



## Sorption and stability of mercury on activated carbon for emission control

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### ABSTRACT

A leading strategy for control of mercury emissions from combustion processes involves removal of elemental mercury from the flue gas by injection of activated carbon sorbent. After particulate capture and disposal in a landfill, it is critical that the captured mercury remains permanently sequestered in the sorbent. The environmental stability of sorbed mercury was determined on two commercial, activated carbons, one impregnated using gaseous sulfur, and on two activated carbons that were impregnated with sulfur by reaction with SO<sub>2</sub>. After loading with mercury vapor using a static technique, the stability of the sorbed mercury was characterized by two leaching methods. The standard toxicity characteristic leaching procedure showed leachate concentrations well below the limit of 0.2 mg/L for all activated carbons. The nature of the sorbed mercury was further characterized by a sequential extraction scheme that was specifically optimized to distinguish clearly among the highly stable phases of mercury. This analysis revealed that there are two forms in which mercury is sequestered. In the sorbent that was impregnated by gaseous sulfur at a relatively low temperature, the mercury is present predominantly as HgS. In the other three sorbents, including two impregnated using SO<sub>2</sub>, the mercury is predominantly present in the elemental form, physisorbed and chemisorbed to thiophene groups on the carbon surface. Both forms of binding are sufficiently stable to provide permanent sequestration of mercury in activated carbon sorbents after disposal.

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### 1. Introduction

Injection of activated carbon is one of the most effective strategies for the control of mercury emissions from combustion processes, such as coal-fired power plants [1,2]. Capture of this mercury will be required by the Canada-Wide Standards for Mercury Emissions and by the US EPA's Clean Air Mercury Rule (CAMR) [3]. Typically, powdered activated carbon is injected into the flue gas to adsorb the gaseous elemental mercury released by combustion and is subsequently captured along with the fly ash in the particulate control device (baghouse or electrostatic precipitator) downstream. It can also be used in granular form in a fixed bed [4]. Fly ash is usually disposed in ash ponds or landfills. While the amount of mercury that leaches from coal fly ash is typically extremely low, the adsorbed mercury on the injected activated carbon might be more easily mobilized and migrate, thus posing significant environmental risk. The Canada-Wide Standards for Mercury Emissions requires a nation-wide reduction of 1.62 t/y in mercury emissions from power plants while the US CAMR requires a reduction of

38 t/y beginning in 2010. Since activated carbon injection is the most promising commercially available technology to achieve this abatement, understanding the environmental consequences of the disposal of the sorbent is critical.

There has been limited investigation of the stability of mercury captured on activated carbon sorbents. The standard method to assess the stability of hazardous materials in disposed solids is the toxicity characteristic leaching procedure (TCLP) which imposes a limit of 0.2 mg/L of Hg in the resulting leachate [5]. There are also a variety of sequential leaching protocols that endeavour to characterize the stability of the hazardous substance by determining the phases with which it is associated through the use of progressively more aggressive lixiviants.

Liu et al. [6] found that when the TCLP was applied to a variety of sulfur-impregnated activated carbons loaded with 1000–2000 µg Hg/g C the mercury levels were below their detection limit of 0.1–0.2 ppb in all cases. The leachate from a non-sulfur activated carbon was also below the detection limit although the mercury loading was much lower (0.7 µg Hg/g C). Similarly, Senior et al. [7] found leachate levels at or below 0.01 ppb for various mixtures of coal fly ash and injected activated carbon containing up to 50 µg Hg/g C. As well, Luo et al. [8] found less than 0.01 ppb in the leachate from both untreated and impregnated activated carbon containing up to 0.6 µg Hg/g C. The exception was for carbon impregnated with MnO<sub>2</sub>, which produced levels as high as 0.04 ppb Hg in the leachate.

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**Table 1**  
Properties of the activated carbons investigated and the concentration of mercury loaded on them.

Carbon	Source	Surface area (m <sup>2</sup> /g)	Average pore size (nm)	Sulfur content (%)	Sulfur source	Mercury loading (μg/g)	Specific mercury loading (μg/(g m <sup>2</sup> ))
BPL	Bituminous coal	1026 <sup>a</sup>	2.48 <sup>a</sup>	0.7 <sup>a</sup>	None	224	0.22
HGR	Bituminous coal	482 <sup>a</sup>	1.95 <sup>a</sup>	10 <sup>a</sup>	Sulfur gas	2960	6.14
BPL-S	Bituminous coal	1142	–	9.8	SO <sub>2</sub>	481	0.42
FC-S	Fluid coke	160	–	11.8	SO <sub>2</sub>	456	2.85

<sup>a</sup> Surface area and sulfur content from Ref. [12], average pore size from Ref. [13].

