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OUTGASSING BEHAVIOR OF EGCR

MODERATOR GRAPHITE

J. P. Blakely
L. G. Overholser

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REACTOR CHEMISTRY DIVISION

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J. P. Blakely and L. G. Overholser

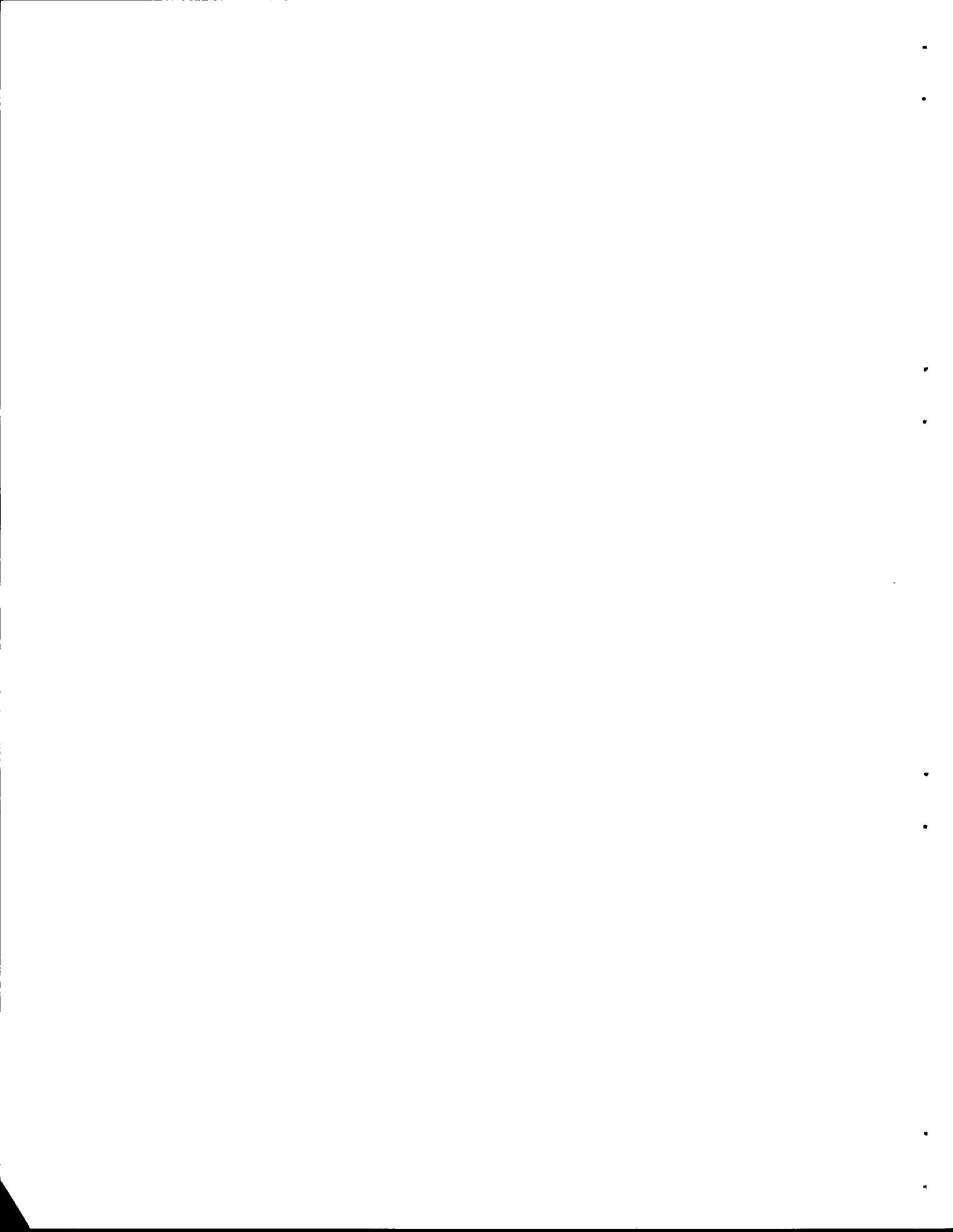
FEBRUARY 1964

OAK RIDGE NATIONAL LABORATORY
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OUTGASSING BEHAVIOR OF EGCR MODERATOR GRAPHITE

J. P. Blakely and L. G. Overholser

ABSTRACT

The outgassing characteristics of specimens of the EGCR moderator graphite stock have been determined in vacuo to a maximum temperature of 1000°C using external resistance heating and to 1800°C by induction heating. The specimens examined were cut from several locations in two of the 18-in. x 18-in. x 20-ft. graphite bars which had been prepared under fabrication conditions comparable to those used for the graphite columns present in the Experimental Gas-Cooled Reactor. Data are given which show the effect of the position of sampling of the bars on the density of the graphite. The volume and composition of desorbates obtained at 300, 600, and 1000°C as a function of specimen size and position of specimen within the bars also are given. The volume-time relationships at 300 and 600°C can be expressed satisfactorily by $v = A \log t + B$ over extended intervals of time. A linear relationship prevails at 1000°C only after heating for longer than ~ 800 min. The volume and composition of the desorbates obtained at 1000, 1400, and 1800°C using induction heating are tabulated.

I. INTRODUCTION

The Experimental Gas-Cooled Reactor (EGCR) core consists primarily of monolithic graphite columns which serve as moderator. The columns, which are 16-in. x 16-in. in cross-section and 20-ft. in length, each have four 5-1/4-in. diameter channels drilled the length of the column to contain graphite sleeves and fuel elements. The helium coolant will

flow upward through the core with the bulk of the gas passing inside the graphite sleeves but with some small fraction of the flow contacting the monolithic columns. Although relatively pure helium is to be charged into the reactor, it is expected that contamination of the coolant may result from inleakage of water and air and from outgassing of the large volume of graphite present. The latter will be most troublesome during the initial heatup. A purification system will be employed to maintain the concentration of the contaminants in the coolant below certain limits and thereby prevent excessive burnoff of the graphite during the life of the reactor. Contaminants such as H_2O , CO_2 , and O_2 will be responsible for the oxidation of the graphite. Excessive buildup of CO in the coolant could lead to the formation of carbon deposits in the heat exchanger through the disproportionation of CO . The CO_2 so produced would be returned to the core for further attack of the graphite. The design of a purification system is dependent mainly on the rate of inleakage of water during prolonged operation of the reactor, but also must be capable of handling the contaminants arising from the outgassing of the graphite during the early stages of reactor operation. Thus, any information related to the outgassing characteristics of the EGCR graphite, including possible catalyst poisons, would be helpful in the design of the purification system.

Considerable outgassing data have been reported¹⁻⁶ for a variety of graphites. In general, however, these results were obtained from material prepared from cokes differing from those used for the EGCR graphite and extruded in much smaller sizes than the EGCR columns. Due to this lack of reliable data for graphites of the EGCR type, experimental studies were undertaken. Two 36-in. long blocks were cut from two of the 20-ft. columns which had been manufactured under the same conditions used for the columns present in the EGCR. These blocks were subdivided and specimens machined from various locations were used in the degassing studies. The density and ash content of specimens cut from various positions were determined. The volume and composition of the desorbate as well as the rate of release of the gas were measured at various temperatures using specimens cut from the various locations. The resulting data

¹R. R. Eggleston, R. L. Carter, W. J. Greening and R. E. Durand, Graphite Outgassing, NAA-SR-Memo-1240 (Jan. 21, 1955).

²R. C. Asher, US/UK Meeting on the Compatibility Problems of Gas-Cooled Reactors, Oak Ridge National Laboratory, Feb. 24-26, 1960, TID-7597, Book 2, p 504.

³J. P. Redmond and P. W. Walker, Jr., Nature 186, 72 (1960).

⁴J. J. Gill, Outgassing Experiments with Mold Grade Graphite for the HNPf, NAA-SR-6291 (Dec. 1, 1961).

⁵L. G. Overholser and J. P. Blakely, Proc. Fifth Carbon Conf. Pergamon Press (1962) Vol. 1, p 194.

⁶L. G. Overholser and J. P. Blakely, Outgassing Characteristics of Various Graphites, ORNL-3396 (Feb. 14, 1963).

give some insight into the variations of these quantities as a function of specimen position and are useful in describing the overall behavior of these large graphite bars.

II. EXPERIMENTAL

A. Materials

The EGCR moderator graphite was manufactured by National Carbon Company as extruded bars having a nominal cross-section of 18-in. x 18-in. and a length of 20-ft. A regular particle size mix (maximum particle size of ~ 0.03 -in.) of Continental Lake Charles No. 1 needle coke was used as filler and coal tar pitch as binder. The so-called "AGOT graphitizing process" was used which involves a maximum graphitization temperature of $\sim 2800^{\circ}\text{C}$ and subsequent cooling in a reactive atmosphere.

Two full-length bars were cut into 36-in. long blocks and one block from each of the two bars was taken for sampling. The blocks, which are designated as File 16, Block 2 and File 3, Block 4, came from positions in the original bar corresponding to a minimum distance of 36-in. from the ends of the bars. Detailed sampling procedures for File 16, Block 2 and File 3, Block 4 are given in Appendixes A and B, respectively. The identification process may appear to be complicated. It will suffice, however, to note that all specimens cut from the central region of the cross sections used carry a B in the code, whereas those from the outer region are marked with either A or C. The purity, density, and dimensions of the graphite specimens are given in subsequent sections.

