

Optimization of Sulfur Impregnation Protocol for Fixed-Bed Application of Activated Carbon-Based Sorbents for Gas-Phase Mercury Removal

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Novel sulfur-impregnated activated carbons for vapor phase mercury uptake (BPL-S series) were designed and developed in this study. Temperature and the initial sulfur to carbon ratio (SCR) during impregnation were the two control parameters for the impregnation procedure. By adjusting these two variables, a series of sulfur-impregnated carbons was created. These new materials together with commercially available sulfur-impregnated activated carbon (HGR) and coal samples were evaluated for the uptake of vapor phase elemental mercury using nitrogen as a carrier gas. The results showed that carbons impregnated with sulfur at high temperature exhibited the highest efficiency for mercury removal. As the impregnation temperature decreased, the performance of the carbons deteriorated. When SCR was varied from 4:1 to 1:2, the sulfur content decreased only slightly, which resulted in a small decrease in mercury uptake capacity. Therefore, the impregnation temperature is the most important factor influencing the efficiency of these sorbents for mercury uptake. Because the impregnation temperature dictates the predominant form of sulfur allotropes, it can be concluded that the actual form of sulfur rather than the total sulfur content is a crucial parameter governing the chemisorption process. Stronger bonding between sulfur and carbon surface was found for carbons impregnated at higher temperatures. This prevents sulfur from agglomerating and clogging the carbon pores during column runs at elevated temperatures. Large surface areas and large fractions of mesopores in these new sorbents also contributed to excellent mercury removal efficiencies.

Introduction

Mercury and its compounds have long been considered very potent neurotoxins. Accumulation of mercury in the lower stem of plants strongly affects their growth. High mercury concentrations in fish can lead to serious epidemic disease, while long-term exposure to mercury can damage eyes, kidneys, or the central nervous system and even cause death (1).

Although the background mercury in the atmosphere is only about 0–3 ng/m³, the lifetime of mercury in air can be

as long as 1–2 yr (2). Furthermore, industrial development, including coal-fired power plants and municipal waste combustors, have the potential to introduce various mercury species into the atmosphere each year. A study by the U.S. Environmental Protection Agency showed that coal-fired utilities, commercial or industrial boilers, municipal waste incinerators, and medical waste incinerators emit about 120 ton of mercury annually. This constitutes 77% of anthropogenic mercury emissions in the United States.

Mercury concentration and speciation in the flue gas varies considerably from site to site. This complexity can be related to several factors. Typically, coals have a wide range of initial mercury concentrations spanning from 0.01 to 8 ppm (3). Unlike most trace metals in coal, mercury is highly volatile and therefore forms the major mercury compound in the flue gases. Finkelman et al. (4) reported that mercury can be volatilized from coals at temperatures as low as 150 °C. The presence of O₂ and HCl can lead to formation of mercuric oxide (HgO) and mercuric chloride (HgCl₂) (5), with HgCl₂ being the predominant form of mercury emissions from municipal waste combustors. In general, the variability in mercury concentration and speciation is a result of many factors, including initial mercury concentration, operational temperature, and solid and vapor phase flue gas constituents.

Various existing emissions control technologies [e.g., electrostatic precipitators (ESP), fabric filters, and wet and dry flue gas desulfurization (FGD) systems] have been evaluated for their ability to reduce mercury emissions from combustion sources. However, limitations of these techniques and erratic performance clearly restrict their applicability. A series of pilot plants studies done by EPRI's High Sulfur Test Center has shown that 90% HgCl₂ was removed from gas stream, while essentially no elemental mercury was dissolved in the FGD scrubbing slurry. Oxidized mercury could also be trapped to a substantial degree by fabric filters (baghouses), while elemental mercury could not be captured due to its small diameter (6). It is clear that mercury speciation governs the performance of these technologies. The mean removal efficiency of ESP and fabric filter was about 30% (7), while FGD can remove between 8% and above 90% of mercury (8, 9).

Activated carbon adsorption offers promising potential for the control of mercury emissions from combustion sources. In fact, fixed-bed or fluidized-bed granular activated carbon (GAC) adsorption (10) or powdered activated carbon (PAC) injection (11) are commonly proposed technologies for this purpose. Fixed-bed or fluidized-bed GAC adsorbents should be installed downstream of the particulate collectors and perhaps FGD units as the final treatment process before the flue gas is discharged into the atmosphere. In situations in which PAC injection is used, the powdered carbon is directly injected into the plant's flue gas stream, where it adsorbs vapor phase mercury, and is collected in devices such as ESP or fabric filters.

