FOREWORD

This report is a supplement to the twelfth volume of WADD Technical Report series 61-72, describing various phases of research and development on advanced graphite materials conducted by National Carbon Company, a Division of Union Carbide Corporation, under USAF Contract No. AF 33(616)-6915.

The work covered in this report was conducted from September 1962 to May 1963 at the Advanced Materials Laboratory of National Carbon Company under the management of R. M. Bushong, Director of the Advanced Materials Project, and of R. C. Stroup, Manager of the Advanced Materials Laboratory.

The contract for this R&D program was initiated under Project No. 7350, "Refractory Inorganic Non-Metallic Materials," Task No. 735002, "Refractory Inorganic Non-Metallic Materials: Graphitic," Project No. 7381, "Materials Application," Task No. 738102, "Materials Processes," and Project No. 7-817, "Process Development for Graphite Materials." The work was administrated by the Air Force Materials Laboratory, Deputy Commander/Research and Engineering, Aeronautical Systems Division, Air Force Systems Command. Captain R. H. Wilson, L. J. Conlon and W. P. Conrardy acted as Project Engineers.

Other volumes in this WADD Technical Report 61-72 series are:

Volume I -	Observations by Electron Microscopy of Dislocations in Graphite, by R. Sprague.
Volume II -	Applications of Anisotropic Elastic Continuum Theory to Dislocations in Graphite, by G. B. Spence.
Volume III -	Decoration of Dislocations and Low-Angle Grain Boundaries in Graphite Single Crystals, by R. Bacon and R. Sprague.
Volume IV -	Adaptation of Radiographic Principles to the Quality Control of Graphite, by R. W. Wallouch.
Volume V -	Analysis of Creep and Recovery Curves for ATJ Graphite, by E. J. Seldin and R. N. Draper.
Volume VI -	Creep of Carbons and Graphites in Flexure at High Temperature, by E. J. Seldin.
Volume VII -	High-Density Recrystallized Graphite by Hot-Forming, by E. A. Neel, A. A. Kellar and K. J. Zeitsch.

Supplement - High-Density Recrystallized Graphite by Hot-Forming, by G. L. Rowe and M. B. Carter.

Volume VIII - Electron Spin Resonance in Polycrystalline Graphite, by L. S. Singer and G. Wagoner.

Volume IX - Fabrication and Properties of Carbonized Cloth Composites, by W. C. Beasley and E. L. Piper.

Volume X - Thermal Reactivity of Aromatic Hydrocarbons, by I. C. Lewis and T. Edstrom.

Supplement - Thermal Reactivity of Aromatic Hydrocarbons, by I. C. Lewis and T. Edstrom.

Volume XI - Characterization of Binders Used in the Fabrication of Graphite Bodies, by E. deRuiter, A. Halleux, V. Sandor and H. Tschamler.

Supplement - Characterization of Binders Used in the Fabrication of Graphite Bodies by E. deRuiter, J. F. M. Oth, V. Sandor and H. Tschamler.

Volume XII - Development of an Improved Large-Diameter Fine-Grain Graphite for Aerospace Applications, by C. W. Waters and E. L. Piper.

ABSTRACT

This report supplements WADD Technical Report 61-72, Volume XII, "Development of an Improved Large-Diameter Fine-Grain Graphite for Aerospace Applications", by C. W. Waters and E. L. Piper, and covers the continuation of development work on large diameter grade RVA graphite. The extension work consisted primarily of fabricating and evaluating raw materials for use as the inert filler in RVA blends, and of attempts to scale up to longer lengths of RVA graphite.

Significant properties of raw materials, as they affect the final properties of grade RVA graphite, were the total porosity and kerosene apparent density. The more porous raw materials imparted higher strength to the finished RVA graphite, whereas those of higher density contributed to higher density of the finished graphite. Long lengths of 33-inch diameter RVA graphite were difficult to process without cracking. The longest length processed successfully under this project was 45 inches.

This report has been reviewed and is approved.

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1. INTRODUCTION

Although existing high density graphites have performed successfully in many aerospace applications, there is a necessity for continued development and scale up of improved high density graphites. Development of one high density graphite (designated grade RVA) has been carried on by National Carbon Company under United States Air Force Contract No. AF 33(616)-6915.

Prior to contract support, a pressure curing process had been partially developed for the forming of RVA in sizes up to 30 inches in diameter by 40 inches in length. Stock produced by this process, however, had a tendency to crack during processing and exhibited more variance in properties than was desired. The objective of development work under the above contract was to determine more completely the effects of forming parameters and raw material variations on the properties of grade RVA and to extend this knowledge to the fabrication of the graphite in useful sizes with reasonable property variance. The initial phase of work completed under AF 33(616)-6915 has been reported(1) including work done on upgrading the strength and developing new processing techniques for RVA graphite.

This supplemental report covers the final phase of RVA development work which was designed primarily to include two areas of investigation: (a) evaluation of raw materials for use as inert filler materials in the RVA blends, and (b) determination of the effect of length on the processability of 33-inch diameter RVA graphite.

Completion of the investigation in these two areas indicated the advisability of making a semi-production run of RVA, using previous forming experience, to determine if, and under what conditions, reproducible material could be formed. As a final step in the development program, grade RVA was characterized from the standpoint of physical properties.

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2. CONTROLLED GRAPHITE FILLER MATERIAL FOR GRADE RVA GRAPHITE

Controlled graphite filler materials were produced to determine the effect of their properties on the properties of grade RVA. The ability to control the properties of filler materials is important in reducing the property variation from piece to piece and in maintaining optimum strength and density of the finished graphite product. The present graphite filler material is a by-product of other graphite processing and has a density ranging from 1.50 to 1.75 g/cc.

The general method used for fabricating and evaluating controlled graphite filler materials was to extrude 2½-inch diameter rods from a known coke base blend, crush and mill the rods after graphitization, and use the resulting material as filler in blends for producing RVA graphite. The precompaction-particle envelope technique of curing was used in the evaluation of the different filler materials.

2.1. Fabrication of a Controlled Graphite Filler Material

The coke base rods used in this study were produced with the use of an auger extruder as pictured in Figure 1. The extruded rods were 2½

Figure 1. Auger Extrusion of 2½-Inch Diameter Rods

inches in diameter by approximately 4 feet in length and were formed from the blend composition shown in Table 1.

