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## Catalytic effects of carbon sorbents for mercury capture

E.S. Olson<sup>\*</sup>, S.J. Miller, R.K. Sharma, G.E. Dunham, S.A. Benson

*Energy and Environmental Research Center, PO Box 9018, Grand Forks, ND 58202-9018, USA*

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### Abstract

Activated carbon sorbents have the potential to be an effective means of mercury control in combustion systems. Reactions of activated carbons in flow systems with mercury and gas stream components were investigated to determine the types of chemical interactions that occur on the sorbent surface. The effects of carbon type, particle size, temperature, and reactive gases were studied. Sorption kinetics and capacities for lignite- and bituminous-based carbons were compared with those for catalytic carbons at temperatures of 107°C, 150°C, and 163°C. In the air and baseline gas studies, the catalytic carbons exhibited far better sorption than the lignite- and bituminous-derived carbons. With the catalytic carbons, the greater sorption kinetics and capacity in an air stream or baseline gas composition compared with nitrogen provides a clear demonstration that O<sub>2</sub> is required in the gas stream for higher reactivities and capacities. Thus, a catalytic chemisorption mechanism predominates for the sorption of mercury at these conditions. The reaction kinetics are inversely proportional to the temperature, indicating that a preliminary physisorption step with mercury associating with a surface site is rate-determining. In synthetic flue gas streams containing HCl (50 ppm), the sorption kinetics of the catalytic carbon are slightly inferior to those of lignite-based carbon. Thus, the reaction is dominated by a different interaction, where HCl reacts with mercury on the carbon surface and the oxidation sites on the catalytic carbon apparently have no advantage. Granular and fine-particle carbons gave similar results in flue gas streams. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Mercury sorption; Chemisorption; Catalytic carbons; Flue gas

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### 1. Introduction

The environmental impact of mercury released during coal combustion is of great concern, as documented in the recently released US Environmental Protection Agency

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<sup>\*</sup> Corresponding author. Tel.: +1-701-777-5155; fax: +1-701-777-5181.

*E-mail address:* eolson@eerc.und.nodak.edu (E.S. Olson).

(EPA) draft *Mercury Study Report to Congress* [1]. On the basis of health studies to date, exposure via ingestion of organic mercury (i.e. methylmercury) poses the most serious health risk. Exposure to elemental and inorganic mercury forms via inhalation and ingestion can present serious health risks if doses are acute; however, most health effects as a result of exposure are of a longer-term, leading to dysfunctional organs/systems. Of major concern are bioaccumulation of organomercury forms in fish and the subsequent impact on waterfowl and other fish-eating species [2,3]. While modes of exposure and dose are certainly important relative to adverse health effects, equally important is mercury speciation. Understanding the various forms (species) of mercury released during coal utilization and subsequently transported in vapor and particulate forms to the environment or preferably transformed to bound forms in a control device is critical to identifying, minimizing, and preventing both short- and long-term adverse health and ecological effects.

Mercury occurs in association with the inorganic (i.e. mineral) and organic components of fuels, which when converted to energy are transformed and released [4]. The mineral and organic hosts of mercury decompose at conversion temperatures of approximately 1500°C, and mercury is liberated as gaseous  $\text{Hg}^0(\text{g})$  because of its volatility (boiling point of 357°C). In the complex environment of the flue gas duct and with decreasing temperature,  $\text{Hg}^0(\text{g})$  may either remain as a monatomic species or react to form additional species. It can react with other gaseous components such as chlorine, sulfur oxides ( $\text{SO}_x$ ), and  $\text{O}_2$  to form various  $\text{Hg}^{2+}$  compounds.  $\text{Hg}^0(\text{g})$  will readily react with  $\text{Cl}_2(\text{g})$  and  $\text{HCl}(\text{g})$  to form  $\text{HgCl}_2(\text{g})$  [5]. The experimental evidence indicates, however, that the formation of  $\text{HgO}(\text{s})$  and  $\text{HgSO}_4(\text{s})$  involves rather complex heterogeneous reaction processes [6]. The formation of  $\text{HgO}(\text{s})$  is apparently catalyzed by the presence of unburned carbon and fly ash particles, but is reversed by the presence of  $\text{SO}_2(\text{g})$  [7] and  $\text{CO}(\text{g})$  [8]. The proposed reactions suggest that mercury speciation is cyclic, whereby the  $\text{Hg}^0(\text{g})$  that is initially released during the energy conversion process and then oxidized may be reduced again. The reaction of  $\text{Hg}^0(\text{g})$  with  $\text{NO}_2$  is well known [9].  $\text{Hg}^0(\text{g})$  may also react with reactive species such as selenide and sulfide compounds, metals, and oxygen atoms on the surfaces of unburned carbon and ash particles entrained in flue gas, as well as on duct surfaces. Reactions between  $\text{HgO}(\text{s})$  adsorbed on particles and  $\text{SO}_3(\text{g})$  may lead to the formation of  $\text{HgSO}_4(\text{s})$ .

The effectiveness of existing air pollution control technologies such as scrubbers, ESPs, and baghouses and novel technologies such as sorbents are being explored to remove various forms of mercury emitted from coal-fired boilers. Most of these technologies are only effective at removing certain mercury species. For example, oxidized mercury species ( $\text{HgX}[\text{s},\text{g}]$ ) are generally water-soluble and can, therefore, be effectively captured by wet scrubber technologies. Conversely,  $\text{Hg}^0(\text{g})$  is difficult to capture and must be converted to an oxidized form for capture.

Most coal-fired boilers are not equipped with wet scrubbers, but most currently employ either an ESP or a baghouse for particulate control. These flue gas purification systems in combustion sources are usually not adequate for control of mercury emissions because of the high volatility at flue gas temperatures of 150°C or lower. Additional treatment of the flue gas streams with mercury sorbents is needed, and current research is directed toward achieving a better understanding of the types of

sorbents that will be effective, the conditions under which different sorbents are effective, and the nature of the sorption mechanisms.

Sorbent injection upstream of an ESP or baghouse has the potential to capture both  $\text{Hg}^0$  and  $\text{Hg}^{2+}$  and could be retrofitted to utility and industrial boilers with these particulate control systems [10]. Powdered activated carbon has been employed for mercury removal in the flue gas stream from an incinerator [11]. The carbon sorbent is injected into the flue gas upstream of a baghouse filter that collects the sorbent along with the ash. This method removed about 95% of the mercury, which may have been mostly  $\text{HgCl}_2$ , in the incinerator gas stream. The method also has great potential for elemental mercury, the major species present in coal combustion gas streams. Three excellent reviews concerning the application of sorbents to control in combustion systems have been published [12–14]. Recent bench-scale studies at the Energy and Environmental Research Center (EERC) indicate that the capacity for sorption of mercury on carbon is highly dependent on the conditions and presence of other flue gas constituents as well as the speciation [15,16].