B. Procedure

Detailed descriptions of the equipment used for the degassing studies are given elsewhere.⁷ Briefly, two systems were used to heat the graphite in vacuo; one utilized a tube furnace for temperatures to 1000°C, the other an induction heater for temperatures to 1800°C. In the latter case, a cylindrical specimen 1-1/4-in. diameter x 1-in. long mounted on a tungsten wire was contained in a water cooled quartz tube. For most of the studies with the tube furnace, a cylindrical specimen 1-1/2-in. diameter x 2-in. long was used (specimens ranging from 3/4-in. in diameter and from 1 to 4-in. in length were examined in a few cases).

The system, with the specimen in place, was evacuated at ~ 30°C to a pressure of 10^{-3} mm Hg or less at the start of a run. The temperature was raised to the desired level and held constant for the designated period of time. The rate of release of gas at the end of the heating period usually was less than ~ 2%/hr of the total volume evolved at this temperature. The desorbate was removed continuously by a Toepler pump and collected in a calibrated manifold equipped with a McLeod gauge and suitable sample bulbs. After collection of the gas was completed at the designated temperature, gas samples were removed and the collection system pumped out prior to raising the graphite temperature to the next desired

⁷GCR Semiann. Prog. Rep., Dec. 31, 1958, ORNL-2676, p. 147; June 30, 1959, ORNL-2767, p. 190.

level. All reported volumes of gas are at STP. Gas analyses were performed by the Analytical Service Groups using a mass spectrometer and a gas chromatograph.

III. RESULTS AND DISCUSSION

A. Density, Ash Content, Weight Loss, and Volume of Gas Evolved

Data presented in Table 1 indicate that the expected "skin effect" arising from the extrusion process produced variations in the density of the graphite. Specimens cut from the outer regions had densities ranging from 1.70 to 1.74 g/cm³, whereas the density of the material from the central regions varied from 1.64 to 1.71 g/cm³. Specimen 34B-28a contained a small inclusion of low density material not found in the adjacent regions. It is not known whether or not similar occlusions were present in other portions of the bars not sampled.

The ash content of the graphite also varied, being higher in the central than the outer regions. The differences, undoubtedly, were due to the less efficient removal of the impurities from the interior of the bar during the graphitization treatment at ~ 2800°C. The major constituents of the ash were Ca, Fe, and V.

Although there is considerable scatter among the values reported in Table 1 for the loss in weight upon degassing the various specimens, significantly lower values were found for the A and C series than for the B series at both 1000

Table 1. Ash Content, Density, Weight Loss and Gas Volume
for EGCR Graphite Specimens

Specimen No.	Specimen Size in Inches (dia x length)	Max. Temp. of Degassing (°C)	Density (g/cm ³)	Total Ash (ppm)	Wt. Loss %	Gas Volume (cm ³ /100 cm ³ of graphite)
162A-121b	1.5 x 2.0	1000	1.74	120	0.009	14.9
162A-131b	1.5 x 2.0	1000	1.74	120	0.015	13.9
162B-223b	1.5 x 2.0	1000	1.71	300	0.019	18.1
162B-213b	1.5 x 2.0	1000	1.71	300	0.019	21.6
34C-12b	1.5 x 2.0	1000	1.70	125	0.005	11.0
34C-11b	1.5 x 2.0	1000	1.71	125*	0.009	11.3
34B-27b	1.5 x 2.0	1000	1.67	275*	0.018	15.7
34B-28b	1.5 x 2.0	1000	1.64	275*	0.016	11.9
34B-29b	1.5 x 2.0	1000	1.69	275	0.013	15.4
34B-29c	1.5 x 2.0	1000	1.70	275	0.016	17.3
34B-25	1.0 x 2.0	1000	1.67	275	0.018	15.5
34B-22	1.0 x 2.0	1000	1.68	275	0.013	14.5
34B-24a	2.25 x 2.0	1000	1.69	275	0.010	14.8
34B-210b	1.5 x 2.0	1000	1.68	275	0.016	17.0
34B-211	1.0 x 4.0	1000	1.70	275	0.011	12.9
34B-213	1.0 x 4.0	1000	1.69	275	0.014	13.1
34B-212	1.0 x 1.0	1000	1.66	275	0.021	12.6

Table 1. (continued)

Specimen No.	Specimen Size in Inches (dia x length)	Max. Temp. of Degassing (°C)	Density (g/cm ³)	Total Ash (ppm)	Wt. Loss %	Gas Volume (cm ³ /100 cm ³ of graphite)
162A-111a	1.25 x 1.0	1800	1.73	120	0.034	14.1
162A-121a	1.25 x 1.0	1800	1.71	120	0.036	23.4
162A-131a	1.25 x 1.0	1800	1.72	120	0.050	37.3
162B-213a	1.25 x 1.0	1800	1.69	300	0.046	45.7
162B-223a	1.25 x 1.0	1800	1.69	300	0.056	43.6
162B-211a	1.25 x 1.0	1800	1.69	300*	0.056	48.6
162A-112a	1.25 x 1.0	1800	1.72	120*	0.026	43.9
162A-122a	1.25 x 1.0	1800	1.70	120*	0.039	48.3
162A-132a	1.25 x 1.0	1800	1.72	120	0.044	48.3
162B-222a	1.25 x 1.0	1800	1.68	300	0.047	46.5
162B-212a	1.5 x 1.0	1800	1.70	300	0.065	54.8
34C-12a	1.25 x 1.0	1800	1.71	125	0.030	49.3
34C-11a	1.25 x 1.0	1800	1.71	125	0.032	56.5
34B-27a	1.25 x 1.0	1800	1.65	275	0.054	48.2
34B-28a	1.25 x 1.0	1800	1.60	275	0.073	75.9
34B-29a	1.25 x 1.0	1800	1.67	275	0.053	59.1
34B-210a	1.25 x 1.0	1800	1.67	275	0.043	46.7
34C-14a	1.25 x 1.0	1800	1.71	125*	0.033	51.2

∞

Table 1. (continued)

Specimen No.	Specimen Size in Inches (dia x length)	Max. Temp. of Degassing (°C)	Density (g/cm ³)	Total Ash (ppm)	Wt. Loss %	Gas Volume (cm ³ /100 cm ³ of graphite)
34C-13a	1.25 x 1.0	1800	1.71	125	0.039	38.4

* Experimental values, with at least one analysis for each location - series of specimens. Numbers listed for other specimens are considered to be representative for specimens cut from that location in the original bar.

and 1800°C. A fair correlation exists between the loss in weight at 1800°C and the original ash content plus the weight of gas removed by heating to 1800°C. Determination of the ash content of a number of specimens after degassing at 1800°C showed that 75 to 90% of the impurities were removed by such treatment. Degassing at 1000°C, however, had no significant effect on the ash content. The loss in weight observed upon degassing to a maximum temperature of 1000°C was greater (in many cases by a factor of 2) than the weight of gas removed. Part of the loss in weight must be associated with the initial pumpdown at 30°C, since the ash content was not changed significantly. A similar effect may be masked in part by the larger changes in weight occurring in the degassing runs at 1800°C.

The total volumes of gas evolved by the various specimens at either 1000 or 1800°C also are given in Table 1 for comparison with the reported loss in weight. The scatter among the data precludes any meaningful comparison of the individual specimens. A comparison of the average values, however, shows that both the loss in weight and volume of gas evolved are less for the A and C series (outer) than for the B series (inner). The data given for the low-density specimen 34B-28a show that, where gross effects occur, the correlation is more easily discernible.

B. Degassing to a Maximum Temperature of 1800°C

The volume and composition of gas evolved by the various specimens upon heating to a maximum temperature of 1800°C are

given in Table 2. Considerable variations in both the volume and composition of the desorbate obtained from the different specimens are evident. Averaged values indicate that the material from the central portion of the bars evolved a somewhat larger volume of gas characterized by a slightly larger CO/H₂ ratio than did material from the outer regions. The bulk of the graphite in the cross sections sampled had a total gas content of 40 to 50 cm³/100 cm³ of graphite. This range also should be applicable not only to the two bars examined but also to the moderator graphite loaded into the EGCR. The hydrogen and carbon monoxide concentrations in the desorbate obtained from the bars at 1800°C should fall in the range of 35 to 40 and 55 to 60 vol %, respectively.

