

## **Carbon From Fly Ash As Sorbents For Mercury**

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### **ABSTRACT**

A laboratory-scale packed-bed reactor system is used to screen carbon sorbents for their capability to remove elemental mercury from various carrier gases. When the carrier gas is argon, an on-line atomic fluorescence spectrophotometer (AFS), used in a continuous mode, monitors the elemental mercury concentration in the inlet and outlet streams of the packed-bed reactor. The mercury concentration in the reactor inlet gas and the reactor temperature are held constant during a test. For more complex carrier gases, sorbent capacity is determined off-line by using a cold vapor atomic absorption spectrophotometer (CVAAS). The capacities and breakthrough times of several commercially available activated carbons, as well as novel carbon sorbents derived from fly ash, were determined as a function of various parameters. The mechanisms of mercury removal by the sorbents are suggested by combining the results of the packed-bed testing with various analytical results.

Activated carbons can remove mercury from flue gas produced by the combustion of coal. However, there are problems associated with the use of activated carbons for mercury removal from flue gas. Since activated carbons are general adsorbents, most of the components of flue gas will adsorb on carbon, with some in competition with mercury. Carbon sorbents operate effectively over a limited temperature range, typically working best at temperatures well below 300EF. The projected annual costs for an activated carbon cleanup process are high, not only because of the high cost of the sorbent, but also because of its poor utilization/selectivity for mercury. Carbon-to-mercury weight ratios of 3,000:1 to 100,000:1 have been projected. In addition, activated carbons can only be regenerated a few times before exhibiting an unacceptably low activity for mercury removal. Therefore, development of improved activated carbons, as well as novel carbons derived from fly ash, merits further research.

Three classes of carbon sorbents have been examined. These categories are: 1) unpromoted activated carbons, 2) chemically promoted activated carbons, and 3) carbons derived from fly ash. The unpromoted carbons exhibit a small capacity for elemental mercury, probably due to physical adsorption. Carbons chemically promoted with chlorine, iodine, or sulfur exhibit much larger capacities; the mechanism of mercury removal being chemisorption and/or chemical reaction. The carbons derived from fly ash were obtained from pilot-scale combustion units located on-site at the National Energy Technology Laboratory (NETL). Initial results suggest that the origin of the carbon, be it coal (activated carbons) or fly ash, does not have a significant effect on sorbent capacity.

Many of the experiments used a gas feed of 585 ppb elemental mercury in argon. This is dramatically different than the composition of a typical flue gas from a coal-fired utility. Most of the

components in a typical flue gas (e.g. acid gases, etc.) can adsorb on an activated carbon and could possibly hinder or help the adsorption of mercury on carbon. The ultra-high purity argon carrier gas was selected to maximize the sensitivity of the AFS for elemental mercury. However, the capacity of the sorbents in argon may be quite different from the capacity in flue gas and will be the subject of future investigations. The effect of oxygen on sorbent capacity has been examined. Initial results are that oxygen does not significantly alter sorbent capacity. Also, the temperatures at which sorbent capacities were determined are 140EF, 280EF, and 350EF. These temperatures were chosen because of their potential relevance to coal-fired utilities. If a sorbent were contacted with the flue gas by injection into the duct work of a coal-fired utility after the air preheater but before the particulate collection device, it would experience temperatures in the range of 350EF to 280EF. If a sorbent was placed downstream of a wet scrubber, it would encounter a temperature near 140EF. The carbons exhibit much greater capacities at the lower temperatures.

The untreated carbons separated from fly ash exhibited a small capacity for the removal of elemental mercury from argon. This is similar to the behavior of the unpromoted commercially available activated carbons. The carbons derived from fly ash showed much larger capacities after treatment with chlorine. This is also in accord with prior experiments in which a commercially available activated carbon was treated with chlorine. Additionally, the carbons extracted from fly ash are not activated, and possess small BET surface areas. A successful effort was made to increase the surface area of the carbons separated from fly ash by thermal oxidation in air at 750EF.

The results obtained from the packed bed unit require judicious interpretation when attempting to extrapolate relevance to sorbent introduction via duct injection on an industrial size combustor. One unpromoted activated carbon was also studied in the NETL 500-lb/hr pilot-scale combustor unit for the removal of mercury from the flue gas. When introduced at sorbent to mercury ratio of around 5,000 to 1, the unpromoted activated carbon used in the 500-lb/hr unit achieved a high level of mercury removal. However, the used carbon recovered from the 500-lb/hr unit had mercury levels of less than 300 ppm (0.3 mg Hg/gram). Unpromoted activated carbons sequester elemental mercury via physical adsorption and therefore exhibit small capacities. Nevertheless, duct injection at large sorbent to mercury ratios allows them to achieve high levels of removal of mercury from flue gas. Future work will focus on testing novel fly ash sorbents in a simulated flue gas containing 2000 ppm SO<sub>2</sub>, 500 ppm NO, 5 % O<sub>2</sub>, 16% CO<sub>2</sub>, 600 ppb Hg, and balance N<sub>2</sub>.