

Sorption of Elemental Mercury by Activated Carbons

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The mechanisms and rate of elemental mercury (Hg^0) capture by activated carbons have been studied using a bench-scale apparatus. Three types of activated carbons, two of which are thermally activated (PC-100 and FGD) and one with elemental sulfur (S) impregnated in it (HGR), were chosen to study the effects of surface area (approximately 550–1000 m^2/g), sorption temperature (23–140 °C), and Hg^0 concentration (30 and 60 ppb of Hg^0 in nitrogen). Investigations revealed that sorption occurs in active sites in PC-100 and FGD which are either depleted or deactivated upon heat treatment at 140 °C. For HGR, sorption at 23 °C occurred in non-S sites residing in the external surface, and sorption of 140 °C primarily occurred through the reaction of Hg^0 and S. Desorption studies for PC-100 and HGR revealed the sorption mechanism to be a combination of physisorption and chemisorption at 23 °C, whereas chemisorption is the primary route at 140 °C.

Introduction

Mercury has long been identified as a potential health and environmental hazard. The source of mercury in water and soil has been most often traced to individual industrial units (1). Anthropogenic global emissions of mercury have been estimated to be $910\text{--}6200 \times 10^3 \text{ kg/yr}$ compared to $100\text{--}4900 \times 10^3 \text{ kg/yr}$ from natural sources (2). A large portion of anthropogenic mercury emissions is from municipal waste combustors (MWCs) and coal-burning utilities. Unlike most other trace elements, the high volatility of mercury causes it to be present in the vapor form in flue gas emissions from combustors.

The European Economic Community (EEC) has set a limit of $50 \mu\text{g}/\text{Nm}^3$ (based on 11 % oxygen [O_2]) for mercury emissions (3) from MWCs. The guidelines expected to be proposed for total mercury emissions from MWCs in the United States are $100\text{--}130 \mu\text{g}/\text{Nm}^3$ at 7 % O_2 (4). However, a limit of $50 \mu\text{g}/\text{Nm}^3$ has been imposed by some states (5). Although there are no current regulations for mercury emissions from electric utilities, the Clean Air Act Amendments of 1990 (Title III, Section 112[b] [1]) require major sources to use maximum available control technology (MACT) and require the U.S. Environmental Protection Agency (EPA) to perform a study of mercury emissions from several sources.

Without additional modifications, conventional flue gas desulfurization systems are capable of removing mercury emissions to some extent (6). However, to achieve high removal efficiencies, additional modifications are required. Among the modifications, employing an activated carbon sorbent (either in a fixed-bed operation or an injection process) has been shown to be a promising technology (6,

3). However, several problems still exist, both economic and technical, concerning the removal of mercury from flue gases.

The main forms of mercury emitted in flue gases (7) are elemental (Hg^0) or its oxidized state (mercuric chloride [HgCl_2] or mercuric oxide [HgO]). The control of mercury emissions has been found to be strongly dependent on the form of mercury. Pilot-scale data (8), where activated carbon injection technology was used, showed the oxidized form to be more easily captured than Hg^0 . This was further supported by MWC Sysav tests (9), which showed that although mercuryspeciation was two-thirds Hg^{2+} (oxidized form) and one-third Hg^0 before the baghouse, stack mercury was 100% Hg^0 . Similarly, preliminary data from the Electric Power Research Institute's (EPRI) High Sulfur Test Center's (HSTC) four MW pilot wet FGD system showed more than 90 % of the oxidized form to be removed with no removal of Hg^0 .

The problem of low Hg^0 removal can be overcome by using activated carbons impregnated with chemicals (10). Chemically impregnated activated carbons were found to possess several times higher Hg^0 sorption than thermally activated carbons (11). Iodine, chlorine, and sulfur compounds are most commonly used as the chemical agents to increase Hg^0 capture. Bansal et al. (12) found that, with increasing S content in their activated carbons, the mercury levels in the airstream at 150 °C decreased. At temperatures of 150–260 °C, Teller and Quimby (11) found activated carbons impregnated with chloride salt to have as much as 300 times greater Hg^0 removal capacity than regular thermally activated carbons. However, the higher costs associated with using chemically impregnated activated carbons require their usage to be optimized.

The apparent difficulty in capturing Hg^0 and the need for expensive carbons impregnated with chemicals require a more fundamental study of the mechanisms of Hg^0 sorption. To this end, investigations have been conducted to study Hg^0 sorption by activated carbons (13, 14) in order to improve the Hg^0 removal process. Gullett and Jozewicz (13) performed bench-scale experiments to study Hg^0 sorption by several types of thermally activated carbons. They noticed decreasing Hg^0 capture by the activated carbons with increasing temperatures, which is indicative of a physisorption mechanism. At 140 °C and higher, they observed evidence of a chemisorption behavior based on their desorption studies. The stronger, more permanent bonds in a chemisorption reaction is supported by Schager (8), who found that for mercury sorbed at 150 °C only 1 % of it leached out when treated with 0.2 M sulfuric acid (H_2SO_4) in agreement with the results of Gullett and Jozewicz (13).

