HIGH ACTIVITY CARBON SORBENTS FOR MERCURY CAPTURE

by

George G. STAVROPOULOS, Irene S. DIAMANTOPOULOU, George E. SKODRAS, and George P. SAKELLAROPOULOS

High efficiency activated carbons have been prepared for removing mercury from gas streams. Starting materials used were petroleum coke, lignite, charcoal and olive seed waste, and were chemically activated with KOH. Produced adsorbents were primarily characterized for their porosity by N_2 adsorption at 77 K. Their mercury retention capacity was characterized based on the breakthrough curves. Compared with typical commercial carbons, they have exhibited considerably enhanced mercury adsorption capacity. An attempt has been made to correlate mercury entrapment and pore structure. It has been shown that physical surface area is increased during activation in contrast to the mercury adsorption capacity that initially increases and tends to decrease at later stages. Desorption of active sites may be responsible for this behaviour.

Key words: *activated carbons, KOH activation, surface area, pore volumes, mercury adsorption*

Introduction

Coal is an abundant fossil fuel that can be used for energy production as substitute of petroleum products. Direct combustion is the conventional route but gasification and even liquefaction are important possibilities to consider. Coal composition is complex and includes between other elements mercury, a substance with known adverse effects in the environment. A potential source of mercury emissions to the atmosphere is coal fired power plants. European Union and United States impose regulations for plant emissions that require the adoption of mercury abatement technologies. The most widely used and well proven is the one based on activated carbon. Flue gases are contacted with carbon materials, which adsorb mercury. Contact can be accomplished in carbon columns but more frequently activated carbon can be directly injected in the flue gas line and recovered in a particle-collecting device, usually an electrostatic precipitator, for disposal. According to literature, mercury is retained either by physical and chemical adsorption mechanisms. Studies have shown that equilibrium adsorptive capacity of activated carbons is high in samples with large percent of micropores and BET surface area [1-3]. Micropores enhance physical adsorption due to the increased potential of small

19

sized pores and surface area enhances the availability of active sites for chemisorption. In this paper attempts are made to prepare activated carbons with unusually high adsorption potential (sometimes called "superactive" carbons, with BET surface areas up to 2500-3000 m^2/g). The mercury adsorption capacity of the products is calculated and correlated with pore structure. In order to minimize production costs, low cost raw materials have been used for the preparation of the carbons, not extensively investigated for mercury entrapment.

Experimental

Mercury adsorption experiments were performed in active carbons prepared from different starting materials selected for their wide availability and low cost of acquisition in the local market. Lignite, charcoal, pet coke, and olive seed waste was activated with KOH in N_2 flow (chemical activation). Samples were crashed and sieved and the particle size fraction less than 180 m was used in the experiments. A tubular fixed bed reactor was used, loaded with one gram of sample maintaining a carbon to KOH ratio of 1:4. Details on experimental set-up and procedure can be found elsewhere [4]. The effect of activation time was investigated by varying reaction times at a constant temperature, 800 °C. Products were characterized for their pore structure based on the N_2 adsorption at 77 K isotherms and application of BET equation for the pore surface area. BET theory [5] is based on a multiplayer adsorption formalism leading to the equation:

$$V_{ads} = \frac{V_m c p}{(p_0 - p)\left[1 + (c-1)\frac{p}{p_0}\right]} \tag{1}$$

Equation 1 can be rearranged in the form:

$$\frac{p}{V_{ads}(p_0 - p)} = \frac{(c-1)p}{V_m c} \cdot \frac{p}{p_0} + \frac{1}{V_m c} \tag{2}$$

A plot of $p/V_{ads}(p_0 - p)$ against p/p_0 gives a straight line (BET plot). Monolayer volume is $V_m = 1/(\alpha + \beta)$, where α and β are the slop and the intercept of the line, respectively.

The specific surface area S can be obtained from:

$$S = \frac{V_m S_0}{w} \tag{3}$$

where S_0 is the nitrogen cross-sectional area (16.3 Å^2/molecule).

The Dubinin-Radushkevich equation [5]:

$$\log W = \log(V_0\rho) - k \left[\log \frac{p}{p_0}\right]^2 \tag{4}$$

was applied for the micropore volume calculation. A plot of $\log W$ *vs.* $\log(p/p_0)^2$ should give a straight line with an intercept of $\log(V_0\rho)$ from which V_0, the micropore volume can be calculated. ρ is the liquid nitrogen density (= 0.808 g/cm^3).

