

Sulfurization of a carbon surface for vapor phase mercury removal – II: Sulfur forms and mercury uptake

Wenguo Feng ^a, Eric Borguet ^b, Radisav D. Vidic ^{a,*}

^a *Department of Civil and Environmental Engineering, University of Pittsburgh, 943 Benedum Hall, Pittsburgh, PA 15261, United States*

^b *Department of Chemistry, Temple University, 1901 N. 13th Street, Philadelphia, PA 19122, United States*

Received 25 October 2005; accepted 18 May 2006

Available online 31 July 2006

Abstract

Sulfur forms deposited on carbonaceous surfaces after exposure to hydrogen sulfide were analyzed using XPS and XANES. Higher temperatures promote the formation of organic sulfur and the presence of H₂S during the cooling process increased elemental sulfur content. Temperatures between 400–600 °C were found to be optimal for producing effective mercury uptake sorbents. The increased amount of sulfur deposited during the cooling process in the presence of H₂S was very effective towards Hg uptake in nitrogen. Correlation of mercury uptake capacity and the content of each sulfur form indicated that elemental sulfur, thiophene, and sulfate are likely responsible for mercury uptake, with elemental sulfur species being the most effective.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Activated carbon; Carbon fibers; Impregnation; X-ray photoelectron spectroscopy; Surface properties

1. Introduction

Mercury is a hazardous air pollutant that has attracted significant public health and environmental attention recently. About 150 tons of mercury are emitted annually by anthropogenic sources in the United States [1]. Control of elemental mercury emissions is very difficult due to its high volatility and low solubility. Effective total mercury removal technologies include wet scrubbers, spray dryer adsorption (SDA), and activated carbon injection [2].

Among technologies mentioned above, activated carbon injection is currently considered to be the most promising technology in terms of Hg removal efficiency and reliability. Although very effective, the high operating cost of this technology [3,4] requires improvements in sorbent performance to facilitate full scale applications. Previous studies showed that introducing oxygen containing functionalities [5,6] and halogens [7,8] can improve Hg uptake capacity.

However, introduction of sulfur onto the carbon surface [9] significantly improved Hg uptake capacity and produced more stable products [10], thus eliminating long-term liabilities of the adsorption technology.

Previous studies [11,12] have observed the increase in mercury uptake capacity at relatively high temperatures (about 150 °C) with an increase in sulfur content. Studies by Vidic and co-workers [7,9,10,13–15] showed that the following factors are important for mercury uptake by sulfur impregnated sorbents: sulfur content, sulfur forms, sulfur distribution, and pore structure/surface area of the sorbent. Their studies suggested that carbons impregnated with sulfur at higher temperatures (400–600 °C) performed better than those produced at lower temperatures (25–150 °C). The authors suggested that higher temperatures produced short-chain sulfur allotropes and more uniform sulfur distribution on the sorbent, surface. The impregnation temperature was found to be more important than the initial sulfur to carbon ratio [9], which was attributed to the fact that sorbents produced at higher temperatures still retained their high surface area and mesopore structure.

* Corresponding author. Tel.: +1 412 624 1307; fax: +1 412 624 0135.
E-mail address: vidic@pitt.edu (R.D. Vidic).

Hsi et al. [16,17] studied the effect of pore structure and sulfur forms using sulfur impregnated activated carbon fibers (ACFs). The authors suggested that both sulfur content and micropore structure are important for the uptake of vapor phase mercury. ACF impregnated with elemental sulfur at 400 °C was found to be the most effective mercury sorbent [17]. This sorbent had a surface area of only 94 m²/g with 86% of the surface area associated with micropores ($d < 2$ nm). Sulfur deposited on activated carbon fiber existed in three forms, namely elemental sulfur, organic sulfur, and sulfate. The authors suggested that only the first two forms act as mercury adsorption sites [16].

Daza et al. [18] evaluated palygorskite (a fibrous mineral with hydrated magnesium silicate, Mg₃Si₄O₁₀(OH)₂) impregnated with sulfur through catalytic oxidation of hydrogen sulfide as a mercury sorbent. They found that the π form of sulfur and a pore diameter larger than about 7.5 nm yielded the best sorbents. They also suggested that a pore structure that creates no steric hindrance for HgS formation is a general requirement for good mercury sorbents [19] and that the minimum pore size per monolayer of deposited sulfur should be around 8 nm.