The surface area of the activated carbons was also found to significantly influence the amount of Hg^0 captured (13). Working with thermally activated carbons ranging in surface area from 550 to 1000 m^2/g , Gullett and Jozewicz (13) observed that Hg^0 capture increased exponentially

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Table 1. Physical Characteristics of Activated Carbons

material	particle diameter (μm)	skeletal density (g/cm^3)	porosity (cm^3/cm^3)	surface area (m^2/g)
PC-100	17.55	1.90	0.35	964
FGD	6.80	2.17	0.49	547
HGR	20-25	2.11	0.36	1078
HGR	250-300	2.11	0.27	797
HGR	2000-4760	2.11	0.24	715

with increasing surface area. However, they observed no trend in Hg^0 capture with pore volume of the activated carbons. Although surface area and pore volume provide limited structural information on the sorbent, a better understanding of mercury capture could be provided by the pore size distribution of the sorbent. In addition, specific sites in the internal surface of the sorbent (active sites) may cause mercury capture.

This study addresses the sorption of Hg^0 by several types of activated carbons. Differences in the internal pore structure and active sites of the activated carbons have been investigated with respect to Hg^0 sorption at a given time. The effect of temperature and inlet Hg^0 concentration on the performance of the activated carbons has also been studied. Understanding the sorption mechanism of Hg^0 in these activated carbons has also been attempted through selected Hg^0 desorption studies. Also, information about the active sites involved in Hg^0 capture by the three activated carbons has been obtained from studying Hg^0 sorption by their heat treated forms.

Physical Characteristics and Chemical Analysis of Activated Carbons

Three types of commercially available activated carbons were chosen for this study. Of the three, PC-100 and FGD (both manufactured by American Norit Company, Inc.) are thermally activated, and HGR (supplied by Calgon Carbon Corporation) is chemically impregnated with elemental sulfur (S). The relative contents of chemical species known to be instrumental in Hg^0 removal were obtained from X-ray fluorescence spectrometry (Siemens, Model SRS303). The thermally activated carbons (PC-100 and FGD) have relatively insignificant amounts of sulfur (less than 1% by weight), chlorine, bromine, and iodine, whereas HGR has 7% (weight basis) of S. Both HGR and PC-100 are bituminous coal based, whereas FGD is lignite based.

The physical and structural properties of the three activated carbons are provided in Table 1. The mass median particle sizes of PC-100 and FGD were obtained using a Micromeritics Sedigraph 5100 system. PC-100 and FGD were used in the study in the same form as supplied by the manufacturer. HGR was supplied in the size range of 2000-4760 μm and was crushed and sieved to obtain the 250-300- μm size range. The 250-300- μm size range of HGR was further crushed and sieved (Alen Bradley Sonic Sifter, Model L3-P, Series A) to obtain the 20-25- μm size range. Unless mentioned otherwise, all results of sorption and desorption of Hg^0 in HGR reported in this paper were obtained using the 20-25- μm size range. The skeletal densities listed in Table 1 were obtained employing helium (He) pycnometry (Micromeritics He pycnometer).

The BET surface areas and porosities of the three activated carbons listed in Table 1 were obtained from

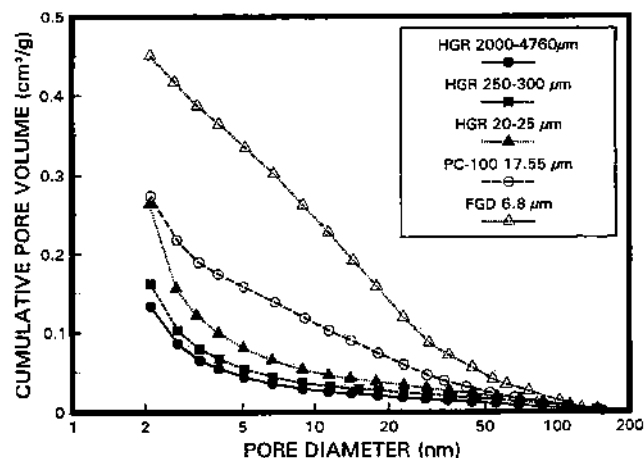


Figure 1. Pore size distributions of the three activated carbons: PC-100, HGR, and FGD.

their respective nitrogen adsorption isotherms (Micromeritics ASAP 2400 analyzer). PC-100 and HGR (20-25 μm) have similar pore volumes and surface areas, whereas FGD has a higher porosity and lower surface area than the other two activated carbons.