The present investigation into the development of mercury sorbent carbons seeks to identify factors that determine the kinetic reactivity of carbon sorbents for mercury vapor at typical flue gas temperatures under controlled gas composition. Although gas streams containing both  $\text{Hg}^0$  and  $\text{HgCl}_2$  have been investigated, only the results for elemental mercury are discussed here. Earlier studies gave conflicting answers to the question of whether the mechanism was physisorption [5,17,18] so further evidence is required to understand the sorption mechanism(s). To elucidate the nature of mercury capture on carbon sorbents, the effects of carbon type, particle size, temperature, and reactive gases were investigated. The approach used here is to first discuss the results for the most simple gas component systems with non-catalytic and catalytic carbons and then progress to more complex systems containing acidic reactive gases with the two types of carbons.

## 2. Experimental

Sorbent tests were performed in a flow-through reactors equipped with continuous vapor-phase mercury analyzers as described in a recent report [19]. Elemental mercury was provided by a standard permeation tube source placed in a double-jacketed glass condenser and heated to the desired temperature. Mercury concentrations were calibrated for the flow rates used.

The granular carbon experiments in nitrogen and air streams used a reaction tube containing the carbon sorbent (0.20 g of  $20 \times 60$  mesh size) that was heated in a gas chromatograph (GC) oven at the desired temperature. Connections to the source and the effluent gas analyzer were Teflon tubing. Mercury concentrations in the effluent were determined by a calibrated continuous mercury UV analyzer (EPM). Flow rates of air or nitrogen were 8 scfh measured at the detector end, and inlet mercury concentrations were  $80\text{--}86 \text{ g/m}^3$ . Blank tests with no sorbent in the tube were performed before each test to determine the mercury concentration.

The tests in the flue gas compositions were performed with powdered sorbents loaded on a quartz filter (2.5 in.). The loaded filter and holder were heated in an oven (107°C or 163°C) in the simulated flue gas stream (containing the following: O<sub>2</sub> [6%], CO<sub>2</sub> [12%], SO<sub>2</sub> [1600 ppm], HCl [50 ppm], Hg<sup>0</sup> [20 μg/m<sup>3</sup>], H<sub>2</sub>O [8%], and N<sub>2</sub> [balance]). Mercury concentrations were determined with a Semtech 2000 analyzer, and a SnCl<sub>2</sub> cell was used to convert oxidized species to elemental, so that both data could be obtained for the effluent concentrations. Spent sorbents were analyzed for mercury to determine the mass balance.

### 3. Results

#### 3.1. Granular carbons in air versus nitrogen

Initial experiments were conducted to compare the sorption kinetics and capacities of activated carbons at 150°C in air and nitrogen streams. These experiments were performed with granular carbons packed in a heated Pyrex tube through which air or nitrogen containing a Hg<sup>0</sup> concentration of 86 μg/m<sup>3</sup> was passed. The mercury concentration in the effluent was continuously determined with the EPM continuous vapor monitor. A convertor furnace was intermittently operated to determine whether oxidized mercury species were in the effluent after breakthrough occurred.

With granular Calgon F-400 in fast flow rates (8 scfh), 100% breakthrough occurred immediately in both nitrogen and air streams (Table 1). There was no significant difference in the breakthrough curves for the two gas streams. The poor sorption activity in air streams demonstrated by the granular Calgon F-400 carbon is consistent with that reported earlier by Sinha and Walker [20], who observed immediate breakthrough for a non-impregnated carbon at 150°C in an air stream. Carey et al. [18] recently reported similar behavior for the lignite-based carbon (Norit FGD) in gas compositions that did not contain HCl.

In an experiment using slow gas flow rates (100 cm<sup>3</sup>/min) with the Calgon F-400 at 150°C, rapid breakthrough of Hg<sup>0</sup> in both nitrogen and air streams at 150°C was again

Table 1  
Mercury sorption on granular carbon sorbents at 150°C

Sorbent	Gas stream	Flow rate (cm <sup>3</sup> /min)	Initial Hg removed (%)	Breakthrough time (min)
Calgon F-400	air	4000		< 1
Calgon F-400	nitrogen	4000		< 1
Calgon F-400	air	100	80	4
Calgon F-400	nitrogen	100		< 1
Norit GAC1240	air	4000		< 1
Centaur <sup>a</sup>	air	4000	100	8
Centaur <sup>a</sup>	nitrogen	4000	100	8
Centaur/5% <sup>a</sup> H <sub>2</sub> SO <sub>4</sub>	air	4000	100	575
Centaur/5% <sup>a</sup> H <sub>2</sub> SO <sub>4</sub>	nitrogen	4000	100	209

<sup>a</sup>Catalytic carbon.

observed. But the time required for 50% breakthrough was shorter in the nitrogen stream (< 1 min) compared to the air stream (4 min). The lack of any sorption in nitrogen shows that nothing present in the carbon, such as a transition metal oxide, is able to directly oxidize mercury. Obviously, physisorption of elemental mercury on activated carbon was not occurring to any significant extent at 150°C. The very small sorption observed in the air stream was attributed to a relatively poor chemisorption activity for this activated carbon. The chemisorption reaction occurring in the air stream is hypothesized to involve catalytic conversion of  $\text{Hg}^0$  to a less volatile oxidized form. In experiments carried out in a stopped-flow reactor, Hall et al. [5] showed that activated carbons prepared from sugar and peat reduced the  $\text{Hg}^0$  concentration in the reactor at temperatures in the range of 100–300°C. Consistent with a catalytic mechanism, Hall observed that the reaction was one-half order with respect to molecular oxygen in the reactor.

### 3.2. Fine-particle carbons in air and baseline gas streams

Since carbon fine particles will be used in a sorbent injection technology, bench-scale tests were conducted with fine particles of a powdered lignite-based activated carbon (LAC) sorbent from Norit America (FGD carbon) and a powdered form of the Calgon F-400 granules used in the previous tests. These tests were performed in air and in a baseline gas composition containing  $\text{O}_2$  (6%),  $\text{CO}_2$  (12%),  $\text{Hg}^0$  (20  $\mu\text{g}/\text{m}^3$ ),  $\text{H}_2\text{O}$  (8%), and  $\text{N}_2$  (balance). The sorbent particles were distributed on a quartz filter to form a very thin bed. The filter is placed in a heated filter holder assembly mounted in the gas stream containing mercury vapor. An  $\text{SnCl}_2$  reduction cell was used to convert oxidized mercury to elemental mercury in the effluent gas stream, so that total mercury as well as elemental mercury in the effluent could be determined. Studies with addition of acidic gases are described later.

The fine-particle LAC was tested in the baseline gas stream at 163°C (Fig. 1 — Run 738). The mercury concentration in the effluent broke through immediately to 100% (Table 2). When the LAC was tested in the baseline gas stream at a lower temperature (107°C), the breakthrough was again immediate to 100%. A comparison test of the LAC at 107°C in an air stream showed immediate breakthrough. Thus, the LAC carbon was relatively inactive for mercury sorption in both air and the baseline gas composition with no reactive flue gas components present.

The powdered Calgon F-400 was tested in air at 150°C (Fig. 2 — Run 749) and broke through less rapidly (50% breakthrough in 30 min). The Calgon F-400 has substantially better activity for mercury sorption in air compared to the LAC.

In the air stream experiments with both the lignite and bituminous carbons where  $\text{Hg}^0$  breaks through very rapidly, the number of catalytic oxidation sites must be very small and the sites must be easily blocked by the oxidized product species. Because of the short breakthrough time on these carbons, not enough mercury was captured in the spent sorbent to determine the form or species of the oxidized mercury present on the sorbent.