Data also are given in Table 2 for several degassing runs in which the desorbates were collected at 1000, 1400, and 1800°C. The total volume and composition of the desorbate obtained under these conditions are in general agreement with those found when a single collection was made at 1800°C. Low concentrations (0.1 to 0.5 vol %) of hydrogen sulfide were found for all of the specimens examined and in a few instances carbon disulfide was detected. The evolution of hydrogen sulfide persisted even above 1400°C. Nitrogen also was evolved in small amounts over the entire temperature range. A low concentration of a complex mixture of hydrocarbons was noted in most cases. Methane was usually the major constituent. Compounds of other mass numbers have

Table 2. Volume and Composition of Gas Evolved by EGCR Graphite from
30°C to 1800°C (specimens 1.25-in. dia x 1.0-in. long)

Specimen No.	Temp. (°C)	Gas Volume (cm ³ /100 cm ³ of graphite)	Gas Constituents, Volume %					
			H ₂	Hydro-carbons	H ₂ O	CO ₂	N ₂	CO
162A-112a	1800	43.9	41	-	-	1	1	57
162A-121a	1800	23.4	38	1	1	1	2	57
162A-122a	1800	48.3	42	1	-	-	1	56
162A-132a	1800	48.3	41	-	-	1	1	57
162A-131a	1000	22.4	35	3	4	5	1	51
	1400	7.7	41	1	1	-	2	54
	1800	7.2	37	-	-	-	3	60
	Total	37.3	37	2	2	3	2	53
162B-211a	1800	48.6	41	1	-	1	2	55
162B-212a*	1800	54.8	33	-	-	1	2	64
162B-222a	1800	46.5	37	-	-	1	2	59
162B-223a	1800	43.6	37	1	1	1	2	59

Table 2 (continued)

Specimen No.	Temp. (°C)	Gas Volume (cm ³ /100 cm ³ of graphite)	Gas Constituents, Volume %					
			H ₂	Hydro-carbons	H ₂ O	CO ₂	N ₂	CO
162B-213a	1000	29.2	37	1	-	-	1	60
	1400	10.3	69	1	1	-	3	26
	1800	6.2	45	1	-	-	5	49
	Total	45.7	46	1	-	-	2	51
34B-27a	1800	48.2	33	-	-	-	2	65
34B-28a	1800	75.9	31	-	-	-	1	67
34B-29a	1800	59.1	33	-	-	-	1	65
34B-210a	1000	24.0	37	1	1	1	2	59
	1400	10.7	45	1	1	-	1	50
	1800	12.0	33	-	-	-	4	63
	Total	46.7	38	1	-	-	2	58
34C-11a	1800	56.5	36	-	1	1	1	61
34C-12a	1800	49.3	28	-	1	1	1	69

Table 2 (continued)

Specimen No.	Temp. (°C)	Gas Volume (cm ³ /100 cm ³ of graphite)	Gas Constituents, Volume %					
			H ₂	Hydro-carbons	H ₂ O	CO ₂	N ₂	CO
34C-13a	1000	21.9	48	2	1	1	1	47
	1400	10.7	35	2	-	-	3	58
	1800	5.8	38	1	-	-	7	54
	Total	38.4	43	1	-	1	2	51
34C-14a	1000	18.0	46	1	1	1	1	50
	1400	19.7	39	1	-	-	1	59
	1800	13.5	24	1	-	-	3	71
	Total	51.2	37	1	-	1	2	59

* This specimen only was 1.5-in. x 1.0-in.

been detected by mass spectrometry but positive identification of these was very difficult or impossible.

C. Degassing at 300, 600, and 1000°C

The volume and composition of the desorbate obtained by degassing various specimens at 300, 600, and 1000°C are presented in Table 3. The customary scatter of data is evident, but averaged values indicate that the material from the central portions of the bars released a larger volume of gas than did that from the outer regions. The gas released by the latter also was characterized by a larger H₂/CO ratio. The differences in gas composition as a function of position are shown graphically in Fig. 1. These averaged values clearly show that the H₂/CO ratio was larger in the desorbate obtained for material from the outer regions of the bar than that found for the specimens taken from the inner regions for temperature intervals of 30 to 1000°C, and 600 to 1000°C. Differences in the CO₂/CO ratio in the desorbate collected between 300 and 600°C are evident although in most cases the ratio is close to unity. It appears that this ratio was somewhat larger in the desorbates obtained from specimens cut from the inner regions than from specimens taken from the outer portions of the bars.

Small quantities of nitrogen were evolved at all temperatures up to and including 1000°C. Data given in Table 2 show that the evolution of nitrogen persisted at temperatures up to at least 1400°C. Water was the main constituent evolved

Table 3. Volume and Composition of Gas Evolved by EGCR Graphite at 300, 600, and 1000°C (specimens 1.5-in. dia x 2.0-in. long, except as noted)

Specimen No.	Temp. (°C)	Gas Volume (cm ³ /100 cm ³ of graphite)	Gas Constituents, Volume %						
			H ₂	Hydro-carbons	H ₂ O	CO ₂	N ₂	CO	SO ₂
162A-121b	300	0.9	2	26	51	9	5	7	-
	600	2.7	10	20	16	20	2	31	1
	1000	11.3	48	2	2	1	2	44	-
	Total	14.9	38	7	7	5	3	40	-
162A-131b	300	0.6	2	15	56	7	9	7	4
	600	2.9	10	19	16	20	2	31	2
	1000	10.4	56	1	1	2	1	41	-
	Total	13.9	44	6	6	5	1	36	-
162B-223b	300	0.6	2	8	67	3	16	1	3
	600	3.1	6	16	17	15	5	14	28
	1000	14.4	35	3	1	4	1	55	-
	Total	18.1	29	5	6	6	3	47	5

Table 3. (Continued)

Specimen No.	Temp. (°C)	Gas Volume (cm ³ /100 cm ³ of graphite)	Gas Constituents, Volume %						
			H ₂	Hydro-carbons	H ₂ O	CO ₂	N ₂	CO	SO ₂
162B-213b	300	0.7	2	10	60	5	17	3	5
	600	2.9	5	17	16	19	4	17	22
	1000	18.0	34	1	1	6	3	55	-
	Total	21.6	29	3	5	7	3	49	3
34C-12b	300	0.4	10	8	45	8	19	7	4
	600	1.9	19	26	18	11	6	16	5
	1000	8.7	45	2	1	1	2	47	-
	Total	11.0	40	5	5	3	4	40	-
34C-11b	300	0.5	1	5	67	5	13	3	5
	600	1.7	10	22	22	13	7	19	5
	1000	9.1	43	2	1	1	1	53	-
	Total	11.3	36	5	7	3	2	46	-
34B-28b	300	0.5	2	4	75	5	13	1	1
	600	2.0	5	23	15	28	6	16	7
	1000	9.4	34	3	1	1	1	59	1
	Total	11.9	27	5	7	6	3	49	1

Table 3. (Continued)

Specimen No.	Temp. (°C)	Gas Volume (cm ³ /100 cm ³ of graphite)	Gas Constituents, Volume %						
			H ₂	Hydro-carbons	H ₂ O	CO ₂	N ₂	CO	SO ₂
34B-29b	300	0.8	1	5	50	13	17	6	6
	600	2.1	5	17	23	22	6	17	10
	1000	12.5	38	2	1	2	1	55	-
	Total	15.4	31	4	7	5	3	48	1
34B-25(1)	300	0.6	1	7	60	5	19	3	4
	600	2.9	5	20	28	17	7	16	6
	1000	12.0	36	2	2	2	2	55	2
	Total	15.5	29	5	9	5	3	46	3
34B-22(1)	300	0.7	1	7	63	3	18	1	5
	600	2.6	8	22	18	19	6	20	6
	1000	11.2	34	3	1	1	2	58	1
	Total	14.5	28	6	7	4	3	49	2
34B-24a(2)	300	0.4	1	4	58	7	22	2	4
	600	2.5	4	18	18	30	5	18	6
	1000	11.9	34	3	1	1	1	59	1
	Total	14.8	28	5	5	5	1	51	2

Table 3. (Continued)

Specimen No.	Temp. (°C)	Gas Volume (cm ³ /100 cm ³ of graphite)	Gas Constituents, Volume %						
			H ₂	Hydro-carbons	H ₂ O	CO ₂	N ₂	CO	SO ₂
34B-211(3)	300	0.6	1	3	47	6	19	3	7
	600	1.7	5	13	28	16	8	17	13
	1000	10.6	28	3	1	2	1	66	1
	Total	12.9	23	4	7	4	2	55	2
34B-213(3)	300	0.5	2	4	51	9	28	3	4
	600	1.7	5	14	23	31	9	13	5
	1000	10.9	24	2	1	2	1	70	-
	Total	13.1	21	4	6	6	4	60	1
34B-212(4)	300	0.5	3	4	51	8	24	4	5
	600	1.9	5	15	16	24	9	15	17
	1000	10.2	24	2	1	1	1	70	1
	Total	12.6	21	4	6	5	3	59	3
34B-29c*	1000	17.3	30	11	5	6	3	40	5

(1) 1.0-in. dia x 2.0-in. long

(2) 2.25-in. dia x 2.0-in. long

(3) 1.0-in. dia x 4.0-in. long

(4) 1.0-in. dia x 1.0-in. long

* Degassed only at 1000°C.