The pore size distributions of PC-100, FGD, and HGR (all three size ranges) are shown in Figure 1. These curves were obtained from the nitrogen adsorption isotherms. It is seen from Figure 1 that the most probable pore size in FGD is larger than that of HGR and PC-100, whereas HGR (20-25 μm), which has a significant fraction of pores below 5.0 nm in pore diameter, exhibits the smallest most probable pore size. PC-100 is seen to have a relatively broad distribution of its pores (2-100 nm in pore diameter).

Bench-Scale Apparatus and Experimental Procedures

The bench-scale apparatus used in this investigation for studying Hg^0 sorption by activated carbons is described by Jozewicz et al. (14). Approximately 20 mg of the activated carbon is loaded in between 10 and 20 mg of glass wool supports in a 1/4-in. (0.64-cm) o.d. polytetrafluoroethylene (PTFE) reactor in all our experiments. A nitrogen flow of 190 cm^3/min (standard temperature and pressure, STP) was maintained in all cases. Inlet Hg^0 concentrations of 30 and 60 ppb in N_2 is used in our experiments.

In our efforts to study desorption of Hg^0 , pure N_2 was passed through the reactor loaded with the activated carbons already exposed to Hg^0 . The temperature of the reactor was increased in steps to observe Hg^0 signals. Once the Hg^0 signal fell to insignificant levels (less than 2 ppb), the reactor temperature was increased to observe desorption at the higher temperature.

Results and Discussions

Sorption Tests. Temperature Effects. Figure 2 shows the Hg^0 sorption vs time curve for the three activated carbons at 23 and 140 $^\circ\text{C}$ when exposed to a concentration of 30 ppb of Hg^0 . A comparison of Hg^0 sorption at the two temperatures for the thermally activated carbons PC-100 and FGD shows the former to capture higher amounts of Hg^0 at all times.

A comparison of their pore size distributions (Figure 1) suggests that the larger pores and pore volume (see Table

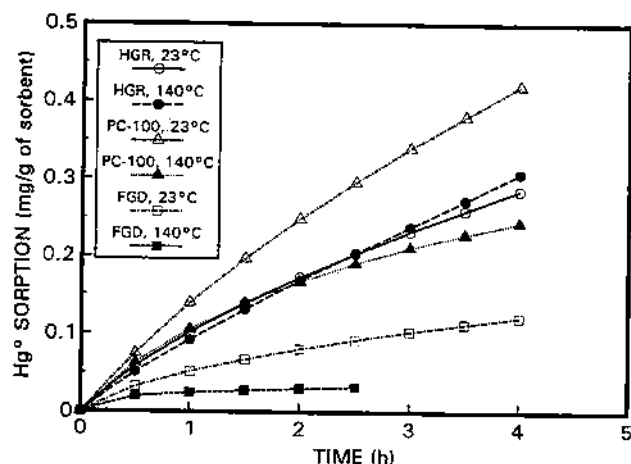


Figure 2. Hg^0 sorption versus time curve for PC-100, HGR, and FGD at 23 and 140 °C exposed to a flow of 30 ppb of Hg^0 in N_2 (190 mL/min).

1) in FGD would cause a lower internal mass transport resistance for diffusing molecules. Also, the smaller particle size for FGD (roughly 2.5 times smaller than PC-100 based on mass median average size) would result in a lower influence of intraparticle mass transport. The only apparent physical evidence to support the higher observed sorptive capacity of PC-100 (versus FGD) is its higher surface area (Table 1). If the sorption of Hg^0 occurred in specific areas of the internal surface (active sites), then the difference may also be attributed to the different coal types (bituminous for PC-100 and lignite for FGD). It is interesting to note that our results from a chemical analysis indicated the more probable chemical sites for Hg^0 sorption (sulfur, chlorine, bromine, and iodine) in PC-100 and FGD were roughly the same implying that, if differences between the two arise because of different active sites, sites different from these would play a role.

Both PC-100 and FGD show lower Hg^0 capture at the higher temperature (Figure 2). Such behavior is normally associated with a physisorption mechanism. The lowering of sorptive capacity with increasing reaction temperature was also observed by Gullett and Jozewicz (13). As shown in Figure 2, both PC-100 and FGD have approximately half the sorptive capacity after 2.5 h at 140 °C than they have at 23 °C. However, this evidence is not conclusive of a physisorption mechanism for Hg^0 capture by PC-100 and FGD since alteration in surface properties at higher temperature may also lead to the same effect. In other words, if the surface active sites leading to Hg^0 capture were the primary centers for Hg^0 sorption, then deactivation or depletion of these at the higher temperature of 140 °C may also result in sorption behavior associated with a physisorption mechanism.