### 3.3. Granular catalytic carbons in air and nitrogen streams

Based on the hypothesis that a catalytic mechanism for oxidative chemisorption is occurring on the carbon sorbents, an improvement in the sorption kinetics and capacity

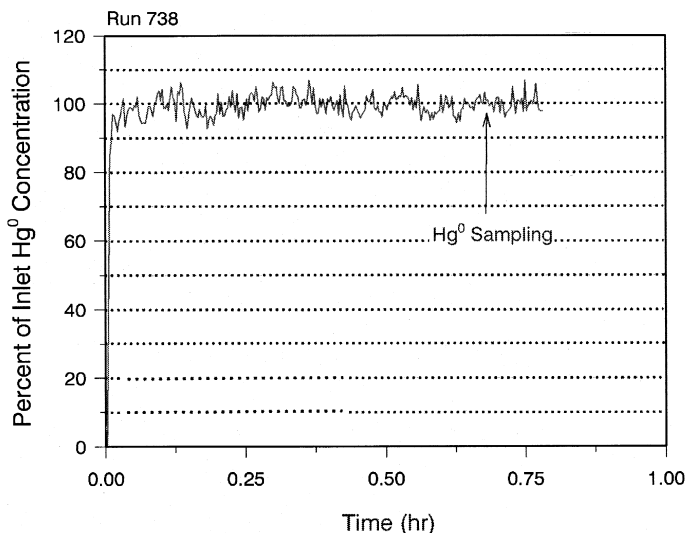


Fig. 1. Hg sorption for LAC fine particles in baseline gas (163°C).

should result from the generation of more catalytic sites or more effective catalytic sites for the activation of  $\text{Hg}^0$  and molecular oxygen. Catalytic carbons are available commercially with enhanced catalytic functionality for aqueous reactions such as the decomposition of peroxides. Catalytic carbons are produced by recarbonization of urea- or ammonia-treated oxidized activated carbons or by impregnation of nitrogen-containing polymers and pitches [21].

Table 2  
Mercury sorption on fine-particle carbon sorbents

Sorbent	Gas stream	Temperature (°C)	Initial Hg removed (%)	50% Breakthrough time (min)
LAC <sup>a</sup>	baseline	163		< 1
LAC	baseline	107		< 1
LAC	air	107		< 1
Calgon F-400 (powdered)	air	149	95	30
EERC 92-5 <sup>b</sup>	air	149	80	≥ 200
LAC	baseline + SO <sub>2</sub> + HCl	107	100	≥ 200
LAC	baseline + HCl (+ SO <sub>2</sub> )	107	95	≥ 200
LAC	baseline + SO <sub>2</sub> + HCl	163	90	≥ 100
Calgon F-400 (powdered)	baseline + SO <sub>2</sub> + HCl	107	90	≥ 200
Calgon F-400 (powdered)	baseline + SO <sub>2</sub> + HCl	163	80	120
EERC 92-5	baseline + SO <sub>2</sub> + HCl	107	80	≥ 200
EERC 92-5	baseline + SO <sub>2</sub> + HCl	163	85	≥ 200

<sup>a</sup>LAC = Norit FGD.

<sup>b</sup>EERC 92-5 = catalytic carbon from indole pitch.

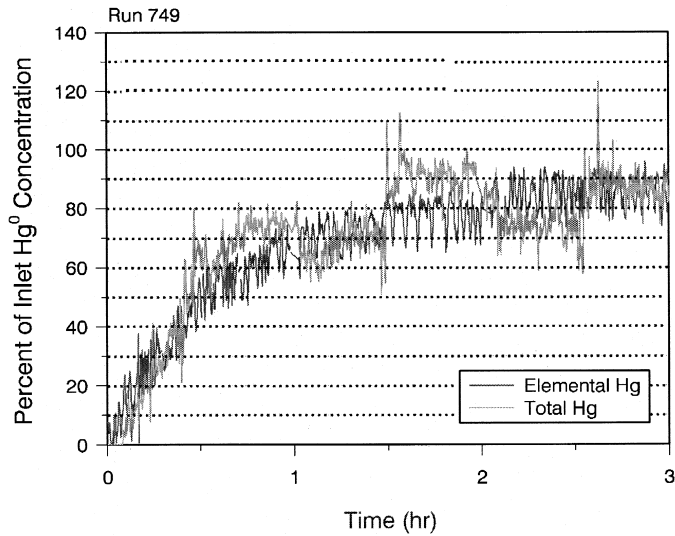


Fig. 2. Hg sorption for Calgon fine particles in air (149°C).

Experiments with a granular catalytic carbon (Calgon Centaur) at 150°C and 8 scfh demonstrated better sorption compared with that of Calgon F-400. An increase in the breakthrough time was observed in both the nitrogen (Fig. 3 — RKS242) and air stream (Fig. 4 — RKS196). Thus, 50% breakthrough occurred after 8 min for the Centaur compared with < 1 min for the Calgon F-400 at 8 scfh. The Centaur activity also decreased more slowly after 50% breakthrough compared with the Calgon F-400, resulting in a higher capacity for the Centaur carbon. This increase in activity for the

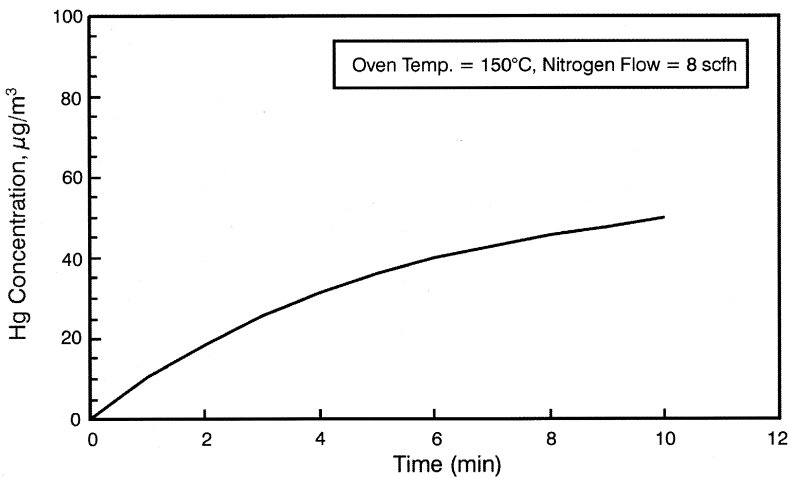


Fig. 3. Hg sorption in nitrogen (150°C).

