

# ROLE OF SURFACE FUNCTIONAL GROUPS IN THE CAPTURE OF ELEMENTAL MERCURY AND MERCURIC CHLORIDE BY ACTIVATED CARBONS

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## Abstract

A laboratory-scale, fixed-bed apparatus was used to study the role of surface functional groups (SFGs) in the capture of mercuric chloride ( $\text{HgCl}_2$ ) and elemental mercury ( $\text{Hg}^0$ ) in nitrogen ( $\text{N}_2$ ) prior to flue gas atmosphere studies. This investigation focused on two activated carbons (FGD and PC-100, Norit Americas, Inc.) with different physical and chemical characteristics. SFGs may be acidic or alkaline. The acidic SFGs include carboxyl, lactone, hydroxyl, and carbonyl functionalities while alkaline properties are believed to arise from two types of active sites, pyrone and chromene structures. The acidic and alkaline SFGs of as-received FGD and PC-100 were determined using surface titration techniques. An attempt was made to correlate the number density of these SFGs to their ability to sorb  $\text{Hg}^0$  and  $\text{HgCl}_2$ . The activated carbons were then treated with acid and alkaline washes to neutralize their alkaline and acidic SFGs, respectively. The mercury capture capabilities of these treated carbons were then compared to those of untreated, as-received samples. The initial hypothesis was that the number of alkaline SFGs should correlate with  $\text{HgCl}_2$  capture. This was proven not to be the case; rather, the concentration of surface chlorine (Cl) sites was related to the  $\text{HgCl}_2$  and  $\text{Hg}^0$  capture. Energy Dispersive X-ray Spectroscopy (EDXS) analysis confirmed the existence of a correlation between the increase in  $\text{HgCl}_2$  and  $\text{Hg}^0$  uptake of acid-treated activated carbon to the increase in surface Cl sites. These Cl sites were strongly bonded to the surface of carbon. It was determined that acidic and alkaline SFGs play no role in the adsorption of  $\text{Hg}^0$  and  $\text{HgCl}_2$  by activated carbons.

## Introduction

There is continuing concern over the anthropogenic emissions of mercury species from combustion sources. One of the control technologies for removal of mercury from flue gas is the adsorption of mercury species through injection of solid sorbents. The attractive features of adsorption processes on dry sorbents has led researchers to evaluate adsorption kinetics and the sorbent capacity of many different solid sorbents [1-9]. The form of mercury species will dictate the mechanism of its capture and its ultimate environmental fate. Similarly the form and concentration of mercury species will determine the rate of its reactions with different solid sorbents.

Typically, elemental mercury ( $\text{Hg}^0$ ) is the prevailing form of mercury in emissions from

coal combustion processes [10], although exceptions have been noted [11]. Based on collected information from the field using existing mercury speciation measurement methods, it appears that combustion of western subbituminous and lignite coals results in a flue gas dominated by  $\text{Hg}^0$  and combustion of eastern bituminous coals leads to a flue gas dominated by oxidized forms of mercury. The form of mercury species is important because oxidized forms of mercury, most probably dominated by mercuric chloride ( $\text{HgCl}_2$ ), are more easily controlled via solid adsorption [1-4, 12] than the elemental ( $\text{Hg}^0$ ) form. Note that a recent study conducted by Olson et al. [13] demonstrated that another form of oxidized mercury, mercury nitrate monohydrate [ $\text{Hg}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ ], can exist in a stable form in combustion flue gases. Oxidized forms of mercury (chloride and nitrate) have higher solubilities in water which make them more amenable to control by wet scrubbers. Research has been conducted to determine conditions that favor formation of oxidized mercury species in combustion processes [14-16]. Since the focus of this study was on the capture of  $\text{Hg}^0$  and  $\text{HgCl}_2$  by activated carbons, a brief review of adsorption processes on activated carbons is warranted.

### **Mercury Species Adsorption by Activated Carbons**

Activated carbons have been found to be effective sorbents for both  $\text{Hg}^0$  and  $\text{HgCl}_2$  [1, 7, 9, 12, 17]. However the projected annual cost for an activated carbon adsorption system is an issue, not only because of the high cost of the sorbent but also because of its poor utilization/selectivity for mercury. Carbon-to-mercury weight ratios of 3,000:1 to 100,000:1 have been projected for various levels of mercury control [18, 19]. Previous investigations [9, 12, 20-22] have shown the role of active surface sites in the adsorption of  $\text{Hg}^0$  and  $\text{HgCl}_2$  by carbon- and non-carbon-based sorbents. The potential importance of reactive surface sites underscores the need for comprehensive research on the characterization of active sites and surface functional groups (SFGs) on the surface of activated carbons. Establishing the nature of those SFGs that are instrumental in mercury capture by activated carbons may result in low-cost technologies for mercury control.