In contrast, temperature is seen to have an insignificant effect on Hg^0 sorption by S-impregnated HGR within the 4-h experimental duration. In an earlier study (14), similar results were found for HGR. However, beyond 5 h of exposure of Hg^0 , HGR reacting at 140 °C captured more Hg^0 than HGR reacting at 23 °C (14). Based on the influence of temperature on the sorptive capacity of HGR, Jozewicz et al. (14) concluded that a chemical reaction ($\text{Hg}^0 + \text{S}$) was the controlling mechanism. However, this mechanism cannot possibly justify the temperature-insensitive sorption results during the initial period (4 h). A possible explanation for this lies in the sorbent structure. HGR was prepared by crushing a 2000–4760- μm precursor.

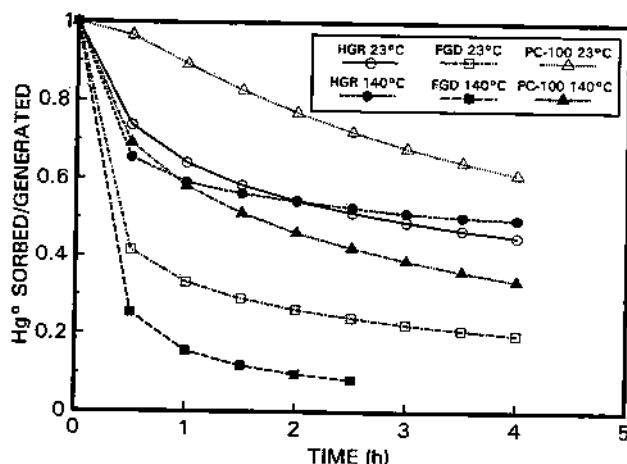


Figure 3. Fraction of generated Hg^0 sorbed by PC-100, HGR, and FGD at 23 and 140 °C exposed to a flow of 30 ppb Hg^0 in N_2 (190 mL/min).

Upon crushing, pore volume doubled for pores of diameter less than 50 nm (Figure 1). The surface area for the 20–25- μm size range also increased to 1078 from 715 m^2/g for the precursor (see Table 1). This increase in surface area would manifest itself in the form of surface roughness since the additional surface area cannot be accounted for based on the decrease in particle size alone. If a chemical reaction of Hg^0 with the S sites was the controlling mechanism at 23 °C during the initial period (4 h), then a strong influence of temperature should have been observed. Also, if mass transport (external or intraparticle) was the controlling step during the 4-h time period, temperature would still have an influence (although lower than if $\text{Hg}^0 + \text{S}$ was the controlling step). Therefore, it appears that, during the initial period of experimentation at 23 °C, the active sites (mostly non-S sites) present on the external surface sorb Hg^0 , resulting in the sorption behavior seen in Figure 2.

The conclusions reached in the earlier investigation (14) and in this study for the sorption mechanism in HGR were found to agree with the findings of Sinha and Walker (15). At 150 °C, they observed Hg^0 sorption only when the activated carbon contained sulfur, suggesting a chemical reaction mechanism between Hg^0 and S. For runs at 25 °C, however, Sinha and Walker (15) found that the presence of S was not required for mercury sorption. Further, addition of sulfur caused decreased mercury sorption, suggesting that S-free sites were the centers of mercury capture at the lower temperature.

Figure 3 shows the amount of Hg^0 captured by the three activated carbons as a fraction of the total amount of Hg^0 generated during a given time period. As shown in Figure 3, PC-100 reacting at 23 °C shows the highest sorption at any given time. After 4 h of exposure, PC-100 at 23 °C captures roughly 65% of the total Hg^0 generated during that time. FGD reacting at 140 °C is seen to have the least efficiency among the three activated carbons with respect to Hg^0 capture (approximately 10% after 2.5 h). Field test results for total mercury capture (no speciation data were available) are available for PC-100 and FGD (6). The field test results show that more than 95% of total inlet mercury (approximately 50–80 ppb) was removed at a carbon injection rate of approximately 450 mg/Nm^3 . These field results correspond to an exposure time of roughly 4 h for our experiments. From Figure 3, the Hg^0 removal is roughly 35 and 10% for PC-100 and FGD, respectively, at 140 °C. Thus, the removal efficiency

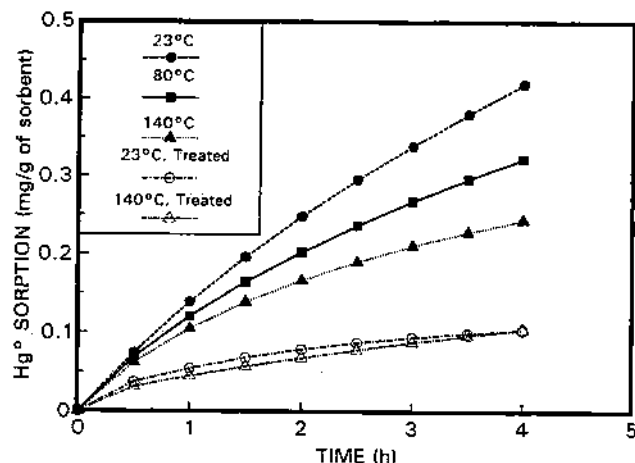


Figure 4. Effect of temperature and heat treating on the Hg^0 sorption versus time curve for PC-100 exposed to a flow of 30 ppb Hg^0 in N_2 (190 mL/min).

