Mercury Binding on Activated Carbon

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Density functional theory has been employed for the modeling of activated carbon using a fused-benzene ring cluster approach. Oxygen functional groups have been investigated for their promotion of effective elemental mercury binding on activated carbon surface sites. Lactone and carbonyl functional groups yield the highest mercury binding energies. Further, the addition of halogen atoms have been considered to the modeled surface, and have been found to increase the activated carbon's mercury adsorption capacity. The mercury binding energies increase with the addition of the following halogen atoms, F > Cl > Br > I, with the fluorine addition being the most promising halogen for increasing mercury adsorption.

Introduction

Emissions from coal combustion processes constitute a significant amount of the elemental mercury released into the atmosphere today. Coal-fired power plants are the greatest anthropogenic source of mercury emissions in the United States [1]. Reducing the emissions of mercury is a major environmental concern since mercury is considered to be one of the most toxic metals found in the environment [2] and additionally is considered a hazardous air pollutant (HAP) by The Clean Air Act (CAA) of 1990. In March 2005, EPA adopted the Clean Air Mercury Rule to reduce mercury emissions from coal-fired power plants, [1] which will ultimately reduce the US emissions of mercury to 15 tons a year, constituting an approximate 70% reduction.

Mercury exists in coal combustion flue gas in a variety of forms depending on the coal type and combustion conditions; i.e., elemental (Hg^0), oxidized ($HgCl_2$ or HgO) and

particulate ($Hg_{(p)}$). Most of the mercury particulates, which comprise 10% of the total mercury in the flue gas can be removed using air pollution control devices. Oxidized mercury, i.e. Hg^{+2}, is easily captured by wet scrubbers, while gaseous elemental mercury passes through the scrubbers readily. It is difficult to capture elemental mercury because of its insolubility in water, higher volatility and chemical inertness [3]. Particulate matter such as fly ash, unburned carbon and activated carbon can be used to capture elemental and oxidized mercury through adsorption processes. Interaction of gaseous mercury with particulate matter can either lead to adsorbed and subsequent retained mercury on the surface, or can serve to oxidize elemental mercury to a water-soluble form for capture in wet scrubbers.

Many studies have been performed to find an effective and affordable sorbent for the removal of elemental mercury from combustion flue gas. Activated carbon (AC) is one of the most studied sorbents for capturing mercury. Activated carbon adsorption can be performed through two different processes, i.e. powdered activated carbon (PAC) injection or fixed-bed granular activated carbon (GAC) adsorption. The use of PAC involves the direct injection of activated carbon into the plant's flue gas stream where it adsorbs gaseous mercury and is collected in downstream particulate control devices, such as fabric filters or electrostatic precipitators (ESP). In the case of using GAC, an adsorber is placed downstream of the flue gas desulfurization (FGD) unit along with particulate collectors, which serve as the final treatment process before the flue gas is discharged into the atmosphere [4].

It has been shown that chemically embedded activated carbon has a higher mercury adsorption capacity than thermally activated carbon. Specifically, sulfur, chlorine, bromine and iodine-embedded activated carbon have been found to be effective sorbents for elemental mercury capture. It has been observed that at 150-260 ºC, activated carbon embedded with chlorine salt has as much as a 300 times greater elemental mercury removal capacity than traditional thermally activated carbon [5]. It has also been reported by Matsumura [6] that oxidized or iodized activated carbon adsorbed mercury vapor 20-160 times more than untreated activated carbon in nitrogen at 30 ºC. Granite et al. [7] stated that hydrochloric acid-treated activated carbon yielded a large capacity of mercury

in the experiments carried out in argon at 138 ºC, which makes it one of the most active sorbents studied to date. However, the cost related to the preparation of chemically embedded activated carbon is high. There have been many attempts to find a low-cost alternative sorbent, but limited success has resulted due to problems associated with removal efficiency [8]. Therefore, it is essential to develop a novel sorbent for the effective and affordable removal of elemental mercury.

Krishnan et al. have shown that the type of activated carbon, reaction temperature and inlet Hg^0 concentration affect sorption rates and capacity for elemental mercury. They have found elemental mercury sorption on thermally activated carbon to be decreasing with increasing temperature [8]. It has been illustrated by many studies that adsorption process of mercury on activated carbon surface is exothermic, indicating a typical physisorption mechanism [8-12]. Moreover, sulfur, iodine and chlorine impregnants are thought to provide sites where the mercury can chemically adsorb onto the carbon surface [13]. For chlorine and sulfur impregnated activated carbons the lower the temperature the higher the adsorption capacity of mercury because of exothermic behavior of mercury reaction with chloride [13-16] or elemental sulfur [17,4]. Conversely, in the case of iodine impregnated activated carbon the amount of mercury adsorbed by the carbon increases as the temperature increases [18].