A clear understanding of mercury reactions on the surface of activated carbons is crucial to the design of more effective sorbents. These reactions may determine both the adsorptive capacity and regeneration efficiency of activated carbons and ultimately their economic viability. A thorough knowledge of carbon surface chemistry may also lead to the development of more mercury-specific activated carbons. Mercury-reactive SFGs on activated carbons may include organic oxygenated species and/or functional groups containing inorganic elements such as chlorine (Cl) or sulfur (S). Organic SFGs are formed through oxygen chemisorption on the surface of activated carbons, forming carbon-oxygen functional groups [23, 24]. These sites can be acidic or alkaline. Acidic oxygenated SFGs include carboxyl, lactone, hydroxyl, and carbonyl functionalities, while alkaline properties are believed to arise from two kinds of active sites: pyrone and chromene structures [23]. The role of oxygenated SFGs on the absorption of organic compounds has been investigated [23, 24]. Not much is known of the role of oxygenated SFGs on mercury species adsorption. In a study conducted by Liu et al. [25], the acidic oxygenated SFGs content of two activated carbons (one virgin and one S-impregnated) were intentionally increased using a procedure described by Tessmer et al. [23]. They observed no impact on  $\text{Hg}^0$  uptake by treated activated carbons, thus concluding that acidic SFGs are not instrumental in  $\text{Hg}^0$

capture. This is probably the only study of its kind and has not been confirmed by other researchers. Moreover, the role of acidic SFGs on  $\text{HgCl}_2$  uptake, and the combined role of alkaline SFGs on  $\text{HgCl}_2$  and  $\text{Hg}^0$  uptake need to be investigated.

The nature of SFGs containing Cl and S is not well understood. These SFGs may contain covalently bound Cl and S to the surface of carbon. The nature of these bonds is not known at this time, although the role of Cl and S in the capture of mercury species is well established. Researchers have investigated mercury removal efficiencies of S-impregnated activated carbons [1, 7, 25]. These carbons have shown enhanced sorption capacity as compared to commercially available virgin activated carbons, due to a higher content of active sulfur atoms. Questions remain as to what constitutes an active S site and what is the nature of surface bonds between active sulfur atoms and carbon. Cl impregnation has shown the same effects. At temperatures of 149-260°C, Teller and Quimby [26] found activated carbons impregnated with chloride salts to have as much as 300 times greater  $\text{Hg}^0$  removal capacity than virgin activated carbons. However, the higher cost associated with using chemically impregnated activated carbons requires their usage to be optimized. The future of understanding the nature of Cl and S bonds on the surface of activated carbons may lead to optimization of impregnation processes for subsequent mercury capture.

Initially, the objective of this study was to determine the role of oxygenated alkaline SFGs on the capture of  $\text{Hg}^0$  and  $\text{HgCl}_2$ . This approach was formulated based on our previous observation [9, 12] that indicated the importance of alkaline sites in the adsorption of  $\text{HgCl}_2$  by a number of calcium-based sorbents. It was hypothesized that alkaline SFGs on the surface of activated carbons play an important role in the capture of  $\text{HgCl}_2$ . In this study, the acidic and alkaline SFGs on the surface of two commercially available, virgin activated carbons were identified and quantitated using the procedures described by Tessmer et al. [23]. Subsequently, using the same procedures, the acidic and alkaline SFGs were neutralized by various treatments on activated carbons. The  $\text{HgCl}_2$  and  $\text{Hg}^0$  uptake capabilities of treated activated carbons were compared to those of untreated ones. The intent was to determine the role of each SFG on the capture of  $\text{Hg}^0$  and  $\text{HgCl}_2$ . However, during the course of this study, it was found that SFGs containing Cl may play a much more important role than oxygenated SFGs. The focus of the study was then shifted to understanding the role of Cl-containing sites. An analytical technique was used to quantify surface-bound Cl in the treated and the untreated activated carbons. An attempt was made to correlate  $\text{Hg}^0$  and  $\text{HgCl}_2$  uptake with surface Cl.

### **Determination of Oxygenated SFGs on Activated Carbons**

Alkaline and acidic oxygenated SFGs were determined using the methods described by Tessmer et al. [23]. Aqueous solutions of sodium bicarbonate ( $\text{NaHCO}_3$ , 0.05N), sodium carbonate ( $\text{NaCO}_3$ , 0.05N), sodium hydroxide ( $\text{NaOH}$ , 0.05 and 0.25N), and hydrogen chloride ( $\text{HCl}$ , 0.05N) were prepared using deionized (DI) water. Each solution was individually added to a predetermined amount (3 g) of activated carbon in a glass bottle. Each bottle was sealed and allowed to equilibrate for 3 days with frequent shaking. Each set of bottles included a blank solution without activated carbon. At the end of the equilibrium period, the activated carbon was separated from the solution using a vacuum filter. The filtered activated carbon was washed

several times with fresh batches of DI water, dried, and stored in labeled bottles, then used for  $\text{Hg}^0$  and  $\text{HgCl}_2$  uptake studies. The filtrate was titrated using standardized acidic or alkaline solutions. The amount of standardized alkaline or acidic solution consumed by each filtrate was then related to the number of the alkaline or acidic SFGs on the surface of activated carbons [23]. SFGs on the surface of fresh activated carbons were quantitated in triplicate.

