Title: **Development of Novel Activated Carbon-Based Adsorbents for Control of Mercury Emissions from Coal-Fired Power Plants**

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Abstract

The objective of this project (Grant No. DE-PS22-96PC96212) is to design and develop new adsorbents for the control of mercury emissions from coal-fired power plants. Activated carbons were selected as the primary adsorbents to evaluate their capacity for mercury uptake under various conditions. Novel sulfur impregnation protocols have been developed in order to enhance the performance of these carbons. Several control parameters were carefully adjusted and the impact of these factors on the carbon performance was investigated. Comparing to commercially available carbons, these sulfur-impregnated carbons demonstrated superior mercury removal capacity in terms of adsorption kinetics and total dynamic adsorptive capacity. Physical and chemical structures of these adsorbents were studied to further understand the adsorbent performance at microscopic level.

A commercially available bituminous coal-based activated carbon (BPL) was supplied by the manufacturer (Calgon Carbon Corporation, Pittsburgh, PA) and was impregnated with elemental sulfur in an inert atmosphere at 250, 400 and 600 ^{o}C. Two different impregnation methods were evaluated in this study. In the first method, carbon and sulfur were placed into two separate ceramic boats in a tube furnace and nitrogen gas was used to carry sulfur vapors to the carbon surface. The second method used only one ceramic boat where carbon and sulfur flakes were mixed together. The designations of these newly developed adsorbents are based on the starting material, the initial sulfur to carbon ratio (SCR), and the impregnation temperature. For instance, BPL-S-4/1-600 means that BPL carbon was impregnated with sulfur at SCR of 4/1 and temperature of 600 ^{o}C. Letter M is added to denote the second impregnation method. 60×80 U.S. mesh size carbon was used to perform the dynamic mercury uptake measurements (column runs), while 170×230 U.S. mesh size carbon was used for the kinetic tests.

The column runs were performed using a fixed-bed reactor to which vapor phase mercury (55 $\mu g/m^3$) was supplied in a down-flow mode at 1.0 L/min. Pure nitrogen, carbon dioxide/nitrogen mixture and oxygen/nitrogen mixture were used as carrier gases. The system was operated in continuous mode at 140 ^{o}C and 1 atm. The effluent mercury concentration was monitored by atomic adsorption spectrophotometer (AAS). The kinetic study was performed in a closed batch system using a high flow rate compressor for gas recirculation. Different initial mercury concentrations (110, 380 and 1080 $\mu g/m^3$) were used for this study, and the concentration decrease inside the system was also monitored by AAS.

Comparing to virgin coal and virgin activated carbon (BPL), a commercially available sulfur-impregnated carbon (HGR) and BPL-S and BPL-S/M demonstrated excellent mercury uptake capacity. For example, virgin carbon and coal only adsorbed about 5 μg Hg/g adsorbent before they reached the 100% breakthrough. HGR could adsorb up to 44 μg Hg/g carbon. However, the amount of mercury captured by BPL-S-250 was about 600 μg Hg/g carbon, while BPL-S-600 adsorbed as much as 2400 μg Hg/g carbon.

It was found that the impregnation temperature was the most important factor influencing the performance of the sulfur-impregnated carbons. For the BPL-S-4/1 series, the capacity increased 4 times as the impregnation temperature increased from 250 to 600 ^{o}C. On the other hand, SCR did not have nearly as pronounced impact on the adsorptive capacity of these adsorbents (the capacity for mercury uptake only varied by 50% as the SCR was reduced from 4:1 to 1:2). The effect was more obvious for the adsorbents prepared by the second impregnation method.

Carbons impregnated with sulfur at higher temperatures possessed more short chain sulfur molecules that were very active, while long chain and ring-structured sulfur molecules were the major sulfur allotropes in carbons prepared at lower impregnation temperatures. Thermogravimetric analysis (TGA) showed that higher impregnation temperature also created stronger bonding between sulfur and carbon surface. Thus, sulfur would not tend to migrate during the column run. BET method was used to analyze the specific surface area and pore size distribution for these adsorbents. The results showed that adsorbents prepared at higher temperatures still had large surface area while the surface area decreased with a decrease in the impregnation temperature. This was mainly due to the condensation of large amount of sulfur molecules at low temperatures. BET results also showed that adsorbents prepared at higher temperatures had more mesopores than the adsorbents prepared at lower temperatures. Obviously, these mesopores provided easy access to the inner pores of the carbon particles and facilitated sulfur-mercury reaction.

