

of silicon content. The purpose of this short note is to reply to a number of inquiries about the relation between the structures and silicon content of PG(Si) prepared in this laboratory.

The conditions for the preparation of PG(Si) were as follows: Deposition temperature (T_{dep}) = 1535, 1635, 1730, 2025°C, total gas pressure (P_{tot}) = 50 Torr, partial pressure of silicon tetrachloride vapor (P_{SiCl_4}) = 0, 4, 6, 13 Torr. The methods for the measurement of density, interlayer spacing and crystallite size have been fully described elsewhere [7].

Figure 1 shows the density (d) of PG(Si) as a

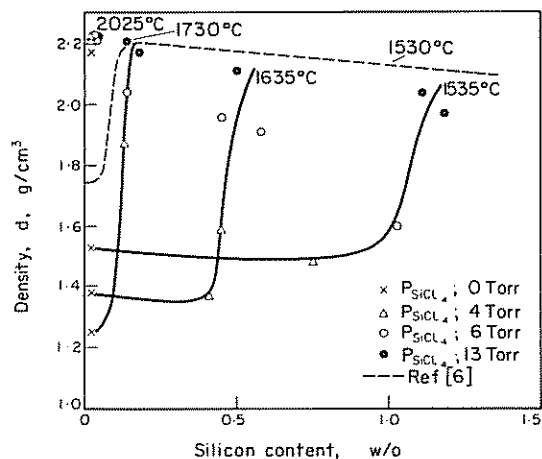


Fig. 1. Relationship between the density (d) and silicon content for PG(Si) prepared at 1535, 1635, 1730 and 2025°C.

function of silicon content. For PG(Si) prepared at 1535°C, d is about 1.5–1.6 g/cm³ in the range of 0–1 wt% Si but increases with silicon content above 1 wt% Si. For $T_{\text{dep}} = 1635^\circ\text{C}$ this critical silicon content is 0.4 wt%. For $T_{\text{dep}} = 1730^\circ\text{C}$, d is increased by the addition of only small amounts of silicon. For $T_{\text{dep}} = 2025^\circ\text{C}$, no remarkable changes in d with silicon content were observed ($d \approx 2.20$ g/cm³). The data by Marinković *et al.* are also included in Fig. 1. They show that the critical silicon content is 0.1 wt% for $T_{\text{dep}} = 1530^\circ\text{C}$.

The relation between the interlayer spacing (C_{002}) and silicon content is shown in Fig. 2. For $T_{\text{dep}} = 1535$, 1635 and 1730°C, C_{002} decreases with increasing silicon content. On the other hand Marinković *et al.* reported that C_{002} is independent of silicon content and is 3.41–3.42 Å for $T_{\text{dep}} = 1530^\circ\text{C}$.

Figure 3 shows the relation of the crystallite size (L_c) vs. silicon content. The critical points are about 1.0, 0.4 and 0.1 wt% Si for $T_{\text{dep}} = 1535$, 1635

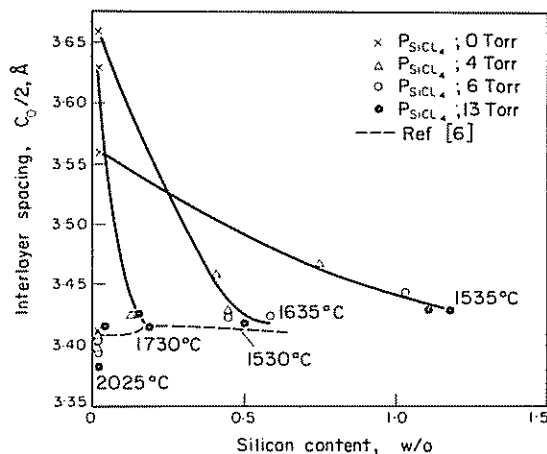


Fig. 2. Relationship between the interlayer spacing (C_{002}) and silicon content for PG(Si) prepared at 1535, 1635, 1730 and 2025°C.