Sinha and Walker (10) showed that virgin carbon could adsorb significantly less mercury at 40 °C when compared to sulfur-impregnated carbon. The adsorption of mercury by the virgin carbon became negligible as compared to that of the sulfur-impregnated carbons as the temperature was further increased to 150 °C. Matsumura (12) showed that oxidized or iodized activated carbons adsorbed mercury vapor 20–160 times more than untreated activated carbon when mercury vapor in concentrations of up to 40 mg/m³ in a nitrogen steam at 30 °C was brought into contact with these adsorbents. Other authors also investigated the

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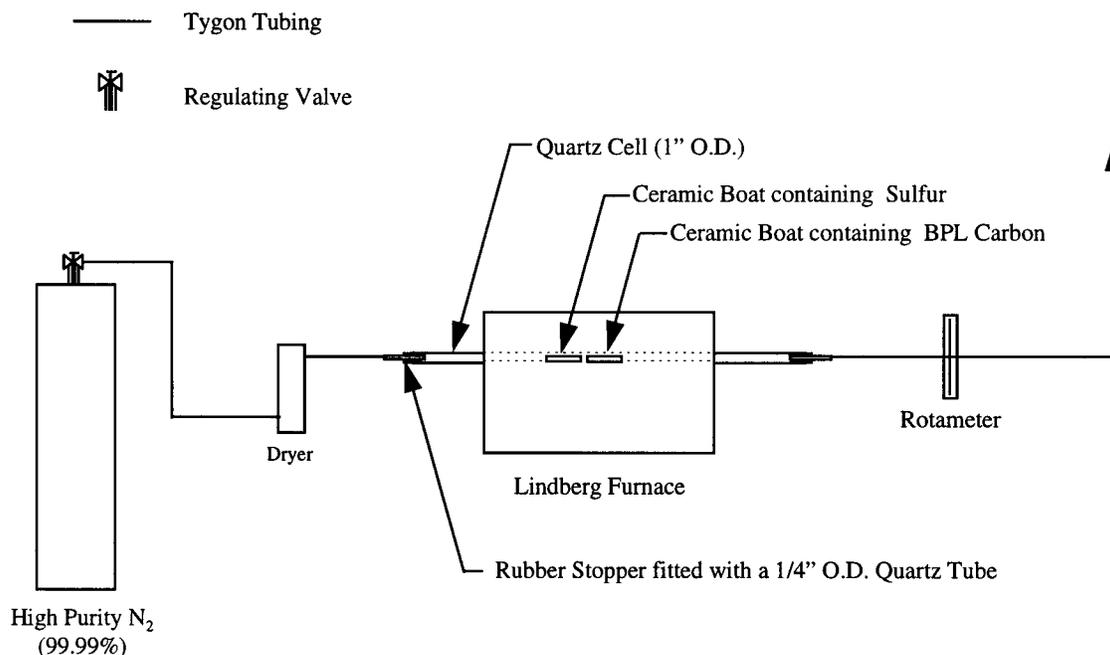


FIGURE 1. Setup of impregnation system.

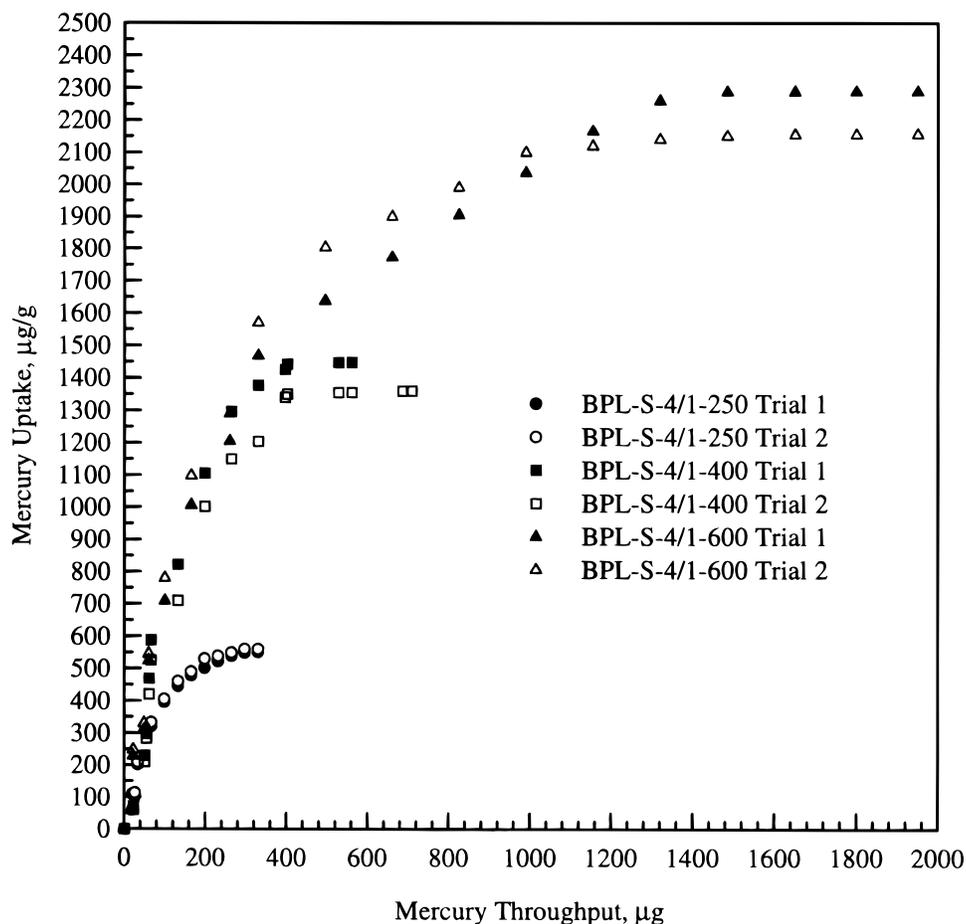


FIGURE 2. Mercury uptake by BPL-S-4/1 series produced at different impregnation temperatures.

feasibility of mercury removal by commercially available sulfur-impregnated carbons (13, 14).

