

Vapor-phase elemental mercury adsorption by residual carbon separated from fly ash

WANG Li-gang¹, CHEN Chang-he², Kruse H. Kolker³

(1. Department of Thermal Engineering, University of Science and Technology, Beijing 100083, China. E-mail: wangligang@tsinghua.org.cn; 2. The State Key Laboratory of Clean Combustion of Coal, Tsinghua University, Beijing 100084, China; 3. Department of Chemical Engineering, University of North Dakota, PO Box 9018, ND58202-9018, USA)

Abstract: The adsorption capacity for vapor-phase elemental mercury (Hg^0) of residual carbon separated from fly ash was studied in an attempt for the control of elemental mercury emissions from combustion processes. At low mercury concentrations ($< 200 \mu\text{g}/\text{m}^3$), unburned carbon had higher adsorption capacity than commercial activated carbon. The adsorbability of unburned carbon was also found to be source dependent. Isotherms of FS carbon (separated from fly ash of a power plant of Shishi in Fujian Province) were similar to those classified as type II. Isotherms of XJ carbon (separated from fly ash of a power plant of Jingcheng in Shanxi Province) were more like those classified as type III. Due to the relatively low production costs, these residual carbons would likely be considerably more cost-effective for the full-scale removal of mercury from combustion flue gases than other technology.

Keywords: mercury; adsorption; residual carbon; fly ash; activated carbon

Introduction

The impact of mercury on the environment and the physiological health of human is well documented (Laudal, 2000; Poissant, 2002; Galbreath, 2000; Palusova, 1991). Mercury, especially methyl mercury, has high affinities for fatty tissues in organisms and can accumulate to toxic levels within those organisms. Mercury can cause damage to the kidney, brain, and eye. Elemental mercury has been shown to methylate in the sediments of contaminated lakes and streams, forming methyl mercury (Carpi, 1997). Because of its tenacity in the environment and toxicity to human and other organisms, mercury has been identified as one of 189 hazardous air pollutants by the Clean Air Act Amendments (CAAA) of 1990 of USA.

Primary anthropogenic sources of atmospheric mercury emissions include coal-fired power plants and municipal waste combustors (MWCs). The coal combustion sources emit an estimated 302.9 tons of mercury in China in 1995 emit an estimated 213.8 tons of mercury into the atmosphere and 89.07 tons of mercury into combustion products. Coal is the main energy sources of electric power industry which consume 1/4 coal output of whole country per year (Wang, 2000). Current air pollution control technologies, such as baghouses, electrostatic precipitators, and wet/dry scrubbers showed to be effective in removing $\text{Hg}(\text{II})$ from the effluent gas stream but contribute little to the removal of elemental mercury (Jung, 2002).

Presently, the most effective and widely used technology for direct control of vapor-phase elemental mercury is injection of powdered activated carbon into the gas stream. Although this technology has been proven effective in removing up to 99% of the vapor-phase elemental mercury, the expenses associated with this process can be quite high, ranging from 14400 to 38200 USAD per pound of mercury removed (Carey, 2000).

Due to the high cost of powdered activated carbon injection technology, various other sorbents were examined with respect to their ability to adsorb vapor-phase mercury and their applicability in industry (Granite, 2000; Lopez, 2002). These include calcium-based sorbents and hydrated lime, silicon and carbon fibers coated with salts and other chemicals, as well as heat-activated and chemically activated

carbons.

Untreated, or virgin, activated carbon is quite inefficient for the removal of elemental mercury at temperatures typical of flue gas streams due to the high volatility of elemental mercury. The adsorption of elemental mercury onto activated carbon can be improved through the introduction of various impregnants onto the carbon surface. Impregnants typically used for mercury adsorption include elemental sulfur, iodine, and chlorine. These impregnated activated carbons are still in investigation and the cost is still in high level.

Price bottle-neck problems mentioned above are aimed at in this study. Residual carbon separated from fly ash is utilized as cheapness sorbent for the substituent of activated carbon in powdered activated carbon injection technology. Mercury adsorption characteristic of residual carbon is the key problem; mercury static adsorption characteristic of residual carbon will be mentioned as following.

1 Materials and methods

1.1 Residual carbon

Two fly ash samples were investigated in this study (Table 1): FS ash from a power plant of Shishi in Fujian Province; XJ ash from a power plant of Jingcheng in Shanxi Province. FS and XJ carbon are the residual carbon separated from FS and XJ ash by froth flotation. For comparison, one commercial activated carbon sample, HXT, was also tested. All samples were dried in air at 105°C .