Studies performed at Energy & Environmental Research Center (EERC) have examined the effects of flue gas acid species such as HCl, SO_2, NO, NO_2 on mercury capture as well as mercury binding and oxidation mechanism. In the model they have proposed, electrons must be accepted by a Lewis acid on activated carbon and then Hg^{+2} which is a Lewis acid can bind to Lewis base sites on the surface competing with other acidic species i.e. HCl and sulfuric acid. [19-22].

Investigations carried out by Carey et al. [23] have found that the type of carbon sorbent and its associated chemical properties are the most important factors affecting elemental mercury adsorption for a given flue gas composition. It has been observed that moisture within the activated carbon matrix plays an important role in promoting elemental mercury adsorption at room temperature [24]. Lee et al. [25] observed that virgin

activated carbon with large oxygen functional groups was superior in mercury adsorption performance. Li et al. [26] also studied the effect of activated carbon's oxygen surface functional groups such as lactone, carbonyl, phenol and carboxyl on elemental mercury adsorption. They found that both lactone and carbonyl groups are the likely active sites for mercury adsorption on an activated carbon surface. They also investigated whether phenol groups may inhibit mercury adsorption and whether the activated carbon surfaces having a lower phenol to carbonyl ratio yield a greater elemental mercury adsorption capacity.

Not only have experimental studies been performed in this area, but theoretical studies have also been carried out to gain an increased understanding of the mechanisms involved in elemental mercury adsorption onto activated carbon surfaces. To the authors' knowledge this is the first ab initio-based investigation involving the adsorption of elemental mercury on halogen-embedded activated carbon thus far. However, there have been theoretical investigations involving adsorption on graphite, which have provided ideas on how to begin modeling a carbon surface.

Chen and Yang [27, 28] have investigated different theoretical methods and different graphite models for describing graphite surface using ab initio methods. Comparing geometry, frequency and bond parameters calculated at different levels of theory to the experiment, B3LYP/6-31G(d)//HF/3-21G(d) has been found to be the most accurate and cost-effective method. Six graphite models with increasing sizes from 1 to 7 seven fused benzene rings were considered at the chosen level of theory. According to their comparison, $C_{25}H_9$ is the most suitable model among the others representing a single layer graphite surface.

Lameon et al. [29] have performed a study on the adsorption of potassium (K) and oxygen on graphite surfaces based on the Monte Carlo simulations. They have used a periodically repeated hexagonal supercell of n graphite layers (n = 1,2,3) and showed that the main physics is correctly described by a single graphite layer. Zhu et al. [30] compared the adsorption of alkali metals on graphite surfaces modeled as seven, ten, twelve and fourteen-fused benzene rings. Since Janiak et al. [31] and Lameon et al. [29]

have found that the difference of K adsorption on single-layer graphite and multilayer graphite is negligible, they chose single-layer graphite for their studies. Their analysis indicated that, comparing two levels of theory, the results from MP2 are not as reliable as those from B3LYP.The binding energies obtained at B3LYP/6-31G(d,p) are in good agreement with other theoretical studies.

Pliego et al. [32] studied the chemisorption of SO_2 on a graphite surface investigating the adsorption sites as well as the stability of the adsorbed complexes. HF/6-31G(d) level of theory was utilized in the geometry optimization. Frequency and single-point calculations were performed at MP2/6-31G(d) to obtain reaction energies. The pyrene structure which has four closely fused aromatic rings ($C_{16}H_{10}$) and two dehydrogenated derivatives corresponding to armchair and zigzag edges were used in modeling the graphite surfaces to simulate different adsorption sites. They have found adsorption to be favorable on an arm chair edge with binding energies of -5 to -51 kcal/mol and found adsorption on a zigzag edge to be the most favorable with binding energies ranging from -61 to -100 kcal/mol. All of these previous studies have focused on understanding the structure of activated carbon and its active sites and the role they play in adsorption mechanisms. Limited theoretical investigations have been performed on the mechanism responsible for the adsorption of mercury on activated carbon surfaces.

Steckel [33] has investigated the interactions between elemental mercury and a single benzene ring, which is quite limited in its potential for representing an accurate carbon surface. However, this previous study is the first to begin the investigations required for elucidating the mechanism by which elemental mercury binds to carbon. No known research has been conducted toward understanding the mechanism of mercury adsorption on simulated halogen-embedded activated carbon surfaces. The objective of the current study is applying theoretical-based cluster modeling to examine the effects of activated carbon's different surface functional groups and halogens on elemental mercury adsorption. This research will provide direction for further experimental studies that will aid in the development of a novel sorbent for effective mercury capture.