Table 1. Blend Composition for Extruded Rods to be Used as Controlled Graphite Filler Materials

Ingredient	Parts by Weight
Calcined Coke Flour	100
110°C Melting Point Coal Tar Pitch	34
Lubricating Oil	4

The properties of the coke flour and the 110°C melting point coal tar pitch used in the raw material extrusion are listed in Tables 2 and 3.

Table 2. Physical and Chemical Properties of Typical Coke Flour*

Property	Average Value
Ash Content, per cent	0.96
Sulfur Content, per cent	0.69
Kerosene, Apparent Density, g/cc	2.118
Particle Size Distribution:	
Per cent through 200-mesh screen	56.3
Per cent through 150-mesh screen	73.2
Per cent through 100-mesh screen	92.9
Per cent through 65-mesh screen	98.9
Per cent through 48-mesh screen	99.0

* Representative sample used (sampling done during milling of coke)

Table 3. Chemical Properties of 110°C Melting Point Coal Tar Pitch*

Property	Average Value
Benzene Insolubles, per cent	34.9
Quinoline Insolubles, per cent	12.0
Flash Point, P.M. closed cup, °C	133
Melting Point, °C	111
Degree of Pitch Coking at 800°C, per cent	59.2

* Representative sample used (sampling done during crushing of pitch)

The extruded rods were processed to graphite in two ways. Half of the rods were graphitized directly to 2800°C and the other half were prebaked to 800°C before graphitizing to 2800°C. The prebaking step allows the 110°C melting point pitch in the rods to pyrolyze slowly and, consequently, to yield a more uniform and a greater amount of pitch carbon residue.

Graphitizing to 2800°C was accomplished in an Acheson furnace. In Figure 2, the rods have been uncovered in the Acheson furnace and are ready to be unloaded after graphitizing to 2800°C. Heating is accomplished in this type of furnace by passing an electrical current through the charge stock, in this case the 2½-inch diameter rods.

Figure 2. Extruded Rods in Acheson Furnace, Uncovered After Being Graphitized to 2800°C

Table 4 lists the physical and chemical properties of the extruded rods, both prebaked and directly graphitized. For comparison, the properties of the standard (by-product) graphite filler also are listed in Table 4. Figure 3 is a plot of the pore distribution of these three graphite materials. The pore distribution indicates two significant properties of porous materials, total porosity and surface area. Surface area is important since a large volume of small diameter pores would signify a high surface area.

Table 4. Physical and Chemical Properties of Controlled Graphite Sources

Type of Graphite Tested	Graphitizing Method	Bulk Density g/cc No. of Samples			Electrical Resistivity with-the-grain 10^{-4} ohm-cm Ave.		Kerosene Apparent Density g/cc	Ash, per cent	Sulfur, per cent
			Ave.	σ		σ			
Extruded Rods (all flour base)	Baked to 800°C, then graphitized to 2800°C	48*	1.51	0.03	8.48	0.75	2.11	0.05	0.04
Extruded Rods (all flour base)	Graphitized directly to 2800°C	33*	1.44	0.04	10.64	1.96	2.22	0.01	0.04
By-Product Filler (25 per cent sized particles, 75 per cent flour)	Baked to 800°C, impregnated, and graphitized to 2800°C	12	1.64	0.06	9.94	0.60	2.19	0.20	0.01

* Samples taken from three separate graphitization runs from an Acheson furnace

The standard deviation in Table 4 shows that direct graphitization of the rods produced a material with greater nonuniformity, in resistivity, indicating that the rods must be prebaked before graphitizing to produce graphite filler material with closely controlled properties. Both the directly graphitized and the prebaked rods, however, were more uniform in bulk density than the standard graphite filler material. The reason for this is that part of the standard graphite had been impregnated before graphitizing, while part had been graphitized with no impregnation. The combination of impregnated and non-impregnated material yielded large variations in density.

The kerosene apparent density of the prebaked rods is low compared to that of the directly graphitized and standard graphites (see Table 4). The low density of the prebaked rods is due to the large volume of inaccessible pores resulting from the high pitch coke content which also accounts for the low resistivities obtained with these rods.

The higher porosity and surface area of the graphite rods shown in Figure 3, as compared to the standard filler material is due to some extent to the difference in initial blend compositions of these two materials. The rods were formed from an all flour blend whereas the standard filler was formed from blends containing 25 per cent particles and 75 per cent filler.