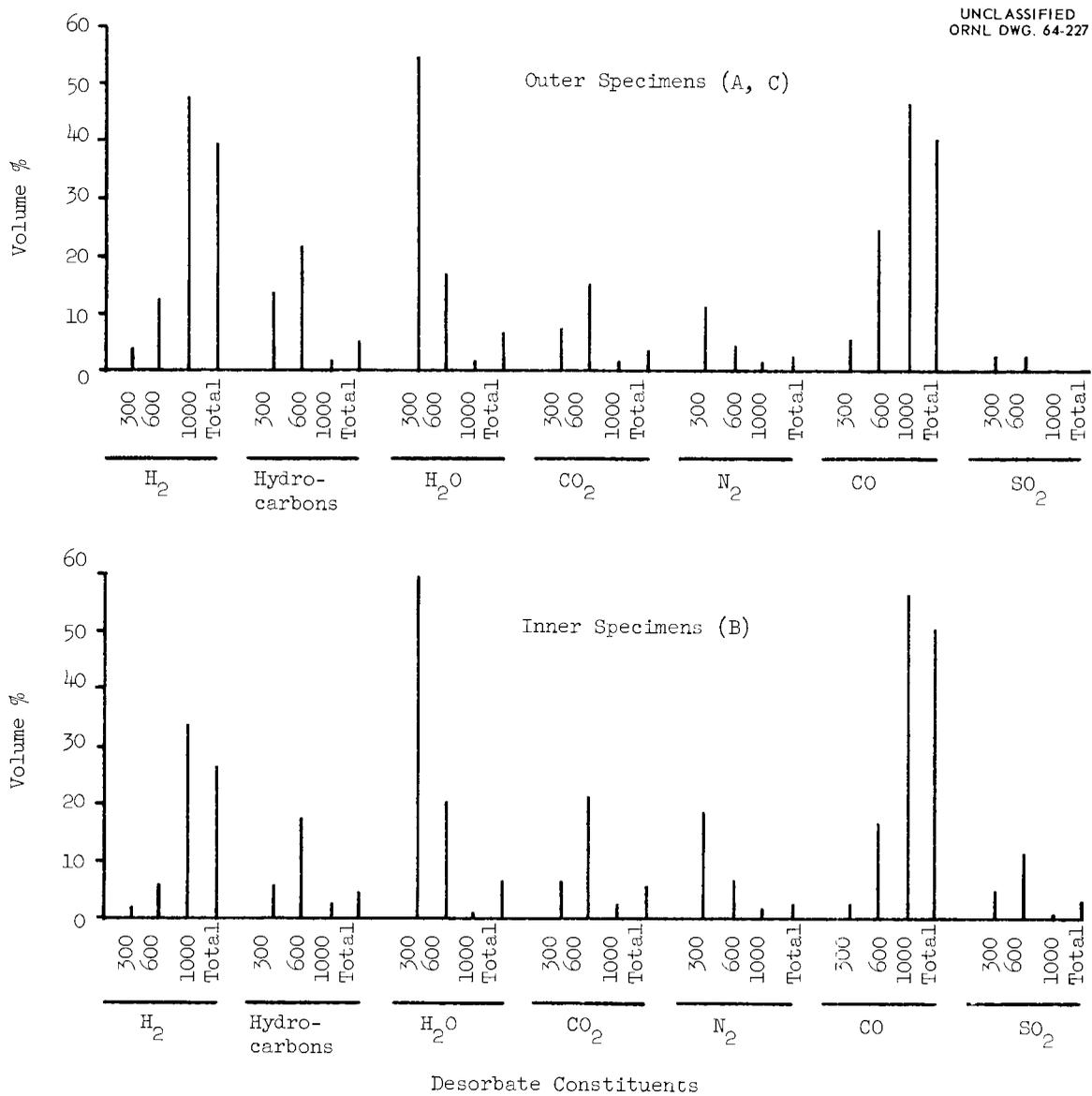


Fig. 1. Averaged Values of Volume Percentages Obtained for the Various Constituents of the Desorbates Evolved (300, 600, 1000°C, and total) by Specimens Machined from Various Locations in the Bars.

between 30 and 300°C. Very little water was found in the desorbate collected above 600°C. The total volume of water collected was a small fraction of the total desorbate, and in most cases did not exceed 1 cm³/100 cm³ of graphite. A complex mixture of hydrocarbons was evolved mainly at temperatures up to 600°C. The small quantity of hydrocarbons found at 1000°C probably was due to cracking of the hydrocarbons at the higher temperatures. It also is possible that the adsorbed hydrocarbons were largely removed at the lower temperatures. Methane was the principal hydrocarbon evolved and usually accounted for about one-half of the total hydrocarbons observed. Positive identification of the other hydrocarbons by means of the mass spectrometer was extremely difficult or impossible in most cases. The evolution of SO₂ is discussed in the following section.

D. Degassing at Smaller Temperature Intervals to a Maximum Temperature of 1000°C

The occurrence of substantial quantities of SO₂ in the desorbate collected at the lower temperatures prompted a more thorough study of its release using smaller temperature intervals. The results obtained for two specimens are given in Table 4. The data indicate that SO₂ was released at the lowest temperature used (200°C), but was not present at temperatures much above 600°C. The maximum release appears to have occurred between 400 and 600°C. Small quantities of H₂S and CS₂ were released over the entire temperature range and, as mentioned in an earlier section, also were found at

Table 4. Volume and Composition of Gas Evolved by EGCR Graphite
at Various Temperature Intervals up to 1000°C
(Sample 1.5-in. dia x 2.0-in. long)

Specimen No.	Temp. (°C)	Gas Volume (cm ³ /100 cm ³ of graphite)	Gas Constituents, Volume %							
			H ₂	Hydro-carbons	H ₂ O	CO ₂	N ₂	CO	SO ₂	H ₂ S + CS ₂
34B-27b	200	0.4	2	3	57	3	27	-	8	-
	300	0.4	1	7	43	9	27	3	8	2
	400	0.8	2	8	27	16	19	9	18	2
	500	0.7	4	11	36	21	8	14	5	-
	600	1.4	7	15	15	27	3	30	1	-
	700	1.4	19	23	11	15	5	26	-	-
	800	2.0	28	9	2	3	2	53	-	0.3
	900	4.2	39	5	1	0.2	2	54	-	-
	1000	4.4	40	2	-	0.2	2	55	-	0.5
	Total		15.7	28	8	9	6	5	42	2
34B-210b	500	2.2	3	18	32	17	12	10	4	5
	600	1.8	6	12	18	36	3	19	5	0.4
	700	2.0	34	21	10	6	4	21	-	2
	800	3.1	34	7	8	1	2	49	-	0.1
	900	2.4	34	4	-	0.3	2	58	-	0.6
	1000	5.5	31	1	1	0.3	2	64	-	0.9
	Total		17.0	26	8	9	7	4	44	1

temperatures above 1400°C. The amounts of sulfur compounds found for the EGCR graphite were larger than those noted for most of the other graphites examined.⁶ This suggests that the coke used for the EGCR graphite contained considerable sulfur and that the graphitization process was not effective in removing the sulfur. Since most of the sulfur will be released during the initial heatup of the graphite, any poisoning of the metal used in the catalytic oxidizer in the purification system is most apt to occur at this time.

The data also indicate that only small amounts of water vapor were released above 700°C. Any adsorbed water present at the higher temperatures reacted with the graphite to form H₂ and CO. The amount of hydrocarbons released became very small as the temperature exceeded 900°C. Cracking of the hydrocarbons at the elevated temperatures would account for the decrease observed. Small amounts of N₂ were found at all temperatures. The CO₂ evolution peaked near 600°C, whereas the amount of CO released increased continuously with increasing temperature.

E. Rate of Release of Desorbate at Various Temperatures

The results of studies of the volumes of gas released by a number of graphites as a function of time at 300, 600 and 1000°C have been reported previously.^{5,6} Plots of the log of time versus the volume of gas released gave essentially linear relationships for most of the graphites examined at 300 and 600°C. The volume-time relationships could be expressed

as an Elovich-type of equation of the form, $\text{volume} = A \log t + B$, where the constant A is the slope and corresponds to the volume of gas released during a tenfold increase in time t . Some departures from linearity were observed at 1000°C , mainly during the early stages of outgassing. A linear relationship usually prevailed after about 12 hours of heating. The increase in slope observed during the early stages was due in part to the uncertainty in assigning a starting time. This was due to the considerable period of time required to heat the specimen from 600 to 1000°C . Another probable cause of the nonlinearity stems from the change in composition of the desorbate with time. Frequently the H_2/CO ratio in the desorbate increased with time particularly during the period in which the slope increased. The rate of desorption of H_2 from graphite has been studied⁸ over the relevant temperature range. Similar data are not available for the desorption of CO and consequently the effect on the slope of varying the H_2/CO ratio must remain a conjectural matter.

Plots of the volume-time relationships and the values for the slopes at 300 and 600°C are given in Fig. 2 and Table 5, respectively. The plots show that an essentially linear relationship between the volume and log of the time prevailed for the several EGCR graphite specimens at 300 and 600°C . Values for the slopes at 300°C ranged from 0.07 to

⁸J. P. Redmond and P. L. Walker, Jr., J. Phys. Chem. 64, 1093 (1960).