Vidic and McLaughlin (15) studied F-400 (virgin bituminous coal-based carbon), HGR (commercially available sulfur-impregnated carbon), and F-400S (F-400 carbon impregnated with sulfur using a novel impregnation pro-

cedure) for their ability to adsorb mercury vapors. The sulfur-impregnated carbons performed much better than the virgin carbon. The main reason was that physisorption dominated the capacity of a virgin carbon while chemisorption, which was facilitated by the formation of HgS, controlled the adsorption ability of sulfur-impregnated carbons.

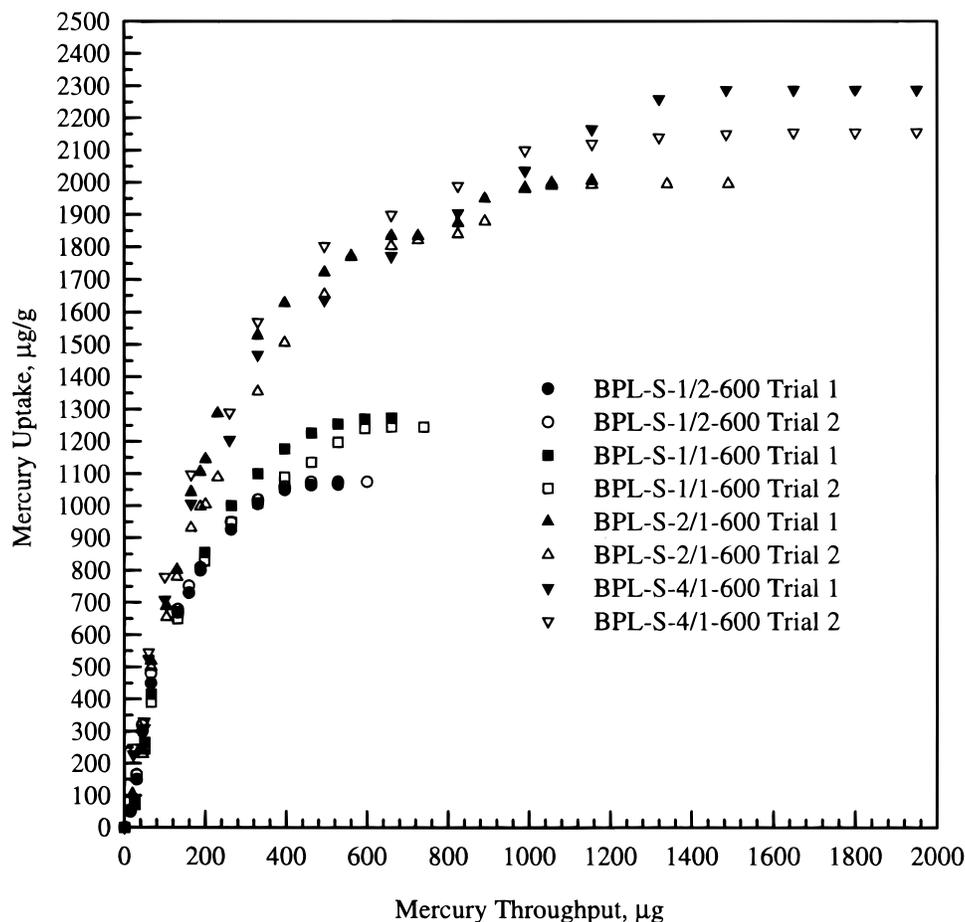


FIGURE 3. Mercury uptake by BPL-S-600 series with different SCR.

TABLE 1. Dominant Sulfur Allotropes at Different Temperatures

temp (°C)	S ₈ (%)	S ₇ (%)	S ₆ (%)	S ₅ (%)	S ₂ (%)	vapor pressure (atm) ^a
180	65	15	15			0.0027
250	49	27	21			0.017
400	22	36	28	5	2	0.496
600			59		16.4	>3.817

^a Calculated based on ref 19.

The primary goal of this study was to further investigate the impact of the 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.

Sulfur allotropes that predominate at higher temperatures have more active terminal atoms and would facilitate more effective mercury uptake. Apparently higher impregnation temperatures are not cost-effective for industrial application. A series of impregnation temperatures were chosen to test the performance of these new carbons. By doing so, an optimal impregnation temperature range can be established for high efficiency of mercury control.