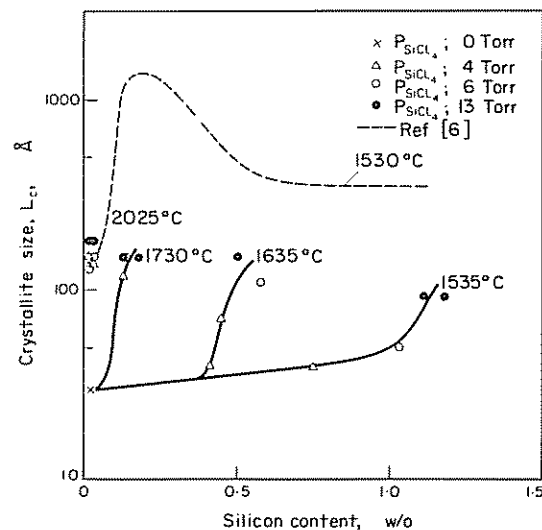


Fig. 3. Relationship between the crystallite size (L_c) and silicon content for PG(Si) prepared at 1535, 1635, 1730 and 2025°C.

and 1730°C, respectively. For $T_{\text{dep}} = 2025^\circ\text{C}$, L_c is independent of the silicon content (150–300 Å). However, as included in Fig. 3, Marinković *et al.* observed a maximum of L_c at 0.2 wt% Si for $T_{\text{dep}} = 1530^\circ\text{C}$.

Figures 1–3 illustrate the great difference between our data and those by Marinković *et al.* The latter authors reported that the silicon entered the PG lattice substitutionally and formed a separate phase of β -SiC below and above 0.15–0.20 wt%

Si and that this concentration corresponded to the solid solubility of silicon in carbon at 1530–1600°C. The results were interpreted by the catalytic effect of silicon on the carbon lattice. As shown in Figs. 1–3, the present experimental results seem to have maximum or minimum values of about 1.1, 0.5 and 0.15 wt% Si for $T_{\text{dep}} = 1535, 1635$ and 1730°C , respectively. From phase diagram considerations, however, it is unreasonable to explain these values as the solubility limit of silicon in carbon at each temperature. Since complex chemical vapor reactions are believed to occur in the process of co-deposition, the structures of the products may not be interpreted by a simple relationship such as a function of additive content [4, 6, 9]. Thus the maximum and minimum values shall not be discussed in this paper.

Schwartz and Bokros [5] investigated the catalytic graphitization of PG(Ti) by titanium and reported that when the deposition rates were very high PG(Ti) was not graphitized during the co-depositing run, while the catalysis by titanium occurred during deposition when the deposition rates were low. The deposition rates of PG(Si) were 50–270 $\mu\text{m/hr}$ in the report by Marinković *et al.* and 1500–2300 $\mu\text{m/hr}$ in our experiments. Such a difference in deposition rates may have a bearing on the different experimental results on the catalytic effect of silicon on the structures of PG(Si).

In order to understand the catalytic effects of additive elements on the properties of co-deposited PG, it is necessary to investigate the mechanism of the decomposition of gases and to know the

behavior of the complex intermediate products, which are formed by the pyrolysis.

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REFERENCES

1. Gridale R. O., Pfister A. C. and Roosbroeck W. van, *Bell Syst. Tech. J.* **30**, 271 (1951).
2. Tombrel F., *Rev. Hautes Temp. Refract.* **3**, 79 (1966).
3. Kotlensky W. V., *Carbon* **5**, 409 (1967).
4. Marinković S., Suznjević Č. and Dežarov I., *Carbon* **7**, 185 (1969).
5. Schwartz A. S. and Bokros J. C., *Carbon* **5**, 325 (1967).
6. Marinković S., Suznjević Č., Dežarov I., Mihajlović A. and Cerović D., *Carbon* **8**, 283 (1970).
7. Yajima S. and Hirai T., *J. Mat. Sci.* **4**, 416, 424, 685, 692 (1969).
8. Yajima S., Hirai T. and Hayase T., *Tanso (Carbons)*, No. 69, 41 (1972).
9. Bokros J. C., In *Chemistry and Physics of Carbon* (Edited by P. L. Walker, Jr.) Vol. 5, p. 1, Marcel Dekker, New York (1969).

Removal of Mercury by Sulfurized Carbons

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There has been much concern in recent years about pollution of our environment by mercury. It is well established now that mercury is present in trace quantities in U.S. coals [1, 2] and that a fraction of it ends up in the atmosphere as vapors through the stacks of power and heat generating plants. Mercury present as a polymerization catalyst on a carbon support has been recovered either by burning the spent carbon in a deficiency of air and condensing the volatilized mercury [3] or by first recovering mercury in solution by contacting with hypochlorite solution and then readsorb-

ing on a fresh batch of activated carbon from which the mercury is vaporized and condensed during carbon regeneration [4]. Use of iodized carbon for recovering mercury from a contaminated air stream was demonstrated by P'Yankov [5, 6].