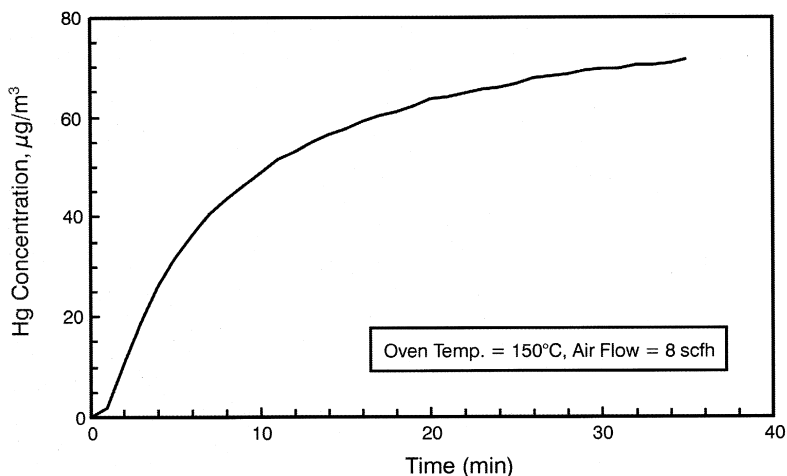


Fig. 4. Hg sorption for Centaur granules in air (150°C).

catalytic carbon could be attributed to catalytic functionality, but could also result from having many nitrogen sites on the carbon edge structure for binding mercury. The increase in breakthrough time for the Centaur was the same in nitrogen as in air at the fast flow rate. Thus, further research was needed to establish the mechanism. Furthermore, the sorption activity of the Centaur was not high enough to justify its use in mercury vapor removal technologies.

### 3.4. Effects of acid promoter

An activation method was applied to the carbons prior to filling of the sorbent tube. This method consisted of adding sulfuric acid (5%) to the activated carbon and drying it briefly in an oven at 110°C. This treatment dramatically increased the  $\text{Hg}^0$  removal rate of the catalytic carbons and increased the capacity by a large factor. In the air stream at 150°C and 8 scfh, the 50% breakthrough time for the acid-promoted Centaur carbon increased to 575 min (Fig. 5 — RKS17). In the nitrogen stream at the same temperature and flow rate, the 50% breakthrough time for the acid-promoted Centaur carbon was 209 min (Fig. 6 — RKS243). Although the breakthrough time for the acid-promoted catalytic carbon in the nitrogen stream was also significantly longer than that of the original Centaur, the large difference in activity in air versus nitrogen for this carbon provides a clear demonstration that a reactive component of the gas stream ( $\text{O}_2$ ) is required for higher reactivities and capacities.

The activation method was also effective in improving the removal rate for activated carbons, such as the Calgon F-400, that are not considered catalytic carbons. The acid-promoted Calgon F-400 carbon experienced 50% breakthrough at 171 min in the air stream at 150°C (Fig. 7 — RKS11) compared with the original Calgon F-400, which broke through in 1 min at 8 scfh. This increase in activity was consistent with that



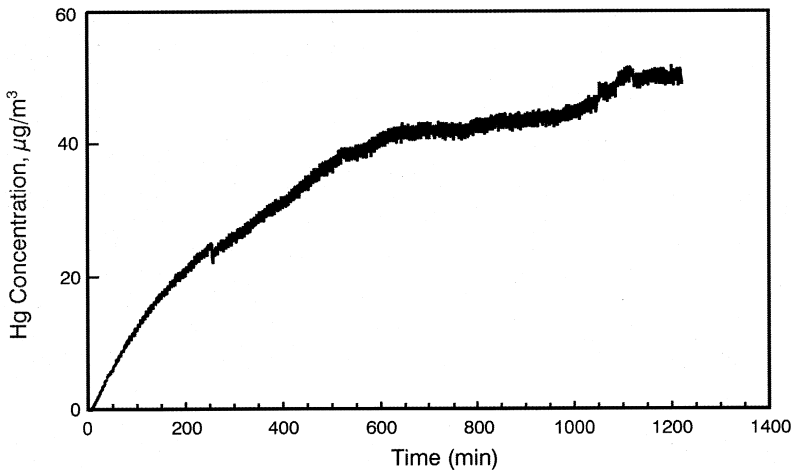


Fig. 5. Hg sorption for Centaur/5% acid granules in air (150°C).

observed for the Centaur carbon, but the acid activation treatment of Calgon F-400 achieved only a fraction of the activity of the acid-promoted Centaur.

Since there is a difference in the activities of acid-treated carbons in air versus nitrogen, the increase in activity seen for the catalytic carbons is not likely due to increased physisorption at the high temperature. The results with the catalytic carbon imply a chemisorption mechanism involving several steps occurring at specific sites on the carbon surface. The catalytic carbon has nitrogenous edge structures that may be

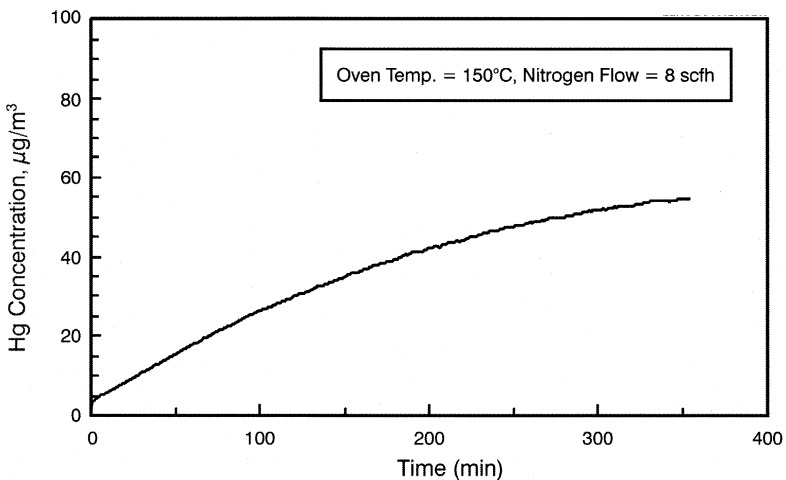


Fig. 6. Hg sorption for Centaur/5% acid granules in nitrogen (150°C).

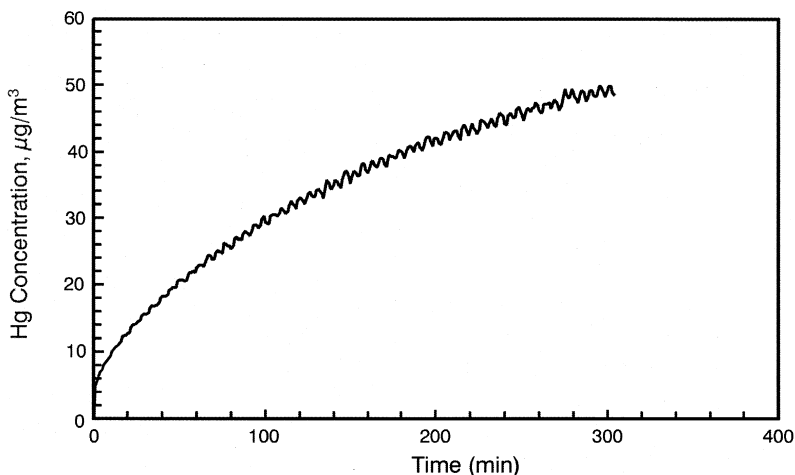


Fig. 7. Hg sorption for Calgon/5% acid granules in air (150°C).

cationic and facilitate ion-induced dipole bonding with  $\text{Hg}^0$ , providing an activation of the  $\text{Hg}^0$ . The chemisorption mechanism could involve generation of a Lewis acid site that can directly accept electrons from the physisorbed  $\text{Hg}^0$  atom. The higher activity of the catalytic carbon may result from a higher oxidation potential of the catalytic carbon. Thus, the mercury is more easily oxidized at the reactive site. If molecular oxygen is present, the carbon is more effective in maintaining the highly active state. The catalytic reaction sites could be blocked as mercuric oxide and sulfate build up over the course of the experiment, resulting in a very gradual type of breakthrough curve.