Another important factor for the production of these sorbents is SCR. In our previous paper (16), we reported that the amount of mercury chemisorbed by sulfur-impregnated carbons was far below the stoichiometric prediction for the formation of HgS, indicating that a large

TABLE 2. Sulfur Content and Surface Area of Sorbents Used in This Study

sample type	sulfur content, (wt %)	specific surface area (m ² /g)
BPL-S-4/1-250	36.2–38.5	164.4–170.6
BPL-S-4/1-400	10.27–10.65	628.7–634.4
BPL-S-4/1-600	10.04–10.18	823.7–845.7
BPL-S-2/1-600	9.12–9.21	897.6–909.5
BPL-S-1/1-600	8.31–8.39	847.6–860.6
BPL-S-1/2-600	7.11–7.23	859.0–888.6
BPL	0.51–0.73	987.7–1026.0
BPL (heated to 600 °C)	0.45–0.51	960.7–989.5
HGR	9.66–10.01	782.6–823.1
React-A-4/1-600	8.56–8.69	826.2–876.2
UFP	1.39–1.47	45–51.3
UFP-4/1-600	4.57–4.65	20.5–24.3

amount of sulfur did not participate in the reaction. Therefore, different SCRs were selected to see if lower amounts of sulfur could be used to achieve the same mercury uptake efficiency.

Materials and Experimental Section

A commercially available bituminous coal-based activated carbon (BPL) was supplied by the manufacturer (Calgon Carbon Corporation, Pittsburgh, PA) in 4 × 10 U.S. mesh size. HGR, which is a sulfur-impregnated activated carbon derived from BPL in 4 × 10 and 12 × 30 U.S. mesh sizes, and React-A, which is a regenerated activated carbon in 4 × 10 U.S. mesh size, were also provided by the same manufacturer. Both BPL and HGR carbons were ground into 60 × 80 mesh size having a geometric mean diameter of 0.021 cm. A sample

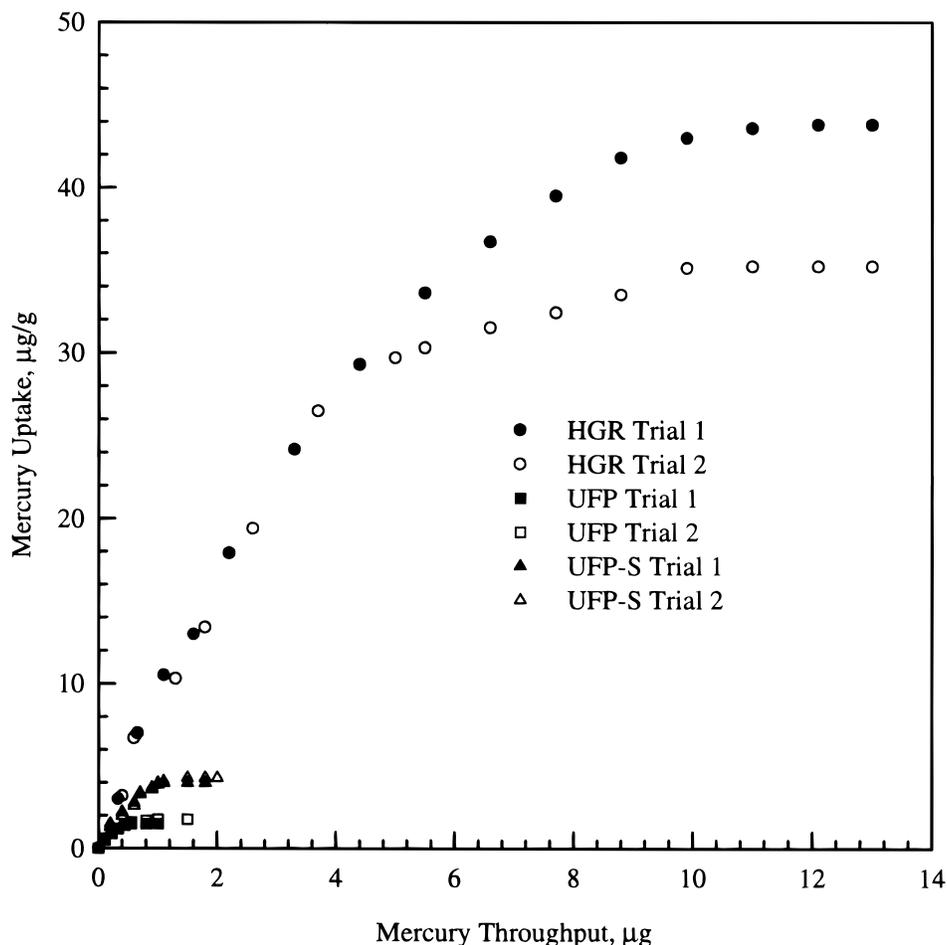


FIGURE 4. Mercury uptake by UFP coal and HGR carbon.

of Upper Freeport (UFP) coal (FETC, Pittsburgh, PA) was also used in this study. This coal sample contained mainly fine particles, and it was sieved to 170 × 230 U.S. mesh size.