Most of the previous studies used elemental sulfur or the oxidation of hydrogen sulfide for sulfur impregnation to produce mercury sorbents. As reported in the first part of this study [20], a significant amount of sulfur can be incorporated into the carbon structure by exposure to H₂S at high temperatures in the absence of oxygen. This is very important because many H₂S containing gas streams are at high temperature and under anoxic conditions (e.g., typical IGCC process gas and the fuel cell supply gas). Sulfurization by hydrogen sulfide may be a simpler way of producing effective mercury sorbents [14]. In addition, the sulfurization process does not change the pore structure of the original sorbent significantly. Following the first part of the study on sulfur content and distribution [20], this part of the study investigated the effect of temperature and sulfurization protocols on sulfur forms and mercury uptake.

2. Experimental details

2.1. Sample preparation and characterization

Preparation of the sorbents is described in the first part of this study [20]. In order to compare the results of this study with those reported earlier [9,10,15], sorbent denoted as “BPL-600C–El. Sulfur” was prepared by impregnating sulfur onto BPL carbon by heating elemental sulfur and BPL carbon with a sulfur to carbon ratio of 1:1 at 600 °C. The details on this procedure can be found elsewhere [9,10,15].

XPS (X-ray photoelectron spectroscopy) analysis was performed using a Physical Electronics Model 550 equipped with a cylindrical, double-pass energy analyzer. The ACF samples before and after sulfurization were attached to a tantalum surface by a conductive silver paste (LADD Research Industries) before insertion into the vacuum chamber.

The sulfur K-edge X-ray absorption fine structure (XAFS) spectra were recorded on X-19 A beam-line at the National Synchrotron Light Source (NSLS) of the Brookhaven National Laboratory, NY. Before analysis, the sulfur impregnated activated carbon samples were ground into powders. The X-ray absorption near-edge structure (XANES) of the spec-

tra were analyzed by least-squares to obtain peaks associated with electronic transition from 1s to 3p levels within the sulfur atoms. Further information about the sulfur K-edge XAFS measurement are reported by Huggins et al. [21–23].

2.2. Mercury uptake test

Virgin and sulfur impregnated BPL activated carbons were tested for vapor phase elemental mercury uptake at 140 °C in a fixed-bed reactor [14]. Industrial grade nitrogen (99.5%) was used as the carrier gas with a flow rate of 550 ml/min, which was controlled by a mass flow controller (Tylan General, Torrance, CA). The inlet mercury concentration was maintained at 350 µg/m³ by controlling the temperature of the permeation tube filled with liquid mercury (VICI Metrons Inc. Santa Clara, CA). Mercury concentration was analyzed continuously using an atomic absorption spectrophotometer (Model 403, Perkin–Elmer, Norwalk, CT) equipped with 18-cm hollow quartz cell (Varian Australis Pty, Ltd., Mulgrave, Vic., Australia) and the mercury adsorption capacity was calculated by integrating the area above the breakthrough curve.

3. Results and discussion

3.1. Forms of sulfurous products on ACFs – XPS results

XPS analysis was conducted to identify the produced sulfur species on ACFs and the typical spectra are shown in Fig. 1. Standard library spectra provide the following information about the peaks related to sulfur species: free elemental sulfur has a peak around 164.05 eV; chemisorbed sulfur has a peak at 161.8–162.6 eV; organic sulfur has a peak between 163–164.1 eV; and oxidized sulfur shows a peak above 167 eV. Unfortunately, there is an overlap between the region of elemental sulfur and that of organic sulfur. The results depicted in Fig. 1 suggest that either organic sulfur or elemental sulfur was the dominant sulfur form on the ACF surface. According to Sugawara et al. [24], thiophene may be the possible structure of organic sulfur products deposited on the carbon surface at high temperatures.

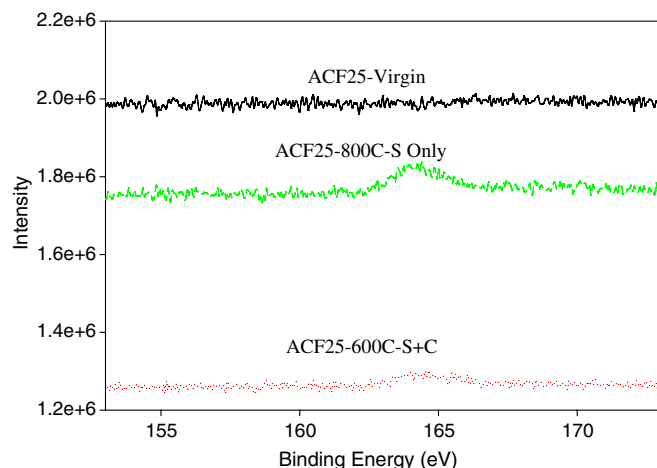


Fig. 1. XPS analysis of ACF25 before and after sulfurization.