Before using carbon dioxide and oxygen as part of the carrier gas, it was confirmed that no reaction occurred between mercury and CO_2 or O_2 under the experimental conditions used in this study. When CO_2/N_2 mixture was used as a carrier gas, the performance of the adsorbents did not change. It was concluded that carbon dioxide was an inert gas and it would not affect the carbon performance. When oxygen /nitrogen mixture was used as a carrier gas, the mercury uptake capacity increased about 15% as the oxygen concentration varied from 3% to 9%. After performing surface acidic functional group analysis, it was found that the presence of oxygen increased the amount of acidic functional groups on the adsorbents. However, these functional groups did not promote mercury adsorption or the reaction between mercury and sulfur. It was concluded that the improved performance of these adsorbents was mainly due to the fact that carbon acted as a catalyst for the reaction between oxygen and mercury.

The kinetics study showed that smaller particle size resulted in faster mercury uptake. In addition, modeling results showed that for the carbon particle size below 40 μm and the contact time below 2 seconds, injection of sorbents with higher capacity would reduce the required injection dosage.

List of Published Journal Articles and Presentations Since the Grant Inception

1. Liu, W., Vidic, R. D., Brown, T. D. "Optimization of Sulfur Impregnation Protocol for Fixed-Bed Application of Activated Carbon-Based Sorbents for Gas-Phase Mercury Removal", *Environmental Science and Technology*, Vol. 32, **1998**, pp. 531-538.

2. Vidic, R. D., Chang, M-T., Thurnau, R. C. "Kinetics of Vapor-Phase Mercury Uptake by Virgin and Sulfur-Impregnated Activated Carbons", *Journal of Air and Waste Management Association*, Vol. 48, **1998**, pp. 247-255.

3. Liu, W., Korpiel, J. A., Vidic, R. D. "Effect of Impregnation Protocol on Physical Characteristics and Adsorptive Properties of Sulfur Impregnated Carbon for Vapor-Phase Mercury", Paper 97-WA72A.02, Air & Waste Management Association's 90th Annual Meeting & Exhibition, June 8-13, **1997**, Toronto, Ontario, Canada.

4. Liu, W., Vidic, R. D. "Selecting a Proper Impregnate to Improve the Performance of Mercury Control by Different Adsorbents", presented at the 5th International Activated Carbon Conference, Pittsburgh, PA, September 17-18, **1997**.

5. Vidic, R. D., Flora, J. R. V., Chang, M. T., "Rate Studies on Vapor Phase Mercury Uptake by Various Activated Carbons", Proceedings of the 23rd Biennial Conference on Carbon, Pennsylvania State University, Station College, PA, July 13-18, **1997**.

6. Liu, W., Vidic, R. D., Korpiel, J. A. "Dynamic of Fixed-Bed Carbon Adsorbents for Vapor-Phase Mercury Uptake", presented at the 23rd Biennial Conference on Carbon, Pennsylvania State University, Station College, PA, July 22-24, **1997**.

7. Korpiel, J. A., Vidic, R. D. "Effect of Sulfur Impregnation Method on Activated Carbon Uptake of Gas-Phase Mercury", *Environmental Science and Technology*, Vol. 31, **1997**, pp. 2319-2325.

List of Articles Submitted for Future Publication and Presentation

1. Liu, W.; Vidic, R. D. “Evaluation of Carbon-Based Substrates for the Production of Economical Mercury Sorbents”, 98-RA79B.05, to be presented at Air & Waste Management Association's 91th Annual Meeting & Exhibition, June 14-18, **1998**, San Diego, CA.

2. Flora, J. R., Vidic, R. D., Liu, W., Thurnau, R. C. “Modeling Powdered Activated Carbon Injection for the Control of Mercury Emissions from Coal-Fired Power Plants”, *Journal of Air and Waste Management Association*, in press.

List of Students Receiving Financial Support from This Grant

Liu, Wei, Ph. D. student.