Figure 1 shows the configuration of the experimental system used for impregnating elemental sulfur onto the solid substrate. High-purity (99.99%) elemental sulfur flakes (Aldrich Chemical Company, Milwaukee, WI) were used in the impregnation process. A 19 in. long, 1 in. o.d., open-ended, hollow quartz tube was used as a holder in the tube furnace (Lindberg Type 55035, Watertown, WI). Two grams of solid substrate was placed evenly in a ceramic boat, and a predetermined amount of sulfur was placed in another ceramic boat. The nitrogen gas flow rate through the quartz tube was set at 60 mL/min, and the upstream rubber stopper on the quartz tube was removed to place the boats into the tube. The system was quickly closed, and nitrogen gas was passed through the quartz tube for 1 h at room temperature to completely remove traces of oxygen from the tube and create inert atmosphere. The furnace temperature was adjusted to the required setting and maintained for 2 h while continuously purging nitrogen gas through the system. After the furnace cooled back to room temperature, the carbon-containing boat was stored in a desiccator.

Three different temperature settings were selected for the impregnation process, namely 250, 400, and 600 °C. Since the chemisorption of sulfur onto activated carbon was maximized at 600 °C (17), this temperature was chosen as the upper limit. 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. The

same sulfur impregnation procedure was also used when impregnating React-A and UFP coal.

Newly developed-sulfur impregnated carbons and other sorbents used in this study were evaluated for their efficiency of vapor-phase elemental mercury removal in the fixed-bed reactor. The empty bed contact time was about 0.012 s. Detailed description of the testing protocol and analytical procedures can be found elsewhere (16).

Sulfur content of HGR, React-A, UFP coal, and newly developed sulfur-impregnated carbon series was measured by a Leco Model SC 132 sulfur determinator (Leco Corporation, St. Joseph, MI). A classic nitrogen BET method was used to determine the surface area and pore size distribution of each sample (Orr Surface-Area Pore-Volume Analyzer Model 2100, Micromeritics Instrument Corporation, Atlanta, GA).

Results and Discussion

Since the performance of sulfur-impregnated activated carbons should be a function of both SCR and impregnation temperature, it was decided to divide sorbents into two groups when evaluating their performance. Three carbons prepared with the SCR of 4:1 and impregnation temperatures of 250, 400, and 600 °C constituted group A. Four carbons produced at the impregnation temperature of 600 °C using the SCR of 4:1, 2:1, 1:1, and 1:2 constituted group B.

To facilitate direct comparison of these mercury sorbents, the experimental conditions for each column run were always kept the same: 100 mg of sulfur-impregnated carbon was placed in the fixed-bed reactor operated at 140 °C using the influent mercury concentration of 55 µg/m³ and a N₂ flow