The addition of the acid provides a substantial benefit and increases the activity such that carbon sorbents become useful for the capture of mercury. Thus, the combination of nitrogenous catalytic carbons and the activation method provides the key to effective elemental mercury sorption in air streams.

### 3.5. Fine-particle catalytic carbons in the baseline gas stream

Several catalytic carbons were prepared by impregnation of ground particles of the Calgon F-400 carbon with solutions of nitrogenous polymers and pitches followed by drying and recarbonization. The fine particles were tested in the thin bed apparatus with an air stream. The results for the carbon prepared by impregnating an indole pitch showed 20% of the inlet mercury in the effluent, but no gradual or further breakthrough (Fig. 8 — Run 739). Thus, the eventual capacity of the catalytic carbon was very high, as with the granular Centaur sorbent. No oxidized mercury was detected in the effluent.

### 3.6. Temperature effects

To better understand the effects of temperature on mercury sorption, it is important that data are obtained for a sorption process that clearly includes a chemisorption

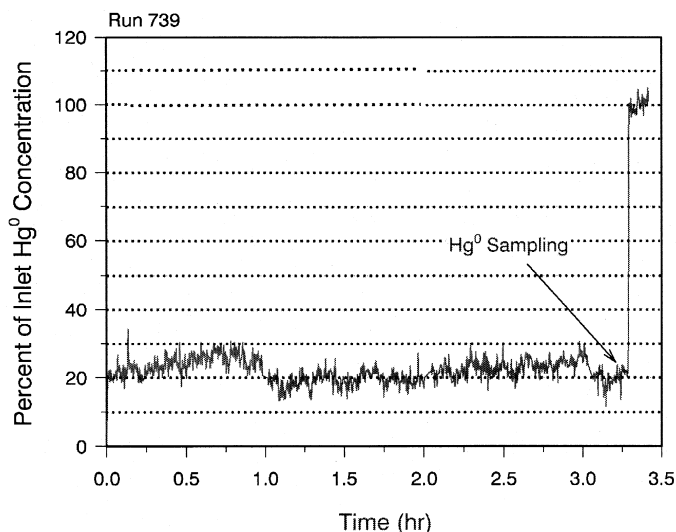


Fig. 8. Hg sorption for EERC Indole pitch carbon fine particles in air (149°C).

component. Earlier studies on temperature effects of activated carbon sorption [17] used a nitrogen stream, where chemisorption by the unimpregnated carbon may not have been maximized.

The chemisorption of Hg<sup>0</sup> is likely a multistep reaction. The rate of each chemical reaction step increases with temperature. In contrast, the exothermic physisorption of Hg<sup>0</sup> at non-oxidizing binding sites will decrease with increasing temperature. If the sorption process includes a preliminary physisorption equilibration where Hg<sup>0</sup> binds and desorbs at the active site, the equilibration will show a negative temperature effect on the overall reaction rate, because desorption is favored at higher temperatures. Thus, although chemisorption may account for the main sorption of mercury, the extent to which increasing the temperature may affect the sorption rate cannot be predicted.

Isothermal experiments were performed with both catalytic (Centaur) and non-catalytic granular carbon sorbents in air streams (8 scfh) at a series of temperatures. For any temperature, all the sorbents captured 100% of the mercury at the start of each run. After a few minutes, small amounts of Hg<sup>0</sup> appeared in the effluent, and the amount increased slowly with time. To compare rate data at the various temperatures, Table 3 shows the percentage of mercury removed for each temperature after 5 and 10 min of run time. The 5-min data are plotted in Fig. 9 for the Centaur carbon with 5% sulfuric acid. Similar curves were obtained for other carbons and the 10-min time interval, but these are not shown. For all carbon sorbents, the removal rates decrease with temperature, but not in a linear fashion. Thus, the rate-determining step of the reaction is clearly an association preequilibrium of Hg<sup>0</sup> at the active site that is less favorable at the higher temperatures. This temperature behavior contrasts with the temperature effects observed for another type of mercury sorbent, the metal oxides, where removal rate increases with

Table 3  
Isothermal mercury sorption at 5- and 10-min run times for catalytic carbon

File name	Sorbent	Temperature (°C)	Percent absorption	
			5 min	10 min
RKS199	Centaur	75	96.3	87.0
RKS198	Centaur	100	91.8	74.8
RKS197	Centaur	125	84.6	63.9
RKS196	Centaur	150	60.1	39.0
RKS190	Centaur/5% H <sub>2</sub> SO <sub>4</sub>	50	99.9	99.8
RKS189	Centaur/5% H <sub>2</sub> SO <sub>4</sub>	75	99.7	99.2
RKS188	Centaur/5% H <sub>2</sub> SO <sub>4</sub>	100	97.4	95.5
RKS187	Centaur/5% H <sub>2</sub> SO <sub>4</sub>	125	97.1	95.3
RKS186	Centaur/5% H <sub>2</sub> SO <sub>4</sub>	150	95.1	91.9
RKS200a	Calgon/5% H <sub>2</sub> SO <sub>4</sub>	75	96.1	94.6
RKS194	Calgon/5% H <sub>2</sub> SO <sub>4</sub>	100	95.7	94.1
RKS193	Calgon/5% H <sub>2</sub> SO <sub>4</sub>	125	89.0	86.7
RKS192	Calgon/5% H <sub>2</sub> SO <sub>4</sub>	150	87.4	84.5

temperature [22]. How temperature affects chemisorption rates of carbons in other gas compositions is discussed below.

### 3.7. Effects of flue gas components

Reactive flue gas components, such as HCl, NO, or NO<sub>2</sub>, can strongly affect mercury sorption at a variety of temperatures, owing to chemical reactions (oxidations) of the elemental mercury. These chemisorption reactions may involve catalysis by the carbon

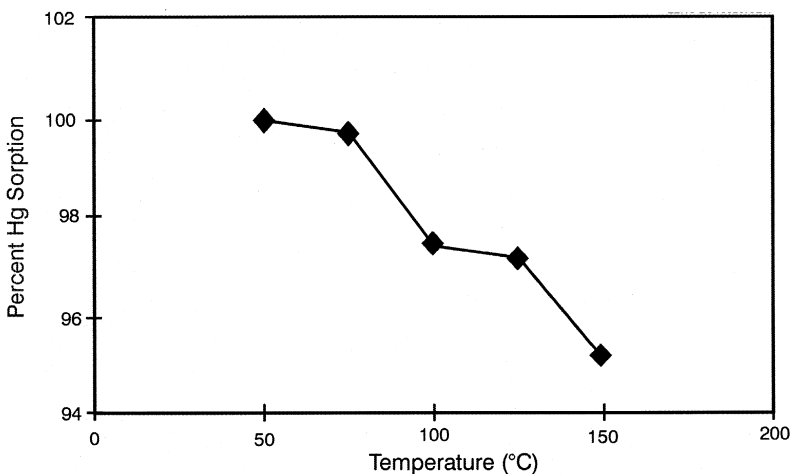


Fig. 9. Plot of % Hg sorption for Centaur/5% acid granules at 5-min run time versus temperature.

surface and subsequent trapping of the less volatile oxidation product. In contrast, the reaction product may be volatile at the gas stream temperature and would then be released into the effluent stream. The analysis of volatile oxidized mercury species in low-microgram per cubic meter concentrations has been previously limited to the distinction between elemental and oxidized mercury.