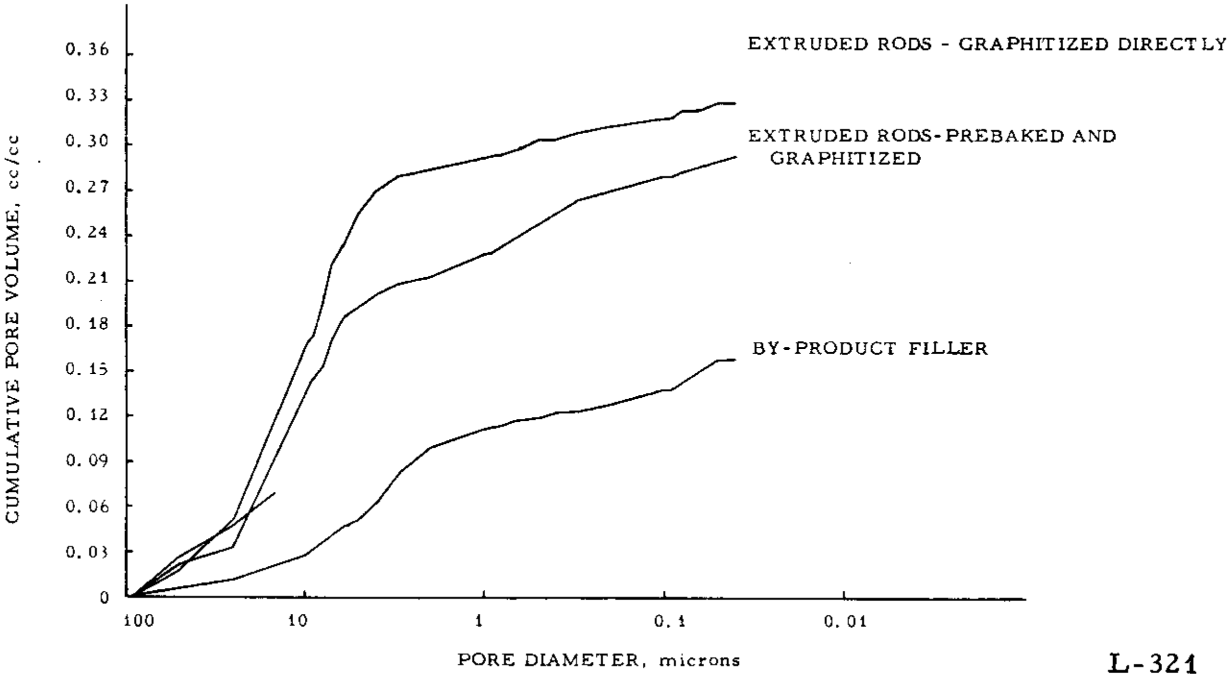

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Figure 3. Pore Spectra for Various Graphite Filler Materials

2.2. Evaluation of the Controlled Graphite Filler Material

The formed graphite rods, as well as the by-product graphite, were crushed and milled into particles and flour and used as the filler material in blends for RVA graphite. Plugs were formed from these blends in 10-inch diameter by 10-inch length sizes. The precompaction-particle envelope technique of forming was employed. The cured plugs were baked to 800°C, impregnated with pitch, and graphitized to 2800°C. The bulk densities of these plugs, as well as their volume and weight changes during baking and graphitizing, are listed in Table 5. The room temperature physical properties of the processed RVA plugs are listed in Table 6. As can be seen from the data in Tables 5 and 6, highly reproducible results (except for the precompacted plug densities) were obtained with the different series.

The data in Table 5 shows that in the cured and baked state, the densities of the plugs formed from both types of controlled graphite filler material are lower than the density of those formed from the by-product filler. The prebaked graphite filler material yielded the lowest density. Some of the density differences observed were either reduced or eliminated with the pitch impregnation step. The differences in densities experienced are believed to be due to the differences in total porosity and in kerosene apparent density of the different graphite materials. The filler materials with greater porosity and/or lower kerosene apparent density produced stock with lower bulk densities (see Figure 3 for porosities and Table 4 for kerosene apparent densities of the graphite filler material sources).

Table 5. Summary of Bulk Properties of Grade RVA Graphite, Filler Material Evaluation, 10-Inch Diameter by 10-Inch Length Plugs

Piece No.	Graphite Source	PPH* 175°C Pitch	Precompacted Density g/cc	Cured Bulk Density g/cc	800°C Baked Density g/cc	Cured to Baked Weight Ratio	Cured to Baked Volume Ratio	Impregnant Pickup per cent	Graphitized Bulk Density g/cc	Baked to Graphitized Volume Ratio
1	Extruded Rods, prebaked	26	1.76	1.73	1.70	1.016	0.998	9.4	1.78	1.047
2	Extruded Rods, before graphitizing	26	1.73	1.73	1.69	1.015	0.994	9.6	1.77	1.042
3	Extruded Rods, before graphitizing	26	1.72	1.73	1.70	1.015	0.998	9.4	1.77	0.047
4	Extruded Rods, before graphitizing	26	1.77	1.74	1.69	1.016	0.989	9.5	1.77	1.040
5	Extruded Rods, graphitized directly	26	1.71	1.79	1.76	1.014	0.998	6.1	1.82	1.043
6	Extruded Rods, graphitized directly	26	1.75	1.77	1.75	1.014	0.998	6.6	1.83	1.053
7	Extruded Rods, graphitized directly	26	1.69	1.78	1.76	1.014	1.003	6.3	1.83	1.048
8	Extruded Rods, graphitized directly	26	1.77	1.78	1.75	1.014	0.996	6.4	1.83	1.048
9	By-Product Filler	26	1.69	1.81	1.77	1.015	0.995	5.3	1.83	1.041
10	By-Product Filler	26	1.78	1.79	1.77	1.014	1.003	5.5	1.83	1.045
11	By-Product Filler	26	1.73	1.79	1.77	1.014	1.001	5.3	1.81	1.038
12	By-Product Filler	26	1.72	1.79	1.77	1.015	1.000	5.4	1.82	1.039
13	By-Product Filler	26	1.74	1.79	1.78	1.012	1.002	5.4	1.82	1.037

* Parts of pitch per hundred parts by weight of filler ingredients

The pore distribution of the RVA material formed from the different graphite fillers is presented in Figure 4 which shows that the high porosity of the extruded rods resulted in high porosity in the finished product.