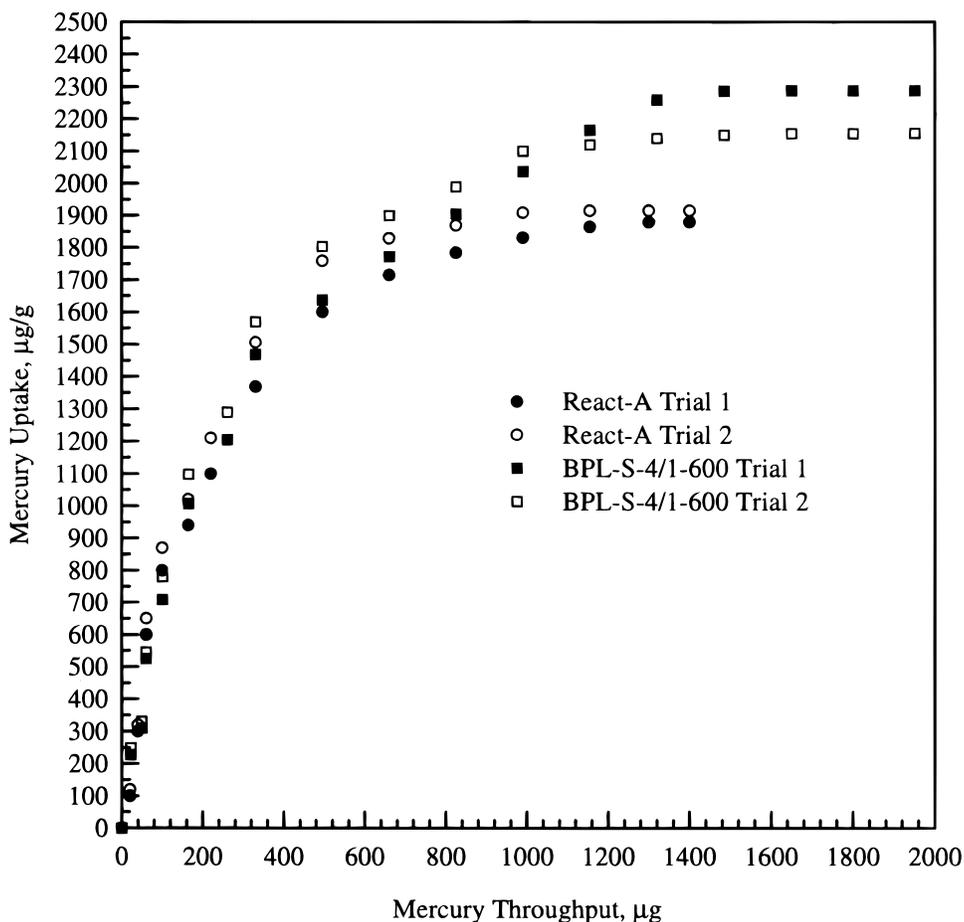


FIGURE 5. Mercury uptake by sulfur-impregnated virgin and reactivated carbons.

rate of 1.0 L/min. The normalized effluent concentration as a function of time (breakthrough curve) is generated for each adsorbent, and the amount of mercury adsorbed in each run can be calculated by integrating the area above the breakthrough curve.

Figure 2 shows mercury uptake as a function of the amount of mercury supplied to the adsorbent (mercury throughput) for the carbons in group A. As can be seen from this figure, mercury uptake is strongly related to the impregnation temperature. As the impregnation temperature increased, the capacity for mercury removal also increased. For example, the maximum mercury uptake for BPL-S-4/1-250 is about 550 µg of Hg/g of carbon, while the capacity for BPL-S-4/1-600 is about 2200 µg of Hg/g of carbon.

Figure 3 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. As shown in Figure 3, both BPL-S-4/1-600 and BPL-S-2/1-600 exhibited high capacity for mercury uptake, while the capacities of BPL-S-1/1-600 and BPL-S-1/2-600 are approximately 40–50% lower.

Figure 4 compares mercury uptake capacity of coal samples and HGR. From the scale of the ordinate, it is clear that the uptake capacity for these three samples is much lower than the capacity of BPL-S series. The amount of mercury adsorbed by HGR was only 35–45 µg of Hg/g of carbon. Mercury uptake capacity of UFP-4/1-600 was only 4 µg of Hg/g of coal, while the uptake capacity of UFP was negligible (less than 2 µg of Hg/g of coal).

Adsorption capacity of React-A-4/1-600 is compared to the performance of BPL-S-4/1-600 in Figure 5. As is apparent

from this figure, React-A-4/1-600 demonstrated very similar performance for mercury uptake to that of BPL-S-4/1-600, yielding the overall mercury uptake capacity of 1900 µg of Hg/g of carbon.

A previous study (10) showed that the mechanism for mercury removal by sulfur-impregnated carbons was primarily through the formation of mercuric sulfide (HgS). Therefore, the physical and chemical properties of sulfur, the predominant form of sulfur, the available surface area, and the pore size distribution are essential factors that influence the performance of these sorbents.

The presence of various sulfur allotropes on the carbon surface depends on their distribution in the vapor phase, which is a strong function of ambient temperature (18) and is provided in Table 1. 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 discussed by Korpiel and Vidic (16).

The last column of Table 1 shows the saturated sulfur vapor pressures at different temperatures, which were calculated based on the empirical equations given by Hampel (19). When the temperature increases, the vapor pressure of sulfur increases rapidly, indicating that sulfur molecules are present mainly in the vapor phase rather than in the liquid phase. Since nitrogen gas was continuously flushing the quartz cell during the impregnation process, lower amounts of sulfur could be attached to the carbon surface at higher impregnation temperatures. As can be seen from Table 2, which provides key properties of sulfur-impregnated sorbents utilized in this study, the sulfur content decreased from about 37% to about 10% as the impregnation temperature increased from 250 to 400 °C. When the impregnation

