DEVELOPMENT OF IMPREGNATED SORBENTS FOR THE CONTROL OF VAPOR-PHASE ELEMENTAL MERCURY EMISSIONS

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Introduction

This study was designed to evaluate the applicability of novel activated carbon-based sorbents for the control of mercury emissions from coal-fired power plants. Sulfur impregnation protocol using hydrogen sulfide as a sulfur source was evaluated for its ability to produce mercury sorbents that are equally effective as sulfur-impregnated activated carbons previously developed in our laboratory. In addition, the adsorption performance of sulfur-, chloride- and chelating agent-impregnated activated carbon for the uptake of vapor-phase elemental mercury was evaluated using a fixed-bed adsorption system.

Experimental

All carbons used in this study were produced from commercially-available, bituminous-coal-based BPL carbon (Calgon Carbon Corporation, Pittsburgh, PA). BPL carbon was impregnated with elemental sulfur (BPL$_S$), hydrogen sulfide (BPL$_H$), copper chloride (BPL$_C$), β-aminoanthraquinone (BPL$_A$), 2-(aminomethyl)pyridine (BPL$_P$), and 2-aminoethanethiol (BPL$_T$).

BPL$_S$ BPL was impregnated with elemental sulfur at 600 °C using the procedure described by Korpiel and Vidic [1].
BPL$_H$ The new sulfuration process involved hydrogen sulfide oxidation with oxygen at relatively low temperatures (below 200 °C) over the substrate surface as suggested by Daza et al. [2].
BPL$_C$ The chloride-impregnated carbon was produced by the method of incipient wetness using a solution of copper chloride in 6N nitric acid.
BPL$_A$ The procedure used for the impregnation of aminoanthraquinone follows that given by Mazur et al. [3].
BPL$_P$ BPL carbon was outgassed and exposed to acrylyl chloride in the same manner as for the production of BPL$_A$ and then contacted with 2-(aminomethyl)pyridine solution.
BPL$_T$ After outgassing at 1000 °C and exposure to acrylyl chloride vapors using the same procedure as for BPL$_A$, BPL carbon was impregnated with 2-aminoethanethiol hydrogen chloride in toluene using the method of incipient wetness.

All sorbents were tested for their ability to adsorb vapor-phase elemental mercury using a fixed bed adsorber charged with 100 mg of sorbent (unless otherwise noted) and operated at 140 °C using an influent mercury concentration of 55 µg/m³ and nitrogen as a carrier gas at a flow rate of 1 L/min. Detail description of the adsorber testing protocol is provided elsewhere [1].

Results and Discussion

Figure 1 compares the performance of BPL$_S$ and BPL$_H$–0.25, which was sulfurized for 0.25 hours and showed the best performance among BPLH series. BPL$_S$ was produced by impregnating BPL with elemental sulfur at 600 °C, which is much higher temperature than that used for the impregnation of BPL with H$_2$S. Due to the higher temperature, the sulfur in BPL$_S$ is more evenly distributed in pore structure, occupying deeper, narrower pores [1]. BET surface area analyses showed that sulfur impregnation with H$_2$S for 15 minutes caused the specific surface area to decrease by about 45 %, while impregnation for 4 hours decreased the surface area by more than 95 %. On the other hand, BPL impregnated with elemental sulfur at 600 °C had only 20 % lower surface area than virgin BPL. However, the use of BPL$_H$ sorbents for mercury control could have positive impact on pollution prevention efforts for refineries and natural gas clean up operations, where H$_2$S is often considered a waste stream.
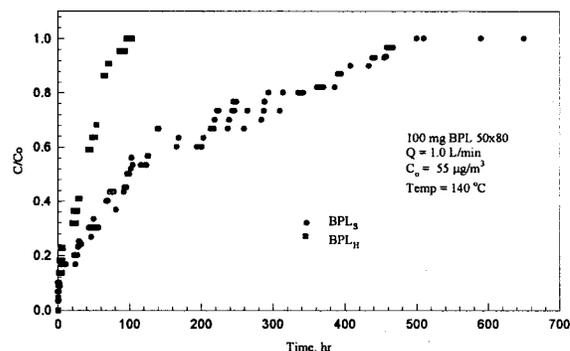