The results of a series of bench-scale tests were recently reported for evaluation of the LAC for mercury removal in simulated flue gases at moderate temperatures [19]. The synthetic flue gas composition included O<sub>2</sub> (6%), CO<sub>2</sub> (12%), SO<sub>2</sub> (1600 ppm), HCl (50 ppm), Hg<sup>0</sup> (20 μg/m<sup>3</sup>), H<sub>2</sub>O (8%), and N<sub>2</sub> (balance). The tests in the flue gas composition indicated that the powdered LAC was very active for mercury sorption. Tests at 135°C and 163°C gave high removal rates in contrast with the poor rates in air streams reported here for LAC.

Further experiments to compare the removal rates of additional sorbents under combustion conditions were performed [16,19]. The gas composition included the baseline gases, O<sub>2</sub> (6%), CO<sub>2</sub> (12%), Hg<sup>0</sup> (20 μg/m<sup>3</sup>), H<sub>2</sub>O (8%), and N<sub>2</sub> (balance) to which was added SO<sub>2</sub> (1600 ppm) and HCl (50 ppm), as in earlier studies. The test procedure used in these studies used fine particles of the sorbent loaded on a quartz filter as described above. Two temperatures were used in the tests (107°C and 163°C).

The results of these tests with the fine-particle LAC sorbent parallel the earlier results. Fig. 10 (Run 689) shows 100% capture initially, and a very slow increase in effluent mercury concentration to 15% breakthrough after 3 h. A repetition of the 107°C experiment but with addition of the SO<sub>2</sub> only after 2 h (Fig. 11 — Run 768) showed nearly 100% capture and only a minimal negative effect of the SO<sub>2</sub> on the high removal rate. Since sorption in the baseline gas was very poor (immediate breakthrough), HCl

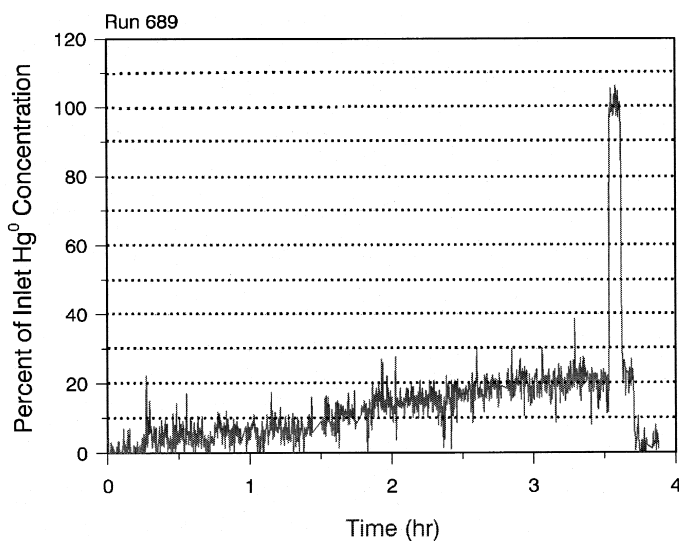


Fig. 10. Hg sorption for LAC fine particles in baseline gas + HCl + SO<sub>2</sub> (107°C).

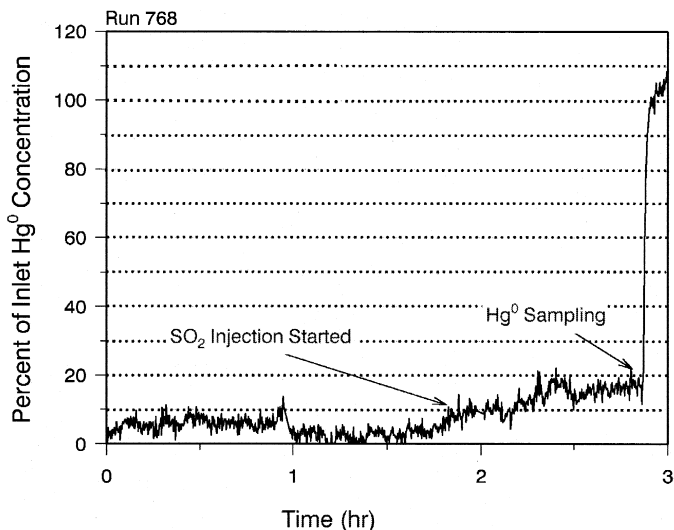


Fig. 11. Hg sorption for LAC fine particles in baseline gas + HCl + SO<sub>2</sub> at 1.8 h (107°C).

was, therefore, demonstrated to have a large positive effect on the sorption. A more complete study of individual reactive flue gas components including NO<sub>x</sub> species and their interactions is currently under way [22] to determine their effects on mercury capture on the sorbent surface and will be reported elsewhere.

The effects of temperature on the sorption kinetics were also investigated for the synthetic flue gas streams. The experiment performed at 163°C in the synthetic flue gas stream gave relatively good mercury capture rates, initially about 15% breakthrough, increasing to 25% breakthrough after 2.5 h (Fig. 12 — Run 709). Since these removal rates are lower than those at 107°C, the negative temperature effect was also demonstrated. Thus, the chemisorption process in HCl is likely to involve a preequilibrium step for binding of at least one of the reactants (HCl or Hg<sup>0</sup>) to the sorbent surface.

Continuous monitor data obtained in the 107°C experiment with LAC (Run 768) when the convertor was switched off at 2.8 h showed that the total mercury concentration corresponded to the Hg<sup>0</sup> concentration; thus, no oxidized mercury species such as HgCl<sub>2</sub> were in the effluent. This is consistent with the granular and fine-particle tests in air, where the HgO stays on the sorbent at the reaction temperature. This is also consistent with tests conducted with HgCl<sub>2</sub> in the influent gas rather than Hg<sup>0</sup>, which showed excellent sorption of HgCl<sub>2</sub> on the carbon surface at this temperature. Thus, the oxidized mercury species resulting from the surface-catalyzed reaction involving the HCl is staying on the sorbent at these temperatures both before and during breakthrough. It is not clear whether the sorbed species is mainly HgO, HgCl<sub>2</sub>, Hg<sub>2</sub>Cl<sub>2</sub>, mercury oxychloride (HgO · HgCl<sub>2</sub>), or some other form. In any case, the HCl promotes high oxidation reaction rates on the carbons, even though they are not catalytic carbons.