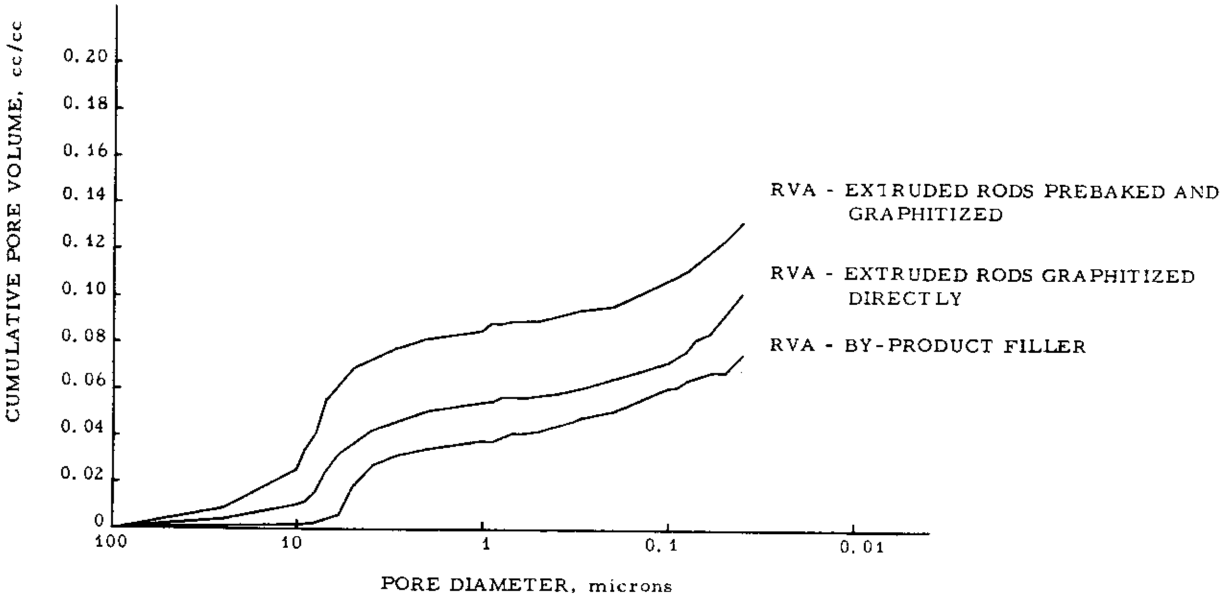

Figure 4. Pore Spectra of Grade RVA Formed from Various Filler Materials

The data in Table 6 show that the extruded graphite rods and the high pitch coke content of the prebaked rods, respectively, imparted high strengths and low resistivities to the RVA materials. The high porosity graphite filler increased the binder capacity and the high surface area graphite filler increased the number of sites available to binder coke, thus imparting high strength to the RVA. All other room temperature properties were approximately equivalent for the three types of graphite tested. The nonuniformity previously observed for the material which was graphitized directly can be detected from the standard deviations of the room temperature properties of RVA formed with this material.

It is concluded from these investigations that the significant properties to consider when choosing a graphite filler material are porosity, surface area and kerosene apparent density. The kerosene apparent density determinations will indicate the volume of pores inaccessible to binders. High porosity and high surface area graphite filler material,within limits yet to be determined,are desirable in obtaining high strength RVA graphite.

Table 6. Room Temperature Properties of Grade RVA Graphite, Filler Material Evaluation, 10-Inch Diameter by 10-Inch Length Plugs

	RVA (Extruded Rods, Prebaked before Graphitizing)			RVA (Extruded Rods, Graphitized Directly)			RVA (By-Product Filler)		
	Pieces Nos. 1 and 2			Pieces Nos. 5 and 6			Pieces Nos. 9 and 10		
Property	No. of Samples	Ave.	σ	No. of Samples	Ave.	σ	No. of Samples	Ave.	σ
Bulk Density, g/cc	47	1.78	0.005	46	1.83	0.005	40	1.82	0.002
Flexural Strength, * lbs/in^2									
w. g.**	24	3980	270	23	4030	410	20	3530	260
a. g.	23	3150	180	23	3020	270	20	2560	115
Electrical Resistivity, 10^{-4} ohm-cm									
w. g.	24	10.6	0.3	23	12.0	0.3	20	11.3	0.2
a. g.	23	15.1	0.6	23	16.1	0.7	20	16.5	0.4
Young's Modulus, 10^6 lbs/in^2									
w. g.	24	1.58	0.06	23	1.69	0.07	20	1.67	0.05
a. g.	23	1.01	0.04	23	1.08	0.05	20	1.01	0.02
Room Temperature, CTE, 10^{-6}/°C									
w. g.	4	1.29	--	4	1.22	--	4	1.28	--
a. g.	4	2.31	--	4	2.22	--	4	2.34	--

* ½- by ½-inch cross section, third point loading

**w. g. = with-the-grain
a. g. = across-the-grain

3. EFFECT OF PRODUCT LENGTH ON PROCESSABILITY OF GRADE RVA GRAPHITE

A series of long plugs (up to 72 inches in length) were formed to determine the effect of length on the processability of 33-inch diameter grade RVA. The plugs were processed to graphite, inspected visually and measured for physical properties. Information gathered during the processing of a series of plugs was used to establish the processing conditions for the subsequent series. This work eventually led to a semi-production run of grade RVA using controlled raw materials and improved processing procedures.

3.1. Description of Equipment and Forming Procedure

A press with 1250 tons pressure was used for the 33-inch diameter forming trials. This press, as well as the 100 ton tamping press used with it, is shown in Figure 5. The 100 ton capacity press, used for pretamping the blend, is required when large quantities of blend are to be processed.

The advantages of the 1250 ton press over the press used for the previous 30-inch diameter RVA trials are as follows:

1) Continuous control of secondary voltage, available with the 1250 ton press, allows continuous and more accurate control of the heating rate.

2) Two separate transformers provide better heating characteristics than normally experienced with the use of only one transformer.

3) Double ram molding minimizes pressure differentials usually present in single ram molding of a semi-fluid material.

4) Molded plugs up to 72 inches in length can be formed.

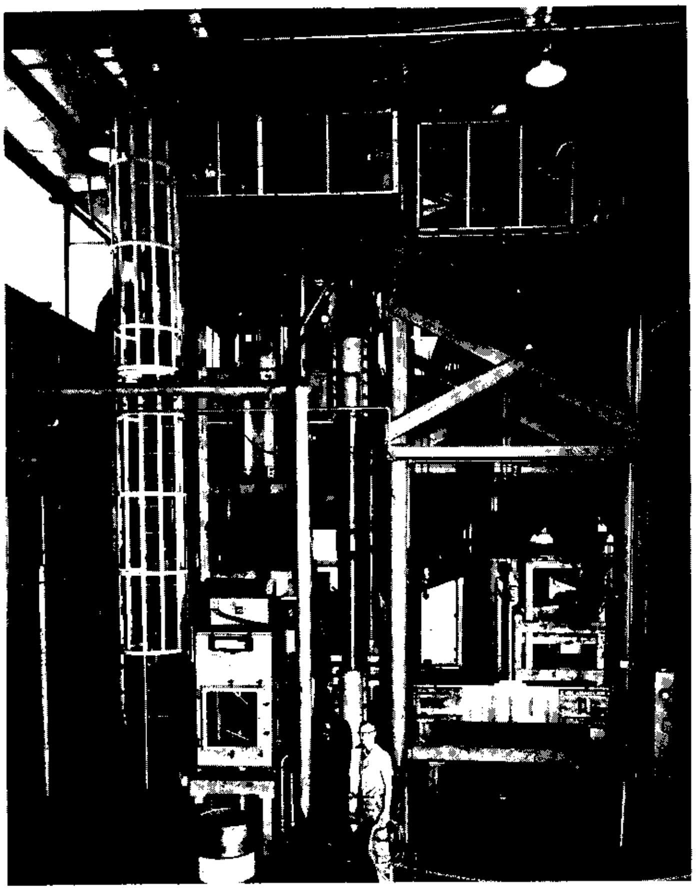

Figure 5. 1250 Ton Press (Left Half of Photograph) and 100 Ton Tamping Press (Right Half of Photograph)

In the initial forming trials, plugs shorter than 65 inches could not be processed due to stroke characteristics of the 1250 ton press. Extensions, shown in Figure 6, were added to the rams of the press so that plugs as short as 45 inches could be molded.