Figure 1. Impact of Sulfur Impregnation method on Mercury Uptake

The performance of chloride impregnated BPL carbons was examined using three different empty bed contact times (EBCTs) to determine the degree to which contact time affects the dynamic adsorption capacity of the impregnated carbon. Figure 2 compares mercury breakthrough from the reactors charged with BPL$_S$ and BPL$_C$ sorbents and operated at EBCT of 0.017.
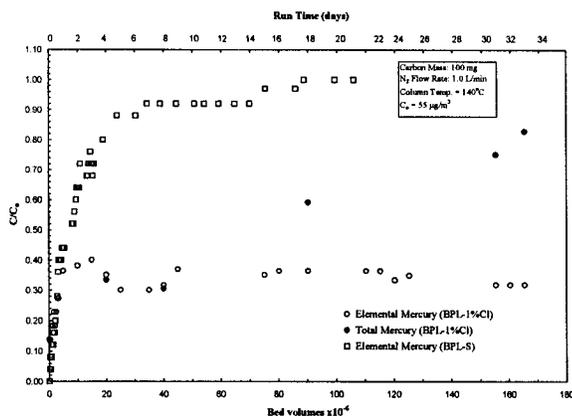
Figure 2. Performance of BPL$_S$ and BPLC (EBCT=0.017s)

Immediately evident in all breakthrough curves is the presence of other species of mercury in the effluent (besides Hg^0) as detected by the impinger analyses. This indicates that a reaction between the copper chloride on the carbon surface and the influent mercury results in a percentage of the reacted mercury that is not adsorbed by the carbon. The comparison of the dynamic adsorption capacities of BPL$_C$ shows approximately a thirteen-fold increase in the capacity with only a two-fold increase (from 0.017 to 0.034 s) in the EBCT. Considering the fact that the dynamic adsorptive capacity of virgin carbon was found to be relatively constant for these EBCTs, it can be concluded that mercury uptake by chloride impregnated carbon is limited by the rate of chemical reaction between chloride and mercury rather than by the rate of mass transfer of mercury onto the carbon surface.

The breakthrough studies with BPL carbon impregnated with various organic compounds are summarized in Table 1. All runs were performed using the EBCT of 0.017 s and 55 µg/m^3 influent mercury concentration. M$_{30}$ represents the adsorptive capacity measured at 30% mercury breakthrough.

Table 1. Performance of BPL$_A$, BPL$_P$, and BPL$_T$

Sorbent	Temp. (°C)	M$_{30}$ (µg Hg/g)
BPL$_A$	140	39
	25	297
BPL$_P$	140	0.2
	25	0.3
BPL$_T$	140	14
	25	1247

The process of impregnation of the AAQ onto the carbon is mediated by the acrylyl chloride which binds with the amine group of the AAQ, leaving the amine group unavailable for subsequent reaction with Hg(g). Therefore, the interaction between the AAQ and Hg(g) most likely occurs at the carbonyl sites of the AAQ where mercury

may be complexed. This hypothesis was further confirmed by the finding that all of the impingers, regardless of the presence or absence of aminoanthraquinone, are equally ineffective in capturing mercury vapors, suggesting that aminoanthraquinone is poor mercury solvent, and that the only mechanism of mercury capture by BPL$_A$ is that proposed above.

BPL$_P$ had negligible dynamic adsorption capacities for mercury at both room temperature and elevated temperatures. One possible explanation is that the functional amine which forms the bond between the acrylyl chloride and the picolyl amine is not available to interact with mercury since it is already utilized.

BPL$_T$ performed significantly better at room temperature than the other sorbents and the complete breakthrough of mercury was not observed even after 30 days of operation. However, at 140°C, the adsorptive capacity of the BPL$_T$ was approximately one third that of BPL$_A$. This is indicative of a relatively weak bond between the thiol ligand and mercury or the lack of thermal stability of the bond between thiol and carbon surface.

Conclusions

The performance of BPL$_S$ and BPL$_H$-series increased significantly over the virgin BPL carbon. BPL impregnated for 0.25 hr (BPL$_H$-0.25) showed best performance for mercury adsorption. Although BPL$_S$ and BPL$_H$-0.25 had similar sulfur content, BPL$_S$ showed much better performance.

The dynamic capacity of BPL$_C$ was found to increase with an increase in EBCT and chloride content and to decrease with an increase in temperature. BPL$_C$ exhibited appreciable initial mercury breakthrough due to slow kinetics of mercury uptake, while substantial concentrations of oxidized mercury species were detected in the effluent from a fixed-bed adsorber. BPL$_A$ and BPL$_T$ exhibited high dynamic adsorption capacities at 25 °C, but had much lower dynamic adsorption capacities at 140 °C. BPL$_P$ exhibited very poor dynamic adsorption capacities at both 25 and 140 °C.

References

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