Table 1 Properties of the carbons used in adsorption experiments

Carbons	Average size, μm	Density, g/cm^3	BET surface area, m^2/g	LOI, %	Remarks
FS	63	2.01	10.747	73.4	Separated from double currents flotation column
SJ	52	2.01	6.189	70.1	Separated from double currents flotation column
HXT	40		739.445		Purchased merchandise (for gas adsorption)

1.2 Static adsorption equipment

The adsorption was conducted in sampling bags (231 series). These bags were fabricated from chemically inert film. The capacity of the bags was 10 L, the procedure employed in this study was as follows:

- Evacuate the bags with a manual-operated evacuation pump;
- Weigh desired amount(m) of carbon with a balance having an accuracy of one ten thousandth grams and put it into the bag through the septum fitting;
- Fill the bag with mercury containing gas through the hose/valve fitting with a flow rate of 1 L/min and a mercury concentration of about $450\text{ }\mu\text{g}/\text{m}^3$, measure the actual mercury concentration C_0 of the gas for each batch and record the total volume of filled gas V with a flow meter and a timer;
- Allow for a 7 d adsorption to attain equilibrium followed by measuring the residual mercury concentration C_{eq} of the bag;
- Calculate the adsorbed mercury q by the following equation:

$$q = \frac{V(C_0 - C_{eq})}{m} \quad (1)$$

During the 7 d adsorption, the bags were periodically shaken to enhance approaching to the equilibrium. The mercury concentrations were measured twice for each bag and the average was then taken.

2 Results and discussion

2.1 Performance of residual carbon and activated carbon

All the tests were conducted at room temperature, 20°C , the carrier gas was nitrogen and the initial mercury concentration in the gas was about $0.45\text{ mg}/\text{m}^3$ at 20°C . The carbons added to the bags weighed about 0.06 g to 0.12 g . Fig. 1 and Fig. 2 present the adsorption isotherms of FS carbon and XJ carbon at 20°C , respectively. For comparison, the isotherm of HXT carbon, a type of activated carbon suitable for gas phase adsorption, is also shown in Fig. 1 and Fig. 2. It is interesting that all the isotherms appear concave in the mercury concentrations of the study range, which are more like type II or type III (Fig. 3) isotherms according to the classification of Brunauer (Brunauer, 1945). At low gas phase mercury concentrations ($< 0.3\text{ mg}/\text{m}^3$), the mercury concentration in carbon increases linearly and gradually with the increase of gas phase mercury concentrations. When gas phase mercury concentration reaches certain levels ($> 0.3\text{ mg}/\text{m}^3$), the mercury concentration in carbon increases rapidly with the increase of mercury concentration in gas phase. The capacity of the carbons at low gas phase concentrations decreases in the order of HXT, XJ and FS. The adsorption capacity of these carbons can be as high as $60\text{ }\mu\text{g}/\text{g}$. However, at high gas phase concentrations, HXT has a much higher capacity, up to about $250\text{ }\mu\text{g}/\text{g}$ at the gas phase mercury concentration of $0.32\text{ mg}/\text{m}^3$. This suggests that, from the economical point of view, unburned carbons are very similar to HXT in removing mercury vapor from utility flue gas streams since it has low mercury concentrations, from 0.05 to $1.20\text{ mg}/\text{m}^3$.

2.2 Analysis of the isotherms of the carbons studied

Brunauer (Brunauer, 1945) have distinguished five types of isotherms involving physical adsorption, although there exists still some others which can not be included in these five types. These five types of isotherms are presented in Fig. 3. According to the classification, type I isotherm approximates monomolecular adsorption and is frequently referred to as Langmuir type. This type of curve is obtained