Mercury removal kinetics were also determined for powdered Calgon F-400 activated carbon in the baseline gas plus SO<sub>2</sub> (1600 ppm) and HCl (50 ppm). The test at 107°C

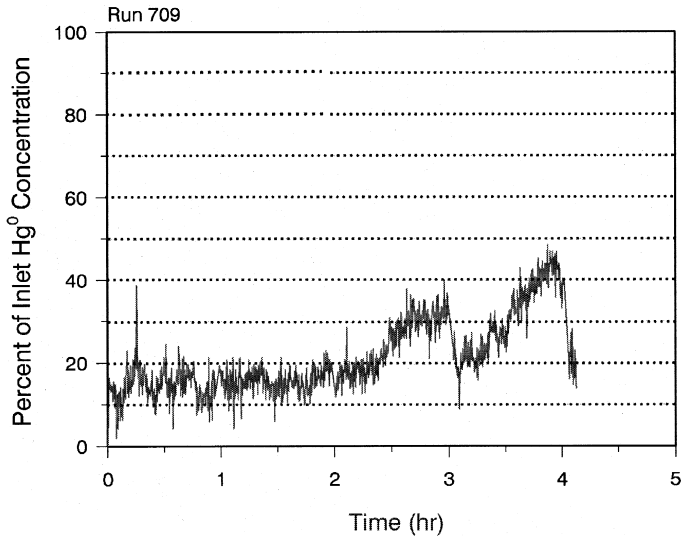


Fig. 12. Hg sorption for LAC fine particles in baseline gas + HCl + SO<sub>2</sub> (163°C).

showed 95% mercury sorption initially, decreasing slightly over 4 h, then increasing in the last hour (Fig. 13 — Run 746). These results are somewhat inferior to those for the LAC in the flue gas composition at 107°C. The test at 163°C showed 80% sorption initially, decreasing over 4 h to 50% (Fig. 14 — Run 777). Again, these results are

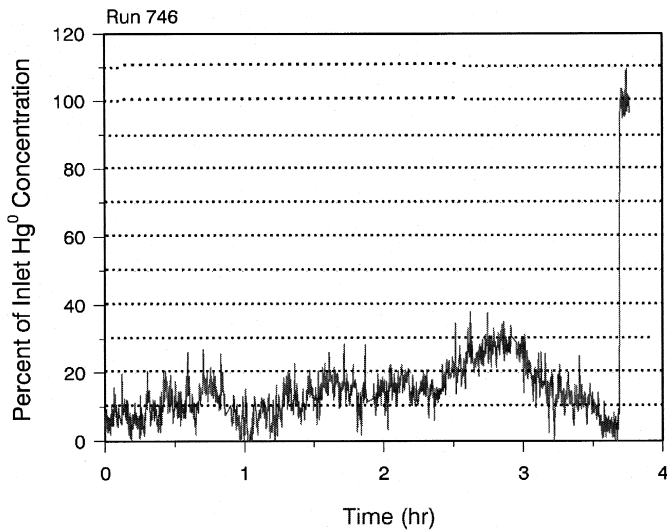


Fig. 13. Hg sorption for Calgon fine particles in baseline gas + HCl + SO<sub>2</sub> (107°C).

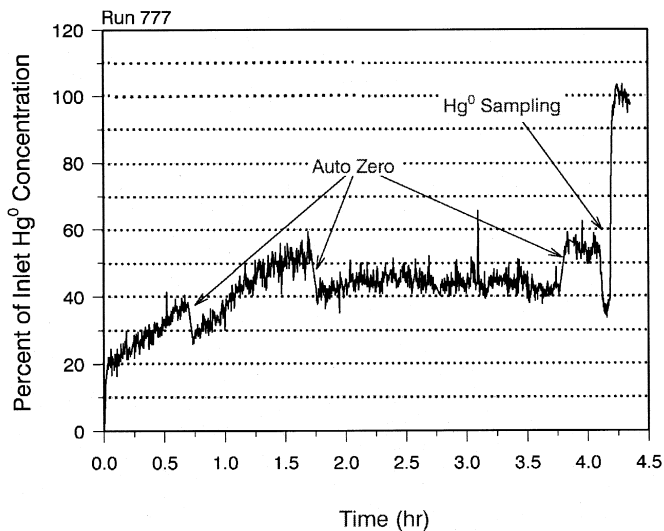


Fig. 14. Hg sorption for Calgon fine particles in baseline gas + HCl + SO<sub>2</sub> (163°C).

inferior to those for the LAC at the corresponding temperature. Both LAC and Calgon carbons show lower sorption rates at higher temperatures.

These results obtained in the series of tests in synthetic flue gas streams are consistent with earlier studies showing that sorbents in gas streams containing HCl give very effective removal of Hg<sup>0</sup>. Hall showed that the gas-phase reaction of Hg<sup>0</sup> with HCl (50–250 ppm) was rapid at high temperatures and gave an oxidized product believed to be HgCl<sub>2</sub> [6]. Previous sorbent studies at the EERC [23] showed that addition of 50 ppm of HCl to the gas feed in a test at 150°C with powdered activated carbon from bituminous coal dramatically enhanced mercury sorption. In that experiment, continuous measurement of Hg<sup>0</sup> in the effluent gas was performed. The effluent gas was then trapped, and EPA Method 29 showed it to contain mainly Hg<sup>0</sup> in very small amounts, consistent with the continuous analyzer data, but the traps did not indicate much oxidized mercury. Thus, HgCl<sub>2</sub> was not breaking through during the experiment. High capacities were recently reported by Carey et al. [18] in studies with the same lignite-derived carbon sorbent used in the EERC tests.

### 3.8. Fine-particle catalytic carbons with flue gas composition

Since the use of catalytic carbons resulted in a considerably higher sorption rate and capacity in an air stream, a comparison of the activities of catalytic carbons with the LAC sorbent in the baseline gas stream was conducted. Tests with powdered forms of the catalytic carbons that had previously exhibited high removal rates in air showed that the EERC catalytic carbon was also active in the synthetic flue gas mixture at 107°C (Fig. 15 — Run 702), initially 80% removal, decreasing to 75%. The activity, therefore, did not really exceed that of the Calgon carbon that was impregnated to generate this



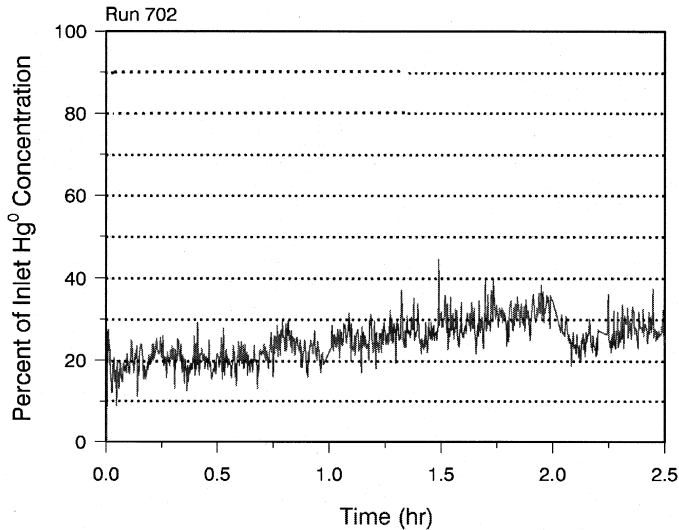


Fig. 15. Hg sorption for EERC indole pitch carbon fine particles in baseline gas + HCl + SO<sub>2</sub> (107°C).

catalytic carbon. Thus, the catalytic carbon actually exhibited a slightly lower mercury removal activity in this system compared with powdered LAC. The experiment at 163°C with the same catalytic carbon (Fig. 16 — Run 707) gave a similar sorption curve, maintaining activity at about 75% removal.

