Darco KB is the least effective sorbent, showing an instantaneous loss in removal efficiency and the most rapid attainment of breakthrough. Similarly to tests without O_2 or SO_2, Barnebey & Sutcliffe CB (iodine-impregnated carbon) retained essentially 100% removal efficiency.

Comparison of the test data indicates an inconsistency in the length of time to achieve breakthrough with the Darco KB, Darco FGD, Darco PC 100, and Mersorb LH. The first tests performed with SO_2 addition (data shown in Figure 2) indicate a substantial increase in the time of breakthrough, for all carbons except Darco PC 100, relative to tests performed without SO_2 (8). Subsequent replicate tests showed more rapid attainment of breakthrough, with Darco PC 100 being superior to all other carbons except the Barnebey & Sutcliffe CB. The differences in apparent effectiveness at seemingly identical conditions may be due to sulfiding of the carbons. During the earlier tests (8), carbons were exposed to SO_2 prior to mercury injection for a shorter duration (several minutes) relative to the carbons in the most recent tests where SO_2 was flowed during the entire carbon preheat period (one hour or more). The data of subsequent tests suggest

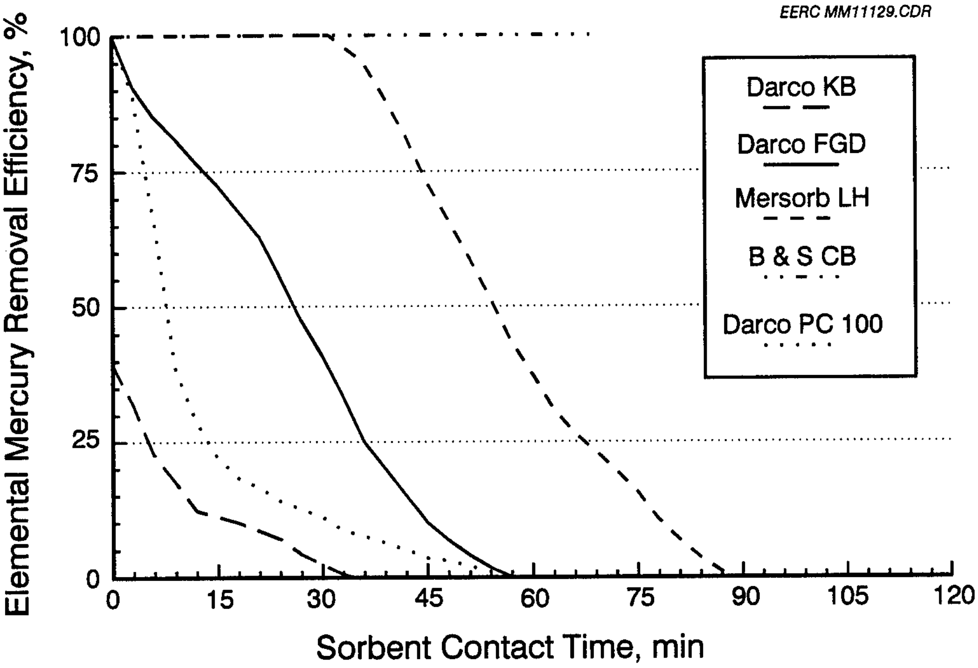

Figure 2. Mercury adsorption curves for activated carbons; 4 vol% O_2, 500 ppm SO_2. (SO_2 exposure time less than several minutes).