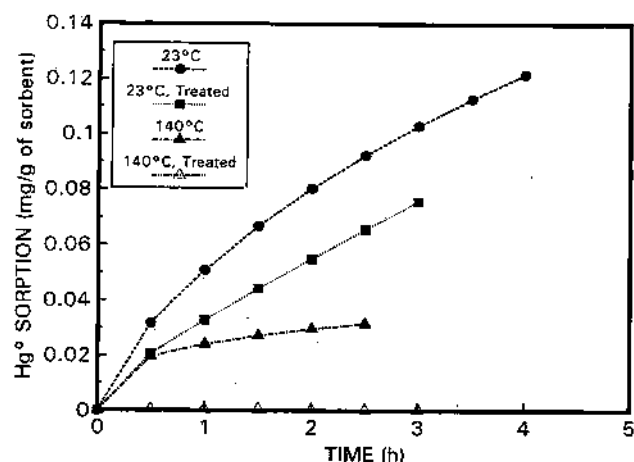


Figure 5. Effect of temperature and heat treating on the Hg^0 sorption versus time curve for FGD exposed to a flow of 30 ppb Hg^0 in N_2 (190 mL/min).

of Hg^0 is far less than that seen in the field tests where mercury exists predominantly in its oxidized form, which emphasizes the difficulties in Hg^0 capture.

Heat Treatment Tests. Experiments were performed to obtain a better understanding of the sorption mechanism in PC-100. Fresh PC-100 was "treated" with a flow of N_2 at 140 °C for 4 h before exposing it to a flow of Hg^0 in N_2 . Figure 4 shows the sorption versus time curve for the treated PC-100 reacted at 23 and 140 °C exposed to an inlet concentration of 30 ppb Hg^0 . As shown, Hg^0 capture by the treated samples is far less than that of the fresh sample at all times.

Heat treatment was also found to have a similar effect on the Hg^0 sorption capacity of FGD as seen in Figure 5. The sorption capacity after 3 h for the heat-treated sample exposed to Hg^0 - N_2 stream at 23 °C is seen to be approximately 65% of that of the untreated sample. The effect of heat treatment was found to be dramatic for the sample exposed at 140 °C to the Hg^0 - N_2 stream. A negligible amount of Hg^0 is seen to be sorbed by the heat-treated FGD sample at the higher temperature of 140 °C. However, the effect of heat treatment on the performance of FGD at 140 °C should be viewed relative to the low capture of Hg^0 by the untreated sample. In contrast to the effect of heat treatment seen for the thermally activated carbons (PC-100 and FGD), exposing HGR for 4 h under

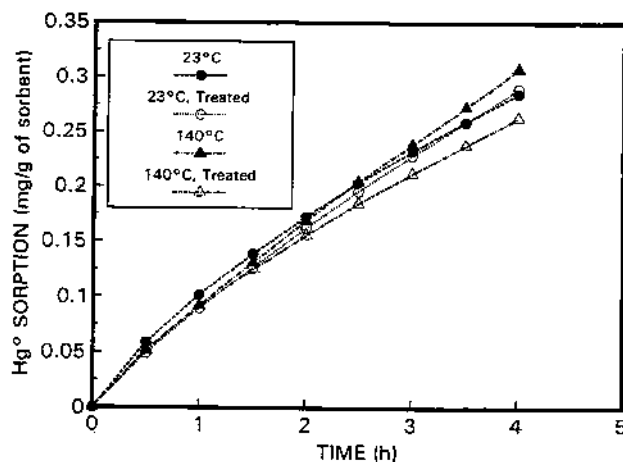


Figure 6. Effect of temperature and heat treating on the Hg^0 sorption versus time curve for HGR exposed to a flow of 30 ppb Hg^0 in N_2 (190 mL/min).

N_2 did not have any effect on its Hg^0 sorption capacity (see Figure 6).

The pore size distribution of all three treated activated carbons was compared with that of the fresh carbons. No change occurred in their pore size distributions, and a BET analysis showed that the treated samples' surface areas were identical to those listed in Table 1. Because we had previously concluded that for PC-100 and FGD the surface area and/or active sites played an important role in Hg^0 capture, a logical conclusion from these results is that active sites residing in the internal surface area of PC-100 and FGD cause Hg^0 sorption and that these active sites are either deactivated or depleted when heat treated. On the other hand, the sorption capacity of HGR is unaffected at 140 °C because the primary sorption site (S) is not depleted or deactivated as seen for PC-100 and FGD. Also, the non-S sites at the external surface that lead to Hg^0 sorption at 23 °C in HGR are not depleted or deactivated at 140 °C.