Computational Methodology

The Gaussian03 software package [34] was used for all of the energetic predictions in this work. Density Functional Theory (DFT) was employed due to its simplicity and accuracy. Considering that mercury has eighty electrons, to account for relativistic effects, a basis set with the inner electrons substituted by effective core potentials (ECP) was chosen. Beck's three-parameter functional with a Lee-Yang-Parr gradient-corrected correlation functional (B3LYP) with LANL2DZ basis set which uses an all-electron description for the first-row elements and an ECP for inner electrons and double-ζ quality valence functions for the heavier elements was used for the energy predictions [35-37].

Results and Discussion

1. Modeling activated carbon surface

For the theoretical model it was assumed that the activated carbon molecular framework is similar to that of graphite. Pyrene was examined to serve as a representative cluster species to model the activated carbon surface. A larger cluster, possibly more accurate, would require greater computational effort. Through comparing the structure predictions of four- and seven-fused benzene rings, the four-fused rings were chosen since the calculations provide a reasonable balance between accuracy and computational expense.

Table 1. C-Cl bond distances (Å) for different positions of Cl_2.

	Armchair edge	Zigzag edge	Center
C-Cl	1.8137	1.8258	4.5093

In order to optimize a halogen-embedded activated carbon surface, halogens were embedded at different sites along the cluster surface, i.e. the armchair edge, zigzag edge and center site. Optimization calculations have been carried out using the B3LYP method with the LANL2DZ basis set. The optimized bond distances of carbon and chlorine atoms are presented in Table 1 with the optimized structures shown in Figure 1. The theoretical geometry predictions convey that there is a minimal difference between the C-Cl bond distance from either the armchair or zigzag edge sites, while this bond distance is much greater at the center site. More calculations have been performed using a bromine-

embedded surface at the HF/SDD and HF/6-311G levels of theory and similar results have been obtained. It has been noted that no stable complex can be formed when halogens are embedded at the center of the cluster.

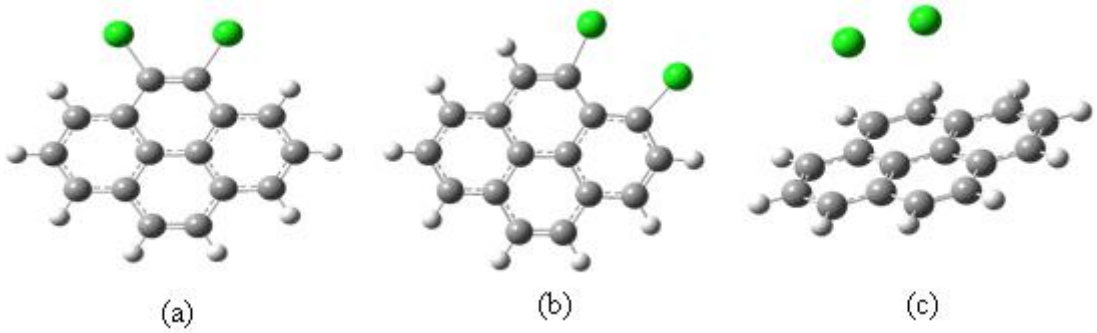

Figure 1. Optimized geometries for Cl_2 on different sites of the cluster (a) armchair edge; (b)zigzag edge; (c) center.

Moreover, a single Hg atom and a Cl atom have been optimized at different sites on the surface and the optimized geometries are shown in Figure 2 while the bond distances are given in Table 2. The same trend has been observed, i.e. that no stable complex can be formed at the center site and therefore, edge sites were chosen to be used in the further calculations. Also, comparison of mercury binding energies for zigzag and armchair edge sites shows that the armchair edge is more favorable for mercury binding with a binding energy of 7.72 kcal/mol while zigzag edge has a binding energy of 3.5 kcal/mol.