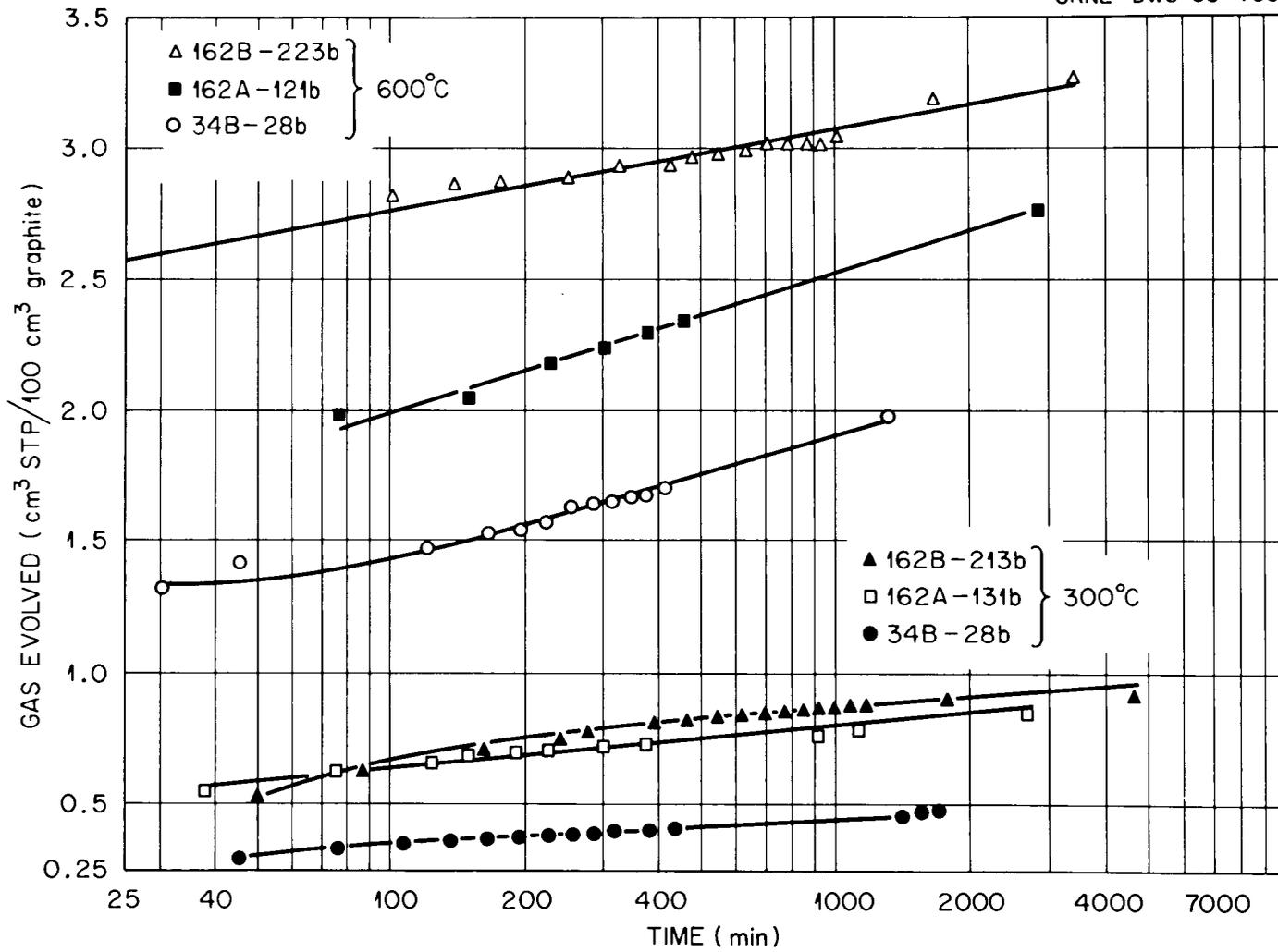


Fig. 2. Volume-Time Plots for EGCR Graphite at 300 and 600°C.

Table 5. Values for the Constants A and B in the Equation
 $V^* = A \log t + B$ for EGCR Graphite Specimens
 at Various Temperatures.

(Size 1.5-in. dia x 2.0-in. long, except as noted)

Specimen No.	Temp. (°C)	Interval t (min.)	A	B
162A-131b	300	30 - 1000	0.13	0.19
162B-213b	300	100 - 1400	0.10	0.34
34C-12b	300	50 - 1200	0.11	0.09
34C-11b	300	60 - 1400	0.082	0.25
34B-28b	300	75 - 1400	0.067	0.22
34B-29b	300	40 - 1360	0.16	0.26
34B-25 (1)	300	150 - 1400	0.080	0.34
34B-22 (1)	300	50 - 1400	0.15	0.25
34B-24a (2)	300	150 - 1400	0.090	0.11
34B-211 (3)	300	100 - 1400	0.090	0.27
34B-212 (4)	300	100 - 1400	0.090	0.21
162A-121b	600	90 - 1100	0.53	0.9
162B-223b	600	100 - 1300	0.35	1.9
162B-213b	600	30 - 2800	0.44	1.3
34C-12b	600	100 - 4000	0.42	0.13
34C-11b	600	120 - 2800	0.42	0.18
34B-28b	600	120 - 1300	0.46	0.50
34B-29b	600	75 - 1000	0.39	0.78
34B-25 (1)	600	70 - 1330	0.82	0.21
34B-22 (1)	600	100 - 1375	0.53	0.70
34B-24a (2)	600	150 - 1250	0.75	-0.01
34B-211 (3)	600	65 - 1350	0.40	0.40
34B-213 (3)	600	50 - 1100	0.28	0.91
34B-212 (4)	600	25 - 1350	0.39	0.60

Table 5 (continued)

Specimen No.	Temp. (°C)	Interval t (min.)	A	B
162A-131b	1000	100 - 600	2.6	0.37
		1250 - 3200	4.6	-5.5
162B-213b	1000	150 - 3000	3.1	4.1
		4000 - 10,000	5.2	-2.8
162B-223b	1000	200 - 1200	2.7	3.1
34C-12b	1000	150 - 400	2.2	-1.3
		1200 - 4100	4.6	-8.0
34C-11b	1000	120 - 300	2.7	-1.8
		1200 - 2600	5.5	-9.8
34B-28b	1000	50 - 440	2.1	1.2
		1125 - 1380	7.0	-12.8
34B-29b	1000	100 - 420	3.2	-1.0
		1080 - 3020	7.0	-12.0
34B-25 (1)	1000	50 - 300	2.6	0.66
		300 - 1375	4.4	-3.8
		1400 - 2750	6.2	-9.5
34B-22 (1)	1000	50 - 350	2.4	1.0
		350 - 1200	3.7	-2.2
		1300 - 2700	5.8	-8.7
34B-24a (2)	1000	150 - 350	3.0	-1.4
		1250 - 5600	5.5	-8.8

Table 5 (continued)

Specimen No.	Temp. (°C)	Interval t (min.)	A	B
34B-211 (3)	1000	50 - 400	2.5	0.73
		1300 - 2200	6.0	-9.5
34B-213 (3)	1000	60 - 375	2.2	2.0
		1050 - 2500	4.7	-4.9
34B-212 (4)	1000	60 - 400	2.3	0.85
		1050 - 2500	5.0	-6.9
34B-210b	500	90 - 1620	0.37	1.0
	600	100 - 1100	0.95	-1.2
	700	100 - 300	0.58	-0.92
		1200 - 2700	1.9	-4.8
	800	125 - 560	1.3	-2.4
		1250 - 3500	2.5	-6.2
	900	100 - 400	0.96	-1.5
		1250 - 2800	2.2	-5.1
	1000	60 - 150	1.0	-1.5
		1075 - 4000	4.2	-10.3

* Volume expressed as cm³ (STP) of evolved gas/100 cm³ of graphite, time in minutes. Specimens were degassed at 300°C prior to degassing at 600°C, and degassed at 300 and 600°C before degassing at 1000°C. The intercepts do not include

Table 5 (continued)

the gas removed at the lower temperatures.

- (1) Specimens 1.0-in. dia x 2.0-in. long
- (2) Specimens 2.25-in. dia x 2.0-in. long
- (3) Specimens 1.0-in. dia x 4.0-in. long
- (4) Specimens 1.0-in. dia x 1.0-in. long.

0.16, those at 600°C from 0.28 to 0.82. No significant effect of the position of sampling of the graphite blocks was evident at either temperature. The outgassing of the graphite can be a problem only at start-up of the reactor or following some subsequent exposure to air because of the logarithmic type of release. After several days at temperature, the rate of evolution of gas would be extremely low and decreasing. For example, at 600°C less than 0.01 ft³ of gas/ft³ of graphite would be released during a 90-day period starting 10 days after the graphite reached this temperature. The data in Table 3 suggest that the main constituents of the gas released at 600°C would be CO, CO₂, H₂O, and a mixture of hydrocarbons.

Plots of the volume-time relationships and values for the slopes at 1000°C are given in Fig. 3 and Table 5, respectively. The plots in Fig. 3 show that the slopes increased with time during the early stages of degassing and that after about 1000 min. they became essentially constant. As mentioned earlier, part of the increase in slope may be associated with the uncertainty in the zero time. These specimens were degassed at 600°C for prolonged periods of time and the temperature then raised to 1000°C. No thermocouple was attached to the specimens and consequently it was not possible to ascertain the time at which the temperature of the specimen reached 1000°C. Also it was noted earlier that the composition of the desorbate changed with time at 1000°C; the H₂/CO ratio