One of the previous conclusions was that the difference in the sorption of Hg^0 between PC-100 and FGD was attributable to surface active sites other than sulfur and halides. It is highly probable that the active site causing Hg^0 sorption in these thermally activated carbons is oxygen. Oxygen is a well-known surface component present in carbons and is known to drastically affect the chemical behavior of carbon surfaces with gases and liquids (16–18). The graphite structure of carbon has an inert planar surface (π -bond) (19) and a very reactive structure (sp^2 electrons) (20). Oxygen is easily chemisorbed on these reactive surfaces as various functional groups which influence further surface reaction (21). As a result of chemisorption, several functional groups, such as carbonyl, quinone, and carboxylic acid, are formed (21). Upon thermal treatment, all these functional groups are known to decompose giving out CO or CO_2 (21), thereby changing the reactivity of the carbon surface. Although high temperatures (>400 °C) have been known to cause such an effect (22), lower temperatures like that used in this study can also lead to the decomposition of the functional groups (21). Using linear temperature-programmed desorption to study energetics of surface complex groups bound to carbon surfaces, they found that decomposition occurred at 75–125 °C. Thus, it is highly likely that heat treatment of PC-100 and FGD caused the decomposition

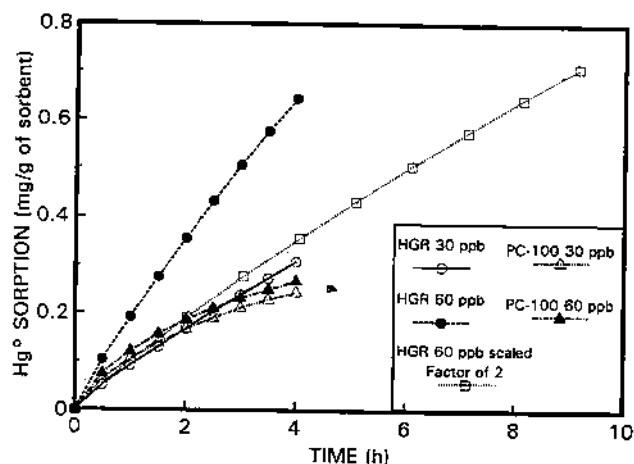


Figure 7. Effect of inlet Hg^0 concentration on the sorption versus time curve for HGR and PC-100 at 140 °C.

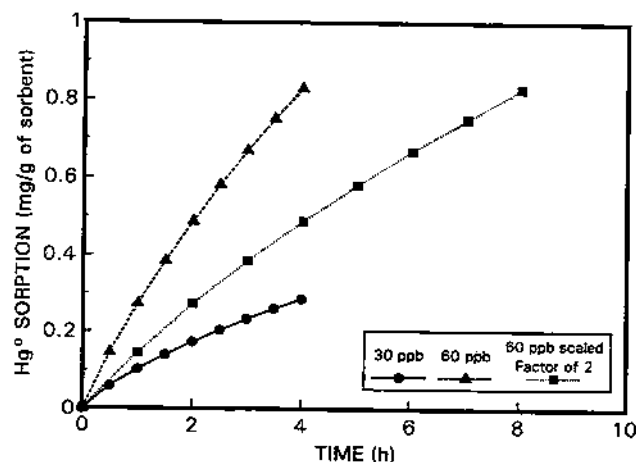


Figure 8. Effect of inlet Hg^0 concentration on the sorption versus time curve for HGR at 23 °C.

of the functional groups, decreasing the reactivity in the carbon surface.

Effect of Hg^0 Concentration. Figures 7 and 8 show the effect of inlet Hg^0 concentration on the sorption behavior of HGR and PC-100. This is of importance in field applications where the feed rate of the activated carbon may need to be varied for flue gases with different levels of Hg^0 . However, Hg^0 sorption versus time curves for the two sorbents are presented here only for two levels of inlet Hg^0 concentration, and readers are advised to exercise caution in generalizing the interpretation from these results.