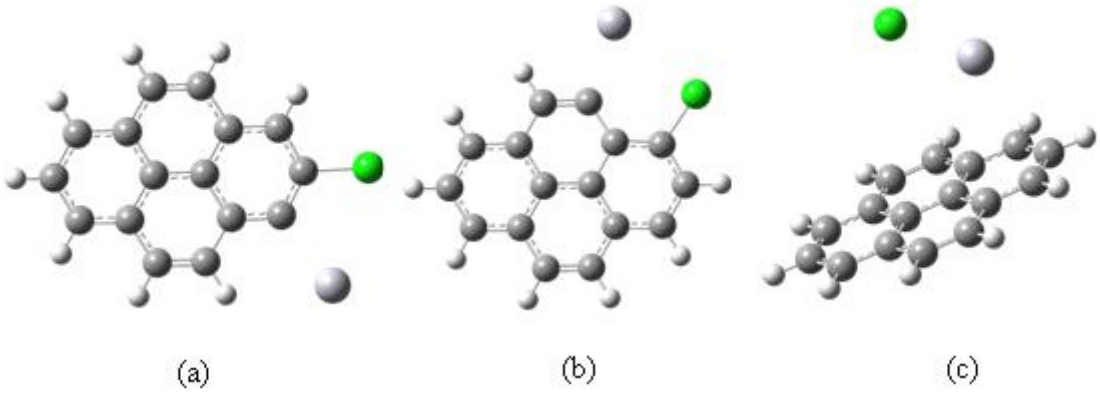

Figure 2. Optimized geometries for Hg and Cl on different sites of the cluster (a) armchair edge; (b)zigzag edge; (c) center.

Table 2. C-Cl and C-Hg bond distances (Å) for different positions on the surface.

	Armchair edge	Zigzag edge	Center
C-Cl	1.8461	1.8345	5.7448
C-Hg	2.4613	2.4788	4.0836

2. Effect of halogens on Hg adsorption capacity

Previous experimental studies have shown that chemically embedded activated carbon has a higher elemental mercury removal capacity than thermally activated carbon. In particular, halogen-embedded activated carbon has been found to be an effective sorbent for elemental mercury capture [5-8,38]. To understand the interactions between elemental mercury and halogen-embedded activated carbon, density functional theory calculations have been performed using different halogens such as fluorine, chlorine, bromine and iodine. The activated carbon cluster having mercury and halogen at the armchair edge has been modeled at the B3LYP/LANL2DZ level of theory. Cluster models with and without halogens are shown in Figure 3.

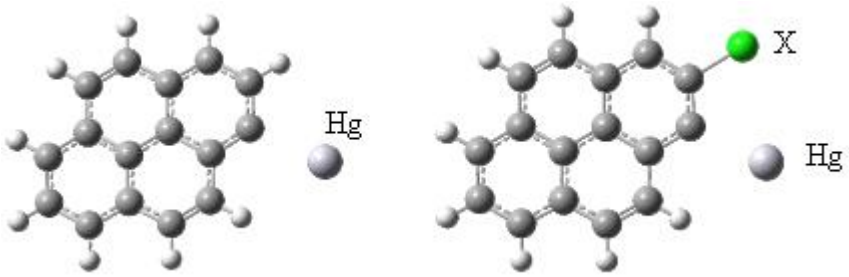

Figure 3. Cluster models of mercury adsorbed on activated carbon (AC) and halogen-embedded activated carbon. X: F, Cl, Br, I

Binding energies of elemental mercury on the activated carbon clusters were calculated using equation (1),

$$\text{Binding Energy} = E(\text{AC-Hg}) - [E(\text{Hg}) + E(\text{AC})] \quad (1)$$

Comparing the binding energies of elemental mercury on the activated carbon surface with and without a halogen indicates that the use of a halogen promotes mercury binding. Examination of the binding energies reported in Table 3 reveals that fluorine yields the highest binding energy, i.e. -9.59 kcal/mol, compared to the other halogens considered.

Table 3. Mercury binding energies (kcal/mol) and C-X bond distances associated with the clusters from Fig. 2.

	Binding energies (kcal/mol)	C-X Bond distances (Å)
AC	-4.3235	-
AC-F	-9.5885	1.4178
AC-Cl	-7.7207	1.8461
AC-Br	-6.6431	1.9809
AC-I	-5.3697	2.1681

3. Effect of oxygen functional groups on Hg adsorption capacity

Experimental studies conducted by Lee et al. [25] indicate that activated carbon with large oxygen functional groups were superior for elemental mercury adsorption. To simulate an activated carbon surface with increased accuracy, oxygen functional groups such as carbonyl, lactone, carboxyl and phenol groups were also considered on the cluster. Each functional group has been investigated separately to note the effect of different functional groups on elemental mercury binding. Carbon-mercury bond distances for the optimized clusters are given in Table 4, with the optimized structures presented in Figure 4.

Table 4. C-Hg bond distances (Å) for the clusters associated with the clusters from Fig. 3.