3.2. Forms of sulfurous products on BPL – XANES results

Fig. 2 shows the sulfur K-edge XANES spectra and the summary of different sulfur forms. By applying the least-squares technique, the relative ratio of different sulfur species can be obtained from the spectra. The total sulfur content was obtained from sulfur analysis and the sulfur content of each species is shown in Fig. 2(b). Sulfur deposited on the carbon surface appears in three major forms, namely elemental sulfur, organic sulfur, and sulfate. This is consistent with the previous results reported by Hsi et al. [16]. It is interesting to point out that sulfate was not detected on ACFs by XPS, which may be due to the extremely low metal content of this carbonaceous material [20].

The major difference among samples is in the elemental sulfur and thiophene content. For those samples prepared without the presence of H_2S during the cooling process, i.e., BPL-400C-S Only, BPL-600C-S Only, and BPL-800C-S Only, thiophene content increased with the increase in temperature, with an abrupt increase in metal sulfide content from 600 °C to 800 °C.

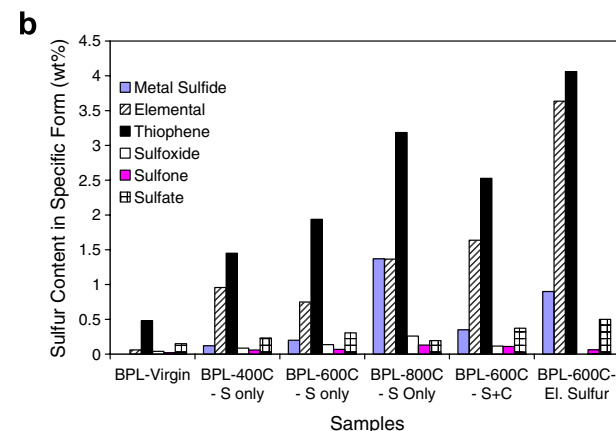
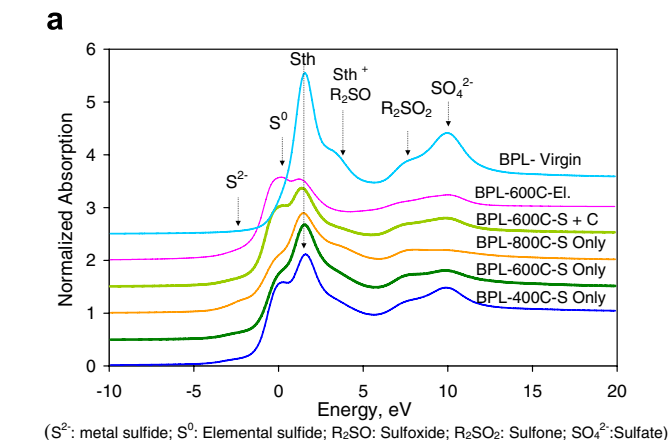


Fig. 2. Contents of different sulfur forms from XANES results. (a) Summary of XANES spectra of prepared samples. (b) Different Sulfur forms in prepared samples.

For samples produced at 600 °C, the presence of H_2S during the cooling process (BPL-600C-S+C versus BPL-600C-S Only) increased both the elemental sulfur content and thiophene content. When elemental sulfur was used as the sulfurizing agent (BPL-600C-El. Sulfur), the majority of the sulfur content was mainly in elemental and organic sulfur form. These observations suggest that exposure to H_2S during cooling process facilitates the formation of low valent sulfur forms. These sulfur species may be formed through the interaction between carbon and sulfur atoms after the decomposition of H_2S [20].

3.3. Mercury uptake studies

3.3.1. Effect of impregnation temperature

As shown in Fig. 3, the H+S+C sulfurization protocol at 400–600 °C produced effective mercury sorbents, with 600 °C being the best impregnation temperature for the production of effective mercury sorbents. This is consistent with previous studies using elemental sulfur for sulfur impregnation onto activated carbons [9,10,17].