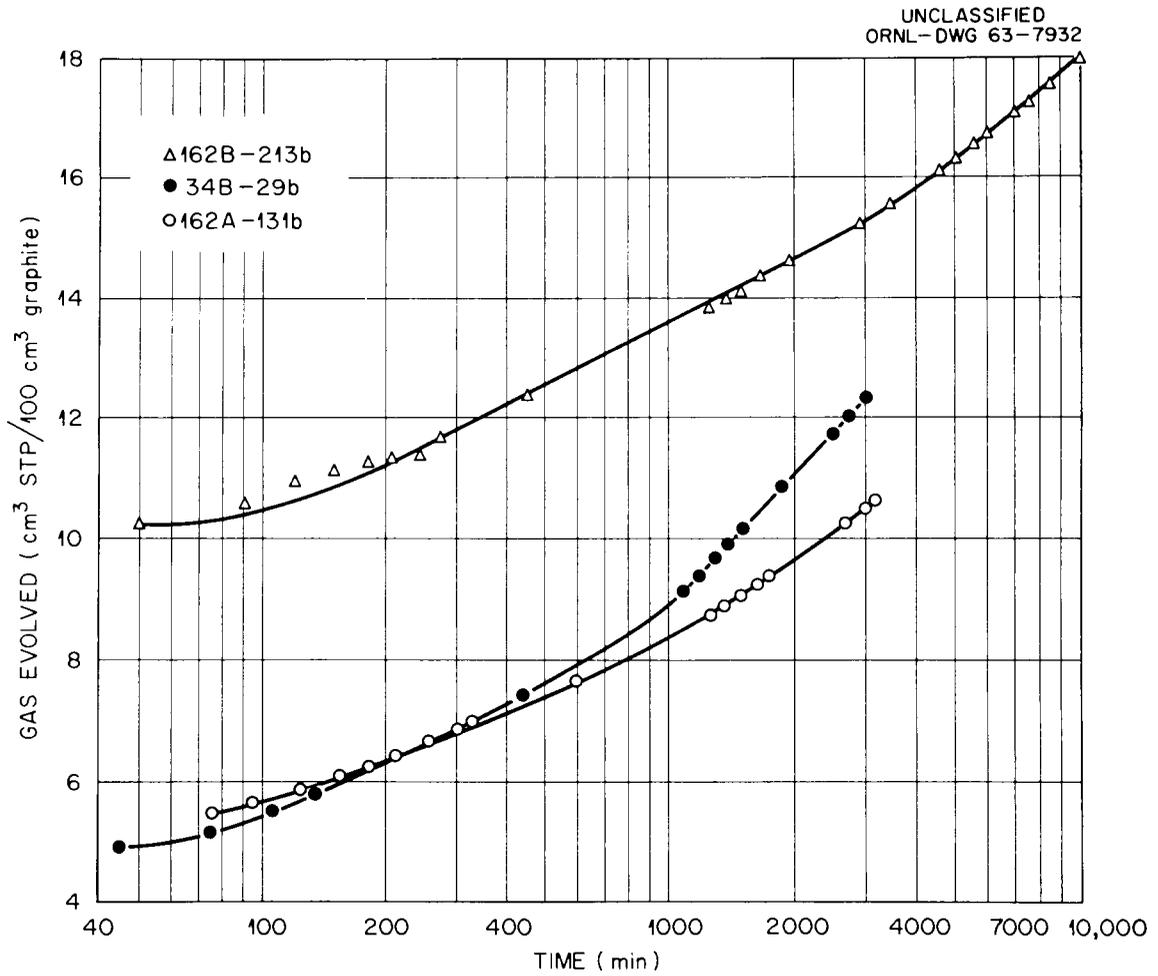


Fig. 3. Volume-Time Plots for EGCR Graphite at 1000°C.

increased with time. This could result in a change in slope, assuming that the desorption energies differ for H_2 and CO . The values given for the slopes at different time intervals in Table 5 were obtained by making a somewhat arbitrary division of the time. The important thing to note is that the slopes in general increased for about the first 1000 min. and then became essentially constant. The final slopes obtained at $1000^\circ C$ are some ten times as large as those measured at $600^\circ C$. The desorbates obtained at $1000^\circ C$ (Table 3) consisted mainly of CO and H_2 with CO/H_2 ratios of approximately 1 and 1.5, respectively, for specimens cut from the outer and central regions of the bars.

Most of the specimens examined were 1.5-in. diameter x 2.0-in. long. A few specimens having different dimensions were studied to ascertain whether or not the size of the specimen had any important effect on the rate of evolution, volume, or composition of the desorbate. The results given in Table 3 show that the specimen size had no significant effect on either the volume or composition of gas evolved. Likewise, the data plotted on Figs. 4 and 5 show that this variable had little effect on the rate of release of the desorbate at 300, 600, and $1000^\circ C$. The variations observed were no greater than those found for different specimens having the same dimensions cut from adjacent positions in the bars. In view of these results, it would appear that the outgassing behavior of the bored moderator columns would

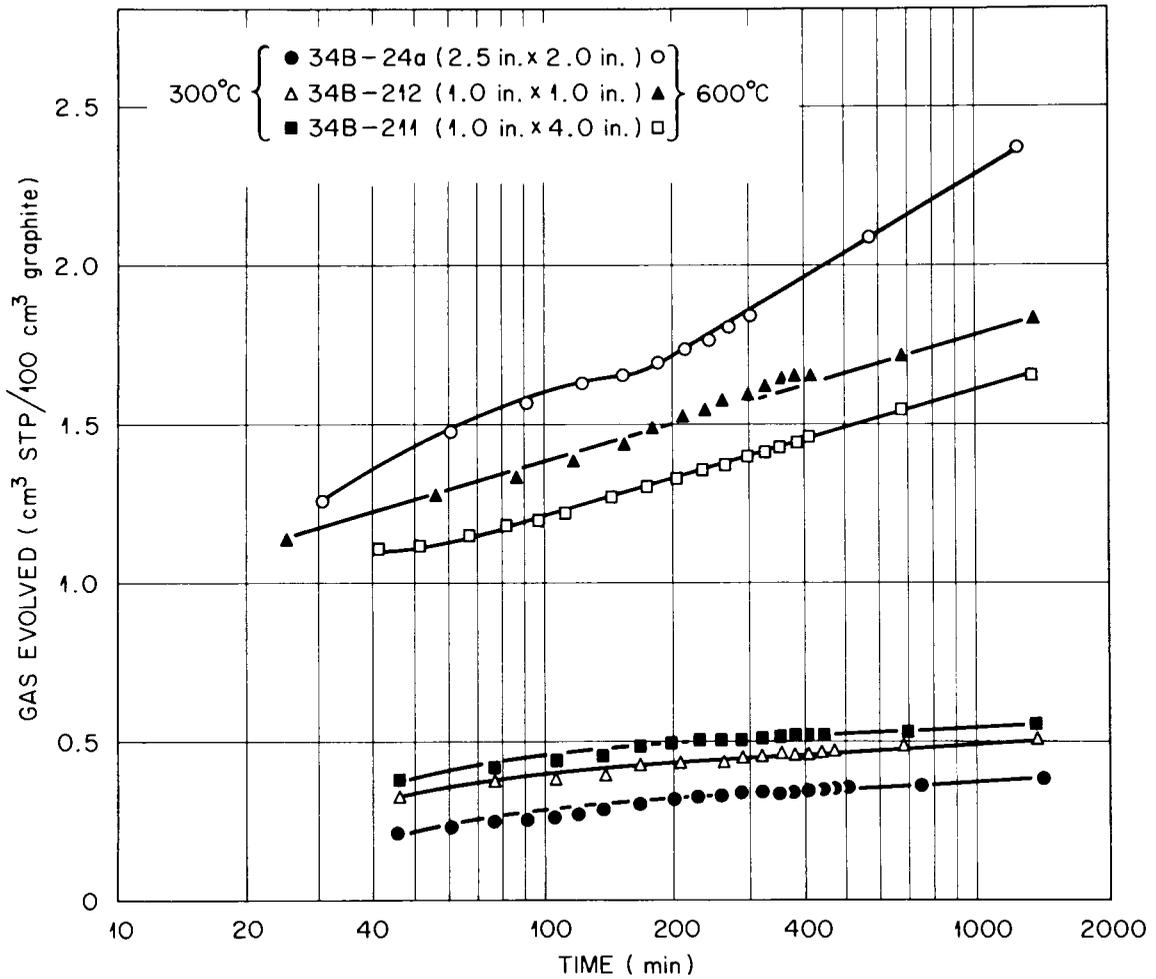
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Fig. 4. Volume-Time Plots for Various Size Specimens of EGCR Graphite at 300 and 600°C.