One method of identifying the forms in which a species exists in a solid is by the use of a series of leachings. A variety of methods of sequential extraction for Hg have been reported [9] although none have been applied to mercury captured on activated carbon sorbents. The scheme chosen for this study was that used by the Geological Survey of Canada (GSC) because a detailed investigation aimed at optimising the distinction between the sulfide forms of Hg and the non-sulfide phases was successfully concluded [10]. Since it is thought that much of the mercury captured by sulfur-impregnated activated carbon is in the form of particles of HgS, it is essential to be able to reliably distinguish this phase from elemental Hg either physically adsorbed or chemisorbed onto the surface of the carbon. The GSC study showed that a 2 h extraction using 40% HNO<sub>3</sub> in a mechanical shaker followed by a rinse was able to dissolve all non-sulfide forms of Hg, including adsorbed elemental Hg, without solubilizing HgS even when present as very fine particles of a few micrometers or less [11].

This sequential extraction procedure has six steps that classify the distribution of Hg into (1) soluble and exchangeable, (2) labile organic, (3) amorphous Fe and Al oxide, (4) crystalline Fe and Al oxides, (5) non-labile organic and elemental Hg, and (6) residual, including HgS [12]. As with any sequential leaching scheme, the results are, to some extent, operationally defined phase associations rather than specific mercury species. However, in this case, the ability of steps 5 and 6 to distinguish between mercury species was carefully investigated using Hg minerals and excellent selectivity was established.

The objective of the present study was to confirm the reported stability of sorbed mercury on activated carbon and sulfur-impregnated activated carbon and to determine the mercury phases that contribute to this stability.

## 2. Experimental

The nature of mercury sorption was studied in four types of activated carbon designated BPL, HGR, BPL-S and FC-S. The first two were commercial activated carbons from Calgon Carbon Corporation, Pittsburgh, PA. BPL is manufactured from bituminous coal and HGR is produced by impregnating BPL with a minimum of 10% sulfur, specifically for use in mercury removal. The remaining sorbents were produced by sulfur impregnation using 30% SO<sub>2</sub> for 3 h at 700 °C. The activated carbons used for sulfur impregnation were produced from fluid coke (FC-S) and from BPL (BPL-S). The BPL and HGR were both ground to ~300 μm to match the particle size of the sulfur-impregnated activated carbons. The properties of the four activated carbon sorbents are given in Table 1.

Each activated carbon was loaded with mercury at room temperature by enclosing it in a small desiccator jar that also contained a pool of liquid Hg in a weighing dish with an exposed area of 12 cm<sup>2</sup>. The amount of mercury loaded on the activated carbon was determined by periodically weighing the weight loss of the liquid mercury on a semi-microbalance. It was found that the amount of mercury loaded by this technique was easily controlled and could

be quantitatively determined within 0.02 mg. The loadings used (Table 1) were at the upper range of that expected from scrubbing flue gas.

The stability of the sorbed Hg was assessed by the TCLP. Since the solids were found to be quite alkaline, the extraction fluid used was 5.7 mL/L of acetic acid at a pH of 2.88 as specified in the TCLP [5]. The test was modified by using only 1 g of the sorbent instead of 20 g while maintaining the 20:1 liquid to solid ratio. The extraction for each carbon was performed in triplicate and the average calculated.

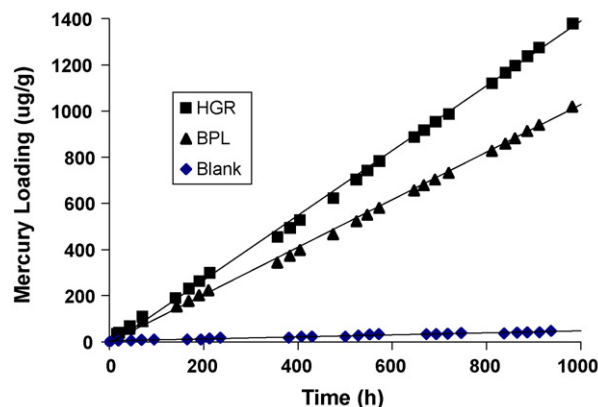
The details of the GSC sequential extraction procedure for determining which phases contain Hg are given by Hall and Pelchat [10]. The successive solutions used were (1) 0.01 mol/L Ca(NO<sub>3</sub>)<sub>2</sub>, (2) 0.1 mol/L Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub>, (3) 0.25 mol/L NH<sub>2</sub>OH·HCl in 0.25 mol/L HCl, (4) 1 mol/L NH<sub>2</sub>OH·HCl in 25% CH<sub>3</sub>COOH, (5) 6.4 mol/L (40%) HNO<sub>3</sub>, and (6) aqua regia. The extraction for each carbon was performed in triplicate and the average and standard deviation calculated.