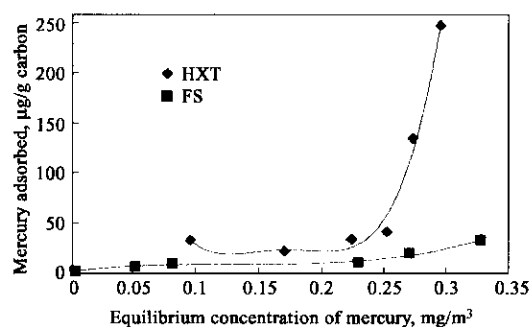


Fig. 1 Adsorption isotherms of FS carbon at 20°C

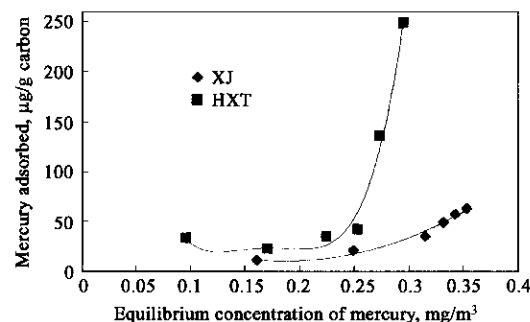


Fig. 2 Adsorption isotherms of XJ carbon at 20°C

by low temperature adsorption of oxygen or nitrogen on certain charcoals and silica xerogels, because a monolayer saturates the surface or fills the pores. Chemisorptions phenomena frequently produce a curve of this type. Type II is the most frequently encountered adsorption isotherm and is referred to as the sigmoid or S-shaped isotherm. The first part of the curve up to a relative pressure of about 0.1 corresponds to monomolecular adsorption (up to point B). A multiplayer region follows this type. Capillary condensation occurs in the region above 0.4 relative pressure. Type IV is similar to Type II, except in that portion of the isotherm approaching 10 relative pressure. The sharp approach to the line corresponding to the saturation pressure indicates a limited pore volume, because the diameter of the pores is only a small multiple of the diameter of the adsorbate molecules. This isotherm is common for many kinds of porous substrates. Type III and V occur only when the forces of monomolecular adsorption are small. They are rarely encountered. A limited pore volume distinguishes the type V isotherm, as compared with type III.

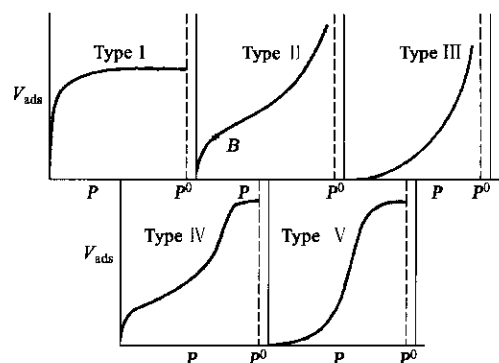


Fig. 3 Brunauer's five types of adsorption isotherms (Brunauer, 1945)

As mentioned earlier, careful examination of the

isotherms of FS carbon (Fig. 1) revealed that they would be more like the type II isotherm if enough data were available at very low mercury concentrations which are well below the emission limit and the detectable limit of the instrument employed in this study. The isotherms of XJ carbon and the active carbons, on the other hand, are similar to that of type III. Since mercury has a high surface tension, the isotherms of XJ carbon and activated carbon are discussed first. Based on this discussion, isotherms of FS carbons will be easily interpreted.

Type III isotherms are characterized by their being convex to the pressure axis. This suggests that the adsorption is co-operative in nature; the more molecules that are already adsorbed, the easier it is for further molecules to become adsorbed. On a prior grounds it seems that the attraction of adsorbate molecules for each other now exceeds their attraction for the adsorbent. If the latent heat of evaporation, L , is assumed to be a measure of the adsorbate-adsorbate interaction, and the differential heat of adsorption, q_{st} , a measure of the adsorbate-adsorbent interaction, it is then deduce that type III isotherms are to be expected in those systems for which q_{st} is close in value to L , i.e. in which the "net heat of adsorption" is not far from zero. Net heat of adsorption here is equal to the difference of the latent heat and the differential heat of desorption.

The similar adsorption behavior of mercury vapor to water vapor could come from their high surface tension (γ) and large contact angle (φ) with carbonaceous materials. γ and φ statistically represents all the interactions between adsorbate and adsorbent molecules, including dispersion, dipole-dipole, π -bonding, hydrogen bonding, metal bonding, ionic, and electrostatic forces. The effect of surface tension and contact angle can be addressed by the work of cohesion (W_{co}) and the work of adhesion (W_{ad}). The former is defined as the work done in reversibly pulling apart a column of liquid unit area in cross-section. The latter is the isothermal reversible work has to be done in order to pull asunder a solid-liquid joint unit area in cross-section. By definition,

