

APPLICATION OF SULFUR-IMPREGNATED ACTIVATED CARBONS FOR THE CONTROL OF ELEMENTAL MERCURY EMISSION FROM COAL-FIRED POWER PLANTS

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Introduction

The adsorptive removal of elemental mercury from flue gases by activated carbons can be significantly improved by impregnating sulfur-based reactive constituents on the carbons that are capable of transforming the mercury into extremely stable sulfur-containing compounds. The primary goal of this study was to investigate the impact of sulfur impregnation method on the efficiency of vapor phase mercury uptake by these sorbents. Two operational parameters that were tested during the impregnation procedure included temperature and the initial sulfur to carbon ratio (SCR) during impregnation, while the performance of these carbons was evaluated using fixed-bed breakthrough studies with nitrogen as a carrier gas.

Experimental

Two types of activated carbon-based sorbents were used in this study: HGR (Calgon Carbon Corporation, Pittsburgh, PA), a commercially available sulfur-impregnated carbon, and BPL-S, which was produced by impregnating a bituminous coal-based virgin activated carbon, BPL (Calgon Carbon Corporation, Pittsburgh, PA), with sulfur in nitrogen atmosphere at elevated temperatures. Detail description of the impregnation protocol is provided elsewhere [1] and will not be repeated here. Three different temperature settings were selected for the impregnation process, namely 250, 400 and 600 °C. The designation of newly derived sorbents was based on the starting material, the initial sulfur to carbon ratio (SCR), and impregnation temperature. For example, BPL-S-4/1-600 denotes a BPL carbon that was impregnated with sulfur at SCR of 4:1 and temperature of 600 °C.

All sorbents used in this study were evaluated for mercury uptake in a fixed bed adsorber according to procedure described by Korpiel and Vidic [1]. QA/QC experiments revealed that there was negligible adsorption of mercury onto the tubing and experimental adsorbers, no interference in the AAS measurement of elemental mercury due to possible HgS formation in the gas phase downstream of the adsorber containing sulfur-impregnated carbon.

Results and Discussion

Thermogravimetric analysis (TGA) conducted on BPL, HGR, and BPL-S carbons showed BPL-S carbon lost a negligible amount of its impregnated sulfur, while HGR carbon lost 88% of its sulfur content (Figure 1). This shows that the bonding of sulfur molecules to the carbon matrix is much stronger in BPL-S than in HGR carbon.

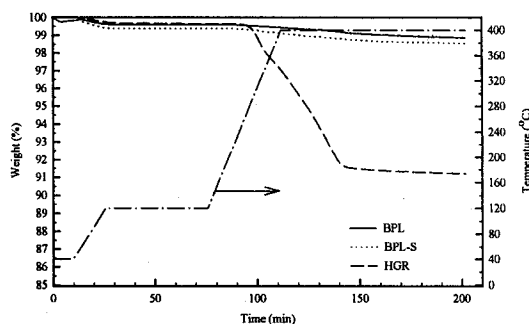


Figure 1. TGA Analyses of Mercury Sorbents

Since the sulfur vapor at 200 °C is in the form of S₈ (76.5%) and S₆ (23.5%) rings [2], it is reasonable to assume that HGR carbon contains sulfur predominantly in the form of voluminous S₈ rings. At 600 °C, sulfur vapor possesses a significant fraction of S₆ (58.8%) and S₂ (16.4%) allotropes [2], which are less voluminous and more reactive because they possess a greater fraction of sulfur terminal atoms. Therefore, the smaller S₂ and S₆ chains can more easily migrate into the narrower pores of the carbon matrix and, as the carbon cools down to room temperature at the completion of the impregnation process, steric hindrance impedes reformation of the more voluminous allotropic S₈ from the other two allotropes. Thus, BPL-S carbon possesses greater proportions of sulfur in the more reactive S₂ form than the normal proportion indicated by the corresponding equilibrium constant.

The breakthrough curves illustrated in Figure 2 show that HGR and BPL-S carbons performed similarly in the uptake of mercury vapor at 25 and 90 °C. However, when the temperature was increased to 140 °C, the performance of BPL-S carbon improved slightly while HGR carbon exhibited significant deterioration in the ability to remove mercury from the feed stream. This may be due to the fact

that 140 °C is above the melting point of sulfur (115.2 °C), which induces the sulfur that is weakly bonded to the surface of HGR carbon to melt and agglomerate as a liquid in the form of long polymer chains and decreases the sulfur surface area available for contact with the incoming mercury molecules. Thus, the performance of HGR carbon at 140 °C may be limited by the slow diffusion of mercury through the liquid state sulfur. The stronger bonding and more uniform distribution of sulfur in BPL-S carbon prevented the sulfur from agglomerating, which ensured that the performance of BPL-S carbon did not deteriorate at higher temperature.