	Lactone	Carbonyl	Phenol	Carboxyl
C-Hg	2.4462	2.2586	2.4497	2.5078

Lactone and carbonyl groups have been found to be active sites for mercury binding, yielding binding energies of -10.29 and -9.16 kcal/mol, respectively. The presence of phenol and carboxyl groups has yielded relatively lower binding energies, -6.72 and -1.22 kcal/mol, respectively. More specifically, the presence of lactone and carbonyl functional groups promotes the chemisorption of elemental mercury while phenol and carboxyl functional groups promote a physisorption mechanism of mercury adsorption. These results agree with the experimental results of Li et al. [26] where they found both lactone and carbonyl groups to be the likely sites for mercury adsorption, with the activated carbon surfaces having a lower phenol to carbonyl ratio yielding a greater elemental mercury adsorption capacity.

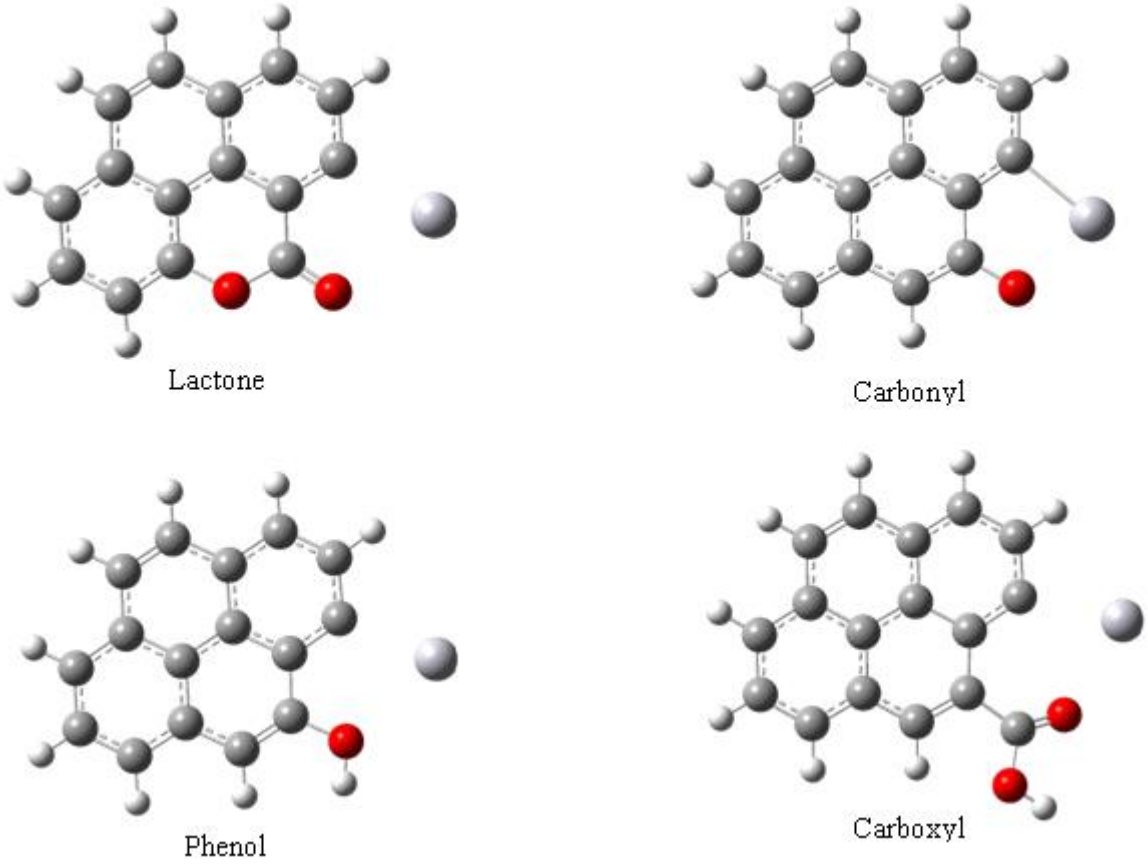

Figure 4. Activated carbon clusters with oxygen functional groups: lactone, carbonyl, phenol, and carboxyl.

Since it is known that halogen-embedded activated carbon has higher elemental mercury adsorption capacities than traditional activated carbon, halogens combined with the oxygen functional groups have been considered. Halogen-embedded clusters with different oxygen functional groups have been investigated and are shown in Figure 5. For these clusters the bond distances of carbon-halogen and carbon-mercury are given in Table 5.

Table 5. Bond distances (Å) of the clusters represented in Fig. 4.