The first part of this study [20] indicated that neither the pore structure nor the sorbent surface area was significantly changed during the impregnation process. Although not all the samples were analyzed for surface area and pore size distribution, the deposition of sulfur is not expected to be the same as that using elemental sulfur as the sulfurization agent because of the high temperature and anoxic conditions. The major process that can lead to pore blockage is the cooling process. The PSD of BPL-600C-S+C (Figure. 8 in reference [20]) showed no obvious PSD change when compared to BPL-Raw, which clearly suggests that elemental sulfur condensation during the cooling process does not have a significant impact on sorbent morphology.

It can be concluded that it is the forms of sulfur species that most likely played a key role in the very high capacity of the sorbent produced at 600 °C. Because elemental sulfur and thiophene are the two major species produced at higher temperatures, it is reasonable to assume that either

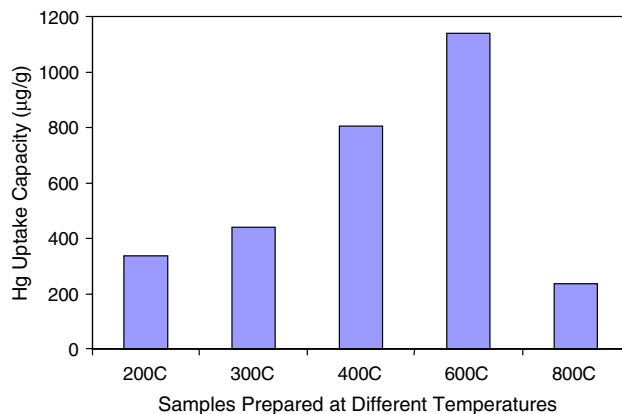


Fig. 3. Effect of impregnation temperature on Hg uptake capacity of sorbents produced using the (H+S+C) protocol.

one or both of the two species function as the key mercury uptake sites.

It is important to note that BPL-800C–H+S+C had significantly lower mercury uptake capacity than BPL-600C–H+S+C despite much higher total sulfur content. As shown in Fig. 2, this sorbent also had the highest metal sulfide contents. It can therefore, be concluded that sorbents prepared at very high temperatures contain sulfur species already combined with metals or other compounds, which are no longer effective for mercury uptake. Metal analysis of raw BPL carbon shows high ash content of 6.6 wt% and high metal contents: Al, 1292 mg/kg; Ca, mg/kg 841; Cu, 251 mg/kg; Mg, 198 mg/kg; Mn, 21 mg/kg; Fe, 2868 mg/kg. The sulfur species formed at very high temperatures may also be imbedded into the graphite structure [20], affecting their mercury uptake capacity.

3.3.2. Effect of impregnation protocol

Besides temperature, the impregnation protocol was found to be important for producing effective mercury sorbents. As shown in Fig. 4, the production of sorbents at 600 °C by exposure to H₂S during the stable phase (600C–S Only) and during both heating and stable phase (600C–H+S) did not produce effective mercury sorbents. The presence of H₂S during the cooling process has a unique impact as can be seen from the performance of 600C–S+C, 600C–H+S+C, and 600C–C Only. The effectiveness of 600C–C Only indicates that the formation of sulfur species effective in mercury capture actually occurs between 400 °C to 600 °C as the sorbent cools. However, heating up to around 600 °C might have created the active sites necessary for the formation of such species during the cooling process. These active sites may be created by decomposing CO₂-yielding oxygen containing functionalities, most probably lactone group [26]. The performance of 600C–S Only and 600C–H+S also indicates that the effective sulfur species are not thermally stable because they are easily removed if H₂S is not present in the gas stream during the cooling process.

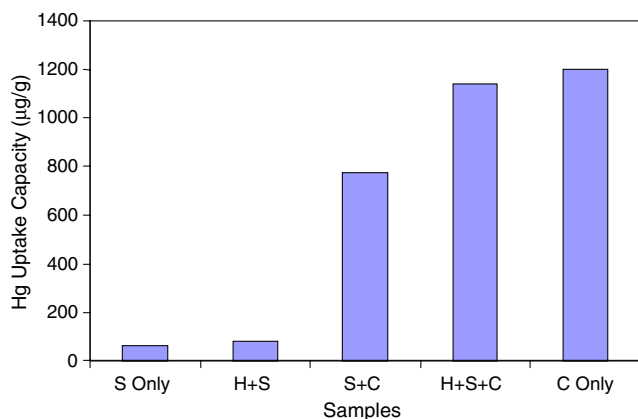


Fig. 4. Effect of impregnation methods at 600 °C on Hg uptake capacity.