Acidic SFGs include carboxyl (-COOH), lactone ( $\text{H}_2\text{COCO}$ ), phenolic hydroxyl (-OH), and carbonyl (-CO) groups. The amount of alkaline solution consumed by each acidic SFG was calculated as the difference in the amount of standardized acidic solution required to titrate the blank to a pH of 4.5 and the amount of acid required to titrate the filtrate to the same pH end point. The carboxyl SFG concentration on the carbon surface was determined as the amount of 0.05N  $\text{NaHCO}_3$  solution consumed by the carbon sample. The lactone SFG content was calculated as the difference between the amounts of 0.05N  $\text{Na}_2\text{CO}_3$  and the amount of 0.05N  $\text{NaHCO}_3$  consumed by the carbon. The hydroxyl SFG content was determined as the difference between the amount of 0.05N NaOH and the amount of 0.05N  $\text{Na}_2\text{CO}_3$  consumed by the carbon. The carbonyl SFG content was found by subtracting the amount of 0.05N NaOH consumed by the carbon from its 0.25N NaOH consumption. According to Tessmer et al. [23], alkaline SFGs are believed to arise from the combination of two groups (pyrone and chromene) which cannot be distinguished using this titration method [23]. The total alkaline SFG content was evaluated by equilibrating activated carbons with a 0.05N HCl solution. The filtrate was titrated to a pH of 11.5 using a 0.05N NaOH solution. The alkaline SFG content was calculated as the difference between the amounts of NaOH required to reach the end point for the HCl blank and for the filtrate.

The above procedure was implemented on two activated carbons: DARCO FGD (FGD) and DARCO PC-100 (PC-100) manufactured by Norit Americas, Inc. These two activated carbons are described in detail elsewhere [12]. Briefly, FGD is a lignite-coal-based activated carbon with a total surface area of about  $500 \text{ m}^2/\text{g}$ , and an average pore diameter of 3.2 nm. PC-100 is a bituminous-coal-based activated carbon with a total surface area of around  $950 \text{ m}^2/\text{g}$ , and an average pore diameter of 1.8 nm. Elemental compositions of these two activated carbons were determined using the X-ray Fluorescence (XRF) technique. A significant difference in calcium content was observed between these two carbons. The calcium content of FGD was 1.8 wt% and that of PC-100 was 0.13 wt%. The Cl and S levels in these two carbons were comparable at 0.23-0.34 and 0.75-0.86 wt%, respectively. The SFG contents of treated and untreated FGD and PC-100, expressed in  $\mu\text{eq}/\text{g}$ , are summarized in Table 1.

Table 1. Acidic and alkaline SFGs in treated and untreated activated carbons (in  $\mu\text{eq/g}$ )

SFGs	Untreated		Alkaline Treated		Acid Treated		Thermally Treated	
	FGD	PC-100	FGD	PC-100	FGD	PC-100	FGD	PC-100
Carboxyl	250 $\pm$ 24	157 $\pm$ 6	95	48	NA	NA	NA	NA
Lactone	217 $\pm$ 11	94 $\pm$ 6	<5	210	NA	NA	NA	NA
Hydroxyl	182 $\pm$ 24	285 $\pm$ 11	<5	60	NA	NA	NA	NA
Carbonyl	2692 $\pm$ 27	1817 $\pm$ 18	767	<5	NA	NA	NA	NA
Alkaline*	1344 $\pm$ 8	363 $\pm$ 11	NA	NA	12.5	513	1670	828

NA: not applicable; \* total (pyrone and chromene)

The intention of acid treating (washing with 0.05N HCl) the activated carbons was to neutralize their alkaline SFGs, and the intention of alkaline treating (with their respective solution) was to neutralize specific acidic SFGs. A thermal treatment method was also used on these activated carbons. The objective of this treatment was to increase alkaline SFGs and thus influence the capture of  $\text{HgCl}_2$  according to the initial hypothesis. This thermal treatment process is described in detail by Papirer et al. [27]. They showed that the amount of oxygen which chemisorbs at 100°C on a pretreated (at 800°C) carbon corresponds to alkaline-like (pyrone) groups which are formed after re-exposure to air. The pyrone group is generated by combination of a heat-resistant oxygen group, which stays on the carbon surface even at 800°C, and another oxygen group created during air re-exposure. Based on this hypothesis, a thermal treatment procedure was implemented on the activated carbons: activated carbons were heated to 800°C in an inert atmosphere (helium) and maintained at this temperature for 1 hour. They were subsequently cooled to room temperature in an inert atmosphere. Activated carbons were then re-exposed to air at 100°C overnight.

As indicated in Table 1, alkaline SFGs increased in both thermally treated activated carbons. This increase was more pronounced for PC-100. Untreated, as-received FGD had higher concentrations of both acidic (except for hydroxyl) and alkaline SFGs as compared to PC-100. The SFG contents of PC-100 are comparable to those reported by Tessmer et al. [23] for a bituminous-coal-based activated carbon. As expected, alkaline-treatment of activated carbons reduced the acidic sites in FGD and PC-100. The only exception was the lactone group in PC-100 which was apparently increased by treatment with 0.05N solution of  $\text{Na}_2\text{CO}_3$ . As expected, acid treatment decreased the number of alkaline SFGs in FGD. However, acid treatment increased the number of alkaline SFGs in PC-100. These anomalies cannot be explained.

