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Gas Content of Graphites

ARTIFICIAL graphite for use in graphite-moderated nuclear reactors, as anodes for mercury vapour rectifiers, and crucibles for vacuum fusion work should contain little gas. Otherwise, when the graphite is heated to operating temperatures, the gas is desorbed, resulting in adverse effects. For example, in the graphite-moderated nuclear reactor, hydrogen and carbon monoxide released from the graphite can interact with the fuel-cladding material (usually zirconium or stainless steel), resulting in hardening and embrittlement of the metal. Released carbon monoxide can disproportionate on cooler metal heat-exchanger surfaces depositing carbon, resulting in an adverse effect on the heat-transfer and flow properties of the system.

The present communication summarizes briefly results on the gas released from typical nuclear graphites (and an electrode graphite, for comparison) when degassed at an upper temperature between 1,500 and 2,000° C. *in vacuo*. For the degassing studies, a pumping system consisting of a liquid-nitrogen cold trap and a two-stage Van-Hespen mercury diffusion pump was used. Power to heat the graphite samples (1 in. long by $\frac{1}{2}$ in. diam.) was supplied by a 5-kW. high-frequency induction generator.

Table 1 presents results for the gas released from a sample of nuclear (*A*) and a sample of electrode graphite. Both graphites were graphitized in an Acheson-type furnace, as described by Abbott[1]. For the nuclear graphite, the graphitizing was done in a chlorine (gas purified) atmosphere[2]; and the cooling

Table 1. GAS RELEASED FROM GRAPHITES WHEN HEATED TO ELEVATED TEMPERATURES*

Property	Nuclear (A)†	Electrode‡
Total gas evolved (c.c./gm. at S.T.P.)	0·12	0·74
Analysis of gas evolved (vol. per cent)		
Hydrogen	59·4	30·8
Carbon monoxide	23·8	53·2
Carbon dioxide	12·7	16·0
Water	2·7	*N.D.*§
Hydrocarbons	1·4	*N.D.*

[*] Nuclear graphite degassed to 1,900° C.; electrode graphite degassed to 1,500° C.

[†] Surface area, 0·3 $m.^2/gm.$; porosity, 25·2 per cent; ash, <0·004 per cent.

[‡] Surface area, 0·4 $m.^2/gm.$; porosity, 31·3 per cent; ash, 0·11 per cent.

[§] Not determined.

was done in helium. For the electrode graphite, the atmosphere during heating and cooling consisted primarily of carbon monoxide and nitrogen which diffused in through the coke packing material. There were also significant pressures of carbon dioxide and oxygen at lower graphitizer temperatures, where the packing material did not completely convert oxygen to carbon monoxide.

For the results given in Table 1, runs were made on three different pieces of each graphite, with the results between each piece agreeing within 10 per cent. As expected[3], a considerably smaller quantity of gas is released from the nuclear than from the electrode graphite. This cannot be accounted for by a difference in Brunauer–Emmett–Teller surface area of the two materials. It is also noted that the percentage of carbon oxides in the evolved gas from the electrode graphite is considerably higher than from the nuclear graphite. Undoubtedly, this is a result of chemisorption by the electrode graphite of carbon monoxide, carbon dioxide and oxygen in the graphitizer and enhanced chemisorption of oxygen (because of the higher impurity content of the electrode graphite) at ambient temperatures following unpacking of the graphitizer. From other studies[4], it is concluded that the hydrogen released from a nuclear graphite is chemisorbed primarily on carbon atoms at crystallite edges.

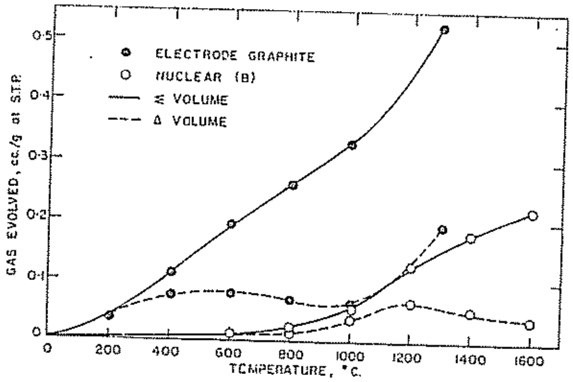

Fig. 1. Comparison of the integral and differential degassing curves for an electrode and a nuclear graphite

Gas-release from a thermally purified nuclear graphite (*B*), as a function of outgassing temperature, is compared with that from the electrode graphite (previously discussed) in Fig. 1 and Table 2. Because of the large amounts of carbon dioxide desorbed from the electrode graphite at low temperatures, a maximum in the differential degassing curve occurs at approximately 500° C. Another maximum (and higher) in the differential degassing curve of electrode graphite will occur above 1,300° C. On the other hand, for the thermally purified nuclear graphite (*B*), gas release below 800° C. is small; and only one maximum in the differential degassing curve is indicated at about 1,200° C. Interesting points to note from the results in Table 2 are:

(1) For the nuclear graphite (*B*), significant amounts of hydrocarbons are found in the gas up to 1,200° C. These gases consist mainly of C_2H_4, C_2H_2, C_2H_6, CH_4, and *iso*-C_4H_8, with C_2H_4 predominant at the lower temperatures and C_2H_2 predominant at the higher temperatures. It is uncertain what fraction of the hydrocarbons recovered is a result of reaction of carbon with desorbed hydrogen (ionized in the high-frequency induction coil)[4]. Carter and Greening[3] also reported hydrocarbons during the degassing of nuclear graphite.

Table 2. Analyses of Gas evolved from Graphites over Different Temperature Increments

Temperature increments (° C.)	Volume percentage of:				Hydrocarbons
	H_2	CO	CO_2	H_2O	
Nuclear (*B*)*					
20–600	34·4	20·8	16·9	7·7	20·2
600–800	43·0	10·8	10·0	4·6	30·7
800–1,000	54·6	7·2	3·1	2·0	32·2
1,000–1,200	63·9	7·3	1·4	nil	27·4
1,200–1,400	85·3	11·1	1·8	nil	1·8
1,400–1,600	70·8	24·4	2·5	nil	2·4
Electrode					
20–200	8·7	14·1	22·8	43·6	10·9
200–400	4·8	21·4	59·5	11·0	2·4
400–600	45·0	36·2	3·8	2·5	12·5
600–800	51·0	38·3	nil	nil	9·8
800–1,000	36·4	63·6	nil	nil	nil
1,000–1,300	24·5	75·0	nil	nil	nil

* Surface area, 0·4 $m.^2$/gm.; porosity, 25·2 per cent; ash content, <0·07 per cent.

(2) Considerably more water is recovered upon the low-temperature outgassing of electrode graphite than nuclear graphite (*B*). Since water adsorption on carbon occurs primarily at sites containing oxygen[5], this result is consistent with the fact that the electrode graphite originally contains more oxygen (ultimately desorbed as carbon dioxide and carbon monoxide).

(3) An increase in the carbon monoxide : hydrogen ratio of the desorbed gas at outgassing temperatures above 1,000° C. for the nuclear graphite (*B*) and above 600° C. for the electrode graphite indicates

Table 3. Effect of Graphitization Temperature and Atmosphere on Subsequent Gas Release upon Degassing at 2,000° C.

Property	Graphite*		
	I	II	III
Ash content (per cent)	0·87	0·044	0·0006
Total gas evolved (c.c./gm. at S.T.P.)	0·93	0·36	0·20
Analysis of gas evolved (vol. per cent):			
Hydrogen	12·5	27·5	32·0
Carbon monoxide	52·0	53·5	48·5
Carbon dioxide	19·5	15·0	11·5
Water	13·5	3·0	7·0
Hydrocarbons	2·5	1·0	1·0
Sample weight loss (per cent)	0·10	0·13	0·05

* The maximum graphitization temperatures for I, II and III are 2,600, 3,000 and 2,700° C., respectively.

that an important fraction of the carbon–oxygen complex leading to carbon monoxide has a higher thermal stability than has the chemisorbed hydrogen.

Table 3 presents results for the gas released from three samples of graphite following heat treatment under different conditions. All samples were outgassed at a maximum temperature of 2,000° C. Graphites I and II were heated and cooled under an atmosphere similar to that used for the electrode graphite. Graphite III was treated in a halogen atmosphere and cooled (flushed) in an inert gas atmosphere to about 1,500° C. It is seen again that the use of a halogen atmosphere during graphitization (and perhaps cooling, in part, in an inert atmosphere) is particularly effective in reducing the subsequent amount of gas released from the graphite. As previously discussed[3], this is related probably to enhanced removal of metallic impurities. These impurities can be oxidized and/or catalyse the chemisorption of gases on carbon. In the former case, the reduction of these metal oxides by carbon at high degassing temperatures leads to gaseous carbon oxides.

The sample weight losses, given in Table 3, are a result of both gas desorption and metal volatilization. For example, for graphite I, each process accounts for about 50 per cent of the loss of weight. Considerable material was collected on the cool walls of the desorption chamber during the degassing of sample I. An emission spectroscopic analysis indicated that the main constituents of the deposit were silicon, iron and magnesium.

The kinetics of the adsorption and desorption of hydrogen on nuclear graphite will be reported on in more detail elsewhere.

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