Sulfurization probably occurred after the decomposition of certain oxygen containing surface functionalities. Temperature programmed desorption studies with virgin BPL carbon found that different oxygen containing surface functionalities decompose at different temperatures [25]. For example, acidic functionalities will decompose to CO₂ at temperatures below 600 °C. Phenolic and carbonyl groups will decompose at higher temperatures, yielding CO as the main product [26]. The results of this study suggest that the decomposition of CO₂ evolving groups is helpful for the formation of sulfur forms active in mercury uptake since effective mercury sorbents were produced at temperatures lower than or at 600 °C.

Fig. 4 also shows that adding H₂S during the heating process can improve the performance of the Hg sorbent created by exposure to H₂S during the stable process and the cooling process. It has been reported that metal sulfides can catalyze the decomposition of hydrogen sulfide into hydrogen and elemental sulfur [27,28]. The difference in the performance of 600C–H+S+C and 600C–S+C suggests that the species (probably elemental sulfur) formed during the heating process are also effective in mercury capture.

The results depicted in Fig. 5 show that the presence of H₂S during the cooling process also significantly increased Hg uptake capacity at 400 °C. However, the 400C–H+S+C was not as effective as 600C–H+S+C. This again indicates the creation of active sites for producing effective sulfur species requires temperature as high as 600 °C. Increasing the temperature to 800 °C resulted in higher sulfur content, but sulfur species created under such conditions are not effective for mercury removal. As mentioned above, this may be related to the formation of other metal sulfides or the removal of certain surface functionalities that were formed at lower temperatures.

The results above indicate that the most effective sulfur species were formed during the cooling process after high temperature (400–600 °C) treatment. Temperatures as high as 800 °C will eliminate or block the active sites for the formation of these sulfur species. Liu et al. [9,10] have

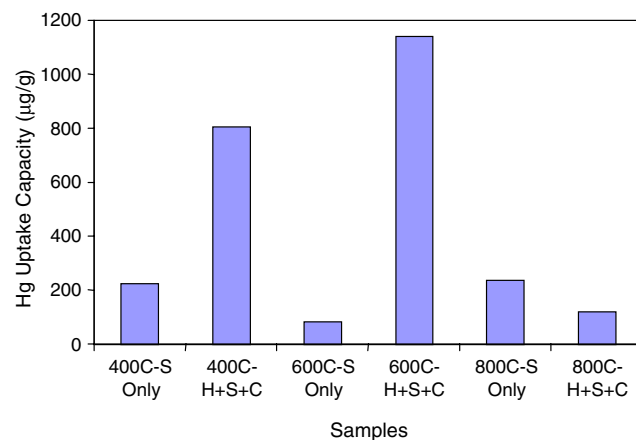


Fig. 5. Effect of exposure to H₂S during heating and cooling on Hg uptake at different temperatures.

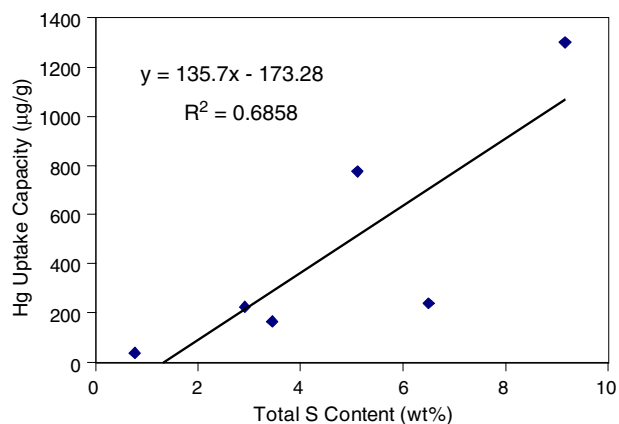


Fig. 6. Correlation of Hg uptake capacity to total sulfur content.

reported that very effective mercury sorbents were produced using elemental sulfur as the sulfurizing agent at

600 °C. The same temperature was found to be effective in this study using H₂S as the sulfurizing agent. However, besides the importance of temperature, the exposure to H₂S during the cooling process is also found to be an important factor in producing effective mercury sorbents.