## Experimental

### Apparatus

Detailed descriptions of the experimental setup, a fixed-bed reactor system (Figure 1), have been presented previously [12]. Briefly, pure  $\text{Hg}^0$  liquid in a permeation tube (VICI Metronics) was the source of  $\text{Hg}^0$  vapor, and pure solid  $\text{HgCl}_2$  crystals in three size D diffusion

vials (VICI Metronics) was the source of  $\text{HgCl}_2$  vapor. The concentration of  $\text{HgCl}_2$  or  $\text{Hg}^0$  in the gas stream was controlled by adjusting the temperature of the permeation tube's or diffusion vial's water bath.  $\text{HgCl}_2$  or  $\text{Hg}^0$  vapor generated was delivered to the fixed bed by an  $\text{N}_2$  stream at a constant total system flow rate of  $300 \text{ cm}^3/\text{min}$  (at standard temperature and pressure, STP). The activated carbon (treated or untreated) to be studied (0.1 g) was mixed to a total of 2 g with sand and placed in the down-flow vertical reactor between two quartz wool plugs and maintained at the desired bed temperature by a temperature controller. A furnace, kept at  $920^\circ \text{C}$ , was downstream of the reactor to convert any oxidized mercury ( $\text{Hg}^{++}$ , as in  $\text{HgCl}_2$ ) to  $\text{Hg}^0$ . The presence of the furnace enabled detection of oxidized, non-adsorbed  $\text{Hg}^0$  or non-adsorbed  $\text{HgCl}_2$  as gas-phase  $\text{Hg}^0$  by the on-line ultraviolet (UV)  $\text{Hg}^0$  analyzer. Thus, continuous  $\text{Hg}^0$  or  $\text{HgCl}_2$  capture data by the fixed bed of sorbent could be acquired.

### *Methodology*

Initial scoping tests were performed to determine the optimum conditions for  $\text{HgCl}_2$  uptake, so that a valid comparison could be made between treated and untreated activated carbons. The optimum conditions were determined to be a bed temperature of  $140^\circ \text{C}$ , inlet  $\text{HgCl}_2$  concentration of 38 ppbv in  $\text{N}_2$ , and an exposure time of 2 hours. In the case of  $\text{Hg}^0$ , scoping tests determined that an optimum comparison between these sorbents could be made at a bed temperature of  $100^\circ \text{C}$ , inlet  $\text{Hg}^0$  concentration of 40 ppbv in  $\text{N}_2$ , and an exposure time of 4 hours. During the  $\text{HgCl}_2$  or  $\text{Hg}^0$  contact period, the exit concentration of mercury was continuously monitored. The instantaneous removal of  $\text{HgCl}_2$  or  $\text{Hg}^0$  at any time ( $Q_t$ ) was obtained as given by:

$$Q_t = [(\text{Hg}_{\text{in}} - \text{Hg}_{\text{out}}) / \text{Hg}_{\text{in}}] \times 100$$

$\text{HgCl}_2$  or  $\text{Hg}^0$  uptake was determined by integrating and evaluating the area under the removal curve.  $\text{HgCl}_2$  or  $\text{Hg}^0$  uptake was defined as a cumulative removal of  $\text{HgCl}_2$  or  $\text{Hg}^0$  up to time  $t$  (4 hours for  $\text{Hg}^0$  and 2 hours for  $\text{HgCl}_2$ ) and was expressed as a weight ratio of mercury species uptake to active sorbent ( $\mu\text{g Hg/g sorbent}$ ). Selected experiments conducted during this test program were run in duplicate and indicated a range of  $\pm 5$  percent about the mean in the experimental results. Blank tests indicated the empty reactor capture of  $\text{Hg}^0$  and  $\text{HgCl}_2$  to be 0.02 and  $< 1.0 \mu\text{g}$ , respectively. These values are significantly lower than uptakes exhibited by the sorbents.

### *Analytical*

An analytical technique was employed to accurately measure the amount of surface Cl in treated and untreated activated carbons. Scanning Electron Microscopy and Energy Dispersive X-Ray Spectroscopy (SEM/EDXS) analysis was performed with a Jeol JSM-6400 interfaced with a SUN SPARC workstation 5. The EDXS detector was a sealed window PRISM detector mounted horizontally. Samples were mounted onto carbon stubs by double-sided tape. The sample was placed in excess on the tape and pressed down lightly with a clean spatula; the excess sample was removed by gently tapping the sample stub. Three separate areas for each sample were magnified to 1000X, and an image and spectra were obtained (only one area was analyzed for the thermally treated FGD and the FGD treated with 0.05 N and 0.25 N NaOH). Spectra were acquired in PRISM quantitative mode at a takeoff angle of  $31^\circ$ , a working distance of 16 mm, and an accelerating voltage of approximately 15 KeV. Quantitative analysis was

performed using the UNIX-based IMIX software. This analysis was performed in the standard-less mode using the "Z-A-F" calculation [28]. ZAF comes from the "atomic number" (Z), "absorption" (A), and, fluorescence" (F). Moreover, the spectra were normalized to account for the slight differences in accelerating voltage between the spectra. Each element present in the samples was calculated in parts per million on a weight basis. Due to the low accelerating voltage, it can be assumed that these elements are on the surface of the carbons within a depth of 1 to 1.5  $\mu\text{m}$  (see the nomograph on page 46 of reference 28). Further studies and computer modeling should result in more accurate estimates of the depth of electron penetration and the depth of excitation of the X-rays for the individual elements.