Mercury adsorption tests were conducted in a column containing 20 mg of carbon sample fed with a N_2 gas stream of 0.35 ng/cm^3 mercury concentrations at 50 °C. A mercury permeation device was used as a source of elemental mercury Hg° (VICI Metronics Inc, Santa Clara, CA, USA). The device, designed to produce constant release of mercury vapour per unit time at specified temperatures, is secured in a temperature-controlled stainless steel U-tube holder, and nitrogen at pre-adjusted constant flow passes through it (200 cm^3/min.). A Mercury Instruments Analyzer GmbH (model: Vapor Monitor 3000-LabAnalyzer 254) was used for the continuous measurement of the outlet elemental mercury concentration. Breakthrough curves showing the retention of mercury as a function of time were constructed based on the inlet-outlet mercury concentration differences. The retained mass of mercury at any time t was calculated from the expression:

$$q_t = \frac{Q}{W} \int_0^t (C_0 - C)\mathrm{d}t \tag{5}$$

in which Q is the volumetric flow rate, W – the mass of adsorbent, C_0 – the mercury vapour concentration at the inlet, and C – the mercury concentration at the outlet. The time t required for the integration was arbitrary chosen to be 6 hours for comparison and therefore equilibrium uptakes of mercury were not necessarily achieved.

Results and discussion

N_2 adsorption isotherms are a simple though potential tool for pore structure characterization of solids. A steep increase of adsorbed volumes at low pressures is due to the enhanced potential of micropores (type I isotherms according to IUPAC classification [6]) and a monotonic or sudden increase at high pressures is shown if mesopores are present in the sample (type IV isotherms). Materials containing both types of pore dimensions exhibit mixed type isotherms (type H3).

As can be seen in fig. 1, isotherms of activated carbons prepared by KOH activation are of mixed type H3 presenting a sudden increase in adsorbed volumes at low relative pressures that continues up to pressures near unity. Therefore the presence of the entire spectrum of pore sizes, both micro- and meso-, can be concluded from the N_2 adsorption isotherms.
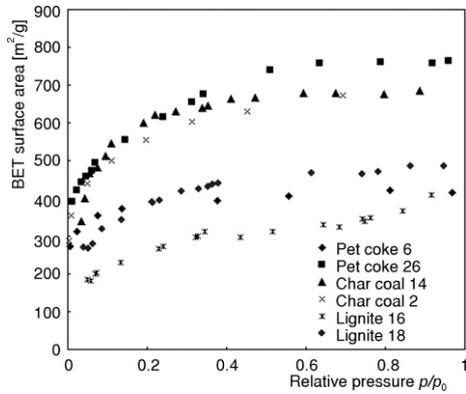
Figure 1. N₂ adsorption isotherms of carbons

Adsorbed amounts generally increase with activation time t, and seem to differ for the materials tested. BET surface areas, S_{BET}, are proportional to the adsorbed volumes and they vary accordingly although areas variation is better correlated with conversion degree X, of the carbon product:

$$X \quad \frac{\text{initial weight} \quad \text{final weight}}{\text{initial weight}}$$

Table 1 shows an increase in areas with conversion that apparently depends on the carbon parent material.

Surface areas of samples are shown to be considerably higher than those of some common, commercially available sorbents. For instance, they have been produced carbons acquiring BET surface areas two- or even threefold higher than F-400 (Calgon Co), tab. 1.

Table 1. Textural properties of activated carbons

Sample number	Starting material	Time [h]	X [wt. %]	S_{BET} [m²/g]	V_μ [cm³/g]	V_m [cm³/g]	W_{Hg} [ng/mg]
2	Charcoal	1	45	1843	0.588	0.402	883
14	Charcoal	2	48	1837	0.585	0.400	559
6	Pet coke	1.5	46	1337	0.476	0.138	909
26	Pet coke	3.5	59	1984	0.634	0.494	647
16	Lignite	1	50	920	0.376	0.236	591
18	Lignite	2	80	1300	0.526	0.190	946
30	Olive kernels	1	40	1340	0.523	0.143	795
31	Olive kernels	3	51	2580	0.845	0.193	833
F-400	–	–	–	881	–	–	505
RWE	–	–	–	343	–	–	363

For the last a pore surface area of 881 m²/g was calculated meanwhile charcoal based carbon 14 posses a BET surface area of 1837 m²/g and olive kernel based carbon 31 presents a BET surface area of 2580 m²/g. Differences are even grater if Rheinbraun RWE carbon is used as a basis for comparison.