3.3.3. Effect of different sulfur forms on Hg uptake

The correlation between mercury uptake capacity and total sulfur content is shown in Fig. 6. The fair correlation shows the importance of sulfur content for sorbents with similar pore structure. Previous studies proposed the effect of pore structure [16,17,29]. However, this study clearly showed that sulfur forms are more important for impregnated sorbents with similar pore structure.

The correlations between mercury uptake capacity and different sulfur forms are shown in Fig. 7. Based on the slope of the linear correlation and the R^2 value, it seems that three forms of sulfur, namely, elemental sulfur,

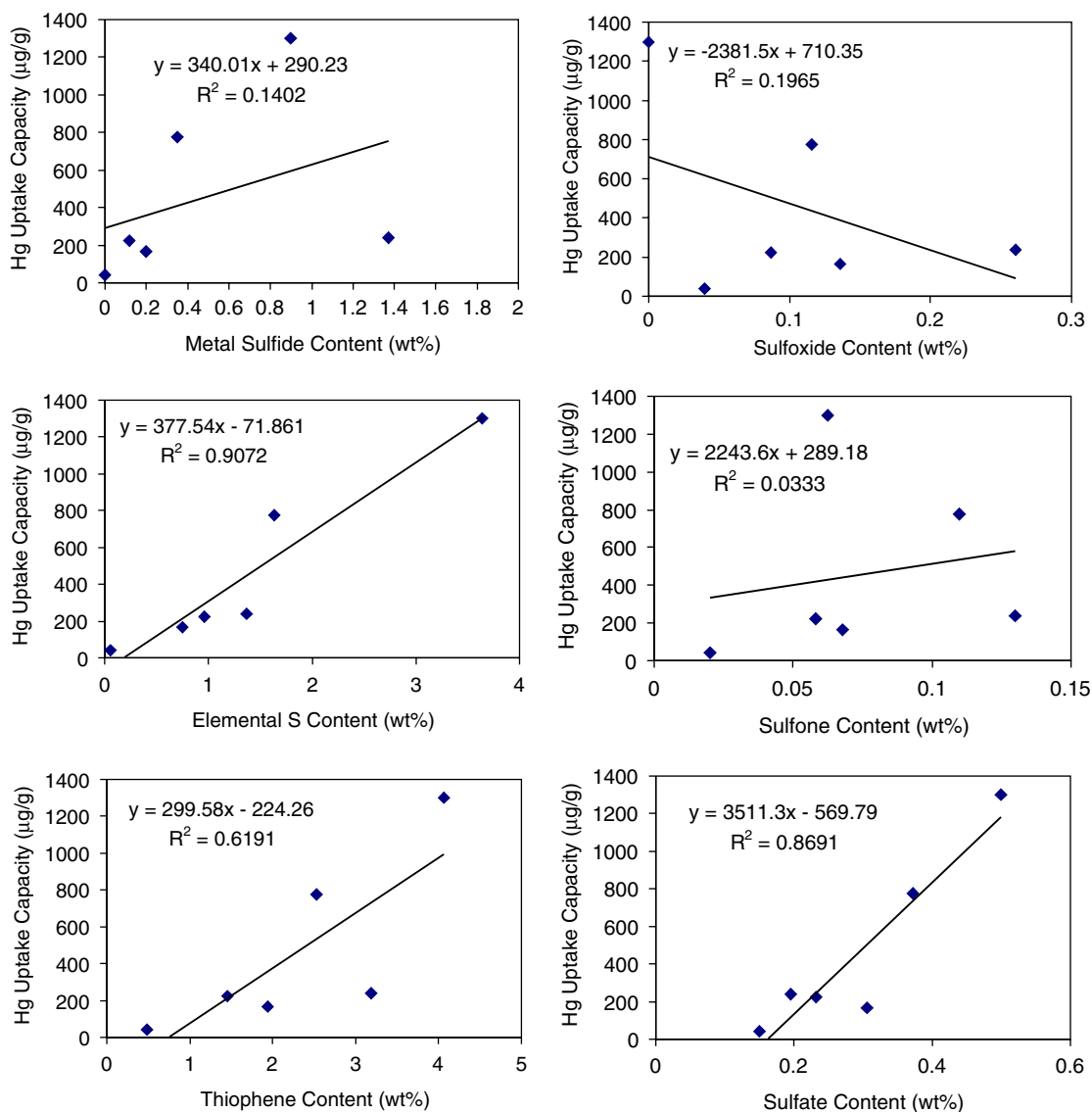


Fig. 7. Correlation of Hg uptake capacity and different sulfur species.