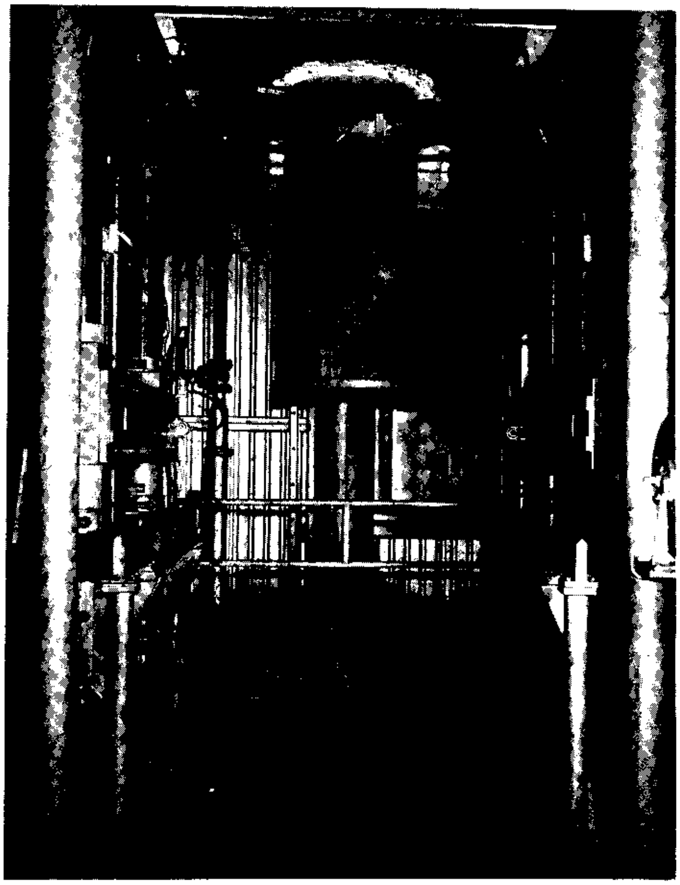

Figure 6. Close-up View of 1250 Ton Press Showing Extensions on Top and Bottom Rams

The precompaction-particle envelope technique of pressure curing was used in all the 33-inch diameter RVA trials. Figure 7 is a sketch of the insulated mold used in these trials. The fiberglass liner is used in the precompaction step only. RVA blend is loaded into the fiberglass liner, pretamped if necessary with the 100 ton press, and then heated in the 1250 ton press to 110-130°C under a product pressure of 1000 lbs/in^2. After cooling, the precompacted plug is ejected from the fiberglass liner.

For the curing operation, the fiberglass liner is removed leaving a 1.75-inch annular space which, when filled with particles, forms the particle envelope around the plug. Figure 8 shows the insulated mold being lowered over a precompacted plug prior to curing the plug. After the mold is in place, the annular space around the plug is filled with coke particles.

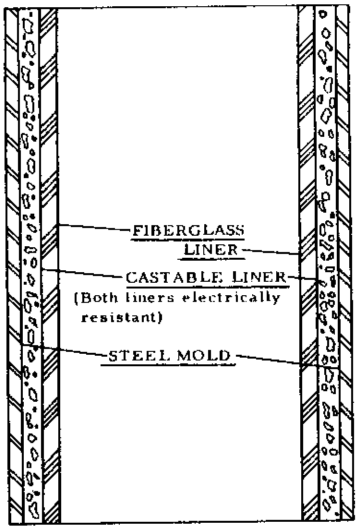

Figure 7. Sketch of 33-Inch Diameter Mold for Fabrication of Grade RVA Graphite

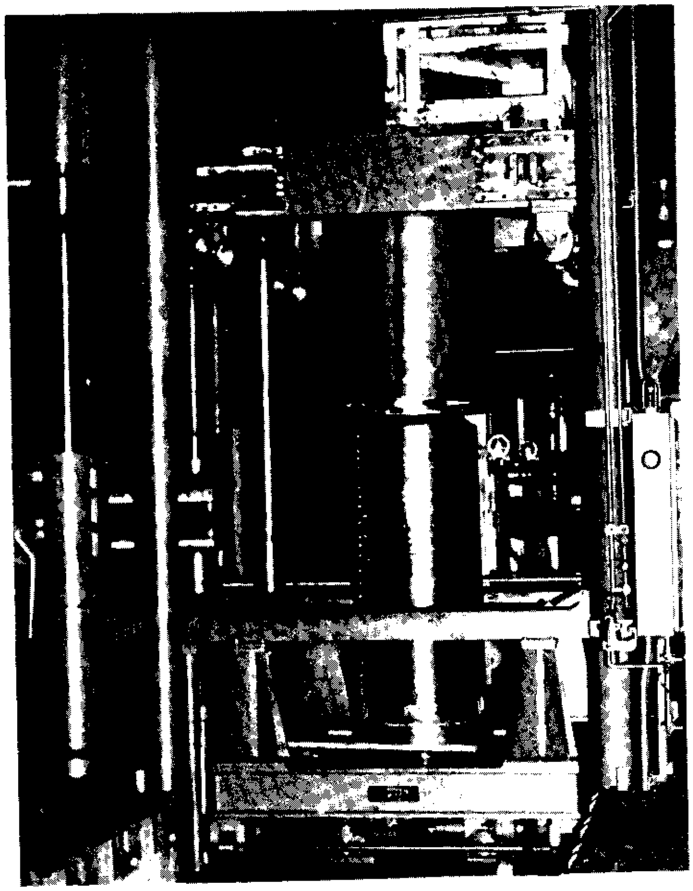

Figure 8. Placing the Insulated Mold Over Precompacted Plug Prior to Curing

The plug is heated to approximately 325°C under a product pressure of from 800 to 1000 lbs/in^2 after which it is cooled and ejected. Figure 9 shows the mold being lifted from around a cured plug in the 100 ton tamping press.