The existence of mercury bonds on the surface of different sorbents was probed using an analytical technique known as X-Ray Absorption Fine Structure (XAFS) spectroscopy [29]. Huggins et al. [29] have shown that different activated carbons (sulfur activated, iodine activated, and lignite-derived activated carbon; FGD) sorbed mercury from an experimental flue gas by three different mechanisms (formation of Hg-S, Hg-I, and Hg-Cl bonds, respectively). XAFS analysis is described in detail elsewhere [29].

## Results and Discussion

The initial hypothesis, and the basis for this study, was that alkaline SFGs on the surface of activated carbons are the active sites for the capture of acidic  $\text{HgCl}_2$ .  $\text{HgCl}_2$  uptake by untreated (as-received) and treated activated carbons was measured in the fixed bed. The uptake results after a 2-hour exposure (expressed in  $\mu\text{g HgCl}_2/\text{g sorbent}$ ) are presented in Figure 2. An unexpected behavior was observed. Acid treating the activated carbons (see 0.05N HCl) promoted the  $\text{HgCl}_2$  capture by both activated carbons as compared to the untreated baseline. Note that the uptake exhibited by HCl-treated activated carbons corresponds to complete removal of inlet  $\text{HgCl}_2$  during the exposure period (2 hours). As mentioned earlier, HCl treatment neutralized alkaline SFGs in FGD and to a slight extent increased them in PC-100. It appears that, in contrast to the initial hypothesis, alkaline SFGs do not provide active sites for the capture of  $\text{HgCl}_2$ . Noted that the treatment of activated carbons did not change the physical properties of these sorbents; e.g., total surface area and pore size distribution. The increase in  $\text{HgCl}_2$  uptake exhibited by the HCl-treated activated carbons is believed to be due to an increase in Cl content of these treated carbons. This treatment process may have acted as a Cl-impregnation process which is a proven method for enhancing mercury uptake capabilities of activated carbons [26]. The increase in Cl content of HCl-treated activated carbons is discussed later. As an additional experiment, samples of HCl-treated activated carbons were exhaustively washed with DI water (total wash time of 96 hours with four batches of fresh DI water) to remove any loosely bound surface Cl. The exhaustively washed HCl-treated activated carbons still exhibited a superior  $\text{HgCl}_2$  removal (see Figure 2), indicating that the active Cl sites created by HCl treatment is of a chemisorbed nature.

Thermal treatment of activated carbons was also used to further show that alkaline oxygenated SFGs do not play a role in the capture of  $\text{HgCl}_2$ . The activated carbons were thermally treated to increase their alkaline SFGs (see Table 1). The  $\text{HgCl}_2$  uptake by thermally treated activated carbons was compared to the untreated activated carbons (Figure 2). The

increase in alkaline SFGs did not result in an increase in  $\text{HgCl}_2$  uptake; rather, thermal treatment decreased the  $\text{HgCl}_2$  uptake. This is believed to be due to the loss of surface Cl sites during the thermal treatment process (see Table 2 and its discussion).

The effect of acidic oxygenated SFGs on  $\text{HgCl}_2$  uptake was studied by comparing alkaline-treated with untreated activated carbons. The activated carbons were treated with 0.05N  $\text{NaHCO}_3$  to neutralize carboxyl groups; 0.05N  $\text{Na}_2\text{CO}_3$  to neutralize carboxyl and lactone groups; 0.05N  $\text{NaOH}$  to neutralize carboxyl, lactone, and hydroxyl SFGs; and 0.25N  $\text{NaOH}$  to neutralize all acidic sites. The  $\text{HgCl}_2$  uptake by these alkaline-treated activated carbons is shown in Figure 2. It was demonstrated that acidic SFGs play no role in capturing  $\text{HgCl}_2$ . The decline in  $\text{HgCl}_2$  uptake by these treated activated carbons may also be due to the loss of surface Cl sites.

Not much is known about the nature of active sites for  $\text{Hg}^0$  capture.  $\text{Hg}^0$  uptake by the acid-, alkaline-, and thermally treated activated carbons was evaluated and compared to that of untreated ones. Results are shown in Figure 3. Treated activated carbons exhibited similar behavior in capturing  $\text{Hg}^0$  as they did in capturing  $\text{HgCl}_2$ . HCl-treated activated carbons showed complete removal of  $\text{Hg}^0$  during the 4 hours of exposure. HCl treatment significantly improved  $\text{Hg}^0$ , as well as  $\text{HgCl}_2$ , uptake. This observation can once again be attributed to an increase in surface Cl content of HCl-treated activated carbons. The exhaustively washed HCl-treated activated carbons still exhibited a superior  $\text{Hg}^0$  (as well as  $\text{HgCl}_2$ ) removal.

Results showed that acidic and alkaline oxygenated SFGs are not instrumental in the capture of both mercury species ( $\text{Hg}^0$  and  $\text{HgCl}_2$ ). Neutralization or generation of these SFGs on activated carbons had little or no effect on mercury species capture. However, it seems that Cl-containing SFGs play an important role in  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture. Chemical impregnation of virgin activated carbons using chlorine compounds has been shown to be effective in increasing  $\text{Hg}^0$  and  $\text{HgCl}_2$  uptake [26, 30]. Quimby [30] showed that treatment of carbons with HCl solution (1:1 weight ratio) can improve mercury adsorption capacity. He observed significant improvement using copper chloride solution as the impregnating agent. It has also been shown that a flue gas stream containing HCl vapor can serve to impregnate activated carbons *in-situ* and improve mercury removal capacity [22, 30]. This *in-situ* impregnation is suspected to play a major role in mercury vapor emission control from municipal, hazardous, and hospital waste incinerators. Granite et al. [31] also showed that HCl-treated activated carbons exhibit a large capacity (up to 4 mg/g) for  $\text{Hg}^0$  and  $\text{HgCl}_2$ . They hypothesized that mercury species will primarily form the tetrachloromercury complex,  $\text{HgCl}_4^{2-}$ , on the surface of HCl-treated activated carbon. The presence of this surface compound has not been verified.