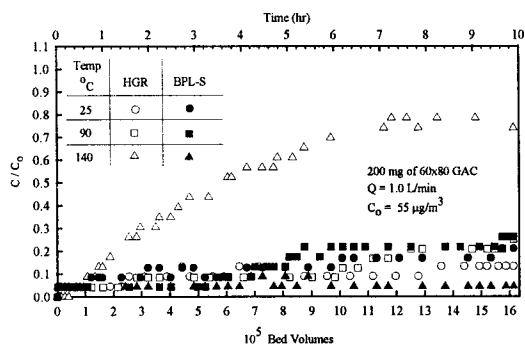


Figure 2. Performance of HGR and BPL-S-4/1-600

Activated carbons impregnated with sulfur at elevated temperatures were divided in two groups: three carbons prepared using the SCR of 4:1 at 250, 400, and 600 °C constituted Group A and four carbons prepared at 600 °C using the SCR of 4:1, 2:1, 1:1 and 1:2 constituted Group B. Figure 3 shows mercury uptake as a function of the amount of mercury supplied to the adsorber (Mercury Throughput) for the carbons in Group A. As can be seen from this figure, mercury uptake increased as the impregnation temperature increased. Figure 4 illustrates the mercury removal efficiency for the four carbons in Group B. When SCR changed from 4:1 to 2:1, the capacity for mercury removal did not experience a significant decrease. Major loss in capacity was observed when SCR was reduced from 2:1 to 1:1.

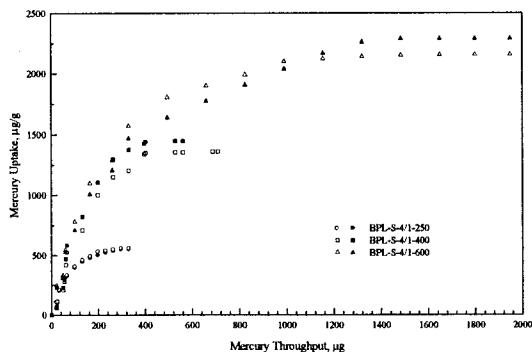


Figure 3. Performance of Group A Sorbents

The difference between various sulfur allotropes in terms of the availability of active terminal sulfur atoms to

react with mercury and associated differences in the performance of sulfur impregnated carbons is already discussed above. The sulfur content among Group A sorbents decreased from 37% to 10% as the impregnation temperature increased from 250 °C to 400 °C. The effect of saturated vapor pressure became less significant when impregnation temperature was further increased to 600 °C. The sulfur content among Group B sorbents decreased from about 10% to about 7% as the SCR decreased from 4:1 to 1:2.

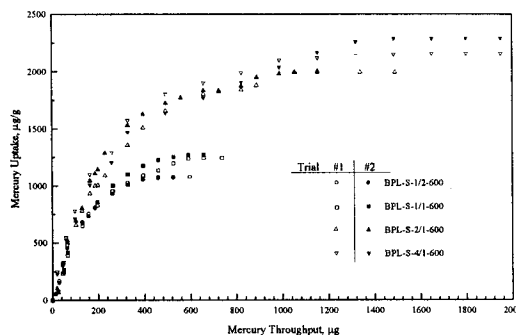


Figure 4. Performance of Group B Sorbents

Conclusions

The effect of the sulfur impregnation method on mercury removal efficiency was examined through experiments conducted on commercially available sulfur-impregnated carbon (HGR) and carbon impregnated with sulfur in our laboratory (BPL-S). Although HGR and BPL-S possess similar sulfur contents, BPL-S is impregnated at a higher temperature which promotes a more uniform distribution of sulfur in the GAC pore structure. At low temperatures, HGR and BPL-S performed similarly in the removal of mercury vapor. However, as the temperature was increased above the melting point of sulfur, the performance of HGR deteriorated significantly, while the performance of BPL-S slightly improved. Temperature and the initial sulfur to carbon ratio (SCR) during production of BPL-S were the two control parameters for the impregnation procedure. The results showed that carbons impregnated with sulfur at higher temperatures exhibited higher efficiency for mercury removal and that the impregnation temperature is the most important factor influencing the efficiency of these sorbents for mercury uptake.

References

1. Korpziel JA, Vidic RD Effect of Sulfur Impregnation Method on Activated Carbon Uptake of Gas-Phase Mercury, Environmental Science & Technology 1997; 31(8):2319-2326.
2. Tuller WN, ed. The Sulfur Data Book. McGraw-Hill Book Company, Inc.: New York, 1954.