Those highly active products were considered as candidate materials for enhanced mercury adsorption capacity. In fig. 2 the samples breakthrough curves are shown reporting the carbon bed outlet-inlet concentration ratio as a function of contact time.

At early stages when carbon is fresh and clean, ratio is quickly decreased due to the strong adsorption potential. At some latter stages when carbon is partly saturated the trend is reversed and the $C_{out/in}$ begins to increase tending for high contact times to unity when carbon active surface area is completely exhausted. The extension of every step is related to the column design parameters but also to the physicochemical characteristics of the samples [7]. The more active the sample, the more pronounced the time for the reversion to take place and the time required for concentration ratio to reach unity. Samples breakthrough curves show that the more active samples are 6 and 18. Breakthrough curves are used to calculate the retention capacities of the samples. Prepared carbons have mercury retention capacities W_{Hg}, higher compared with the F-400 and RWE products (tab. 1). Lignite based sample 18 presents the highest adsorbing capacity, 946 ng/mg, the lowest been 559 ng/mg for the charcoal sample 14, compared to the F-400 carbon having a capacity of 505 ng/mg and RWE with only 363 ng/mg. The mercury retaining capacity was correlated with the samples BET surface areas (fig. 3) in order to reveal if porosity correlates with mercury retention. It can be seen that mercury adsorption capacity is increased proportionally to the areas up to some value but afterwards remains constant with a tend to decre- ase. Samples with high surface areas do not adsorb proportionally high amounts of mercury. BET surface area is a measure of total geometric (physical) area of a solid where active sites for chemisorption reside. Carbons with high surface areas are produced at high activation times (tab. 1) and have high conversions. An increase in BET surface areas not accompanied by a proportional increase in mercury adsorption capacity may indicate that active sites are created early and further activation affects only the physical structure but not the chemical. Experimental points of fig. 3 anticipate a decrease in mercury adsorption capacity of samples

Figure 2. Mercury breakthrough curves
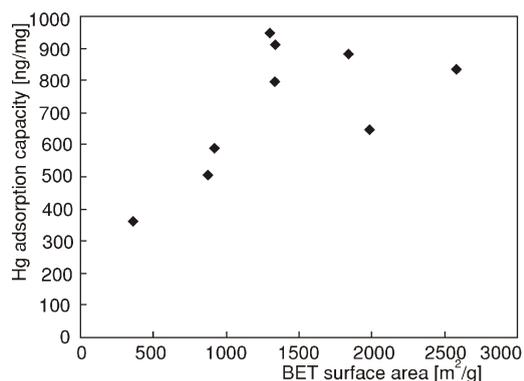
Figure 3. Variation of mercury adsorption capacity with surface area

with high surface areas. One can speculate on the existence of a active site loss mechanism that most probably is due to thermal desorption of oxygen functionalities that constitute large part of active sites for chemisorption in carbon materials. Previous studies indicated possibly lacton and carbonyl surface groups to be the active centres [8].

Retained amounts of mercury are increasing in samples with increased micropore and mesopore volumes reaching a plateau with a decreasing trend at late stages of activation (tab. 1) in a similar way with surface area. So far, samples with low conversion adsorb large quantities of mercury either in micro- and mesopores. These results do not confirm the results reported in literature that mercury adsorption takes place preferably in micropores. On the contrary they show adsorption activity in all pore sizes. It is generally accepted that micropores are major active sites for most adsorbates while mesopores act as adsorption sites especially for larger molecules and also as transportation paths for small molecules. One cannot exclude *a priori* the existence of active centres for mercury adsorption in mesopores while physisorption in micropores is greatly enhanced by the low pore sizes together with chemisorption. Therefore except porosity, active carbon surface chemistry is also important in determining the mercury adsorption capacity in accordance with the results of other works [9, 10].

In order to elucidate the adsorption topology *i. e.* confirm the sorption of mercury in the total surface area, the mercury adsorption isotherms need to be constructed, (work in progress). The shape of the curves will give information on whether mercury adsorbs in micro- and/or mesopores and will serve as a guide for the selection of active carbons with the appropriate pore structure. Anyhow, porosity results confirm the previous conclusions that "young" carbons with relatively low degree of conversion are more active in mercury adsorption and that the high N_2 adsorption capacity does not necessarily reflects high mercury adsorption capacity. Thus, carbons activated with KOH for low times are best suited in mercury adsorption applications.

