

DYNAMICS OF FIXED-BED CARBON ADSORBERS FOR VAPOR-PHASE MERCURY UPTAKE

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Introduction

Air pollution control processes capable of controlling mercury emissions from combustion processes include activated carbon adsorption and wet scrubbing. Vidic and McLaughlin (1) investigated the effects of temperature, mercury concentration, and method of sulfur-impregnation on mercury removal performance using virgin and sulfur impregnated carbons. They observed that the sulfur-impregnated GACs showed much greater adsorptive capacity than virgin activated carbon due to the chemisorption of mercury facilitated by the formation of HgS on the carbon surface. They also documented that the method of sulfur impregnation has a major impact on the observed performance for mercury uptake. The main objective of this study was to further understand the role of different impregnation methods on the availability of sulfur to bond vapor-phase mercury and the corresponding impact on the dynamics of a fixed-bed adsorption systems.

Experimental

Two types of activated carbon were used in this study: HGR and BPL-S. HGR, a commercially available sulfur-impregnated carbon, was supplied by the manufacturer (Calgon Carbon Corporation, Pittsburgh, PA), while BPL-S was produced by impregnating a bituminous coal-based virgin activated carbon, BPL (Calgon Carbon Corporation, Pittsburgh, PA), with sulfur in a pure nitrogen atmosphere at 600 °C. The sulfur contents of HGR and BPL-S are 9.7% and 10.0%, respectively. Detailed description of the experimental protocols and analytical procedures used in this study is available elsewhere (2) and will not be repeated here.

Results and Discussion

Although different impregnation methods yielded similar sulfur content, sulfur-impregnation of HGR and BPL-S carbons caused a 53% and 20% decrease in the initial BET specific surface area of 4x10 U.S. Mesh size BPL carbon, respectively (Table 1). Due to the higher impregnation temperature, the sulfur in BPL-S carbon is suspected to be more evenly distributed in the pore structure, occupying the deeper, narrower pores. The

sulfur in HGR carbon, on the other hand, is most likely condensed at the external surface of the carbon, blocking the access to the narrower high energy pores.

Table 1. Comparison of GAC Types

GAC Type	Sulfur Content (wt.%)	BET (m ² /g)
BPL	0.7	1026
HGR	9.7	482
BPL-S	10.0	824

Thermogravimetric analysis (TGA) conducted by heating samples of BPL, HGR, and BPL-S carbons up to 400 °C in an argon atmosphere showed that BPL and BPL-S carbons underwent negligible decreases in weight, while the weight of the HGR carbon sample decreased by 8.5%. Since both HGR and BPL-S carbons are manufactured by impregnating BPL carbon with sulfur, this outcome implies that BPL-S carbon lost a negligible amount of its impregnated sulfur, while HGR carbon lost 88% of its sulfur content.

Sulfur exists in several allotropes, including S_λ (S₈ rings), S_π (S₈ chains), and S_μ (chains of variable length), with S₈ rings as the only form at room temperature (3). Since the sulfur vapor at 200 °C is in the form of S₈ and S₆ rings (3), 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%) molecules (3), 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 S_λ from the other two allotropes.

All adsorber experiments conducted at short EBCT (≤ 0.11 second) utilized 60x80 U.S. Mesh size GAC. As shown in Figure 1, the performance of HGR carbon improved as the flow rate increased from 0.1 to 5.0 L/min. Although the dynamic mercury adsorptive capacity was observed to increase with increasing flow rate, it was in all cases negligible compared to the capacity predicted by the stoichiometry of HgS formation (0.607 g Hg/g HGR).