It was discovered accidentally during a study of the catalytic oxidation of H_2S over carbon that a large amount of mercury from a mercury diffusion pump and mercury manometer was taken up by the sulfurized carbon catalyst at 140°C . The present note reports on the use of sulfurized carbons for removing mercury vapors from contaminated streams at 150°C .

Carbon prepared by carbonizing Saran at 900°C was selected as the support material for sulfur [7]. Sulfurization of this carbon to three sulfur load-

ings of 1.0, 4.0, and 11.8%, by weight, was carried out through oxidation of H_2S by O_2 in a fluidized bed at $140^\circ C$. Surface areas of the sulfurized carbons (65×150 mesh size) are given in Table 1. Areas were calculated from N_2 and CO_2 isotherms obtained at $-196^\circ C$ and $25^\circ C$, respectively. The original Saran carbon had a helium density of 2.18 g/cm^3 and a mercury density of 1.16 g/cm^3 —or a porosity of 47%.

Table 1. Physical properties of sulfurized Saran carbon

%S	Surface area, m^2/g	
	N_2	CO_2
0.0	875	932
1.0	738	—
4.0	718	—
11.8	< 1.0	580

The concentration of mercury in the air stream before and after contacting the sulfurized carbons was monitored, using a Perkin-Elmer Model 303 atomic absorption spectrometer. The spectrometer was calibrated by saturating the air stream with mercury maintained in thermostated baths at -15 , -20 , and $-30^\circ C$. The amounts of mercury in the saturated air stream was calculated from the known vapor pressures of mercury at these temperatures. Levels of mercury as low as 5 ppb, by volume, in the contaminated air stream could easily and reproducibly be detected. The contaminated air stream was prepared by bubbling air through a mercury bath maintained at $24^\circ C$. A concentration of 2.2 ppm, by volume, of mercury in air was calculated from a knowledge of its vapor pressure.

The contaminated air stream, with a contact time of 0.05 sec, flowed through a bed of 1 g of sulfurized carbon maintained at room temperature. Breakthrough profiles of mercury from beds of different sulfur loadings, are shown in Fig. 1. Increased sulfurization of the carbon decreased the breakthrough time for mercury at room temperature. Once breakthrough occurred, the rate of mercury build-up in the effluent from carbons of up to at least 4% sulfur loading was independent of amount of sulfur on the carbon, suggesting that adsorption was physical. A much higher rate of mercury build-up in the effluent stream when the 11.8% sulfur-containing bed was used is consistent with a substantial decrease in surface area of this carbon and obvious narrowing of the

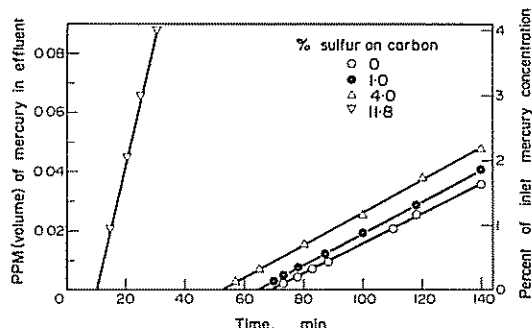


Fig. 1. Breakthrough curves of mercury in a dry air stream at $25^\circ C$ from Saran carbon beds containing varying amounts of sulfur.

diameter of the micropores. That is, the carbon dioxide area was much greater than the nitrogen area [8].

Moisture, deliberately added to the contaminated stream at 1.5% by volume, has a marked effect on reducing the breakthrough time, as can be seen from Fig. 2. For example, for the original

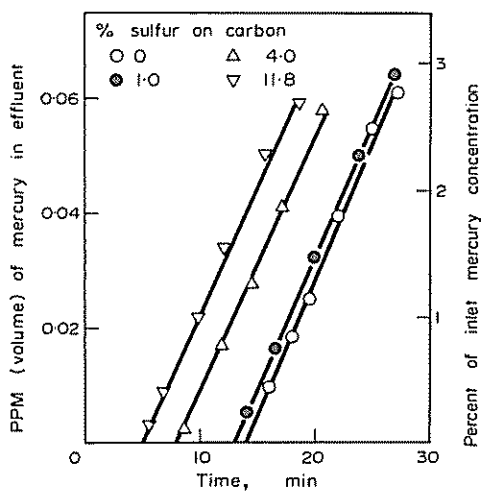


Fig. 2. Breakthrough curves of mercury in a wet air stream at $25^\circ C$ from Saran carbon beds containing varying amounts of sulfur.