The concentrations in the extracted liquids from both procedures were sufficiently high that the Hg could be analysed by inductively coupled plasma optical emission spectrometry (ICP-OES). A Perkin-Elmer Optima 3000 in the axial mode was used to measure concentrations at the 194.17 nm wavelength. The detection limit was 0.02 ppm.

## 3. Results and discussion

### 3.1. Mercury loading

The static technique used to load Hg onto activated carbon at concentrations relevant to those resulting from flue gas adsorption was found to be both simple and accurate, requiring only a balance. An example of the adsorption of Hg onto 20 g of BPL and HGR activated carbons as given by the weight loss of the mercury is shown in Fig. 1. A blank consisting of mercury in a desiccator containing no sorbent shows that very little mercury is lost to the walls of the jar or during weighing. The adsorption of Hg is approximately linear with time and is higher for HGR than BPL (1.41 and



**Fig. 1.** Adsorption of mercury on BPL and HGR activated carbons at room temperature. The results for a blank with no adsorbent are included.

1.03  $\mu\text{g Hg/g C}$  per h), indicating a more rapid uptake by the sulfur-impregnated activated carbon. The small irregularities observed are due to a lower rate of Hg transport when there was a longer time interval between weighings. This lower transport rate was caused by the re-formation of a film of oxide on the surface of the liquid Hg over a period of time after the previously formed oxide film had been disrupted mechanically by the movement of the mercury surface that inevitably occurs during the weighing process. The nearly linear rate of transfer allows precise control of the amount of Hg that is loaded on the activated carbon. The mercury content of BPL and HGR after loading was determined by total digestion in aqua regia followed by ICP analysis. These results agreed within better than 3% with the concentrations determined by weighing.

While the equilibrium vapor pressure of Hg at room temperature (21.5 °C) is 16,090  $\mu\text{g/m}^3$ , hindrance of evaporation by the surface oxide film and constant removal of the mercury vapor result in a gaseous Hg concentration far below this.

### 3.1.1. TCLP

The TCLP results were all less than the detection limit of 0.02 ppm with the exception of BPL, the only non-sulfur-impregnated carbon, which showed 0.05 ppm. These results are consistent with the previous studies of the leachability of mercury adsorbed on activated carbon, despite the somewhat higher Hg loading used in this study. The latter amount is much higher than the leachate levels of less than 0.0002 ppm found for BPL by Liu et al. [6], but their samples were much more lightly loaded with Hg than in the present study (0.66 vs. 224  $\mu\text{g/g}$ ). The amount of Hg leached here was less than 0.5% of the total loaded.

It is clear from these results that little of the acid-soluble forms of mercury – oxides and halides – were present in the sorbents and that mercury is very effectively immobilized by all activated carbon sorbents, even with loadings as high as 3.0 mg Hg/g C. Therefore, when combined with fly ash in the particulate control device, any mercury leached in the TCLP test will likely be primarily determined by the amount leached from the fly ash.

### 3.1.2. Sequential extraction

The results of the six sequential extractions for each of the four activated carbons are shown in Fig. 2. The total amount of mercury extracted, TL, is given as a percentage of the amount that was originally loaded (Table 1). TL thus represents the mass balance for the entire procedure and is within  $\pm 11\%$ , excellent for sequential extractions. As expected from the results of the TCLP test, there was very little Hg extracted in the first four steps, which involve increasing acidity but neutral or reducing conditions. BPL does show a small amount of Hg in the first step of the sequential extraction that leaches ‘easily soluble’ phases. This probably arises from the hydrolysis of a minor amount of mercury oxide:



The mercury oxide itself is leached in step 3. There is also a small amount leached from HGR in steps 3 and 4 when acid is used. While the soluble Hg in BPL does appear in its TCLP, Hg was not found in the TCLP for HGR, presumably because of its resorption onto the sulfur present on the activated carbon during the much longer leaching time that is used in this test. In all cases, the vast majority of the mercury is leached only in the final two steps under oxidizing conditions.