Figure 9. Removing the Insulated Mold from Around a Cured Plug

The blends from which RVA graphite is made (Table 7) are prepared in the twin shell blenders shown in Figure 10. These blenders are equipped with a rotating bar which intensifies the blending action.

Table 7. Blend Composition Used in 33-Inch Diameter RVA Trials

Ingredient	Parts by Weight
Graphite Particles	50
Graphite Flour	50
Thermatomic Black	8
175°C Melting Point Pitch	28.1
Sulfur	5.6
Total Parts	141.7

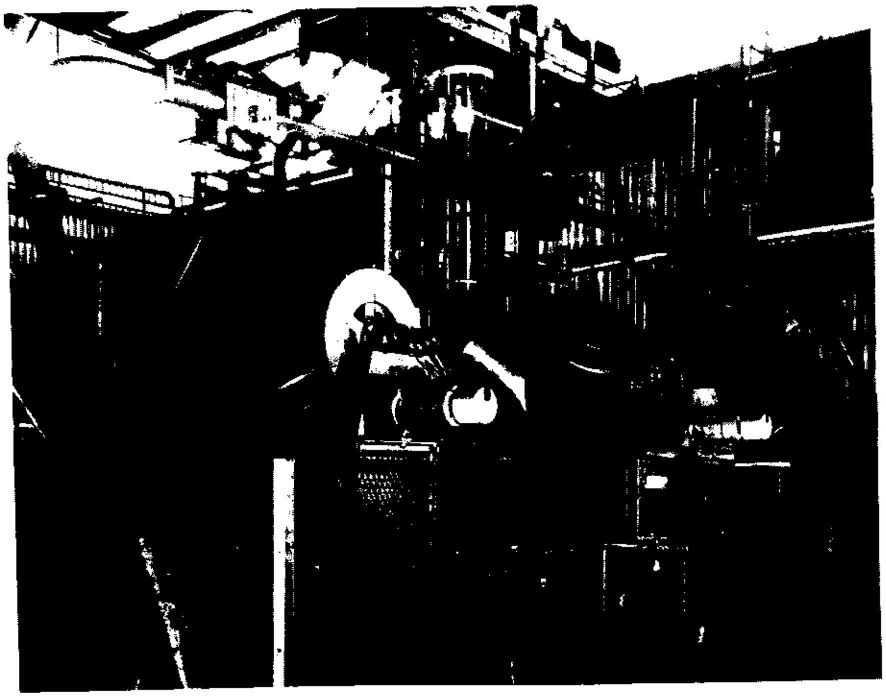

Figure 10. 30 cu. ft. Twin Shell Blenders

3.2. Fusion of Precompacted Plugs During Pressure Curing

The large fill ratio (2.1 to 1)* of the blend used for grade RVA necessitates using a press having a long stroke and a large dimension between the fully retracted rams in order to fabricate long sections. The production of these long sections also requires molds of excessive height

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* Ratio of the length of cured plug to the depth of loose blend placed in the mold.

and weight. In present practice these problems are somewhat reduced by pretamping the mix before precompaction and curing operations. A method for extending the length capability of presses used prior to the 33-inch diameter trials involved the fusion of two precompacted plugs to form one long plug during pressure curing.

Two 10-inch diameter and three 24-inch diameter fusion trials were attempted. All three 24-inch diameter plugs cracked at the joint, two after curing and one after graphitizing to 2800°C. In the 10-inch diameter trials two fusion approaches were used.

1) The machined ends of two precompacted plugs were butted together and cured in a particle envelope.

2) Loose blend was placed in the joint between two precompacted plugs and the assembly was cured in a particle envelope.

The plug using the loose blend between the pieces cracked at the joint on curing. The other piece, formed by butting two precompacted plugs together, was found to be intact after graphitizing to 2800°C. Strengths across the joint of the graphitized plug and strengths of the basic material are listed in Table 8.

Table 8. Flexural Strengths of Grade RVA Graphite Formed by Fusing Two Precompacted Plugs During Curing

	Across-Grain Flexural Strength* lbs/in^2			
Sample Location	No. of Samples	Average	Maximum Value	Minimum Value
Across the Joint	26	1410	2120	650
Outside the Joint	26	1590	2150	1280

* ½- by ½-inch cross section, third point loading

Although the strengths across the joint were somewhat lower, they compared favorably with the strengths of the base material. Additional work in this direction was not initiated because of the lack of success in the forming of flaw-free 24-inch diameter fused RVA.

3.3. Forming Trials of Grade RVA Graphite, Large Sizes

In the 33-inch diameter RVA trials, a total of 22 plugs were precompacted, of which 17 were cured. The material was processed in three series, which were comprised of 6, 4 and 12 plugs, respectively. The first two series were attempts to form long plugs. The last series included a semi-production run of 8 plugs, 6 from blends containing standard graphite filler and 2 using blends with controlled filler material. Table 9 lists the precompaction and curing data and Table 10 lists the bulk densities of the three series of plugs. The piece numbers missing in Tables 9 and 10 were trials on the press with other types of materials.

3.3.1. Grade RVA Trials, Series 1

The objectives of the trials in Series 1 were basically to check out the mechanical operations of precompacting and curing in the 1250 ton press (firing rate, pressure control, ram travel indication, etc.) and to gain an insight into the problems involved in the forming of long sections.

The press performed satisfactorily for all of the runs with the exception of running out of press stroke in the precompaction of pieces A-1 and A-2. However, this did not seem to affect the results of these two trials.

Run No. A-7 was an attempt to precompact a hot mix of RVA blend. This was done to eliminate the problem of particle-flour segregation which is caused by free fall of blend during loading of the mold and which can result in cracked stock. Heating of the blends was accomplished with the use of a turbulizer mixing apparatus. Results of this trial were inconclusive as difficulty was encountered in maintaining uniform mix temperature.