$$W_{co} = 2\gamma_l, \quad (2)$$

and

$$W_{ad} = \gamma_l + \gamma_s - \gamma_{sl}, \quad (3)$$

where W_{ad} is the work of adhesion, γ_l is the surface tension of liquid, γ_s is the surface tension of solid, and γ_{sl} is the interface tension. According to the Young-Dupre equation, for a drop of the liquid adsorbate standing in equilibrium on the plane surface of a solid which is covered with an adsorbed film,

$$\gamma_s = \gamma_l \cos \varphi + \gamma_{sl}, \quad (4)$$

where φ is the contact angle. Combining Eq. (3) and Eq. (4) gives

$$W_{ad} = \gamma_l (1 + \cos \varphi). \quad (5)$$

The adsorption of a liquid on a solid may be judged by a parameter called spreading coefficient S , which is the difference of the work of cohesion and the work of adhesion:

$$S = \gamma_l (1 - \cos \varphi). \quad (6)$$

From this definition, the larger the S , the more the adsorbate molecules tend to tie together as a liquid rather than to adsorb on the solid. In contrast to most of

hydrocarbon compounds which have low surface tension and contact angle (with carbons), mercury has a surface tension of 485 dyne/cm and a contact angle of 135° with activated carbon, while water has a surface tension of 72 dyne/cm and a contact angle of about 90° with graphite. As a result, mercury and water have a much higher S value than many organic compounds. This leads to a low adsorption of mercury or water on carbonaceous materials which is not accord with our mercury static adsorption test of residual carbon unless "primary sites" are available to propagate the adsorption process. At these primary sites, however, the contact angle φ is small and the S is small too, resulting in a high adsorption on these sites.

3 Conclusions

The adsorption capacity was found to be carbon source dependent rather than surface area and pore size dependent. At low mercury concentrations corresponding to those of utility flue gas. FS carbon and XJ carbon had similar adsorption capacities with activated carbons. The isotherms of FS carbon were more like type II isotherm according to the classification of Brunauer while those of XJ carbon are similar to type III or type V isotherms because of the insufficient data in XJ curve. The curve of HXT activated carbons is similar to type III isotherms. The high surface tension (γ) and large contact angle (φ) with carbonaceous materials could lead to weak adsorption of mercury on carbonaceous materials. Judge from the test result, "primary site" are existed on carbonaceous materials which result in a high adsorption on these site.

References:

- Brunauer S, 1945. The adsorption of gases and vapors [M]. Vol. 1. New Jersey: Princeton University Press.
- Carey T R, Richardson C F, Chang R *et al.*, 2000. Assessing sorbent injection mercury control effectiveness in flue gas streams [J]. *Environmental Progress*, 19(3): 167—174.
- Carpi A, Lindberg S E, Prestbo E M *et al.*, 1997. Methyl mercury contamination and emission to the atmosphere from soil amended with municipal sewage sludge [J]. *Journal of Environmental Quality*, 26(6): 1650—1655.
- Galbreath K C, Zygarlicke C J, 2000. Mercury transformations in coal combustion flue gas [J]. *Fuel Processing Technology*, 65(1): 289—310.
- Granite E J, Pennline H W, Hargis R A, 2000. Novel sorbents for mercury removal from flue gas [J]. *Industrial and Engineering Chemistry Research*, 39(4): 1020—1029.
- Jung J, Lee T C, Lee G W *et al.*, 2002. Mercury removal from incineration flue gas by organic and inorganic adsorbents [J]. *Chemosphere*, 47(9): 907—913.
- Laudal D L, Brown T D, 2000. Effects of flue gas constituents on mercury speciation [J]. *Fuel Processing Technology*, 65(1): 157—165.
- Lopez M A, Tascon J M, Martinez M R, 2002. Retention of mercury in activated carbons in coal combustion and gasification flue gases [J]. *Fuel Processing Technology*, 77(20): 353—358.
- Palusova O, Ursinyova M, Uhnak J, 1991. Mercury levels in the components of the environment and diets [J]. *Science of the Total Environment*, 101(1): 79—83.
- Poissant L, Dommergue A, Rerrari C P, 2002. Mercury as a global pollutant [J]. *Journal De Physique IV*, 12(10): 143—160.
- Wang Q C, Shen W G, Ma Z W, 2000. Estimation of mercury emission from coal combustion in China [J]. *Environmental Science and Technology*, 34(13): 2711—2713.
- Wu S D, Chang M B, 1997. Dissemination and fate of mercury in the environment [Z]. *Bulletion of Environmental of "National" Central University*, 1997, 4.

(Received for review July 21, 2004. Accepted December 29, 2004)