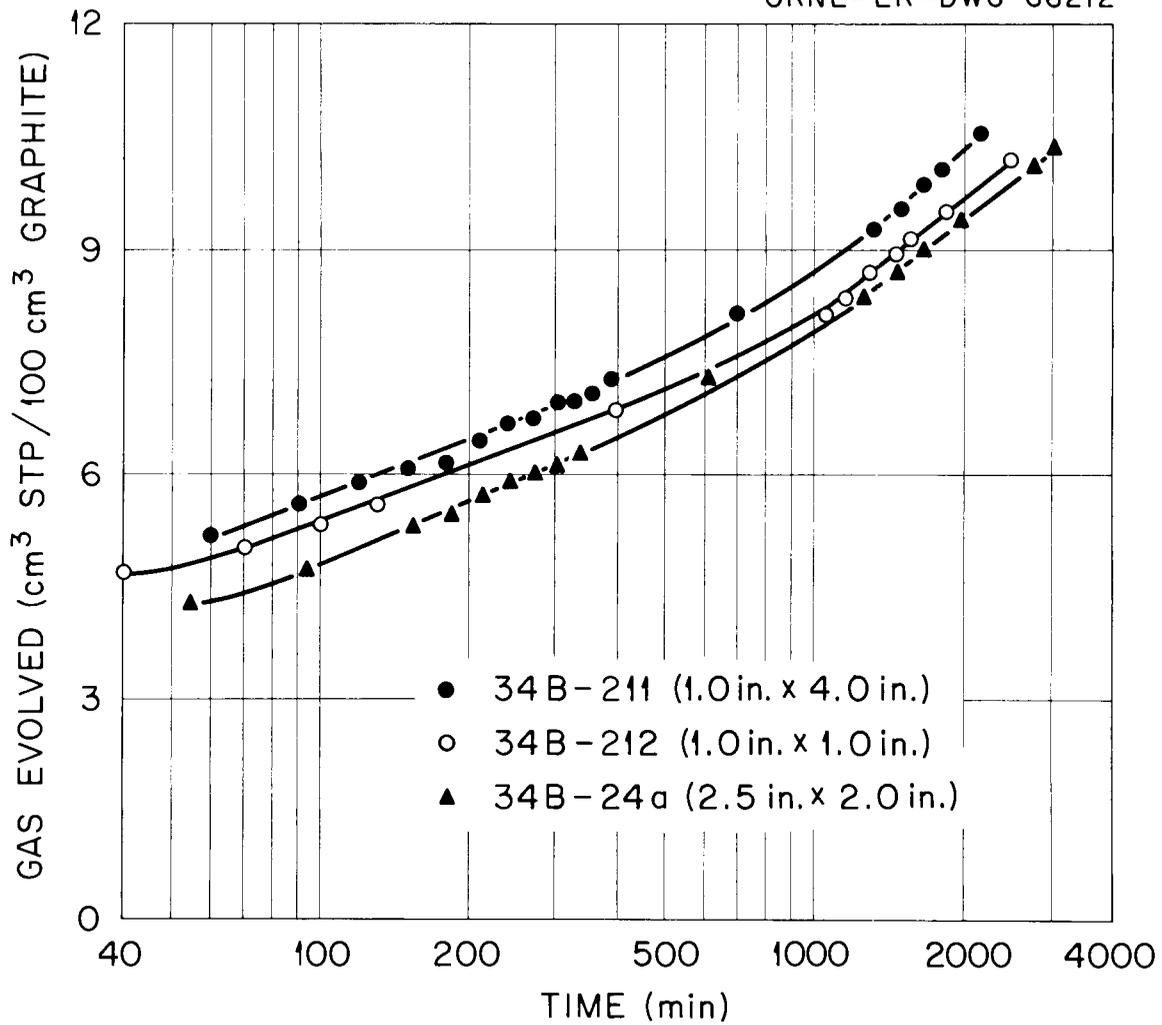
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Fig. 5. Volume-Time Plots for Various Size Specimens of EGCR Graphite at 1000°C.

not differ markedly from the specimens studied, even though the geometry is different.

Data are given in Table 5 and Fig. 6 which show the volume-time relationships obtained by degassing a single specimen of graphite at successively higher temperatures in the range 500 to 1000°C. The general shape of the 500 and 600°C plots are similar, both showing an essentially linear relationship between the volume of gas evolved and the log of time. The slope is larger at 600 than at 500°C, as anticipated. Starting at 700°C, the type of desorption must be different as evidenced by the change in shape of the curves. As seen in Table 4, this also is the temperature at which a marked increase in the concentration of H₂ and a decrease in the concentration of CO₂ were observed. The general appearance of the curves obtained at 700°C and above is similar and, except for the 800 to 900°C interval, the slope increases with temperature as might be expected. No satisfactory explanation can be offered for the slight decrease in slope noted upon going from 800 to 900°C.

These data illustrate quite vividly the changes in the character of the outgassing behavior which may occur when a single specimen of graphite is degassed at various temperatures for prolonged periods of time. Not only may the evolution process change with temperature, but also with time at a constant temperature as evidenced by the change in composition of the desorbate. This suggests that the kinetics of

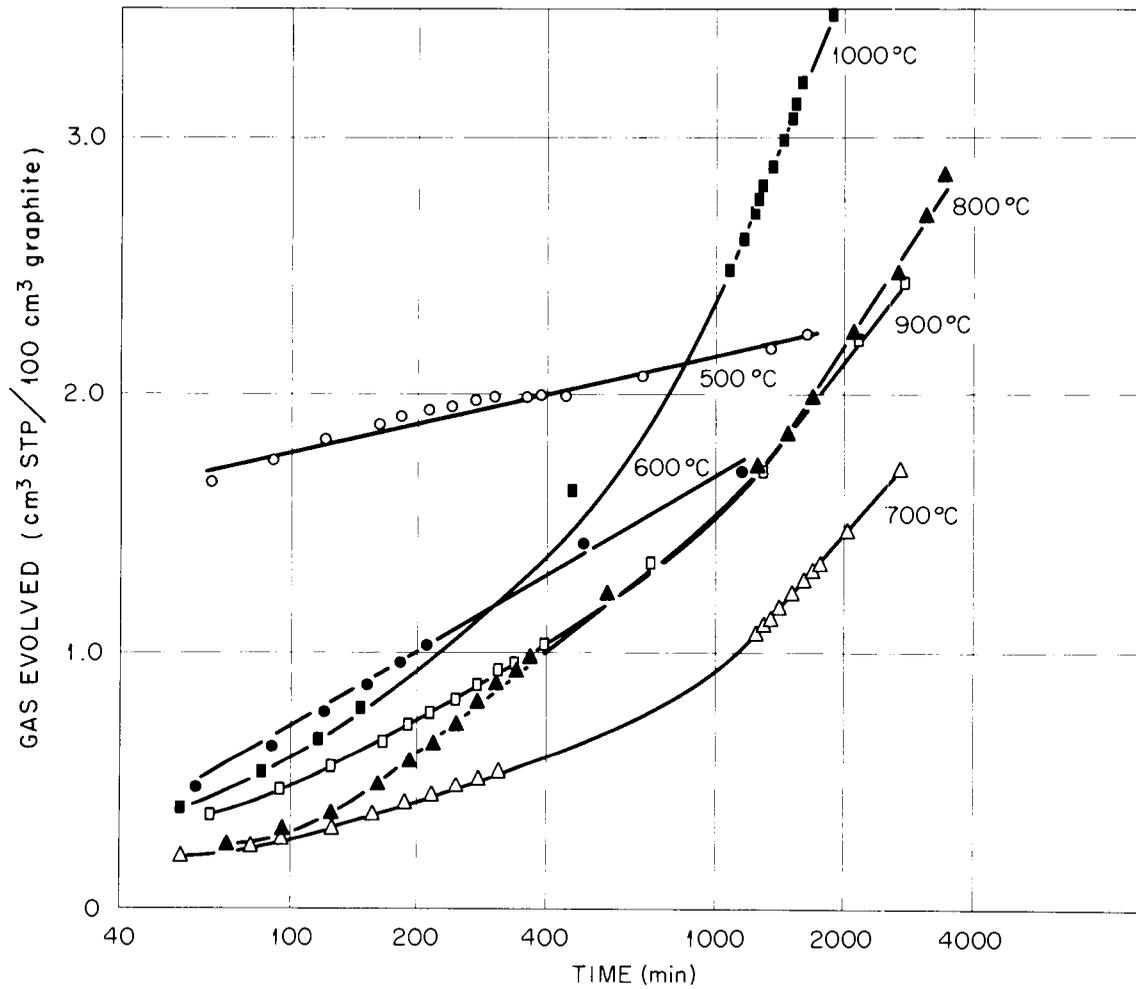
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Fig. 6. Volume-Time Plots for EGCR Graphite in the Range 500-1000°C.

desorption are complex, and consequently activation energies for the process are difficult to establish. In view of the complexity of the system, it is surprising that the Elovich plots are linear in so many instances. One must remember that the data presented were collected under a more or less empirical set of experimental conditions, and that the effects of a number of variables, including the pressure over the specimens, have not been examined.

IV. CONCLUSIONS

The extrusion process used in the manufacture of the large bars of EGCR moderator graphite produced some variations in density, but these do not appear to be greater than those occurring in bars of smaller cross sections of other nuclear-grade graphites. The density is significantly higher in the outer regions than in the interior. The presence of one inclusion of low density material in the portions sampled suggests that small pockets of such material may occur occasionally in this grade of graphite.

The ash content varies from ~ 120 ppm in the outer regions to ~ 300 ppm in the interior. These values compare favorably with those observed for other nuclear-grade graphites and probably result from the use of a coke having a relatively low ash content. The principal impurities present are iron, vanadium, and calcium.

Slightly larger volumes of desorbate were released by specimens cut from the interior than were released by those cut from the outer regions. The latter gave desorbates having

larger H₂ to CO ratios. These observations, along with the larger ash content found in the interior, indicate that the graphitizing furnace temperatures were too low and/or the heating period too short to remove the metallic impurities and the carbon oxide as effectively from the center material as from the outer material.

An abnormally large amount of sulfur is present in the interior regions as evidenced by the release of substantial volumes of SO₂ at temperatures below 600°C. Poisoning of platinum catalysts present in the purification system by the sulfur compounds could occur during the initial heat-up of the graphite if the gas is circulated through the catalytic converter at this time.

Results obtained for various sizes of specimens show that neither the volume nor the rate of desorbate evolved is particularly sensitive to changes in geometry. The scatter in the data precludes any rigorous examination of this variable.

The evolution of the gas can be satisfactorily described at 300 and 600°C by an Elovich expression of the form $v = A \log t + B$ for all periods of time examined. A linear relationship was noted at 1000°C only after heating for longer than ~ 800 minutes.