Functional groups	X=F		X=Cl		X=Br		X=I	
	C-Hg	C-F	C-Hg	C-Cl	C-Hg	C-Br	C-Hg	C-I
Lactone	2.4096	1.4116	2.4239	1.8395	2.4307	1.9891	2.4382	2.1640
Carbonyl	2.2608	1.4096	2.2671	1.8336	2.2678	1.9809	2.2730	2.1525
Phenol	2.3954	1.4165	2.4150	1.8468	2.4254	1.9959	2.4314	2.1718
Carboxyl	2.4428	1.4220	2.4616	1.8564	2.4690	2.0069	2.4747	2.1824

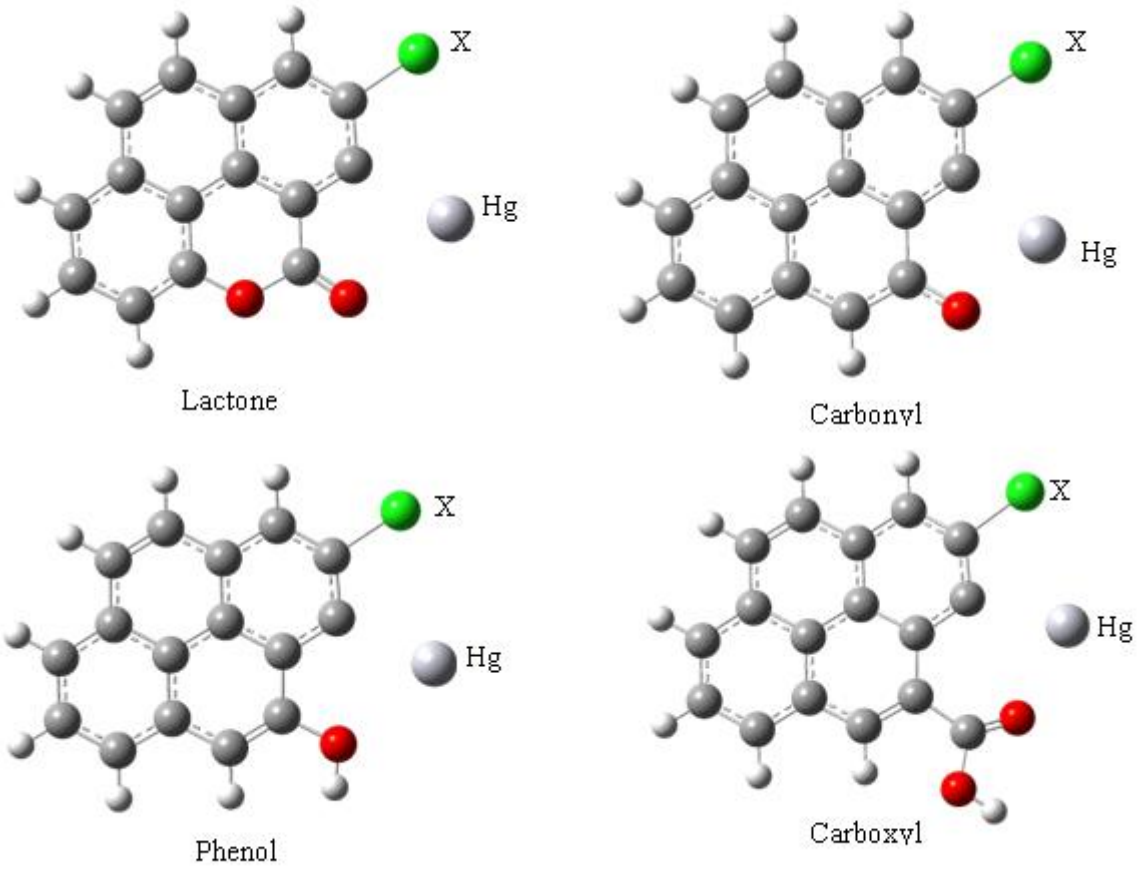

Figure 5. Halogen-embedded activated carbon clusters with oxygen functional groups: lactone, carbonyl, phenol, and carboxyl. X = F, Cl, Br, I

The binding energies reported in Table 6 show that adding a halogen to the cluster increases the elemental mercury adsorption capacity. It is interesting to note that the mercury binding energy increases with decreasing halogen distance to the activated carbon cluster surface as it is seen from Table 3. Further investigations would be required to determine whether the halogen proximity directly influences the activity of the binding sites.

Using different halogens with surface functional groups, the same trend has been observed where fluorine yields the highest binding energy of elemental mercury. The best binding performance has been obtained with the fluorine atom and lactone functional group combination, which has a mercury binding energy of -16.71 kcal/mol, while the second best is a carbonyl functional group with fluorine atom having a binding energy of

-14.5 kcal/mol. Although the phenol functional group does not yield a promising adsorption capacity, when fluorine is used, it may exist as an active site for elemental mercury adsorption.