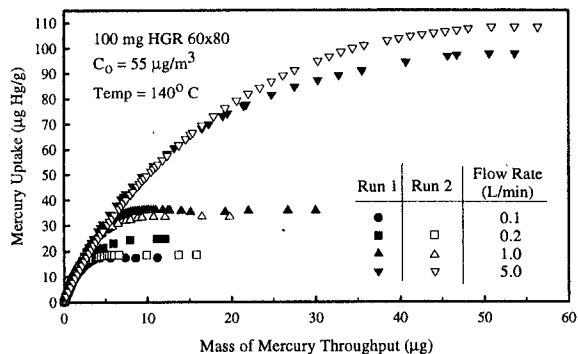


Figure 1. Effect of Flow Rate on Hg Uptake by HGR

One possible explanation for the behavior shown in Figure 1 is that the rate of mercuric sulfide formation and subsequent diffusion into the sulfur bulk phase is the rate limiting step in the adsorption dynamics of HGR carbon. The increasing mercury loading rates at higher gas flow rates accelerate the exothermic reaction of HgS formation, resulting in thermal agitation which breaks up the sulfur chains more rapidly. The resulting increase in the number of sulfur terminal atoms causes the reactivity of the impregnated sulfur to increase.

An adsorber experiment in which the mercury laden gas was periodically diverted around the adsorber was conducted using 100 mg of 60x80 U.S. Mesh HGR carbon. As shown by the breakthrough curve in Figure 2, four mercury loading steps were performed over a period of 8 days.

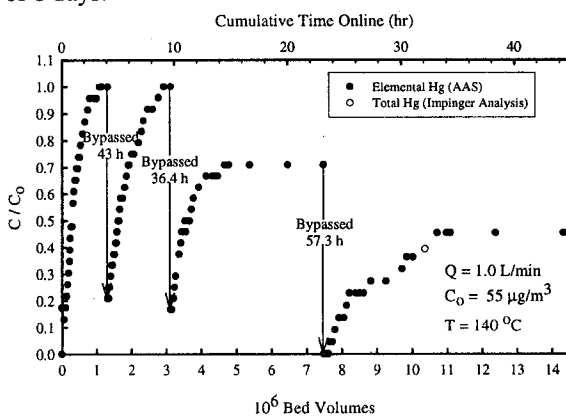


Figure 2. Breakthrough of Hg from HGR Adsorber

By the time 100% breakthrough is reached in the first loading step, the available surface area of the sulfur agglomerates is completely covered by a monolayer of HgS, which blocks the incoming Hg molecules from reacting with the bulk sulfur that is still available in the carbon pores. During the period that the adsorber was bypassed, the HgS molecules had sufficient time to diffuse into the sulfur liquid phase, breaking up sulfur chains to provide additional sulfur terminal atoms to react with mercury molecules in a subsequent loading step. The

observation that the mercury removal performance actually improved in the third and fourth loading step may be due to the fact that the sulfur polymer chains began to break apart into smaller chains as more and more mercury reacted with sulfur, thereby increasing the fraction of sulfur terminal atoms which led to an increase in the rate of HgS in the later part of the column experiment.

In order to compare the effect of temperature on the performance of HGR and BPL-S carbons, adsorber experiments were conducted at 25, 90 and 140 °C. The breakthrough curves illustrated in Figure 3 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.

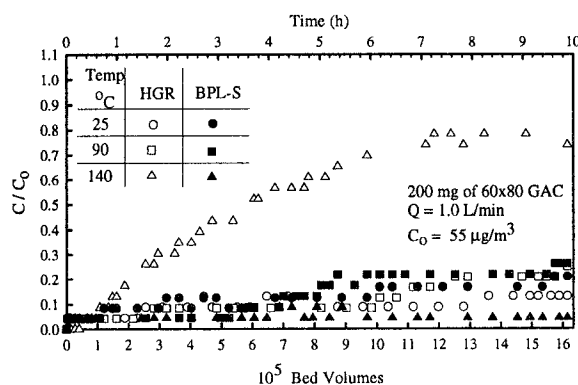


Figure 3. Effect of Temperature on Hg Uptake by HGR and BPL-S Carbons

References

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