Conclusions

Active carbons with substantially higher mercury adsorption capacities than commercial products have been prepared from cheap raw materials. The high surface area and porosity of samples does not ascribe a correspondingly high mercury adsorption capacity. Adsorption takes place on the total porosity presumably by both physical and chemical adsorption mechanisms.

Low activation times are required for the preparation of active carbons in mercury adsorption applications. Extension of the activation times seem to not contribute in the generation of active surface area for mercury adsorption despite the creation of physical surface area. On the contrary there are indications of an active site loss mechanism.

Nomeclature

C – column outlet concentration, [ng/cm^3]
C_0 – column inlet concentration, [ng/cm^3]

c – BET constant, [–]
k – parameter depending on structure and temperature, [–]
p – pressure, [atm]
p_0 – N_2 saturation vapor pressure, [atm]
Q – volumetric flow rate, [cm^3/min.]
q_t – mercury retention, [ng/mg]
S_{BET} – BET surface area, [m^2/g]
t – time, [min.]
V_μ – micropore volume, [cm^3/g]
V_m – mesopore volume, [cm^3/g]
W – mass of adsorbent, [mg]
W_{Hg} – mercury retention, [ng/mg]
w – sample weight, [g]
X – conversion, [wt. %]

References

[1]   Serre, D. S., Silcox, D. G., Adsorption of Elemental Mercury on the Residual Carbon in Coal Fly Ash, *Ind. Eng. Chem. Res.*, *39* (2000), 6, pp. 1723-1730
[2]   Krishnan, S. V., Gullett, K. B., Jozewicz, W., Sorption of Elemental Mercury by Activated Carbons, *Environ. Sci. Technol.*, *28* (1994), 8, pp. 1506-1512
[3]   Hsing-Cheng, H., Rood, J. M., Rostam-Abadi, M., Shiaoguo, C., Ramsay, C., Effects of Sulfur Impregnation Temperature on the Properties and Mercury Adsorption Capacities of Activated Carbon Fibers (ACFs), *Environ. Sci. Technol.*, *35* (2001), 13, pp. 2785-2791
[4]   Stavropoulos, G. G., Precursor Materials Suitability for Super Activated Carbons Production, *Fuel Processing Technology*, *86* (2005), 11, pp. 1151-1240
[5]   Rouquerol, F., Rouquerol, J., Sing, K., Adsorption by Powders and Porous Solids, Academic Press, London, 1999, pp. 110-111
[6]   Rouquerol, F., Rouquerol, J., Sing, K., Adsorption by Powders and Porous Solids, Academic Press, London, 1999, pp. 19-20
[7]   Mendioroz, S., Guijarro, M. I., Bermejo, P. J., Munoz, V., Mercury Retrieval from Flue Gas by Monolithic Adsorbents Based on Sulfurized Sepiolite, *Environ. Sci. Technol.*, *33* (1999), 10, pp. 1697-1702
[8]   Mercedes Maroto-Valer, M., Zhang, Y., Granite, E. J., Tang, Z., Pennline, H. W., Effect of Porous Structure and Surface Functionality on the Mercury Capacity of a Fly Ash Carbon and Its Activated Sample, *Fuel*, *84* (2005) 1, pp. 105-108
[9]   Guijarro, M. I., Mendioroz, S., Munoz, V., Effect of Morphology of Sulfurized Materials in the Retention of Mercury from Gas Streams, *Ind. Eng. Chem. Res.*, *37* (1998), 3, pp. 1088-1094
[10] Hancai, Z., Feng, J., Jia, G., Removal of Elemental Mercury from Coal Combustion Flue Gas by Chloride-Impregnated Activated Carbon, *Fuel, 83* (2004), 1, pp. 143-146

Authors' adresses:

G. G. Stavropoulos[1], I. S. Diamantopoulou[1],
G. E. Skodras[1,2], G. P. Sakellaropoulos[1,2]

[1] Chemical Process Engineering Laboratory,
    Department of Chemical Engineering,
    Aristotle University of Thessaloniki,
    P. O. Box 1520, 54006, Thessaloniki, Greece

[2] Laboratory of Solid Fuels and Environment,
    Chemical Process Engineering Research Institute,
    4th km Nat. Rd Ptolemais-Kozani (AEVAL),
    P. O. Box 95, 50200, Ptolemais, Greece

Corresponding author (G. G. Stavropoulos):
e-mail: gstaurop@cheng.auth.gr