Following is a summary of observations and conclusions of the Series 1 precompaction and curing trials (pieces Nos. A-1 through A-5 in Table 9).

1) Precompaction Trials

   a. Sidewall friction problems as a result of length is indicated by comparing runs A-1 and A-2 (density of plug A-2 being greater than the density of the longer plug A-1).

Table 9. Precompaction and Curing Data of 33-Inch Diameter Grade RVA Graphite Trials

Precompaction Data

Series No.	Nature of Trial	Piece No.	Graphite Filler Source	Thickness of Particles Used inches Top	Bottom	Thickness of Thermax Used inches Top	Bottom	Final Side Temp. °C	Hold Time hours	Plug Length inches	Bulk Density g/cc
1	Length Scale Up	A- 1	Standard	5 Coke	5 Coke	0	0	128	0	71.9	1.77
	Length Scale Up	A- 2	Standard	8 Coke	6 Coke	0	0	126	0.7	57.1	1.81
	Length Scale Up	A- 3	Standard + Extruded Rods	12 Coke	12 Coke	0	0	125	2.5	60.9	1.75
	Length Scale Up	A- 4	Extruded Rods	8 Coke	6 Coke	0	0	116	1.3	68.0	1.67
	Length Scale Up	A- 5	Extruded Rods	8 Graphite	6 Graphite	0	0	---	1.3	66.6	1.60
	Length Scale Up	A- 7	Standard	None	None	0	0	---	---	67.7	1.52
2	Length Scale Up	A- 8	Standard	None	None	1	1	---	15.0	61.4	1.82
	Length Scale Up	A- 9	Standard	None	None	1	1	122	13.5	70.7	1.80
	Length Scale Up	A-10	Standard	None	None	0	0	118	4.7	61.0	1.76
	Length Scale Up	A-11	Standard	None	None	0	0	123	8.3	61.1	1.76
3	Length Scale Up	A-17	Standard	None	None	½	2	116	5.0	53.7	1.70
	Length Scale Up	A-18	Standard	None	None	½	1½	112	5.0	51.5	1.74
	Semi-Production	A-19	Standard	None	None	½	1½	116	14.0	49.1	1.81
	Semi-Production	A-20	Standard	None	None	¾	1½	115	14.0	49.9	1.81
	Semi-Production	A-21	Standard	None	None	½	1½	116	14.0	49.6	1.80
	Semi-Production	A-22	Standard	None	None	½	1½	116	14.0	49.8	1.82
	Semi-Production	A-23	Standard	None	None	½	1½	117	14.0	50.7	1.79
	Semi-Production	A-24	Standard	None	None	½	1½	118	14.0	48.6	1.84
	Semi-Production	A-26	Extruded Rods (Prebaked)	None	None	½	1½	114	14.0	49.3	1.83
	Semi-Production	A-27	Extruded Rods (Graphitized Directly)	None	None	½	1½	116	14.0	49.4	1.83
	Production of Pre-compacts for Induction Curing	A-28	Extruded Rods + Standard	None	None	½	1½	118	15.0	49.3	1.85
		A-31	Extruded Rods (Graphitized Directly)	None	None	½	1½	115	10.0	---	1.84

Curing Data

Series No.	Thickness of Particles Used inches Top	Bottom	Final Curing Temperatures °C Side	Top	Bottom	Diameter Increase per cent	Plug Length After Machining inches	Bulk Density After Machining g/cc	General Appearance After Baking to 800°C
1	-	-	343	248	285	2.1	65.5	1.75	Piece OK
	8	6	---	---	---	3.6	53.2	1.80*	Piece cracked horizontally
	8	4	305	280	280	2.1	56.8	1.79*	Piece cracked horizontally
	-	-	---	---	---	1.8	63.0	1.70*	Piece cracked horizontally
	8	5	332	---	293	2.7	54.0	1.74	Piece OK
	Piece not cured								
2	3	3	---	---	---	5.7	57.8	1.73*	Piece cracked vertically
	3	3	---	---	---	6.0	61.1	1.77*	Piece OK
	3	3	---	---	---	5.4	54.9	1.77*	Piece cracked vertically
	3	3	---	---	---	5.4	52.9	1.80	Piece OK
3	Piece not cured								
	Piece not cured								
	3	3	---	290	---	4.5	42.2	1.79	Piece OK
	3	3	---	---	---	4.8	42.4	1.79	Piece OK
	3	3	320	299	---	4.7	41.5	1.79	Piece OK
	3	3	328	307	325	5.0	42.5	1.79	Piece OK
	3	3	316	298	318	5.4	42.8	1.79	Piece OK
	3	3	306	295	316	5.9	42.3	1.79	Piece OK
	3	3	312	312	319	5.9	43.5	1.78	Piece OK
	3	3	321	296	325	6.0	42.8	1.76	Piece OK
	Piece not cured								
	Piece not cured								

