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

ICCI Project Number:	96-1/4.2A-1
Principal Investigator:	Shiaoguo Chen, Illinois State Geological Survey (ISGS)
Other Investigators:	Massoud Rostam-Abadi, ISGS; Hsing-Cheng Hsi and Mark Rood, University of Illinois; William A. Rosenhoover, CONSOL, Inc.; Carl F. Richardson, Radian International; Ramsay Chang, EPRI
Project Manager:	Daniel Banerjee, ICCI

ABSTRACT

Carbon-based processes are believed to have the best prospect for low-cost, near term commercial use for control of mercury emissions from utility flue gas. The goal of this project is to develop and produce novel activated carbons from Illinois coal that can meet or exceed the mercury removal performance of commercial activated carbons, but at a lower production cost.

This project is a cooperative effort between ISGS, University of Illinois (UIUC), CONSOL, Radian and EPRI. ISGS/UIUC will develop, produce, and characterize low-cost activated carbons. Radian, will perform bench-scale mercury screening tests with the ISGS developed carbons. CONSOL will conduct mercury performance tests of the carbon sample in a 0.25 MWe flue gas treatment pilot plant. EPRI provides funds for mercury tests at Radian and will be an advisor to the project during the course of the research.

The results from this study show that low-cost activated carbon can be produced from some Illinois coals for removal of trace amounts of vapor phase mercury from utility flue gas. ISGS produced more than 100 pounds of an Illinois coal-derived activated carbon (ICDAC) in an 18-inch ID fluidized-bed pilot reactor at Svedala (Oak Creek, WI). This sample was tested at CONSOL's toxics control pilot-plant and at two EPRI/DOE sponsored utility demonstration sites (slip-stream). In these tests, the mercury removal performance of the ICDAC was comparable to or better than that of a most commonly used commercial activated carbon (Norit FGD). Results from bench- and pilot-scale tests indicated that both physical and chemical properties of activated carbon influence the adsorption of elemental mercury but only the chemical properties affect adsorption of ionic mercury. 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. Future work is, however, needed to further improve both reactivity and capacity of MCS.

The effects of physical and chemical properties of carbon-based sorbents on removal of vapor phase mercury from utility flue gas were investigated.

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 because of perceived risks from its environmental release, and because it is present mainly in the vapor form and is 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 these data cannot be used directly for coal-fired utilities because mercury concentrations, species, and process conditions differ greatly. Injection of activated carbon upstream of a particulate control system has the potential of providing a low-cost method for control of 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 the process conditions. Tests have shown that the carbon to mercury ratio require 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 could be a result of either mass transfer limitations or a low mercury capacity of carbon due to 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, either a more efficient sorbent that can operate at a lower C/Hg ratio, or a lower-cost sorbent, or both are 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 Year 1

Significant progress were made during the first year of this program. A mass transfer analysis was conducted for 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. The intraparticle diffusion, by contrast, was found not to be important. For an activated carbon with typical 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 carbon injection process.

A study was initiated to evaluate the importance of both the internal structures and surface chemistry of carbon for vapor phase mercury capture. This study showed that activated carbon used in injection process should be microporous and contain certain type of surface functional groups. Guided by this theoretical analysis, more than 20 activated carbon samples were prepared from two Illinois coals. The results showed that low-cost activated carbon can be produced from some Illinois coals for removal of trace amounts of vapor phase mercury 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 an 18-inch ID fluidized-bed 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 toxics 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.

Goals and Objectives

The goals of the program during the second year of this project were to continue the development of low cost, high reactivity activated carbon from Illinois coal and identify and quantify the effects of physical and chemical properties of carbon-based sorbents on removal of vapor phase mercury from utility flue.

The project had seven tasks. In Task 1, the role of physical and chemical properties of activated carbon on mercury sorption rate and capacity were systematically studied. Both Illinois-coal-derived and commercial activated carbons were used in these studies.

In Task 2, activated carbons with varying physical and chemical properties were produced from Illinois coal.

In Task 3, ICDAC samples were tested in a 0.25 MWe sorbent injection pilot-plant at CONSOL to determine the effects of sorbent properties, key process and flue gas variables on mercury capture under realistic flue gas conditions.