Table 6. Binding energies of mercury on halogen-embedded activated carbon with different oxygen functional groups: lactone, carbonyl, phenol, and carboxyl.

Functional groups	Binding Energies (kcal/mol)				
	AC	AC-F	AC-Cl	AC-Br	AC-I
Lactone	-10.2851	-16.7144	-14.6622	-13.4594	-11.8763
Carbonyl	-8.8298	-14.5008	-13.0570	-12.1202	-10.9199
Phenol	-6.7242	-12.6310	-10.5091	-9.2009	-7.7716
Carboxyl	-1.2231	-7.6798	-4.0432	-2.4707	-0.6746

Conclusions

Note that these calculations do not represent real flue gas conditions and the calculated mercury binding energies have yet to be compared directly to experiment since such specific data is currently lacking in the literature. Effects of other flue gas constituents have not been considered and the simulations have been performed at room temperature. Density functional theory calculations have been carried out to provide a possible mechanism associated with mercury binding on various typed of activated carbon. These results can provide a direction for the further experiments in terms of through the recognition of binding trends and how the binding capacity changes by modifying the surface. In light of these results, activated carbon with the best combination of halogen and oxygen surface functional groups yielding the highest mercury removal capacity can be used in the experiments.

Through comparing the binding energies of elemental mercury on simulated activated carbon surfaces, it can be concluded that increasing the amount of lactone and carbonyl groups and decreasing carboxyl group can increase the binding capacity of elemental mercury. In addition, embedding halogen, especially fluorine, into the activated carbon matrix, can possibly promote elemental mercury binding.

Acknowledgements

This work was supported by the U.S. Environmental Protection Agency (Cooperative Agreements CR-83291001-0).

References

1. U.S. Environmental Protection Agency. Fact Sheet: EPA's Clean Air Mercury Rule. 2005.
2. Clarkson, T. W. Mercury: major issues in environmental health. Environ. Health Perspect. 1993, 100, 31-38.
3. Change, R.; Offen, G. R. Mercury emission control technologies: an epri synopsis. Power Engng, 1995, 99, 51-57.
4. Korpiel, J. A.; Vidic, R. D. Effect of sulfur impregnation method on activated carbon uptake of gas-phase mercury. Environ. Sci. Technol. 1997, 31, 2319-2325.
5. Teller, A. J.; Quimby, J. M.; 84th Annual Meeting and Exhibition, AWMA, Vancouver, BC, 1991, 95, 35.5.
6. Matsumura, Y. Atmosph. Environ. 1974, 8, 1321.
7. Granite, E. J.; Pennline, H. W.; Hargis, R. A. Novel sorbents for mercury removal from flue gas. Ind. Eng. Chem. Res. 2000, 39, 1020-1029.
8. Krishnan, S. V.; Gullett, B. K.; Jozewicz, W. Sorption of elemental mercury by activated carbons. Environ. Sci. Technol. 1994, 28, 1506-1512.
9. Karatza, D.; Lancia, A.; Musmarra, D.; Zucchini, C. Study of mercury absorption and desorption on sulfur impregnated carbon. Exp. Therm. Fluid Sci. 2000, 21, 150-155.
10. Ghorishi, B.; Gullett, B. K. Sorption of mercury species by activated carbons and calcium-based sorbents: effect of temperature, mercury concentration and acid gases. Waste Management Res. 1998, 16, 582-593.
11. Gullett, B. K.; Jozewicz W. International Conference on Municipal Waste Combustion, Williamsburg, VA, 1993.
12. Zeng, H.; Jin, F.; Guo, J. Removal of elemental mercury from coal combustion flue gas by chloride-impregnated activated carbon. Fuel. 2004, 83, 143-146.
13. Vidic, R. D.; Siler, D. P. Vapor-phase elemental mercury adsorption by activated carbon impregnated with chloride and chelating agents. Carbon. 2001, 39, 3-14.
14. Van Wylen, G. J.; Sonntag, R. E.; Borgnakke, C. Fundamentals of classical thermodynamics, 4th ed., New York, John Wiley and Sons, 1994, 555-646.
15. Smith, J. M.; Van Ness, H. C. Introduction to chemical engineering thermodynamics, 4th ed., New York, McGraw-Hill, 1987, 105-133.
16. Chase, Jr M. W.; Davies, C. A.; Downey, Jr, J. R.; Frurip, D. J.; McDonald, R. A; Syverd, A. N. JANAF thermodynamic tables. J. Phys. Chem. Ref. Data. 1985, 14, 1-1856, Supplement 1.
17. Liu, W.; Vidic, R. D.; Brown, T. D. Optimization of sulfur impregnation protocol for fixed-bed application of activated carbon-based sorbents for gas-phase mercury removal. Environ. Sci. Tech. 1998, 32, 531-538.
18. Lee, S. J.; Seo, Y. Jurng, J.; Lee, T. G. Removal of gas-phase elemental mercury by iodine- and chlorine-impregnated activated carbons. Atmosph. Environ. 2004, 38, 4887-4893.