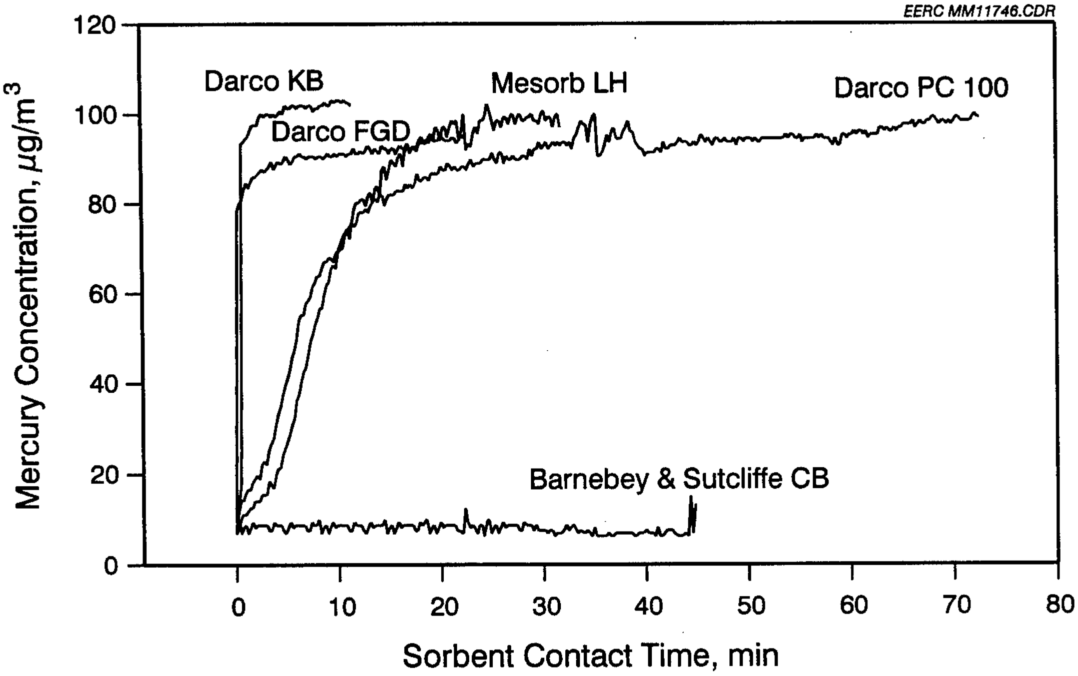

Figure 3. Comparative effectiveness of five activated carbons for elemental mercury adsorption; 4 vol% O_2, 500 ppm SO_2 (SO_2 exposure time up to 2 hours).

that Darco PC 100 is more effective than Mersorb LH which, in turn, is more effective than Darco FGD.

The EPA Method 101A test using Barnebey & Sutcliffe CB 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 Mersorb LH and Darco PC 100 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 flowed) is presented in Figure 4 for a test performed with Mersorb LH. 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 while flowing HCl, contrasts with the curve for Mersorb LH in Figure 3, 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 3. Upon injection of HCl, the return to essentially 100% mercury removal was immediate.

A replicate test with Mersorb LH and a single test with Darco PC 100 using 50 ppm HCl produced similar results. The EPA (draft) Method 29 with Darco PC 100 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

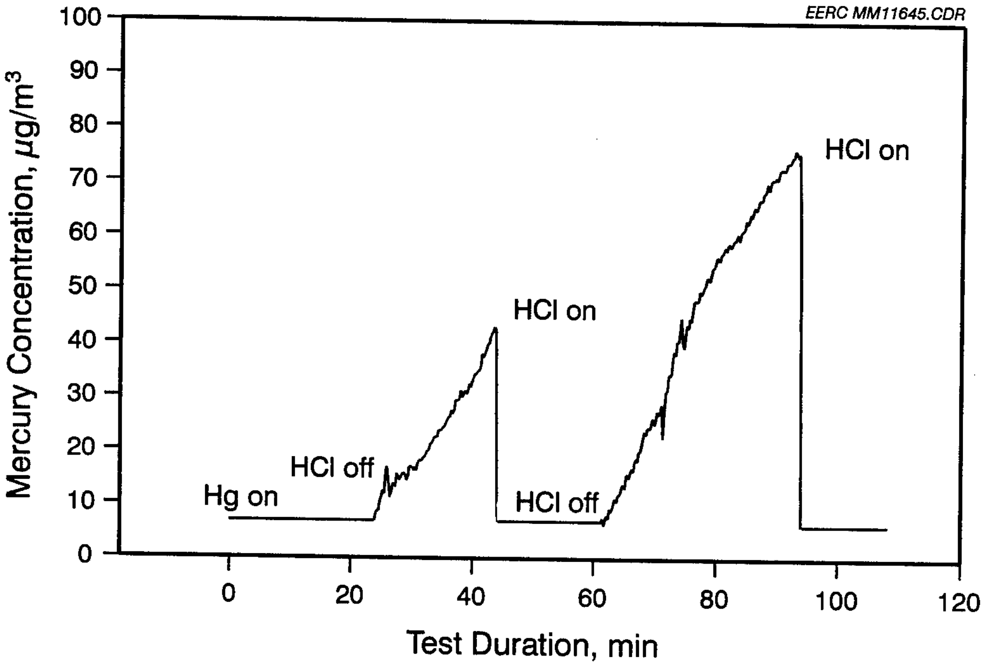

Figure 4. Mercury adsorption by sulfur-impregnated, steam-activated bituminous coal; 4 vol% O_2, 500 ppm SO_2, 50 ppm HCl.

mercury removal was over 97 wt%, agreeing well with the analyzer output. The detection of mercury in the peroxide trap further suggests that oxidized forms of mercury were produced and, as such, were also removed by the Darco PC 100.

4.0 CONCLUSIONS

The Barnebey & Sutcliffe CB (iodine-impregnated) activated carbon was the consistently superior sorbent and the Darco KB (chemically activated hardwood) was the consistently least effective sorbent for elemental mercury removal from simulated combustion flue gas containing SO_2 at 500 ppm. Adding SO_2 appeared to have the effect of increasing the sorbent removal efficiency of some carbons, possibly via carbon sulfiding. However, the level of sulfiding or increase in mercury removal efficiency may be related to the length of time the carbons are exposed to SO_2 prior to mercury injection.

Adding HCl at 50 ppm had the apparent effect of enhancing the mercury removal efficiency of the sulfur-impregnated and chemically activated bituminous coal-based carbons to a level comparable to that of the iodine-impregnated carbon.

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M97002298

Report Number (14) DOE/MC/30097-- 5668

Publ. Date (11) 199708

Sponsor Code (18) DOE/FE, XF

UC Category (19) UC-101, DOE/ER

DOE