There are two distinctive patterns observed in these last two steps. The non-sulfur-impregnated BPL and both of the activated carbons impregnated using  $\text{SO}_2$  show at least 75% of the Hg leaching at step 5. This indicates that most of the mercury has not formed a sulfide but rather is present either physically adsorbed or chemisorbed onto the carbon surface. The other pattern is seen in HGR, which shows that nearly 60% of the mercury has been bound

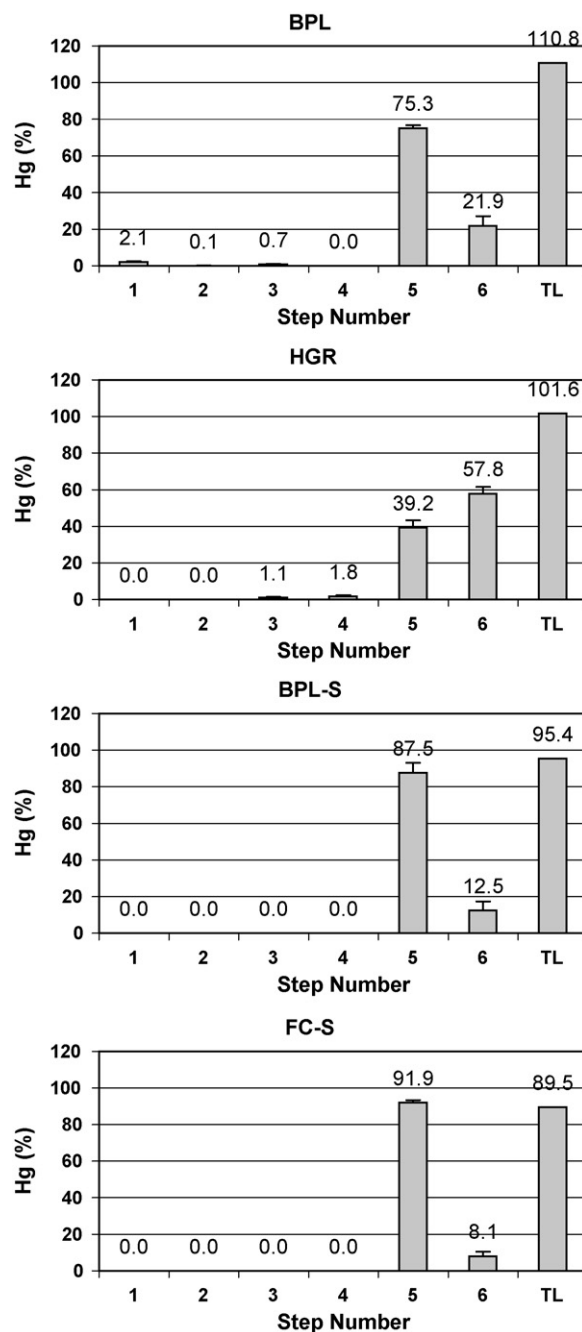


Fig. 2. The amount of mercury leached in each step of the sequential extraction has been given as a percent of the total leached for each of the four activated carbons, BPL, HGR, BPL-S and FC-S. The standard deviation for three replicates is also shown.

as sulfide and thus is leached only in the final, highly oxidizing step. The dramatic difference in the leaching behavior of HGR is probably due to the different method used for its sulfur impregnation. Rather than using  $\text{SO}_2$  at elevated temperatures, HGR is impregnated using sulfur gas at low temperatures between 150 and 200 °C [12,13]. This results in less strongly bound elemental sulfur that reacts more readily with elemental mercury to form mercuric sulfide.

It is well established that activated carbon, especially when impregnated with sulfur, is an excellent sorbent for gaseous mercury even when the mercury is present at very low concentrations [12]. It is also found that, after being loaded with mercury, the spent sorbents consistently perform extremely well in environmental leach tests with the concentrations of mercury in the leachate

often several orders of magnitude below the regulatory limits and hence appearing eminently suitable for disposal [6–8]. Thus, it is not surprising that little mercury is released in steps 1–4 of the sequential leach test, which involve increasing acidity under reducing or neutral conditions.