The HCl-treated activated carbons in this study exhibited similar behavior. Their improved  $\text{Hg}^0$  and  $\text{HgCl}_2$  removal capabilities may be due to an increase in Cl-containing SFGs. Both  $\text{Hg}^0$  and  $\text{HgCl}_2$  in the flue gas are attracted to these sites. As mentioned, and to test this hypothesis, an analytical SEM/EDXS method was employed to measure surface Cl content of treated and untreated activated carbons (Table 2). A sample of SEM/EDXS spectra for HCl-treated and untreated activated carbons is shown in Figures 4 (for FGD) and 5 (for PC-100). SEM/EDXS analysis showed that the surface of FGD and PC-100 carbons is predominately

composed of carbon (C) and oxygen (O), with trace levels of calcium (Ca), aluminum (Al), silicon (Si), iron (Fe), magnesium (Mg), and sulfur (S). The surface of FGD carbon contains significantly more Ca than the surface of PC-100 carbon (Table 2).

The results of the SEM/EDXS analysis showed that the level of Cl on the surface of the HCl-treated carbons is significantly higher than on the untreated, alkaline-, and thermally treated carbons (Table 2, and Figures 4 and 5). The exhaustively washed HCl-treated carbons also showed higher levels of Cl than the untreated carbons, but a lower level of Cl compared to the non-exhaustively washed HCl-treated carbons. It can be hypothesized that the exhaustive wash of carbons removed all the loosely bound surface Cl and established the amount of those Cl atoms that are strongly bound to the surface. The exhaustively washed, HCl-treated carbons and non-exhaustively washed HCl-treated carbons removed the same amount of  $\text{HgCl}_2$  and  $\text{Hg}^0$  (Figures 2 and 3), suggesting that the strongly bound surface Cl provides active sites for the capture of mercury species.

XAFS analysis was also performed on HCl-treated and untreated activated carbons to determine the nature of mercury bonds on the surface of activated carbons. Possible formation of Hg-Cl type bonds were detected on the surface of HCl-treated and untreated FGD when exposed to  $\text{Hg}^0$  and  $\text{HgCl}_2$  in the flue gas. However, in the case of PC-100 (both treated and untreated), the presence of Hg-S type bonds may have been detected. XRF analysis on PC-100 and FGD indicated identical sulfur content (0.75-0.85 wt%). Sulfur in PC-100 may be more active than that in FGD. Note that XAFS analysis is a qualitative method, and the interpretation of the results should be regarded with caution. Other analytical techniques (such as infrared spectroscopy) need to be developed to detect mercury surface species.

Table 2. Concentration of Cl and Ca on treated and untreated activated carbons

Treatment	Cl (ppmw)		Ca (ppmw)	
	FGD	PC-100	FGD	PC-100
As-received (untreated)	NC	150±71	10267±2272	267±58
0.05N HCl	833±153	1900±608	1033±351	250±71
0.05N HCl (exhaustively washed)	167±58	633±58	800±173	100
0.05N $\text{NaHCO}_3$	NC	NC	14000±2921	367±58
0.05N $\text{Na}_2\text{CO}_3$	NC	NC	13700±2193	533±208
0.05N NaOH	100	NC	14200	400±100
0.25N NaOH	100	NC	15500	333±58
Thermally treated	NC	NC	13600	367±115

NC: Not Calculated, below system/standard quantitation limit (100 ppmw).

## Summary

The content of oxygenated acidic and alkaline surface functional groups (SFGs) on the surface of two activated carbons was manipulated to investigate their role in  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture. Acidic SFGs on the surface of activated carbons were neutralized by a variety of alkaline washes. The alkaline-treated activated carbon showed no enhancement in  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture, thus indicating that acidic SFGs play no role in capturing mercury species. The alkaline SFGs contents were increased by a thermal treatment process. The thermally treated activated carbons did not exhibit any improvement with regard to their  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture capabilities as compared to the untreated ones. The activated carbons were then treated with a very dilute HCl solution to decrease their alkaline SFGs content. The HCl-treated activated carbon showed a very significant improvement in its  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture capabilities. This observation was contrary to the initial hypothesis that alkaline sites are needed to capture acidic  $\text{HgCl}_2$  from the flue gas. It was then hypothesized that HCl treatment increases the number of active surface chlorine sites, which subsequently enhance  $\text{Hg}^0$  and  $\text{HgCl}_2$  capture. An analytical technique, Energy Dispersive X-ray Spectroscopy (EDXS), was used to quantify surface Cl sites. A strong correlation between the increased amount of surface Cl and  $\text{Hg}^0/\text{HgCl}_2$  uptake enhancement was observed. The role of SFGs containing Cl atoms in providing  $\text{Hg}^0/\text{HgCl}_2$  active sites was established. Future investigation using SEM/EDXS and Fourier Transform Infrared (FTIR) will focus on understanding the nature of Cl bonds on the surface of carbon, so that more effective mercury species sorbents can be manufactured.