thiophene (typical organic sulfur on carbon surface), and sulfate, could possibly contribute to mercury uptake capacity. Elemental sulfur and organic sulfur were previously considered to be effective mercury removal agents [16,17]. However, sulfate also showed good correlation with mercury uptake capacity in this study.

It should be noted that the thiophene content on the samples produced in the presence of H₂S at stable temperatures only (BPL-400C–S Only, BPL-600C–S Only, and BPL-800C–S Only), increased up to three times with the increase in temperature, but the mercury uptake capacity remained unchanged. Such behavior suggests that thiophene might not be the major active site for mercury uptake although a reasonable correlation was found between mercury uptake capacity and thiophene content. Comparing to the other two possible effective sulfur species, the sulfate content is very low. This also indicates that sulfate may not be the most effective sulfur forms for mercury uptake regardless of the fair correlation between mercury uptake capacity and sulfate content.

Elemental sulfur can react with elemental mercury even at room temperature. However, not all elemental sulfur forms function equally. As described in Part I of this study [20], temperature programmed reaction between H₂S and carbon surface released H₂ at temperatures around 600 °C. This suggests the decomposition of H₂S into H₂ and S that is likely catalyzed by the carbon surface. This reaction pathway can easily create short-chain elemental sulfur species, such as S₂ and S₄, which are believed to be much more effective in Hg uptake than long-chain elemental sulfur [9,10,13].

4. Conclusions

XPS and XANES analysis of the BPL carbon-based sorbents produced at different temperatures and different sulfurization protocols showed that most of the produced sulfur is either organic, elemental or metal sulfide. High temperatures promote the formation of organic sulfur, and the presence of H₂S during the cooling process increased elemental sulfur content. Hg uptake tests indicate that 400–600 °C is the optimum temperature range to produce effective mercury sorbents. The presence of H₂S during the cooling process creates the most effective sulfur species for mercury binding. Elemental sulfur species are probably the most effective for capturing mercury although thiophene and sulfate content also showed fair correlation with mercury uptake capacity.

Acknowledgements

This study is supported by the NSF Grant No. BES-0202015. The authors would like to thank Dr. Waldeck's group at the Department of Chemistry, University of Pittsburgh for providing assistance with XPS analysis. The authors would also like to thank Dr. Huggins from the

University of Kentucky for the help in the sulfur K-edge XAFS analysis.