It has been postulated that the excellent performance both in capturing gaseous Hg and sequestering it during leaching has been due to formation of the totally insoluble and stable HgS [12]. Indeed, one study has detected this species on sulfur-impregnated activated carbon after exposure to mercury [14]. It is thus surprising that steps 5 and 6 of the sequential leach, which have been carefully optimized to distinguish between HgS and mercury present in other forms, have revealed a second form of mercury sequestration that does not involve formation of HgS.

However, the sequential extraction patterns observed for each activated carbon are in accord with a number of investigations that studied the forms of sulfur found on activated carbon impregnated with sulfur. Although scanning electron microscopy with energy dispersive spectrometry [16], X-ray diffraction [6] and Fourier transform infrared spectrometry [15] were found to reveal little of the nature of the sulfur, X-ray photoelectron spectrometry (XPS) has been successfully applied to distinguish among elemental, chemisorbed, and oxidized sulfur. Unfortunately, the organic sulfur species, particularly thiophene, cannot be differentiated from elemental sulfur since their peaks are both at 164 eV. XPS consistently shows the presence of elemental and/or organic sulfur and sometimes also sulfate [17,18].

Sulfur K-edge X-ray absorption near-edge spectrometry (XANES) is able to not only distinguish elemental sulfur from organic sulfur but also to detect the species thiophene, sulfoxide and sulfone separately as well as sulfate and metal sulfide. Over a range of impregnation temperatures and types of impregnating gases and using a variety of activated carbons, the dominant species found are elemental sulfur and thiophene, while the other organic species are minor components and sulfate is variable. Furthermore, it is consistently found that elemental sulfur predominates at impregnation temperatures up to 400 °C, while thiophene increases and may exceed elemental sulfur above this temperature [16,17,19].

BPL is not sulfur-impregnated, but retains minor sulfur from its bituminous precursor. This sulfur has been found to be present mainly in the form of thiophene and sulfate [17]. From the results of the sequential extraction of BPL, it appears that the Hg chemisorbed to thiophene is removed at step 5. As well, it is known that BPL also retains mercury by adsorption of the elemental form [6] and it is well established that physically adsorbed elemental mercury is very selectively extracted by step 5 [11]. These two forms of sorbed mercury are probably the main types found in BPL in addition to minor amounts of mercury sulfide.

When activated carbon is impregnated with gaseous sulfur at low temperatures, XANES reveals that sulfur is deposited only in the elemental form [19]. Thus, the sulfur in HGR is primarily elemental together with minor thiophene from its BPL precursor. When gaseous mercury reacts with the elemental sulfur, it forms mercuric sulfide, which is not extracted until step 6.

In contrast, when the same precursor, BPL, is impregnated at temperatures above 400 °C (with H<sub>2</sub>S), at least a 2:1 ratio of thiophene to elemental sulfur is found [16]. This is reflected in the predominance of Hg leached in step 5 from BPL-S, which has been impregnated at 700 °C. A similar extraction pattern is also seen with FC-S.

In summary, the sequential extraction results reveal that there are two distinct types of sorbed mercury. One type consists of elemental mercury either physisorbed directly or chemisorbed to thiophene groups on the surface of the activated carbon, which are extracted in step 5. The other type is a true mercuric sulfide com-

pound formed by reaction with elemental sulfur that is extracted in step 6. Both types of sorption provide the very stable immobilization of mercury on activated carbon that is consistently observed in TCLP leach tests and would provide permanent sequestration after disposal.

#### 4. Conclusions

The environmental consequences of disposal of activated carbon sorbents used to remove elemental mercury from the gas stream of combustion processes have been investigated. The reason for the excellent performance of these mercury-containing sorbents observed in the TCLP was determined by a sequential leaching test that was optimized to reliably distinguish between the two most stable phases with which mercury was likely to be associated. Mercury was found to be sequestered in two distinct forms—adsorption on the carbon surface and by formation of mercury sulfide. The predominant type of mercury capture depends on the type of activated carbon sorbent used.

In HGR, impregnated with sulfur vapor, nearly 60% of the mercury was bound in the sulfide phase. In contrast, BPL and both activated carbons impregnated at 700 °C using SO<sub>2</sub> bind more than 75% of their Hg in non-labile organic and elemental forms. In the latter two carbons, most Hg is chemisorbed to the thiophene and physisorbed to the carbon while only 8–13% is present as sulfide. This distribution reflects the relative abundances of these phases found in activated carbons that are sulfur-impregnated at temperatures above 400 °C.

Regardless of which phase the mercury is associated with, it is highly stable and would remain immobilized after disposal.

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