The results of the tests in the gas streams containing HCl indicated that the mercury sorption activity of the lignite-based carbon was better than that of the catalytic carbons

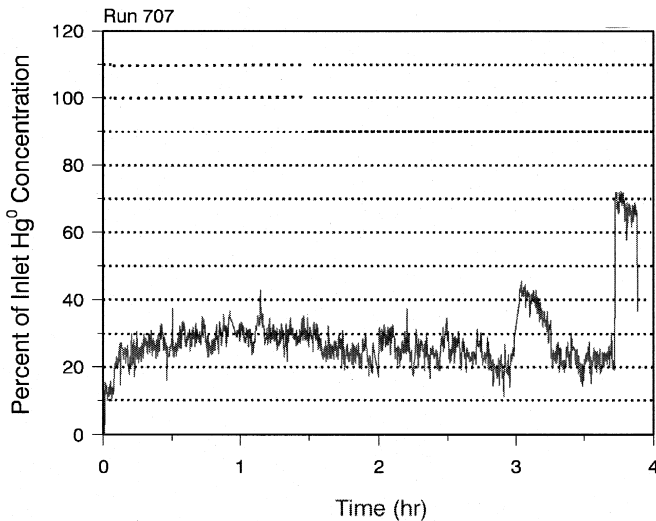


Fig. 16. Hg sorption for EERC indole pitch carbon fine particles in baseline gas + HCl + SO<sub>2</sub> (163°C).

and the bituminous activated carbons, especially at 163°C. This contrasts significantly with the activities in air streams. Thus, the large positive HCl effect on the sorption kinetics dominates the sorption when HCl is present. This behavior appears to show that the chemisorption mechanism that occurs in HCl gas streams operates at least partly independently of the carbon-catalyzed molecular oxygen mechanism. Different reaction sites may be utilized in the two types of oxidative mercury capture. A possible reason for the somewhat greater activity of the lignite-based carbon is its greater macropore structure. Further work is in progress to elucidate the differences in these and other sorption mechanisms.

Although HCl exerts a considerable positive effect on sorption, the addition of HCl to flue gas to maximize the sorption kinetics would be environmentally unacceptable for treatment of flue gas produced by burning a low-chlorine coal unless the sorbent was backed up by effective scrubbing. Preliminary studies in gas compositions containing NO<sub>2</sub> in the baseline mixture indicated that NO<sub>2</sub> also has a significant positive effect on mercury sorption kinetics [15,16,22]. However, an early breakthrough was noted to occur in this gas composition, which limits the capacity. Further efforts to understand these effects are planned.

#### **4. Summary**

Mercury control with activated carbon depends on sorbent properties, process conditions, and other flue gas constituents. In the absence of acidic gases, a large improvement in mercury sorption kinetics and capacity can be obtained using catalytic carbon sorbents. For coal-fired and incinerator systems, the acid gases produced will dominate the sorption chemistry on the surface. Under these conditions, the catalytic carbon sorbents have no advantage.

It is obvious that the type of fuel (coal or waste materials) and burning conditions will determine the flue gas composition with respect to acidic gases, and thereby determine the effectiveness of the carbon sorbents used in the mercury control. Criteria for predicting sorbent effectiveness in acid gases are lacking. Thus, further effort is needed to better understand the complex heterogeneous reactions that occur on sorbent surfaces and develop criteria for selecting the most effective sorbent for various fuels and conditions.

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## References

- [1] US Environmental Protection Agency, Mercury Report to Congress, EPA-452/R-97-101, December 1997.
- [2] J.G. Sorenson, G.E. Glass, K.W. Schmidt, J. Huber, G. Rapp, *Environ. Sci. Technol.* 24 (1990) 1716–1727.
- [3] W.F. Fitzgerald, D.R. Engstrom, R.P. Malm, E.A. Nates, *Environ. Sci. Technol.* 32 (1) (1998) 1–7.
- [4] D.J. Swaine, *Fuel Process. Technol.* 39 (1994) 121.
- [5] B. Hall, P. Schager, J. Weesmaa, *Chemosphere* 30 (1995) 611.
- [6] B. Hall, P. Schager, O. Lindqvist, *Water, Air, Soil Pollut.* 56 (1991) 3.
- [7] W.H. Schroeder, G. Yarwood, H. Niki, *Water, Air, Soil Pollut.* 56 (1991) 653.
- [8] C. Seigneur, J. Wrobel, E. Constantinou, *Environ. Sci. Technol.* 28 (1994) 1589.
- [9] E.S. Freeman, S. Gordon, *J. Am. Chem. Soc.* 78 (1956) 1813.
- [10] R. Chang, G. Offen, *Power Eng.* 5 (1995) 51.
- [11] L. Liberti, M. Notarnicola, V. Amicarelli, V. Campanoro, F. Roethel, L. Swanson, *Waste Manage. Res.* 16 (1998) 183.
- [12] J. Pavlish, *Power online*, <http://news.powerline.com/technical-news/19990114-1131.html>.
- [13] T.D. Brown, D.N. Smith, R.A. Hargis Jr., W.J. O'Dowd, *J. Air Waste Manage. Assoc.* 49 (1999) 628.
- [14] F.B. Meserole, R. Chang, T.R. Cavey, J. Machac, C.F. Richardson, *J. Air Waste Manage. Assoc.* 49 (1999) 694.
- [15] S.J. Miller, E.S. Olson, G.E. Dunham, R.K. Sharma, Preparation methods and test protocol for mercury sorbents, in: *Air and Waste Management Association 91st Annual Meeting*, San Diego, CA, June 14, 1998.
- [16] S.A. Benson, S.J. Miller, E.S. Olson, *Prepr. Pap. — Am. Chem. Soc., Div. Environ. Chem.* 38 (2) (1998) 163.
- [17] R.D. Vidic, J.B. McLaughlin, *J. Air Waste Manage. Assoc.* 46 (1996) 241.
- [18] T.R. Carey, O.W. Hargrove, C.F. Richardson, R. Chang, F.B. Meserole, *J. Air Waste Manage. Assoc.* 48 (1998) 1166.
- [19] G.E. Dunham, S.J. Miller, R. Chang, P. Bergman, *Environ. Prog.* 17 (1998) 203.
- [20] R.K. Sinha, P.L. Walker, *Carbon* 10 (1972) 754.
- [21] E.S. Olson, R.K. Sharma, S.J. Miller, G.E. Dunham, *Prepr. Pap. — Am. Chem. Soc., Div. Fuel Chem.* 43 (1998) 867.
- [22] S.J. Miller, G.E. Dunham, E.S. Olson, T.D. Brown, in: *Proc. Conf. Air Qual.*, McLean, VA, 1998, p. 1, Miller.
- [23] B.C. Young, M.A. Musich, *Prepr. Pap. — Am. Chem. Soc., Div. Fuel Chem.* 40 (1995) 833.