

FINAL TECHNICAL REPORT
September 1, 1995, through August 31, 1996

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

ICCI Project Number: 95-1/4.2A-3
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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 substantially lower production cost.

This project was a cooperative effort between ISGS, University of Illinois (UIUC), CONSOL, and EPRI. ISGS/UIUC has developed, produced, and partially characterized a low-cost activated carbon. CONSOL conducted mercury performance tests of the carbon in a 0.25 MW_e flue gas treatment pilot plant. EPRI has funded three organizations (Radian, ADA, and UNDEERC) to test carbons and has been an advisor to the project during the course of the research.

During the past year, the results from a mass transfer analysis showed that film mass transfer plays an important role in the mercury removal process. Theoretical analyses were also carried out to evaluate the importance of carbon internal structures and surface functional groups. Guided by the mass transfer analysis and the results from theoretical calculations, more than 20 activated carbon samples were prepared from two Illinois coals. The optimal processing conditions for producing an activated carbon with desired properties were identified through these lab-scale studies. Several of these samples showed mercury (metallic and HgCl₂) reactivity and capacity comparable to those of commercial activated carbons. The estimated production cost of the Illinois-coal-based activated carbon is approximately one-fourth of its commercial counterpart. Two U.S. patent applications have been filed.

The ISGS has produced more than 100 pounds of activated carbon from an Illinois coal. Pilot-scale production showed little difficulty with the scaling-up of our process. The activated carbon samples produced at pilot-scale have been tested in a toxics control pilot plant at CONSOL R&D. The results from CONSOL test indicated that the ISGS activated carbon has significantly higher mercury removal capacity than a commercial carbon tested. The ISGS carbon will also be tested in a utility demonstration site (slip-stream) sponsored by EPRI/DOE in Pueblo, Colorado.

Page 4 through 19 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 MSW 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.

Goals and Objectives

The goal of this project is to develop and produce a low-cost, high reactivity activated carbon from Illinois coal and to evaluate the effectiveness of the product for removal of trace amount of mercury from coal combustion flue gases. This project is cost-shared with EPRI and CONSOL R&D.

The project has seven tasks.

Task 1 (Funded as a part of the EPRI study), the role of internal surface area, pore structure, and surface chemistry (surface functional groups) of activated carbon on mercury sorption rate and capacity were determined. Both Illinois-coal-derived and commercial activated carbons were used in these studies.

Task 2. A low-cost activated carbon that is suitable for removal of mercury from combustion flue gases was produced from an Illinois coal. Activated carbon samples, with varying physical properties (surface area, pore size and volume, particle size, etc.) and

different types and amounts of functional groups, were also produced.

Task 3. CONSOL has used a 0.25 MW_e sorbent injection pilot plant to determine the effects of sorbent properties, key process and flue gas variables on mercury capture under realistic coal combustion systems. The process and flue gas variables tested include: mercury concentration in the flue gas, flue gas temperature, activated carbon residence time in the duct and mercury species (Hg and HgCl₂).

Task 4. A selected number of activated carbons which have been tested for mercury removal will be thermally regenerated. This Task was not conducted in the past year and will be performed in the second year of the contract. The results of these tests will be used to evaluate the feasibility of the reactivation of the activated carbon for multiple use.

Task 5. Activated carbon samples were characterized for their physical and chemical properties to gain additional insight into the fundamentals of preparation and properties of the product. The mercury removal performance of the carbon sorbent from the parametric tests were correlated with the characterization data to elucidate properties which impact performance.

Task 6. A process analysis and economic study including the technical issues involved in producing activated carbon from Illinois coal, the operating conditions controlling the mercury capture from flue gas, and the fundamental chemical and physical mechanisms which control sorbent capture of mercury at conditions applicable to coal combustion systems will be conducted. A process flow sheet for the production of the novel activated carbon/char from Illinois coal will be developed.

Task 7. Technical and management reports are prepared and submitted to the ICCI.

Results and Discussion

Significant progress has been made during the first year of this contract: 1). A mass transfer analysis was conducted for the carbon injection process; 2). Theoretical investigations of the effects of the internal structures of activated carbons on mercury capture were carried out; 3). On the basis of the theoretical investigations, several activated carbons have been designed and prepared at the bench-scale; and finally, 4). the data obtained in bench-scale experiments have been used at pilot scale activated carbon preparation.

Mass transfer analyses showed that mercury transfer from the bulk flue gas phase to the external surface of carbon particles (film mass transfer) plays an important role in determining carbon/mercury ratio of the injection process. The intraparticle diffusion, by contrast, was found not to be important. The predicted carbon/mercury ratios, were calculated using a residence time of 3 seconds, carbon particle density of 0.5 g/cm³, inlet mercury concentration of 10 µg/Nm³ (600 µg/Nm³ for MSW flue gas), and outlet mercury concentration of 1 µg/Nm³ (60 µg/Nm³ for MSW flue gas). In these calculations it was assumed that the mercury adsorption capacity of the carbon and the carbon reactivity are not limiting the mercury removal process. Therefore, the results obtained in the mass transfer analyses represent the minimum amount of carbon needed to achieve a specific mercury removal. For an activated carbon with a typical particle size of 10 µm, the minimum C/Hg ratio is about 13,600.

The importance of both the internal structures and surface chemistry of carbon for mercury

capture has been analyzed. Our analysis showed that carbon used to remove mercury from utility flue gas by injection process should be microporous and with functional groups on its surface.

Four activated carbon fiber samples, ACF-10, ACF-15, ACF-20, ACF-25, were acquired to study the pore size effect on the mercury capacity of the material.

Guided by our theoretical analysis, more than 20 activated carbon samples were prepared from two Illinois coals. The results showed the Illinois coal-derived carbons are comparable in mercury capacity to their commercial counterpart--the Norit FGD carbon (both about 2000 $\mu\text{gHg/gC}$). These samples have also been used to investigate the roles that the internal structures and surface functional groups of carbon play in the process of mercury removal.

Encouraged by the results, EPRI has arranged for a pilot-plant (slip-stream) demonstration test of the ISGS carbon material at a utility test site in Pueblo, Colorado in August 1996 and ISGS has conducted a two phase pilot-scale production program.

In phase I, three Illinois coals from three different operating mines were located. Lab-scale experiments were performed with a 5-cm ID fluidized-bed reactor to obtain scale-up data and identify optimum processing conditions for producing an AC sample with desirable properties.

In phase II, the production conditions identified at the ISGS have been used to produce more than 100 pounds of activated carbon from Illinois coal. The ISGS engineers worked with Svedala Inc., a chemical process equipment firm located in Oak Creek, WI, to produce the activated carbon product in a 46-cm ID fluidized-bed reactor. The carbon product was tested at Radian and CONSOL R&D. The results showed that the mercury capture of ISGS activated carbon is significantly better than its commercial counterpart. The cost of ISGS carbon, however, is more than 75% lower than the commercial carbon.

Two U.S. patent applications have been filed and a paper titled "Mercury Removal from Combustion Flue Gas by Activated Carbon Injection: Mass Transfer Effects" was presented at the American Chemical Society Annual Meeting of Fuel Chemistry Division in New Orleans on March 23-28, 1996.