19. Miller, S. J.; Dunham, G. E.; Olson, E. S.; Brown, T. D. Flue gas effects on a carbon-based mercury sorbent. Fuel Process. Technol. 2000, 65-66, 343-363.
20. Olson, E. S.; Laumb, J. D; Benson, S. A.; Dunham, G. E.; Sharma, R. K.; Mibeck, B. A.; Miller, S. J.; Holmes, M. J.; Pavlish, J. H. An improved model for flue gas-mercury interactions on activated carbons. Proceedings of Mega Symposium and Air & Waste Management Association's Specialty Conference, Washington, DC, 2003.
21. Laumb, J. D; Benson, S. A.; Olson, E. S. X-ray photoelectron spectroscopy analysis of mercury sorbent surface chemistry. Fuel Process. Technol. 2004, 85, 577-585.
22. Olson, E. S.; Crocker, C. C.; Benson, S. A.; Pavlish, J. H.; Holmes, M. J. J. Air & Waste Manage. Assoc. 2005, 55, 747-754.
23. Carey, T. R.; Hargrove, O. W.; Richardson, C. F.; Chang, R.; Meserole, F. B. J. Factors affecting mercury control in utility flue gas using activated carbon. Air Waste Manage. Assoc. 1998, 48, 1166
24. Li, Y. H.; Lee, C. W.; Gullett, B. K. The effect of activated carbon surface moisture on low temperature mercury adsorption. Carbon. 2002, 40, 65-72.
25. Lee, S.; Park, Y. Gas phase mercury removal by carbon-based sorbents. Fuel Process. Technol. 2003, 84, 197-206.
26. Li, Y. H.; Lee, C. W.; Gullett, B. K. Importance of activated carbon's oxygen functional groups on elemental mercury adsorption. Fuel, 2003, 451-457.
27. Chen, N.; Yang, R.T. Ab initio molecular orbital calculation on graphite: Selection of molecular system and model chemistry. Carbon. 1998, 36, 1061-1070.
28. Chen, N.; Yang, R.T. Ab initio molecular orbital study of the unified mechanism and pathways for gas-carbon reactions. J. Chem. Phys. A. 1998, 102, 6348-6356.
29. Lamoen, D.; Persson, B.N.J. Adsorption of potassium and oxygen on graphite: A theoretical study. J. Chem. Phys. 1998, 108, 3332-3341.
30. Zhu, Z.H.; Lu, G.Q. Comparative study of Li, Na, and K adsorptions on graphite by using ab initio method. Langmuir. 2004, 20, 10751-10755.
31. Janiak, C.; Hoffmann, Rr.; Sjovall, P.; Kasemo, B. The potassium promoter function in the oxidation of graphite: an experimental and theoretical study. Langmuir, 1993, 9, 3427-3440.
32. Pliego, J. R.; Resende, S. M.; Humeres, E. Chemisorption of SO_2 on graphite surface: A theoretical ab initio and ideal lattice gas model study. J. Chem. Phys. 2005, 314, 127-133.
33. Steckel, J. A. Ab initio modeling of neutral and cationic Hg-benzene complexes. Chem. Phys. Lett. 2005, 409, 322-330.
34. Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A.

Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 2003.

35. Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg. J. Chem. Phys., 1985, 82, 270-283.
36. Hay, P. J.; Wadt, W. R. Ab initio effective core potentials for molecular calculations. Potentials for K to Au including outermost core orbitals. J. Chem. Phys., 1985, 82, 299-310.
37. Wadt, W. R. Hay, P. J.; Ab initio effective core potentials for molecular calculations. Potentials for main group elements Na to Bi. J. Chem. Phys., 1985, 82, 284-298.
38. Morimoto, T.; Wu, S.; Uddin, M. A.; Sasaoka, E. Characteristics of the mercury vapor removal from coal combustion flue gas by activated carbon using H_2S. Fuel, 2005, 84, 1968-1974.