FINAL TECHNICAL REPORT
September 1, 1997, through February 28, 1999

Project Title: **PREPARATION AND EVALUATION OF NOVEL ACTIVATED CARBONS FROM ILLINOIS COAL FOR MERCURY REMOVAL**

ICCI Project Number: 97-1/1.4A-4
Principal Investigator: Shiaoguo Chen, Illinois State Geological Survey (ISGS)
Other Investigators: Massoud Rostam-Abadi, ISGS; Hsing-Cheng Hsi and Mark Rood, University of Illinois; Carl F. Richardson, Radian International; Ramsay Chang, EPRI
Project Manager: Ron Carty, ICCI

ABSTRACT

The US EPA's Mercury Study Report to Congress in December 1997 identifies carbon-based processes as one of the lower-cost technologies for control of mercury emissions from utility flue gas. The goal of this project is to demonstrate that Illinois coal is a suitable and cost-effective precursor for commercial development and production of activated carbon for removal of mercury and other air toxics from coal combustion flue gas.

This project is a cooperative effort between the ISGS, UIUC, Radian and EPRI. ISGS and UIUC designed, prepared and characterized low-cost activated carbons. Radian performed bench-scale screening adsorption tests with the samples developed by the ISGS. EPRI provided funds for the carbon development program at the ISGS, bench-scale tests at Radian, pilot-scale tests at selected utility demonstration sites, and gave guidance to the technical direction of the research.

The process for producing activated carbon from Illinois coal and its application for removal of vapor phase mercury from combustion flue gas has been demonstrated at a pilot-plant level. More than 100 pounds of activated carbon was prepared from an Illinois coal in a 16-in. ID fluid-bed reactor. The carbon product was tested at two EPRI sponsored pilot utility demonstration sites which involved the injection of activated carbon into a slipstream of coal combustion flue gas. Under comparable test conditions, Illinois coal-derived activated carbon removed an equal or greater amount of mercury than a commercial vapor phase carbon manufactured by American Norit. Research in this year was focused on the development of low-cost sorbents for injection processes and super-sorbents for fixed-bed or moving-bed configurations. Several low-cost coal-based sorbents have already been developed at the ISGS. A modified coal sorbent (MCS) was recently tested on a slipstream of a coal combustion flue gas at the EPRI's Environmental Control Test Center (Barker, NY). MCS showed very promising mercury removal capacity. This type of low-cost coal sorbent would be suitable for fixed-bed or moving-bed configurations.

Significant progress has been made towards the understanding of the mechanism of vapor phase mercury adsorption onto activated carbon and other sorbents. The study has provided information relating to the role of functional groups at carbon surfaces on mercury adsorption and will guide the development of low-cost and super-sorbents.

Pages 4 through 10 contain proprietary information

EXECUTIVE SUMMARY

Background

The Clean Air Act Amendments of 1990 listed 189 substances as hazardous air pollutants, of which 37 substances have been detected in power plant emissions. Of the 37 hazardous air pollutants, 11 are trace metal species. Mercury is the trace metal species of greatest concern due to perceived risks from environmental release, and because it is present mainly in a vapor form not captured effectively by existing particulate removal systems.

Carbon-based processes (both direct injection and fixed-bed) have been developed for control of mercury emission from municipal- and hazardous-waste incinerators. Existing data from incinerators provide some insights on mercury control, but this data cannot be used directly for coal-fired utilities as mercury concentrations, species, and process conditions differ greatly between utilities. Injection of activated carbon upstream of a particulate control system has potential for providing a low-cost method of controlling mercury emissions from utility flue gas. The low concentrations of mercury in the flue gas and limited exposure time (<3 seconds) of the sorbent generally require large amounts of activated carbons in these sorbent injection tests. To achieve high Hg removal (>90%), the required ratio of carbon to mercury (C/Hg) in the flue gas has generally been found to be 3,000-20,000 (on weight basis), depending on process conditions. Tests have shown that the C/Hg ratio required in M.S.W. incinerators is more than an order of magnitude lower than that necessary to achieve similar mercury removal in coal combustors.

The high C/Hg ratio is a result of either mass transfer limitations or a low mercury capacity of carbon. The low mercury capacity can be due to either the extremely low concentration of mercury in the flue gas, or the low reactivity of the carbon. To reduce the operating cost of the carbon injection process, a more efficient sorbent that can operate at a lower C/Hg ratio or a lower-cost sorbent, or both, is required. A study of the physical and chemical processes that affect mercury removal from flue gas and a systematic sorbent development project would be required to develop an efficient, cost-effective carbon injection process for removal of mercury from coal-fired utility flue gas.

Results from Years 1 and 2

Significant progress was made during the last two years of this program. A mass-transfer analysis was conducted on the carbon injection process. Mass-transfer analyses showed that mercury transfer from the bulk flue gas phase to the external surface of carbon particles (film mass-transfer) plays a dominant role in determining carbon/mercury ratio of the injection process. Intraparticle diffusion, by contrast, was found not to be important. For an activated carbon with average particle size of 10 μm, the predicted minimum C/Hg ratio by mass transfer is about 13,600. This minimum C/Hg ratio gives some guidance to lower the cost of the carbon injection process.

A study was initiated to evaluate the importance of internal structure and surface chemistry of carbon-to-mercury capture. The study showed that activated carbon used in the injection process should be microporous and contain surface functional groups. Guided by this theoretical analysis, more than 20 activated carbon samples were prepared from several Illinois coals. The results showed that low-cost activated carbon can be produced from some Illinois coals for mercury removal from utility flue gas. Results from lab-scale experiments performed at Radian showed that the adsorption capacity of the Illinois coal-derived activated carbon (ICDAC), for both the elemental and oxidized mercury, is comparable to a commonly used commercial product (Norit FGD carbon).