References

- [1] U.S. EPA, Mercury study report to congress. EPA-452/R-97-003, 1997.
- [2] Pavlish JH, Sondreal EA, Mann MD, Olson ES, Galbreath KC, Laudal DL, et al. State review of mercury control options for coal-fired power plants. *Fuel Process Technol* 2003;82(2–3):89–165.
- [3] Chang R, Owens D. Developing mercury removal methods for power plants. *EPRI J* 1994:46.
- [4] Biswas P, Senior C, Chang R, Vidic R, Laudal D, Brown T. Mercury measurement and its control: what we know, have learned, and need to further investigate. *J Air Waste Manage Ass* 1999;49(12):1469–73.
- [5] Li YH, Lee CW, Gullett BK. Importance of activated carbon's oxygen surface functional groups on elemental mercury adsorption. *Fuel* 2003;82(4):451–7.
- [6] Krishnan SV, Gullett BK, Jozewicz W. Sorption of elemental mercury by activated carbons. *Environ Sci Technol* 1994;28(8):1506–12.
- [7] McLaughlin JB. Activated carbon adsorption for the removal of mercury from flue gas emissions. MS Thesis. Pittsburgh (PA, USA): University of Pittsburgh; 1995.
- [8] Vidic RD, Siler DP. Vapor-phase elemental mercury adsorption by activated carbon impregnated with chloride and chelating agents. *Carbon* 2001;39(1):3–14.
- [9] Liu W, Vidic RD, Brown TD. Optimization of sulfur impregnation protocol for fixed bed application of activated carbon-based sorbents for gas-phase mercury removal. *Environ Sci Technol* 1998;32(4):531–8.
- [10] Liu W, Vidic RD, Brown TD. Optimization of high temperature sulfur impregnation on activated carbon for permanent sequestration of elemental mercury vapors. *Environ Sci Technol* 2000;34(3):483–8.
- [11] Shinha RK, Walker PL. Removal of mercury by sulfurized carbons. *Carbon* 1972;10:754–6.
- [12] Otani Y, Emi H, Kanaoka C, Uchiwa I, Nishino H. Removal of mercury vapor from air with sulfur-impregnated adsorbents. *Environ Sci Technol* 1988;22(6):708–11.
- [13] Korpiel JA, Vidic RD. Effect of sulfur impregnation method on activated carbon uptake of gas-phase mercury. *Environ Sci Technol* 1997;31(8):2319–25.
- [14] Kwon S, Vidic RD. Evaluation of two sulfur impregnation methods on activated carbon and bentonite for the production of elemental mercury sorbents. *Environ Eng Sci* 2000;17(6):303–13.
- [15] Liu W. Development of novel adsorbents for the control of vapor-phase mercury emissions. PhD Thesis. Pittsburgh (PA, USA): University of Pittsburgh; 1999.
- [16] Hsi HC, Rood MJ, Rostam-Abadi M, Chen SG, Chang R. Mercury adsorption properties of sulfur-impregnated adsorbents. *J Environ Eng-ASCE*. 2002;128(11):1080–9.
- [17] Hsi HC, Rood MJ, Rostam-Abadi M, Chen SG, Chang R. Effects of sulfur impregnation temperature on the properties and mercury adsorption capacities of activated carbon fibers (ACFs). *Environ Sci Technol* 2001;35(13):2785–91.
- [18] Daza L, Mendioroz S, Pajares JA. Influence of texture and chemical composition on sulphur deposition onto sepiolites. *Appl Clay Sci* 1989;4(5-6):389–402.
- [19] Daza L, Mendioroz S, Pajares JA. Mercury elimination from gaseous streams. *Appl Catal B: Environ* 1993;2:277–87.
- [20] Feng W, Borguet E, Vidic RD. Sulfurization of a carbon surface for vapor phase mercury removal – I: effect of temperature and sulfurization protocol. *Carbon*, doi:10.1016/j.carbon.2006.05.019.
- [21] Huffman GP, Ganguly B, Zhao J, Rao K, Shah N, Feng Z, et al. Structure and dispersion of iron-based catalysts for direct coal-liquefaction. *Energ Fuels* 1993;7(2):285–96.

- [22] Taghiei MM, Huggins FE, Shah N, Huffman GP. In-situ X-ray absorption fine-structure spectroscopy investigation of sulfur functional-groups in coal during pyrolysis and oxidation. *Energ Fuels* 1992;6(3):293–300.
- [23] Huffman GP, Shah N, Huggins FE, Stock LM, Chatterjee K, Kilbane JJ, et al. Sulfur speciation of desulfurized coals by XANES spectroscopy. *Fuel* 1995;74(4):549–55.
- [24] Sugawara K, Enda Y, Kato T, Sugawara T, Shirai M. Effect of hydrogen sulfide on organic sulfur behavior in coal and char during heat treatments. *Energ Fuels* 2003;17(1):204–9.
- [25] Figueiredo JL, Pereira MFR, Freitas MMA, Orfao JJM. Modification of the surface chemistry of activated carbons. *Carbon* 1999;37(9):1379–89.
- [26] Leon y Leon CA, Radovic LR. Interfacial chemistry and electrochemistry of carbon surfaces. In: Thrower PA, editor. *Chemistry and physics of carbon*, vol. 24. New York: Marcel Dekker; 1994. p. 213–310.
- [27] Alqahtany H, Chiang PH, Eng D, Stoukides M, Robbat A. Electrocatalytic decomposition of hydrogen sulfide. *Catal Lett* 1992;13(3):289–95.
- [28] Nelen LM, Fuller K, Greenlief CM. Adsorption and decomposition of H₂S on the Ge(100) surface. *Appl Surf Sci* 1999;150(1–4):65–72.
- [29] Daza L, Mendioroz S, Pajares JA. Mercury elimination from gaseous streams. *Appl Catal B–Environ* 1993;2(4):277–87.