In Task 4, the feasibility of the reactivation of spent the activated carbon for multiple use were evaluated.

In Task 5, the physical and chemical properties of carbon samples were obtained to gain additional insight into the structure-property relationship and to elucidate key properties which have impact on mercury adsorption reactivity and capacity.

In Task 6, a process analysis and economic study including the technical issues involved in producing activated carbon from Illinois coal were conducted. A process flow sheet for the production of the novel activated carbon from Illinois coal was developed.

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

Results and Discussion---A mass transfer analysis conducted last year 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. For an activated carbon with typical particle size of 10 microns, the predicted minimum C/Hg ratio by mass transfer is about 13,600 (90% removal, 2 seconds exposure time). To grind carbon to a smaller particle size would be expensive. The very large C/Hg ratio implies that the minimum theoretical saturation capacity of the carbon required for 90% mercury removal will also be low. Therefore, one of the practical ways to reduce the cost of injection process is to reduce the cost of sorbent. A major focus during the reporting period was to develop low cost sorbent with required minimum mercury capacity.

More than a dozen of modified coal sorbent (identified as MCS) samples were prepared by using two different techniques from high volatile bituminous Illinois coals. The elemental mercury capacity of all MCS samples were negligible. However, the mercuric chloride capacity of some samples ranged from 300 to about 800 μg/gC. This value is comparable to the capacity of most activated carbon samples reported last year. Because the production cost

of MCS is expected to be substantially lower than that of the activated carbon, the MCS is a promising sorbent for mercury removal in an injection process.

About 50 pounds each of three MCS samples were prepared in a rotary kiln. The samples were tested both in bench scale and in a utility demonstration (slip-stream) site in New Jercy. Although bench-scale tests showed excellent mercury chloride capacity for the sample tested, very low mercury removal were observed in the in the utility slip-stream site tests. The reasons for the discrepancy between the bench- and pilot-scale results are still not determined. Two possible explanations are: 1) MC samples had very little reactivities, and thus showed no mercury removal during slip-stream test (where the residence time is shorter), and 2) C/Hg weight ratio used in these tests ranged from 10,000 to 20,000. Tests with higher C/Hg might have resulted in moderate mercury removal.

The physical (BET surface area, pore size and pore size distribution) properties of more than a dozen of activated carbon samples were systematically measured. Attempts were made to correlate these data with mercury adsorption data. Little correlation was found between mercury capacity of the carbon samples and their BET surface area. This is because BET total surface area includes all of the surface areas accessible to nitrogen molecule which may not be accessible to mercury molecules.

Some correlation between elemental mercury capacity and the mesopore volume and micropore volumes were found. The elemental mercury capacity increases with increasing micropore volume and mesopore volume. This may indicate that mercury adsorption on activated carbon is chemical in nature and is enhanced by the micropore structure of carbon. In other words, both physical and chemical properties of carbon are important. This information will help optimize the pore structure of activated carbon for mercury adsorption.

No correlations was found between ionic mercury capacity and any of the physical properties tested. The ionic mercury capacity was less predictable than elemental mercury capacity.

For an activated carbon with a mercury capacity of 3000 μgHg/gC, only about 0.1% of BET surface area (assuming 700 m^2/g) is utilized by mercury molecules. This means that the potential to increase mercury capacity of an activated carbon is tremendous. The elemental capacity could be as high as 1 gHg/gC if all the carbon surface is occupied by mercury molecules. The role of carbon surface functional groups on mercury adsorption can potentially help identify ways to achieve high mercury adsorption capacity. . X-ray absorption near-edge spectrum (XANES spectrum) and X-ray photon spectroscop(XPS) were used to differentiate different functional groups on carbon. Results from this study are being analyzed and will be presented in the future reports to the ICCI.

CONSOL used a 0.25 MWe sorbent injection toxics control pilot plant to study the effects of sorbent properties, process and flue gas variables on mercury capture performance under realistic flue gas conditions. The variables investigated include: flue gas temperature, HCl concentration in the flue gas, fly ash concentration, carbon residence time in the duct and baghouse, and mercury speciation. CONSOL has completed the tests and the results are currently being analyzed.

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