

## STRUCTURE OF GRAPHITES

### Interlayer Spacings of Graphitic Carbons

BASED upon the X-ray diffraction studies of Nelson and Riley<sup>1</sup> on Ceylon natural graphite, Franklin<sup>2</sup> assigned an interlayer spacing of 3.3538 Å. (15° C.) to a carbon of 100 per cent graphite structure. Any carbon having a spacing of greater than this value is said to contain less than 100 per cent graphite structure—the amount less being given by the Franklin relationship<sup>2</sup>. We have looked at many graphitized carbons heat treated between 2,500 and 3,000° C. which have been produced from petroleum coke and coal-tar pitch coke materials. The lowest interlayer spacing found is  $3.3569 \pm 0.0004$  Å. (15° C.), indicating, according to the Franklin correlation, that the best artificial 'graphite' obtainable under usual graphitization conditions contains about 10 per cent turbostratic structure<sup>3</sup>.

In this work, four commercial graphitized carbons have been further heated in argon in the vicinity of 3,600° C. under a pressure of 10 atm. to investigate the possibility of lowering the interlayer spacing of the carbon down to or below that of Ceylon natural graphite. The above pressure prevented any significant sublimation of the carbon. The X-ray procedures used have been thoroughly described in a previous publication<sup>4</sup>.

Table 1 presents the X-ray diffraction data and other pertinent information on the samples. The interlayer spacing for the Ceylon graphite used is in close agreement with the value found by Nelson and Riley, particularly considering the probability that the two samples were not exposed to precisely similar geological conditions. The change in interlayer spacing of the carbons upon heat treatment is seen to be in qualitative agreement with the amount of impurities evolved. It is of further interest to note the parallel between the decrease in interlayer spacing and the irreversible change in thermal expansion above 2,200° C. during the first heating.

Even though increasing the graphitization temperatures of the carbons to 3,600° C. did produce some additional decrease in interlayer spacing, the lowest spacing obtainable still is indicative of a carbon containing only 90 per cent graphite structure. It is felt that the higher interlayer spacing values found for the artificial 'graphites' in comparison with that for Ceylon graphite is a result of the inability of the crystallites to grow as large in artificial 'graphites'. As Bacon<sup>5</sup> and Pinnick<sup>6</sup> have discussed, the inter-

Table 1. INTERLAYER SPACINGS OF CARBONS

Sample	d-Spacing (A.) (15° C.)	Relative amount of impurities evolved on heat treatment*	Per cent irreversible decrease in thermal expansion above 2,200° C. during first heating†
Ceylon natural graphite	3.3544 ± 0.0001		
Type A, < 3,000° C.	3.3623 ± 0.0004	Moderate	0.05
3,600	3.3604 ± 0.0001		
Type B, < 3,000° C.	3.3534 ± 0.0004	Moderate‡	0.03
3,600	3.3569 ± 0.0001		
Type 1, < 3,000° C.	3.3536 ± 0.0001	Negligible	0.00
3,600	3.3535 ± 0.0003		
Type 2, < 3,000° C.	3.3660 ± 0.0003	Large	0.25
3,600	3.3534 ± 0.0003		

\* The impurities consisted of lacy, white material appearing in the cooler regions of the furnace.

† The irreversible effects were only noticed in the direction normal to the extrusion axis or parallel to the moulding axis, that is, along the preferred c-axis orientation in both cases.

‡ There was somewhat less impurity for sample B than for A.

layer spacing decreases as crystallite diameter increases. This variation in interlayer spacing is due to the competition between the aligning forces between planes and the 'pinning' forces at their edges, the competition being a function of crystallite size. It is thought that the factor restricting crystallite growth in the graphitized carbons is the porosity developed previously during the coking cycle. These pores within the coke particles act as boundaries across which crystallite growth cannot occur. In comparison with this, Ceylon natural graphite particles are dense and non-porous, crystallite growth not having been restricted. Coking under a high static pressure would probably produce a better-ordered, lower porosity material, which upon subsequent graphitization would yield a carbon with an interlayer spacing more closely approaching that of Ceylon natural graphite.

We thank the Atomic Energy Commission, Contract No. AT(30-1)—1710, for support, in part, of this work. We express particular appreciation to N. S. Razor, of Atomics International, for heat-treating the samples, supplying the data on impurity release and thermal expansion, and offering many constructive criticisms on the manuscript.