Figure 7 shows the effect of inlet Hg^0 concentration (30 and 60 ppb) on the sorption versus time curve for HGR and PC-100 at 140 °C. Inlet Hg^0 concentration has a strong effect on the total Hg^0 captured at any time. The quantitative effect of inlet Hg^0 concentration on the sorption behavior of HGR can be obtained by scaling the time axis of the sorption curve (60 ppb case, dashed line) by a factor of 2 to obtain the scaled curve (dotted line). A comparison of the scaled curve with the sorption versus time curve for HGR exposed to a flow of 30 ppb Hg^0 (solid line) shows that the two nearly overlap for the 4-h duration, implying a linear effect of inlet Hg^0 concentration on sorption by HGR. It was observed by Jozewicz et al. (14) and by Sinha and Walker (15) that at 140 °C the primary mode of sorption is via the $\text{Hg}^0 + \text{S}$ reaction. If the intraparticle mass transport does not play a significant

role during the 4-h sorption period of our experiment, this then implies that the intrinsic kinetics are linear with respect to inlet Hg^0 concentration. In an earlier study (14), similar effects of inlet Hg^0 concentration were seen for HGR; however, beyond the 4-h exposure period, nonlinear effects were observed. The difference between the effects of inlet Hg^0 concentration between short and long exposure times could be the reaction zone of Hg^0 and S since HGR possesses a large external surface area (see Table 1). For longer exposures, the interaction between Hg^0 and S would primarily occur inside the particle. Here, a combined influence of concentration on reaction and intraparticle mass transport would occur. The nonlinear effect of concentration at longer exposures would therefore be attributable to a nonlinear driving force for Hg^0 mass transport if the $\text{Hg}^0 + \text{S}$ reaction is linear with respect to Hg^0 concentration. At shorter exposures, the $\text{Hg}^0 + \text{S}$ reaction occurs at the external surface since both reaction and external mass transfer (from the bulk gas phase) are linear functions of concentration of Hg^0 in the bulk phase.

The effect of inlet Hg^0 concentration was found to be minor for PC-100 reacting at 140 °C (Figure 7). From our previous discussions, it was found that sorption in PC-100 occurred in specific sites that are either deactivated or depleted at higher temperatures. Therefore, the sorption by PC-100 at 140 °C could possibly be limited by the number of active sites available to sorb Hg^0 . In other words, the higher amounts of Hg^0 prevalent in PC-100 on account of the doubling in bulk-phase Hg^0 concentration may not get sorbed because of the lack of active sites. Nevertheless, if the number of active sites is the same for both cases (a reasonable assumption), then the sorption amounts should have been higher for PC-100 reacted under 60 ppb of Hg^0 during the initial exposure periods (e.g., 1 h) since the sorption curve has not reached a plateau. Therefore, it appears that the sorption kinetics for PC-100 are zero order with respect to Hg^0 concentration at 140 °C.

Figure 8 shows the effect of inlet Hg^0 concentration on the sorption behavior of HGR reacting at 23 °C. Again, the two inlet concentrations are 30 and 60 ppb of Hg^0 in N_2 flowing at 190 cm^3/min . The quantitative effect of inlet Hg^0 concentration on the sorption behavior can be obtained by scaling the time axis of the sorption curve (60 ppb case, dashed line) by a factor of 2 to obtain the scaled curve (dotted line). Unlike the linear effect of Hg^0 concentration observed for HGR reacting at 140 °C within the same time frame, increasing the inlet Hg^0 concentration by two is seen to increase the sorption by more than a factor of 2 (compare the solid and the dotted lines in Figure 8). On the basis of our previous discussions and the results of Sinha and Walker (15), the main mode of Hg^0 sorption is not through the $\text{Hg}^0 + \text{S}$ reaction at 23 °C. Therefore, the nonlinear effect of inlet Hg^0 concentration is attributable to the sorption behavior of the non-S active sites contributing to Hg^0 sorption at 23 °C.

Desorption Tests. The samples of PC-100 and HGR exposed to a set time of Hg^0 vapors at 23 and 140 °C were tested for desorption of Hg^0 as a function of temperature. Detailed desorption characteristics for the two sorbents as a function of temperature are given by Jozewicz et al. (14). The limited desorption of Hg^0 from PC-100 and HGR exposed to Hg^0 at 23 °C suggests that the primary route of Hg^0 capture is chemisorption. That is, the majority of interaction between the active sites and Hg^0

Table 2. Summary of Sorption Capacities, Mechanisms, and Effect of Heat Treatment for PC-100, FGD, and HGR

	PC-100 (thermally activated)	FGD (thermally activated)	HGR (S-impregnated)
23 °C	high capture of Hg ⁰ ; capture of Hg ⁰ is a combination of physisorption and chemisorption and occurs on active sites	low capture of Hg ⁰ ; sorption occurs on active sites	medium capture of Hg ⁰ on non-S sites located on external surface via physisorption and chemisorption; order of sorption kinetics greater than 1 with respect to Hg ⁰ concentration
140 °C	medium capture of Hg ⁰ via zero-order chemisorption on active sites	lowest capture of Hg ⁰ ; sorption occurs on active sites	medium capture via chemisorption; first-order reaction of Hg ⁰ and S on external surface (initially)
heat treatment	destroyed active sites leading to lower Hg ⁰ sorption at 23 and 140 °C	destroyed active sites leading to lower Hg ⁰ sorption at 23 and 140 °C	no effect on Hg ⁰ capture; active sites (both S and non-S are not destroyed)

is of a chemical nature. At the higher exposure temperature of 140 °C, the interaction is solely chemisorption.