The ISGS produced more than 100 pounds of activated carbon from an Illinois coal in a pilot reactor located at Svedala Industries, Oak Creek, WI. There were no processing problems during the production runs. The activated carbon sample was tested in a toxins control pilot plant at CONSOL R&D and at two EPRI/USDOE-sponsored utility demonstration sites (slip-stream). The results from these tests indicated that the ICDAC has comparable or higher mercury removal capacity than the commercial carbon (Norit FGD) tested. The production cost of the ICDAC is estimated to be less than $400/ton.

In addition to ICDAC, a new class of low-cost, coal-based sorbent, identified as MCS, was developed. In bench-scale tests, several MCS samples showed significant ionic mercury equilibrium capacity. This type of sorbent may find application in flue gas where the ionic mercury species is dominant.

Goals and Objectives

The US EPA Mercury Report to Congress in December 1997 identifies carbon-based processes as one of the low-cost technologies for control of mercury emissions from utility flue gas. The goal of this project is to demonstrate that Illinois coal is a suitable and cost-effective precursor for commercial development and production of activated carbon for removal of mercury and other air toxics from coal combustion flue gas.

The project had seven tasks.

In Task 1, ISGS used an existing rotary kiln to produce the low cost activated carbon from Illinois coals (ICDAC).

In Task 2, the samples of ICDAC and low-cost modified coal sorbent (MCS) were tested at several utility sites.

In Task 3, More low cost sorbents were prepared and tested. Pound quantities (>20 pounds) of MCS samples were prepared for utility site mercury test to evaluate the performance of these exciting sorbents under realistic carbon injection conditions.

In Task 4, the roles of physical and chemical properties as well as surface chemistry of ICDAC and MCS samples were determined to understand critical properties for enhancing both the reactivity and the capacity of these samples for mercury capture. In addition to standard physical and chemical characterization techniques, X-ray absorption near edge structure (XANES) were used to study the role of certain carbon surface functional groups believed to be important for vapor-phase mercury adsorption.

In Task 5, regeneration of spent carbons from pilot scale tests was conducted.

In Task 6, a process economic analysis was performed by Svedala and ISGS to determine the manufacturing cost of the ICDAC and MCS based on an assumed production rate in a central Illinois location.

In Task 7, technical and management reports will be prepared and submitted to the ICCI.

Results and Discussion

Pound quantity of ICDAC and modified coal sorbent were produced by ISGS engineers. These samples were tested at several utility sites under real flue gas conditions. These tests showed that ICDAC is comparable or superior to commercial available FGD carbon at both cost and mercury removal performance. MCS also showed moderate adsorption capacity, but its cost has huge advantage over activated carbon.

More than a dozen low-cost sorbent samples were prepared and tested at Radian. These sorbents are not designed for large mercury adsorption capacity but are selected for their low cost. Some of these samples showed promising elemental and ionic mercury capacity. They could be used in injection processes.

The mechanism of mercury adsorption onto carbon surface was investigated to guide the development of low-cost coal-based sorbents. Bench-scale experimental results showed that concentration of mercury in flue gas influences adsorption capacity onto carbon. Mercury capacity increases linearly with increasing mercury concentration in flue gas for both elemental mercury and mercuric chloride.

In a carbon injection process, the injection temperature might be as high as 325 F. However, bench- and pilot-scale tests have shown that at temperatures above 275 F mercury adsorption capacity of carbon-based sorbents decreases sharply. To determine the effect of temperature on adsorption capacity, the experimental data obtained at several adsorption temperatures were used to calculate the heat of adsorption of mercury onto carbon. Both elemental mercury and ionic mercury showed a heat of adsorption of about 10 kcal/mol. This value represents a mercury-sulfur bond. Sulfur-impregnated carbons have been shown to be suitable for low-temperature vapor phase mercury adsorption. Experimental results obtained in this project indicate that 1-2 wt% sulfur deposition onto carbon improves mercury adsorption capacity of activated carbon. Higher concentrations of sulfur did not improve the capacity. These results indicate that sulfur is not the best functional group for preparing super sorbent for high temperature mercury adsorption.

The effect of flue gas composition on mercury adsorption was also investigated. Results showed that the presence of HCl in the flue gas increases mercury adsorption capacity onto carbon. When HCl was not present in flue gas, most carbon samples showed significant decrease in mercury adsorption capacity. HCl was responsible for enhancing the oxidation of elemental mercury in the presence of activated carbon. These results were used to conclude that adsorption of elemental mercury onto activated carbon is not only by physical interactions but may also involve chemical adsorption. This information is useful in identifying and developing super sorbents for mercury adsorption.

Regeneration of spent carbon was carried out. Results showed that regeneration under isothermal conditions was not successful. Leaching test of the spent carbon showed mercury adsorbed on activated carbon is stable, indicating that mercury-bearing activated carbon may be safely disposed with fly ash.

An economic analysis of ICDAC production process was conducted based on previous research conducted at ISGS. Results showed that the break-even price of an 80,000 ton/year plant for ICDAC is less than $350/ton. Which is considerable lower than the commercial product, which sells at more than $800/ton.

The remainder of this report contains proprietary information and is not available for distribution except to the sponsor(s) of this project.