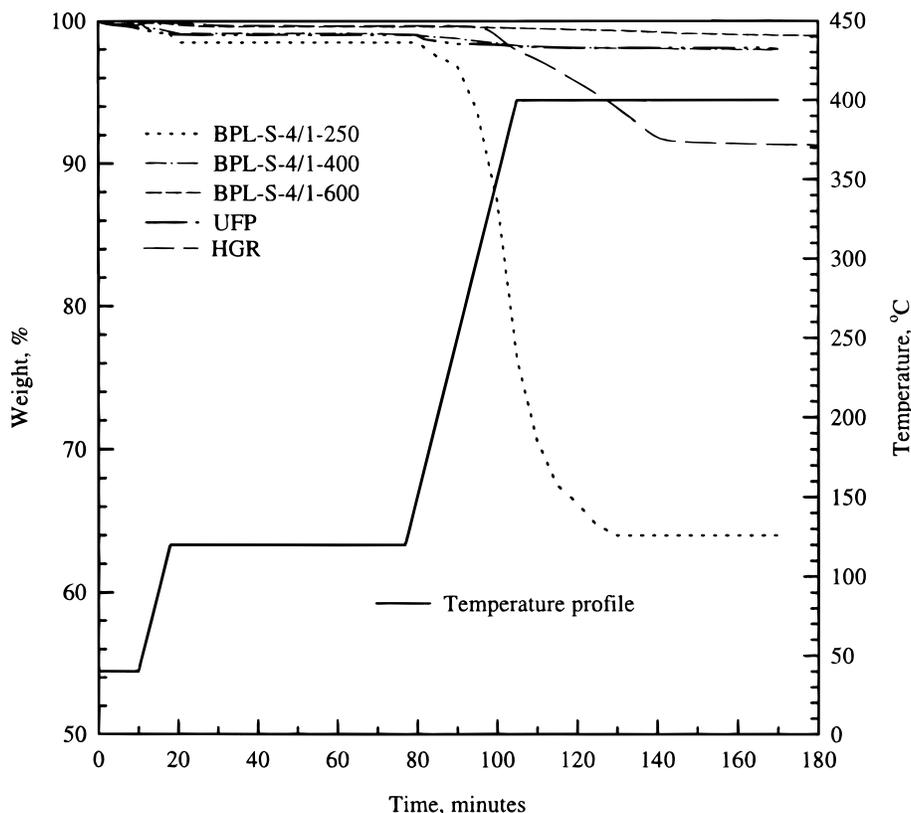


FIGURE 6. TGA analyses for different sorbents.

temperature was further increased to 600 °C, the effect of saturated vapor pressure became less significant since the sulfur content of BPL-S-4/1-600 was only slightly lower than that of BPL-S-4/1-400.

The data in Table 2 also show that the sulfur content in BPL-S-600 series decreased from about 10% to about 7% as the SCR decreased from 4:1 to 1:2. This change in SCR not only decreased the absolute amount of sulfur on the carbon surface but also reduced the number of terminal active sulfur atoms. The direct consequence was that the mercury removal capacity became smaller.

As discussed above, the mechanism for mercury adsorption is governed by the reaction between active sulfur atoms and vapor phase mercury molecules. Although the impregnation temperature was the most important factor influencing the efficiency of these new adsorbents, lower SCR values also decreased their efficiency for mercury removal. However, SCR did not exhibit as strong influence on the performance of these novel carbons as did the impregnation temperature. Therefore, the assessment of the performance of sulfur-impregnated carbon for mercury removal cannot rely solely on the measured sulfur content of the sorbent.

Figure 6 provides the results of TGA tests performed on the sorbents used in this study according to procedure described by Korpiel and Vidic (16). As can be seen from this figure, all sorbents prepared at impregnation temperatures above 400 °C (BPL-S-4/1-600, BPL-S-4/1-400, UFP-4/1-600) exhibited negligible weight loss while those prepared at lower temperatures (HGR and BPL-S-4/1-250) lost more than 90% of the sulfur content during the heating process. A detailed explanation of such behavior and the associated impact on mercury uptake is provided by Korpiel and Vidic (16).

Classical nitrogen BET method was used to study the microstructure of these new activated carbons. The specific surface area for each adsorbent is listed in Table 2. For the BPL-S-4/1 series, the specific surface area decreased with a

decrease in the impregnation temperature. For instance, the specific surface area of BPL-S-4/1-250 was only 20% of BPL-S-4/1-600 surface area. Comparing the surface area of virgin and heated (at 600 °C without the addition of sulfur) BPL carbons, it can be seen that the surface area does not change significantly as a result of exposure to 600 °C (Table 2). This indicates that the major reason for the loss of surface area for all these carbons is the impregnation with sulfur.

As shown in Table 1, the major forms of sulfur allotropes at low temperature are S_8 and S_7 . These ring-structured molecules could only enter large pores and easily form clusters. Consequently, these clusters blocked pore entrances and reduced the total surface area measurable by BET method. Since BPL-S-600 carbons were prepared at high temperature, clogging was not a problem, and as shown in Table 2, none of them exhibited significant loss of surface area due to impregnation process regardless of the variations in SCR.

Table 2 also shows that both UFP and UFP-4/1-600 have very small specific surface area, which minimizes the chances for sulfur to attach to the coal surface. The actual sulfur contents for UFP and UFP-4/1-600 were only about 1.4% and 4.6%. As shown in Figure 4, their capacities for mercury removal are negligible since both sorbents have very low surface area and low sulfur content.

React-A-4/1-600 exhibited similar physical characteristics as the BPL-S-4/1 series. Its high surface area and large portion of active sulfur terminal atoms facilitated effective mercury removal. Figure 5 shows that React-A-4/1-600 is a highly efficient adsorbent like the sulfur-impregnated adsorbents derived from virgin activated carbons.