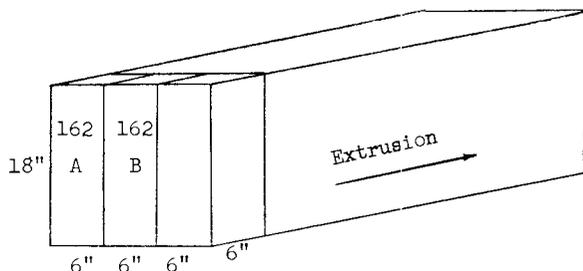
A rapid initial heat-up of the graphite to 600°C in the EGCR would release at most ~ 4 ft³ (STP) of gas/100 ft³ of graphite. The principal constituents would include H₂O, CO,

CO₂, and CH₄ plus other hydrocarbons. Lesser amounts of SO₂, N, and H₂ would be present. A slow heat-up program, as planned for the reactor, would permit removal of the evolved gas without any large buildup. Since the evolution of gas is a logarithmic function of time, the rate of release would be very low during reactor operation, excluding possible radiation effects.

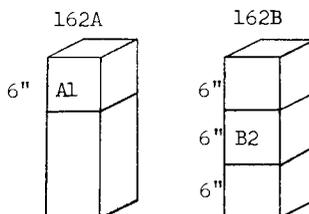
APPENDIX A

Cutting Charts for EGCR Graphite Specimens for File 16, Block 2

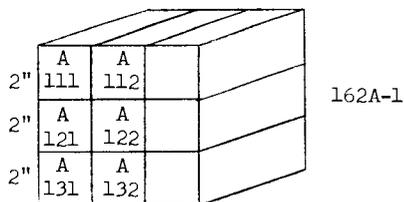
- (1) A six-inch slab was cut from the end of the 18-in. x 18-in. No. 162 and divided as shown.



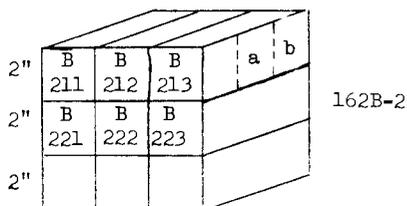
- (2) The resultant 162A (6-in. x 6-in. x 18-in.) and 162B (6-in. x 6-in. x 18-in.) were further divided as shown



- (3) Sections 162A-1 (6-in. x 6-in. x 6-in.) and 162B-2 (6-in. x 6-in. x 6-in.) were further subdivided.



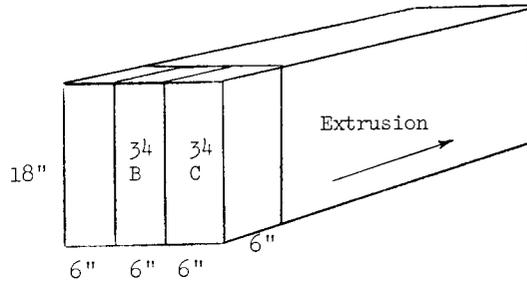
- (4) From the numbered sections (all 2-in. x 2-in. x 6-in.) were machined two cylinders each, the *a* cylinders being 1.25-in. dia. x 1.0-in. long, and the *b* cylinders being 1.5-in. dia. x 2.0-in. long. The un-numbered sections were reserved for future use or discarded.



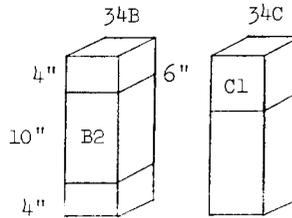
APPENDIX B

Cutting Charts for EGCR Graphite Specimens for File 3, Block 4

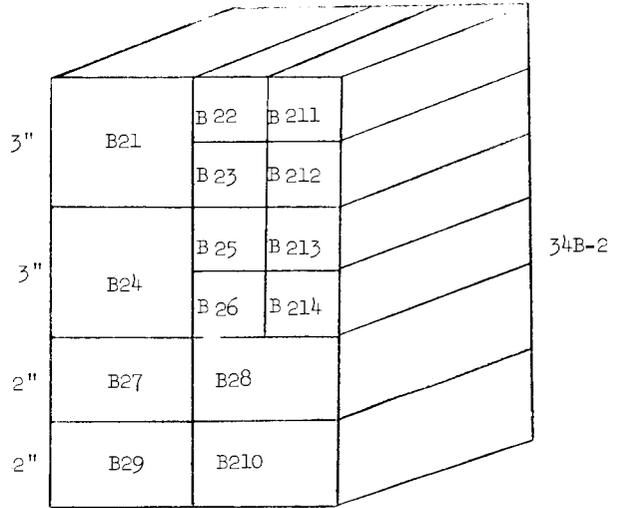
- (1) A six-inch slab was cut from the end of the 18-in. x 18-in. No. 34 and divided as shown.



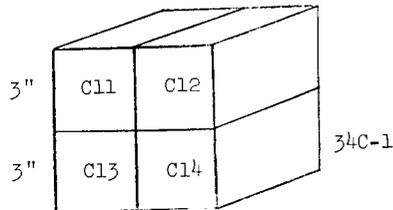
- (2) The resultant 34B and 34C (both 6-in. x 6-in. x 18-in.) were further divided as shown.

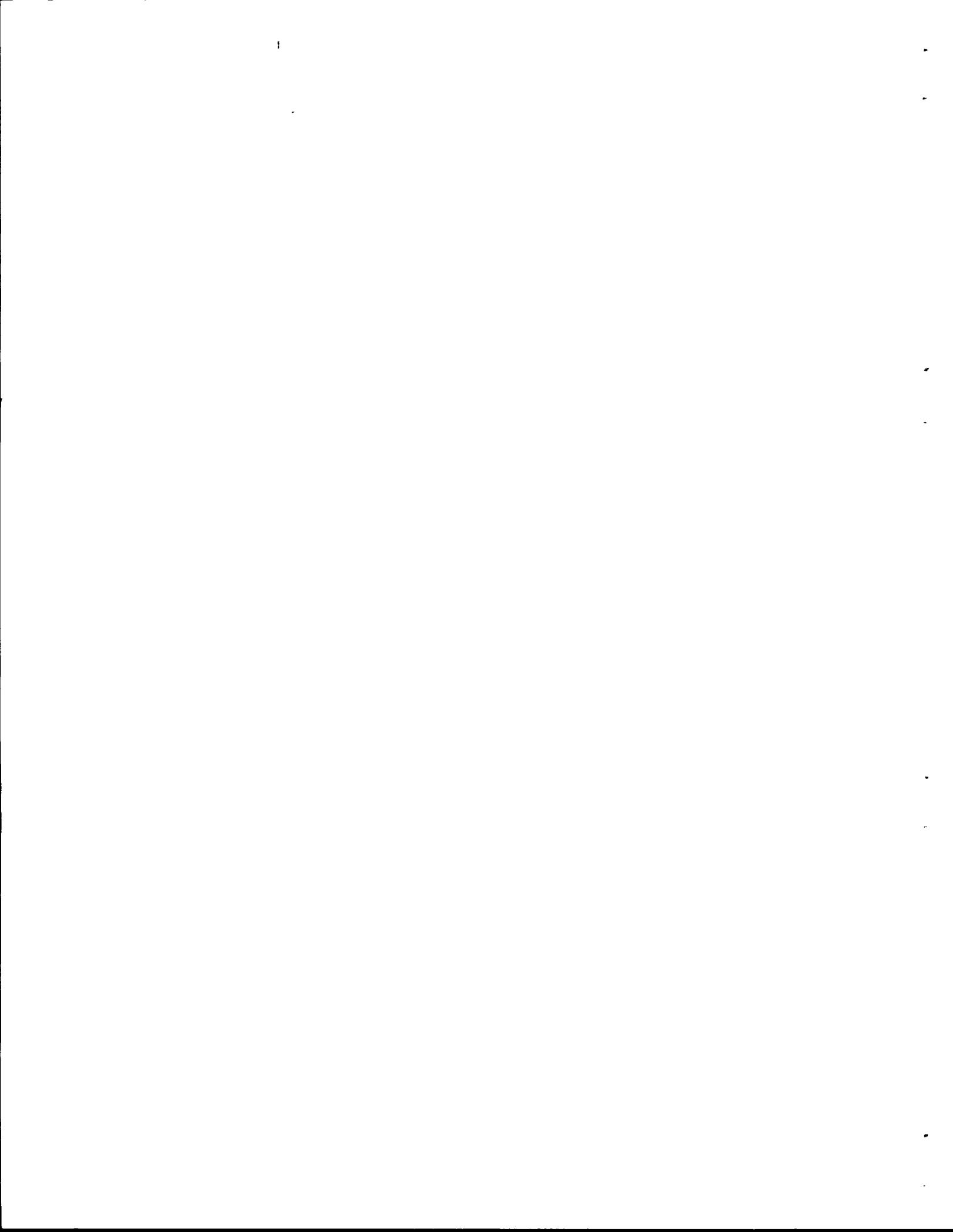


- (3) Sections 34B-2 (6-in. x 6-in. x 10-in.) and 34C-1 (6-in. x 6-in. x 6-in.) were further subdivided.



- (4) Cylinders were machined from the numbered sections as follows:
 B21, 24: two each, 2.25-in. dia x 2.0-in. long.
 B22-23, 25, 26: two each, 1.0-in. dia x 2.0-in. long.
 B27, 28, 29, 210: two each, 1.5-in. dia x 2.0-in. long; plus one each 1.25-in. dia x 1.0-in. long.
 B211, 212, 213, 214: one each, 1.0-in. dia x 4.0-in. long.
 C11, 12, 13, 14: two each, 1.5-in. dia x 2.0-in. long; plus one each 1.25-in. dia x 1.0-in. long.





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