Summary and Concluding Remarks

Sorption rates and capacities for Hg⁰ were found to vary in our study with the type of activated carbon, reaction temperature, and inlet Hg⁰ concentration. Table 2 summarizes sorption capacities, mechanisms, and effect of heat treatment for each activated carbon.

Both of the thermally activated carbons, PC-100 and FGD, showed decreasing sorption of Hg⁰ with increasing temperature. Although such behavior is associated with a physisorption mechanism, investigations with heat-treated samples of PC-100 and FGD revealed that this evidence was not conclusive. The lower Hg⁰ sorption by the heat-treated samples of PC-100 and FGD compared to that of the fresh samples indicated that either deactivation or depletion of surface active sites in PC-100 was responsible for lower sorption of Hg⁰. It is believed that the functional groups formed by chemisorption of O₂ cause sorption of Hg⁰ in PC-100 and FGD. These functional groups decompose upon heat treatment, decreasing the sorption capacity of PC-100 and FGD.

Either physisorption or chemisorption could occur in these active sites depending on the temperature of operation. However, further investigation of samples of PC-100 already exposed to Hg⁰ by attempting to desorb Hg⁰ suggested that both physisorption and chemisorption occurred at 23 °C, whereas the sorption mechanism at 140 °C was solely chemisorption.

PC-100 was found to sorb larger amounts of Hg⁰ than FGD at all times and reaction temperatures. Analysis of the two carbons revealed a similar distribution of sulfur, chlorine, bromine, and iodine. Therefore, the difference between the sorption capacity of the two sorbents was caused by an active site other than these (most probably the functional groups formed by sorption of O₂). The number of these active sites is a factor causing differences in the sorption capacity of PC-100 and FGD since the surface area of PC-100 is nearly twice that of FGD.

At 140 °C, the chemically activated carbon (HGR) exhibited sorption of Hg⁰ through the reaction of Hg⁰ and S, whereas at 23 °C, the majority of the sorption of Hg⁰ occurred at sites other than elemental S. This was determined based on the sensitivity of Hg⁰ sorption with respect to temperature during the initial exposure period and for larger exposure times (14). Also, heat-treated HGR and a fresh sample showed identical sorption capacities for Hg⁰, indicating that the site of Hg⁰ sorption is not destroyed when heated, unlike in PC-100 and FGD. This confirms that the most likely route for Hg⁰ capture by HGR at 140 °C is through the Hg⁰ + S reaction. A similar

conclusion was reached by Sinha and Walker (15). Also, the relative insensitivity with respect to temperature shown by HGR for Hg⁰ sorption during the initial period of exposure suggests that the sorption occurs at the external surface.

Based on the limited information available on the effect of temperature, heat treatment, and inlet Hg⁰ concentration on the capture of Hg⁰ by activated carbons, operating conditions can be tuned toward optimizing the Hg⁰ removal process. When thermally activated carbons are used, lowering the temperature of operation would result in higher removal. Also, depletion of active sites in these activated carbons can be minimized by limited exposure to heat. However, for S-impregnated HGR, temperature and heat effect were insignificant.

Bulk Hg⁰ concentration was found to have a linear effect on the sorption behavior of Hg⁰ by HGR at 140 °C during the initial 4-h exposure. At longer exposures, the effect is seen to be nonlinear (14). This is indicative of the Hg⁰ + S reaction occurring at the external surface during the initial period and in the internal surface afterward. However, at 23 °C, HGR showed disproportionately higher Hg⁰ sorption with increasing Hg⁰ concentration in the bulk phase, indicative of nonlinear sorption by non-S sites.

Desorption studies of samples of PC-100 and HGR showed that both physisorption and chemisorption occurred at 23 °C, whereas only chemisorption occurred at 140 °C.

The simulated flue gas in this study consisted of Hg⁰ in N₂. Future studies are planned to study the capture of mercury in a gas stream consisting of water vapor, sulfur dioxide, hydrochloric acid, and nitrous oxides. The study of the capture of other prevalent forms of mercury-like mercuric chloride and mercuric oxide is also planned.

Acknowledgments

The authors would like to acknowledge the help of the late George Gillis (EPA/AEERL) for equipment support and the assistance of Lisa Adams (Acurex Environmental Corp.) with the experiments. Helpful discussions with C. W. Lee (EPA/AEERL) are also acknowledged.

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Received for review November 29, 1993. Revised manuscript received May 10, 1994. Accepted May 18, 1994.*

* Abstract published in *Advance ACS Abstracts*, June 15, 1994.