Saran carbon the breakthrough time was reduced from 68 to 14 min in going from the dry to the moist stream. Also the rate of mercury build-up in the effluent from the moist stream following breakthrough was about twenty times faster than from the dry stream.

The breakthrough profile of mercury from a bed of carbon maintained at 150°C is shown in Fig. 3. The flow rate of the contaminated stream for this series of experiments was suitably adjusted so as to give the same residence time of 0.05 sec in the bed at 150°C as that at room temperature. Mercury from the unsulfurized bed broke through immediately and built up to 95% of the inlet concentration in less than 30 sec. For the sulfurized carbons, breakthrough occurred in the

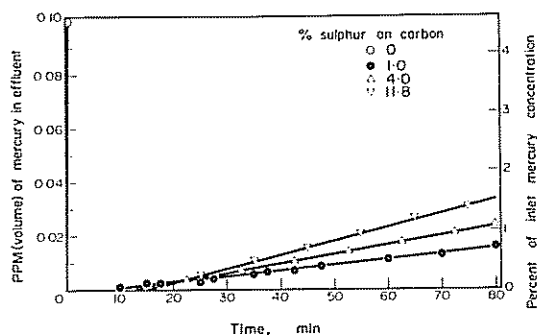


Fig. 3. Breakthrough curves of mercury in a dry air stream at 150°C from Saran carbon beds containing varying amounts of sulfur.

effluent between 7 and 15 min, but the rate of mercury build-up in the effluent was low. For the 1% sulfur-containing carbon, mercury broke through the bed after 7 min, but the rate of build-up was such that after 80 min only 0.8% of the inlet mercury was breaking through the bed. For carbons containing more than 1% sulfur, the breakthrough occurred later, but the rates of build-up were also somewhat higher.

The fact that the amount of mercury pick-up on the original Saran carbon at 150°C was negligible indicates that physical adsorption of mercury at this temperature is small. The much greater capacity of the sulfurized carbons at 150°C for mercury strongly suggests that mercury is reacting with sulfur on the carbon surface forming mercuric sulfide. Comparison of the ability of the original Saran carbon to remove mercury from dry air at 25°C with that of the Saran carbon sulfurized to 1% to remove mercury at 150°C is interesting. Whereas breakthrough of mercury

at 150°C was considerably shorter (7 min) than breakthrough at 25°C (68 min), the rate of build-up of mercury in the effluent was less at 150°C (0.013 ppm Hg/hr) than the rate at 25°C (0.030 ppm Hg/hr). Thus, it is probable that for longer times mercury concentration in the effluent from the original Saran carbon at 25°C would surpass that from the 1% sulfurized carbon at 150°C. It of course, would depend upon the long time capacity of the beds.

Since the spectrometer analyzed mercury present only as atoms, we do not know whether any mercuric sulfide that may have formed at 150°C left the carbon bed. However, TGA analysis on pure mercuric sulfide at 150°C showed a cumulative weight loss of less than 0.7% in 8 hr. On this basis we think it is likely that negligible mercuric sulfide left the sulfurized carbon bed.

The effect of moisture in the contaminated stream was briefly studied at 150°C for the carbon bed containing 1% sulfur. Mercury broke through the bed in 2 min, and the initial rate of build-up in the effluent was five times more rapid than for the dry stream. However, after about 8 min the mercury build-up rate in the effluent decreased and approached closely that observed for the dry stream.

Attempts to remove Hg^{2+} from aqueous solutions by Saran carbon sulfurized by H_2S oxidation or by Na_2S solution did not show promise.

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REFERENCES

1. Joensuu, O. I., *Science* **172**, 1027 (1971).
2. O'Gorman, J. V., Suhr, N. H., and Walker, P. L., Jr., *Appl. Spectrosc.* **26**, 44 (1972).
3. Knapsack, A. G., Brit. Pat. 1,162,328, (1969).
4. Parks, G. A. and Baker, R. E., Can. Pat. 875,476, (1971).
5. P'Yankov, V. A., *J. Gen. Chem. (USSR)* **6**, 1528 (1936).
6. P'Yankov, V. A., *J. Gen. Chem. (USSR)* **7**, 198 (1937).
7. Lamond, T. G., Metcalfe, J. E., and Walker, P. L., Jr., *Carbon* **3**, 59 (1965).
8. Walker, P. L., Jr. and Kini, K. A., *Fuel* **44**, 453 (1965).