<sup>1</sup> Nelson, J. B., and Riley, D. P., *Proc. Phys. Soc. Lond.*, 57, 477 (1945).

<sup>2</sup> Franklin, R. E., *Acta Cryst.*, 4, 253 (1951).

<sup>3</sup> Biscoe, J., and Warren, B. E., *J. Appl. Phys.*, 13, 364 (1942).

<sup>4</sup> Walker, P. L., jun., McKinstrey, H. A., and Pustinger, J. V., *Indust. and Eng. Chem.*, 46, 1651 (1954).

<sup>5</sup> Bacon, G. E., *Acta Cryst.*, 3, 137 (1950).

<sup>6</sup> Pluniek, H. T., *J. Chem. Phys.*, 20, 756 (1952).

## Graphitic Character of Kish

KISH is a waste product which forms on the surface of molten iron of high carbon content during the manufacture of steel. It is carbon which has been taken into solid solution with the iron and is afterwards evolved when the iron cools. Kish particles are shiny and flaky, resembling large particles of natural graphite. It is of interest to compare the graphitic character of kish with Ceylon natural graphite by interlayer spacing measurements. X-ray procedures used have been thoroughly described in a previous publication<sup>1</sup>.

Table 1 presents interlayer spacing data for kish and Ceylon natural graphite before and after various treatments. It is noted that the raw kish has an interlayer spacing significantly less than that of the Ceylon natural graphite. However, after acid treatment or graphitization at 2,800° C. the spacing is found to increase to the same value as Ceylon natural graphite.

The increase in interlayer spacing upon purification suggests that the carbon in the raw kish is subjected to considerable internal pressure because of the contraction of the molten iron. Assuming a volume compressibility of  $4.4 \times 10^{-6}$  cm.<sup>3</sup>/kgm. for carbon<sup>2</sup>, an internal pressure of ca. 100 kgm./cm.<sup>2</sup> is calculated for this particular kish sample. It is significant that acid treatment with only hydrochloric acid, which would remove the iron but not the silicon, increases the interlayer spacing to the Ceylon natural graphite value. This suggests that iron alone is subjecting the carbon to the high internal pressure.

It is suggested<sup>3</sup> that Ceylon natural graphite was crystallized from an iron melt in the same manner as kish. However, in the case of Ceylon graphite, it is not clear what happened to the iron which had to be originally present to produce the high internal pressure. Thus it is seen in the present work, since the interlayer spacing of Ceylon graphite does

Table 1. INTERLAYER SPACINGS OF KISH AND CEYLON NATURAL GRAPHITE BEFORE AND AFTER VARIOUS TREATMENTS

Sample	Treatment	d-Spacing (A.) (15° C.)	Ash content (per cent)
Kish	None	3.3523 ± 0.0002	48.4*
Kish	HCl	3.3544 ± 0.0001	23.2
Kish	HCl + HF	3.3540 ± 0.0001	2.9
Kish	2,800° C.	3.3543 ± 0.0003	0.6
Ceylon natural graphite	None	3.3543 ± 0.0001	2.1
Ceylon natural graphite	2,800° C.	3.3543 ± 0.0001	0.0

\* The main constituents were iron and silicon.

not change after graphitization, that the carbon (after mining) is not under an internal pressure. In the formation of Ceylon graphite, it would seem that the pressure necessary to produce good ordering and consequent large growth of the carbon crystallites, with an attendant small interlayer spacing, could be produced by the depth of the deposit. Assuming a density of 3.0 gm./c.c. for the Earth, a material at a depth of ca. 330 m. would be under a pressure of 100 kgm./cm.<sup>2</sup>.

We thank the Atomic Energy Commission, Contract No. AT(30-1)—1710, for support, in part, of the above work.

P. L. WALKER, JUN.  
GEORGE IMPERIAL

Fuel Technology Department,  
Pennsylvania State University,  
University Park, Pennsylvania.

October 15.

- <sup>1</sup> Walker, P. L., jun., McKinstry, H. A., and Pustinger, J. V., *Indust. and Eng. Chem.*, 46, 1651 (1954).  
<sup>2</sup> Basset, J., *C.R. Acad. Sci., Paris*, 213, 829 (1941).  
<sup>3</sup> Seeley, Sherwood B., and Emendorfer, Earl, "Encyclopedia of Chemical Technology", 3, 92 (The Interscience Encyclopedia, Inc., New York, 1949).