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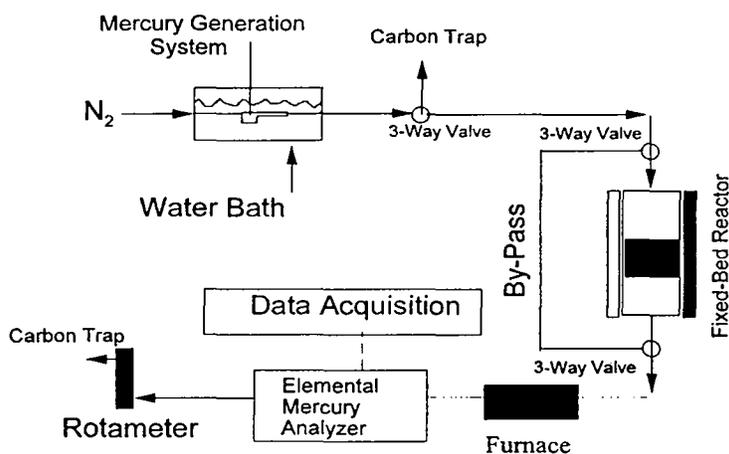


Figure 1. Schematic of the bench-scale, fixed-bed adsorption system.

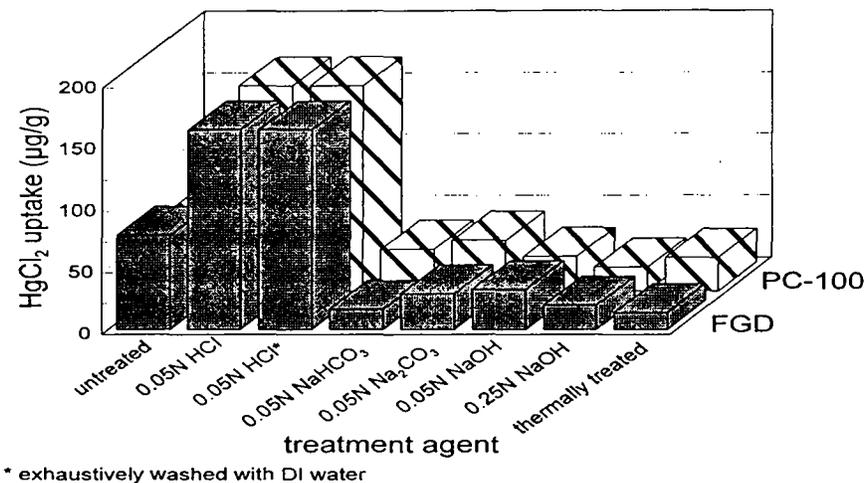


Figure 2. HgCl<sub>2</sub> uptake by treated and untreated activated carbons, bed temperature of 140°C, inlet HgCl<sub>2</sub> concentration of 38 ppbv, 0.1g sorbent/2 g sand, and exposure period of 2 hours.

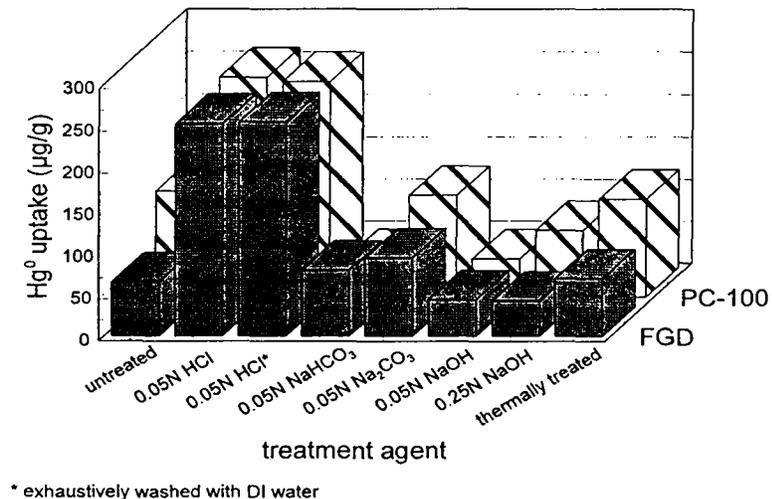


Figure 3. Hg<sup>0</sup> uptake by treated and untreated activated carbons, bed temperature of 100°C, inlet Hg<sup>0</sup> concentration of 40 ppbv, 0.1 g sorbent/2 g sand, and exposure period of 4 hours.