The liquid nitrogen desorption method was used to measure the pore size distribution of HGR and BPL and its derivatives. All pore size distribution measurements on the BPL-S-4/1 series are summarized in Figure 7. As can be seen from this figure, the undersized pores (radius less than 20 Å) and the oversized pores (radius greater than 180 Å)

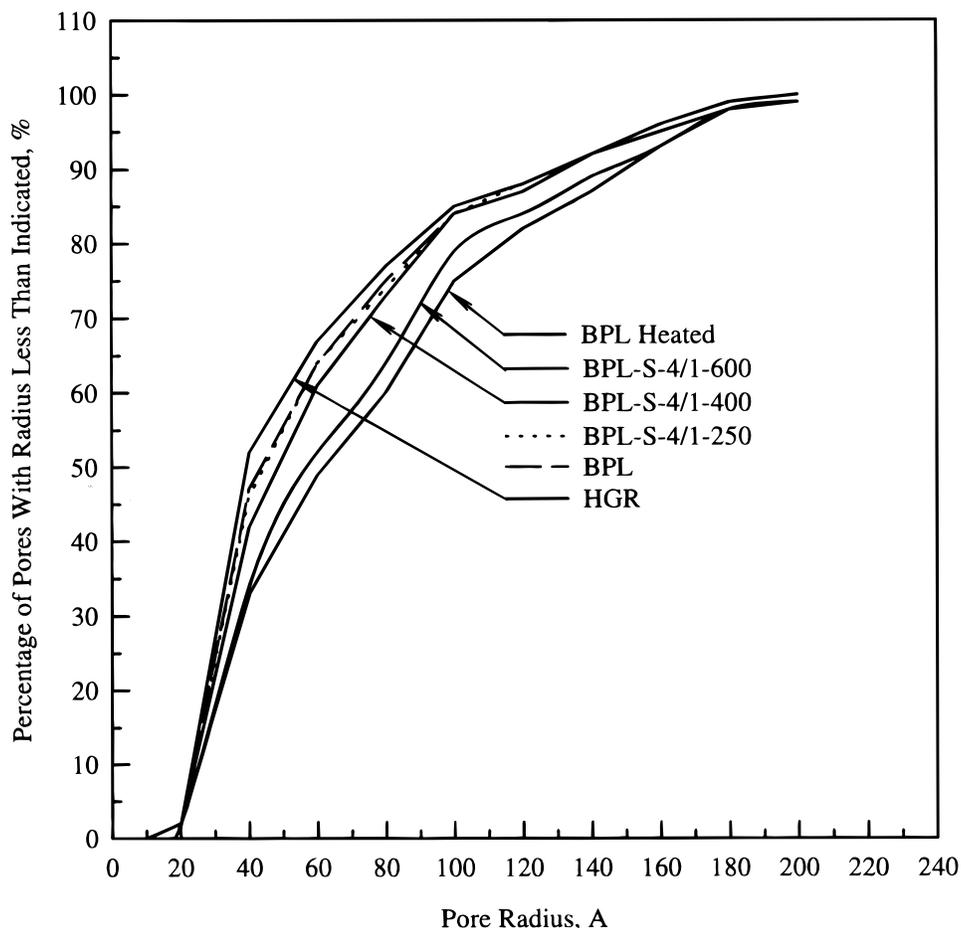


FIGURE 7. Pore size distribution for BPL-S-600, BPL, and HGR carbons.

consist only of a small portion of total pores for all carbons used in this study. The major differences among these carbons can be found in the distribution of 40–100 Å pores. In order to study the temperature effect on pore size distribution, virgin BPL carbon was heated at 600 °C for 2 h. As can be seen in Figure 7, heated BPL has larger volume of pores in the range of 40–100 Å than virgin BPL. Apparently, 600 °C was sufficiently high temperature to induce changes in the inner structure of BPL carbon, resulting in pore opening.

It is postulated that this difference in pore size distribution among BPL-S carbons is a direct result of impregnation temperature and sulfur loading. First, the amount of sulfur attached to the carbon increased as the impregnation temperature decreased. As a result, more pores will be filled for BPL-S-4/1-250 carbon. The existing form of sulfur molecules is another important factor. At lower impregnation temperatures, sulfur molecules are mainly in the form of rings or long linear chains. Although these molecules will have little steric hindrance for oversized pores, they may form barriers in the medium size pores. As these large sulfur molecules attach to the carbon surface, they tend to block the entrance to medium pore openings and form multilayers to further reduce the surface area. At higher impregnation temperatures, smaller and shorter chain sulfur molecules are dominant. They can migrate easily along the carbon pores, resulting in a more uniform sulfur distribution. Thus, more medium size pores are available in the carbons prepared at higher temperatures. As stated earlier, HGR is a commercially available sulfur-impregnated activated carbon. Although the detailed preparation steps for HGR are not available, the temperature range for HGR manufacturing is estimated to be between 150 and 200 °C. It showed similar

sulfur content to BPL-S-4/1-600, and its specific surface area was also high. But the major portion of internal pores was in the 20–60 Å range. Since the impregnation temperature was low, it contained lower amounts of active terminal sulfur atoms, which was the key reason that HGR had a much lower capacity for mercury removal as compared to the BPL-S series. It should be noted that SCR does not have nearly as much influence on pore size distribution since very similar distributions were measured for carbons prepared using the SCR that varied by a factor of 8 (data not shown).

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