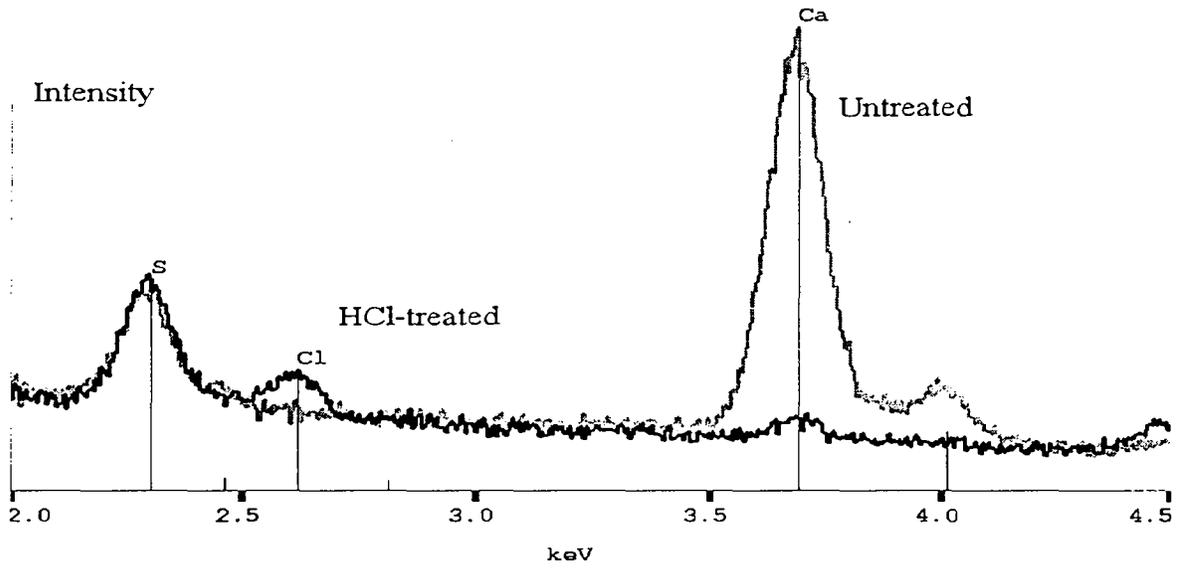


Figure 4. EDXS spectra of HCl-treated and untreated activated carbon FGD.

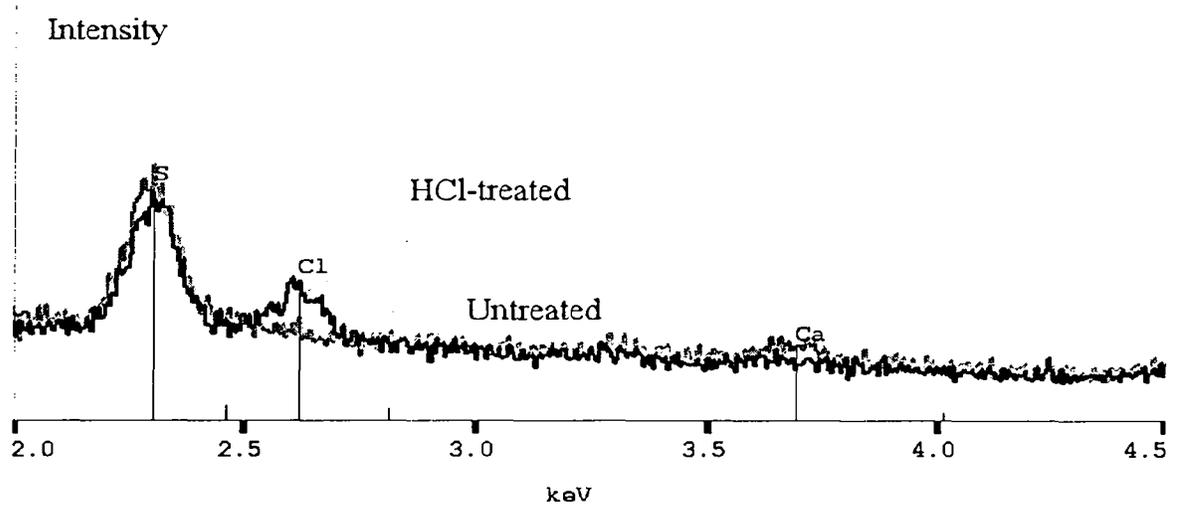


Figure 5. EDXS spectra of HCl-treated and untreated activated carbon PC-100.

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16. ABSTRACT <b>The paper discusses using a laboratory-scale, fixed-bed apparatus to study the role of surface functional groups (SFGs) in the capture of mercuric chloride (HgCl<sub>2</sub>) and elemental mercury (Hgo) in nitrogen (N<sub>2</sub>) prior to flue gas atmosphere studies. The study focused on two activated carbons (FGD and PC-100, Norit Americas, Inc.) with different physical and chemical characteristics. SFGs may be acidic or alkaline. Acidic SFGs include carboxyl, lactone, hydroxyl, and carbonyl functionalities, while alkaline properties are believed to arise from two types of active sites, pyrone and chromene structures. The acidic and alkaline SFGs of as-received FGD and PC-100 were determined using surface titration. An attempt was made to correlate the number density of these SFGs to their ability to sorb Hgo and HgCl<sub>2</sub>. The activated carbons were then treated with acid and alkaline washes to neutralize their alkaline and acidic SFGs, respectively. The mercury capture capabilities of these treated carbons were then compared to those of untreated as-received samples. The initial hypothesis was that the number of of alkaline SFGs should correlate with HgCl<sub>2</sub> capture. This was proved not to be the case; rather, the concentration of surface chlorine (Cl) sites was related to the HgCl<sub>2</sub> and Hgo capture. Acidic and alkaline SFGs play no role in the adsorption of Hgo and HgCl<sub>2</sub> by activated carbons.</b>		
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