*Estimated Density on unturned piece

Table 10. Bulk Properties of 33-Inch Diameter Grade RVA Graphite Trials

Series No.	Nature of Trial	Piece No.	Graphite Filler Source	Precompacted Bulk Density g/cc	Bulk Density After Curing and Machining g/cc	800° C Baked Bulk Density g/cc	Impregnation Pitch Pick up per cent	Graphitized Bulk Density g/cc	Comments - Condition of Pieces
1	Length Scale up	A- 1	Standard	1.77	1.75	1.73	---	1.83	Piece OK-inside structure unknown
	Length Scale Up	A- 2	Standard	1.81	1.80*	---	---	---	Piece horizontally cracked in baked state**
	Length Scale Up	A- 3	Standard + Extruded Rods	1.75	1.79*	1.64	---	1.71	Piece horizontally cracked in precompacted and baked state**
	Length Scale Up	A- 4	Extruded Rods	1.67	1.70	1.68	---	---	Piece horizontally cracked in baked state*
	Length Scale Up	A- 5	Extruded Rods	1.60	1.74	---	---	---	Piece OK-stored in cured state
	Length Scale Up	A- 7	Standard	1.52	---	---	---	---	Precompact horizontally cracked
2	Length Scale Up	A- 8	Standard	1.32	1.73*	---	---	---	Piece vertically cracked in baked state**
	Length Scale Up	A- 9	Standard	1.80	1.77	1.76	7.1	1.85	Contained internal horizontal crack in graphite state
	Length Scale Up	A-10	Standard	1.76	1.77*	---	---	---	Piece vertically cracked in baked state**
	Length Scale Up	A-11	Standard	1.76	1.80	1.78	6.4	1.85	Piece OK-internal structure OK
3	Length Scale Up	A-17	Standard	1.70	---	---	---	---	Precompacted plug OK
	Length Scale Up	A-18	Standard	1.74	---	---	---	---	Precompacted plug horizontally cracked
	Semi-Production	A-19	Standard	1.81	1.79	---	6.7	---	Contained internal horizontal crack in graphite state
	Semi-Production	A-20	Standard	1.81	1.79	1.79	6.6	1.87	Piece OK-internal structure OK
	Semi-Production	A-21	Standard	1.80	1.79	---	6.5	---	Contained internal horizontal crack in graphite state
	Semi-Production	A-22	Standard	1.82	1.79	---	6.5	---	Piece burned-internal structure unknown
	Semi-Production	A-23	Standard	1.79	1.79	1.78	6.4	1.85	Contained external horizontal crack in graphite state
	Semi-Production	A-24	Standard	1.84	1.79	1.78	6.5	1.85	Piece OK-internal structure OK
	Semi-Production	A-26	Extruded Rods (Prebaked)	1.83	1.78	1.76	8.0	1.85	Piece OK-internal structure unknown
	Semi-Production	A-27	Extruded Rods (Graphitized Directly)	1.83	1.76	1.74	7.7	1.84	Piece OK-internal structure unknown
	Production of Pre-compacts for Induction Curing	A-28	Extruded Rods + Standard	1.85	---	---	---	---	Precompact OK
		A-31	Extruded Rods	1.84	---	---	---	---	Precompact OK

*Estimated Density on unmachined piece

** Piece condition in cured state unknown due to layer of particles stuck on all surfaces

b. The coke particles used on the ends of the plugs in runs A-1 through A-4 contributed to the problem of sidewall friction. The thicker the layer of coke particles, the greater was the resulting sidewall friction (compare pieces Nos. A-2 and A-3 in Table 9).

Table 11 lists the top and bottom ram travel obtained in the precompaction of plugs A-1 through A-5. Since the fiberglass mold is tapered from top to bottom (largest diameter at the bottom) any significant sidewall friction effect would be aggravated at the bottom. Less ram travel would therefore be obtained at the bottom. This was observed for runs A-1 through A-4 (see Table 11). The use of graphite particles in the precompaction of A-5 lessened the sidewall friction problem and, consequently, yielded equal top and bottom ram travel.

Table 11. Top and Bottom Ram Travel, Precompaction Runs Nos. A-1 through A-5

Piece No.	Thickness of Particles Used inches		Ram Travel inches			Approximate Precompacted Length, inches
	Top	Bottom	Top	Bottom	Total	
A-1*	5	5	14.5	10.0	24.5	71.9
A-2*	8	6	16.5	9.0	25.5	57.1
A-3*	12	12	12.1	9.4	21.5	60.9
A-4*	8	6	11.9	8.3	20.2	68.0
A-5**	8	6	9.7	9.1	18.8	66.6

* Coke particles used on ends of plug

** Graphite particles used on ends of plug

c. The final temperature greatly affected the precompacted plug density, with higher temperatures producing more dense plugs. This can be seen by comparing the final side temperature and the large density differences obtained in runs A-3 and A-4 shown in Table 9.

The temperature at the ends of the plug also affects the density. The high heat losses in the ends of piece A-5 (due to the high thermal conductivity of the graphite used) resulted in a very low density for this piece.

d. Cooling rates of the precompacted plug in the fiberglass liner were of the order of 4 to 6°C per hour. This very slow rate of cooling necessitated leaving the precompacts in the mold for periods of about 16 hours to prevent cracking the plug on ejection.

2) Curing Trials

a. The low precompacted densities of A-4 and A-5 resulted in very low densities for the cured plugs. Low cured densities are due, in part, to increased sidewall friction caused by the extra slump obtained when curing low density precompacts.

b. The extra thickness of the layers of coke particles used in curing runs A-1 through A-5 resulted in additional sidewall friction, although this problem could not be related directly to cured densities.

c. Cracking of pieces A-2, A-3 and A-4 when they were baked to 800°C is believed to have resulted from a combination of sidewall friction and nonuniformity in final temperature obtained on curing. No visible flaws were observed after baking pieces Nos. A-1 and A-5.

It was tentatively concluded from the results of Series 1 that a high density (about 1.80 g/cc) of the precompacted plug and a reduction in the amount of coke particles used top and bottom of the plug during the curing operation was required to minimize sidewall friction problems. The plug density can be raised by eliminating the use of particles on the top and bottom during precompaction and by providing extra heat at the ends of the plug.

3.3.2. Grade RVA Trials, Series 2

The objective of the trials in Series 2 (see Tables 9 and 10, pieces Nos. A-8 through A-11) was to minimize the sidewall friction problems observed in the precompaction and curing trials of Series 1. Series 2 trials also made use of a 7-inch long bottom ram extension on the 1250 ton press to insure adequate ram travel in the precompaction step.

Following is a summary of observations and conclusions of the Series 2 precompaction and curing trials.

1) Precompaction Trials

a. High densities were obtained on the precompacted plugs from runs Nos. A-8 and A-9 by providing extra heat at the ends of the plugs with the use of thermatomic black instead of coke particles at the top and bottom of the plugs. When heating by passing an electrical current through the charge, more heat will be generated in the thermatomic black than in the product since the electrical resistivity of the black is greater than the product blend. Elimination of the carbon black heat dams from the ends of the plug in runs Nos. A-10 and A-11 resulted in lower densities of the precompacted plugs.

b. Several trials were run in which the precompacted plug was held under pressure after heating. No conclusions can be drawn from the data on the effect of this hold time (compare runs Nos. A-1 and A-2 with A-8 through A-11 in Table 9).

2) Curing Trials

a. The estimated densities obtained on the unmachined pieces A-8 and A-10 are undoubtedly inaccurate due to the layer of particles stuck to these pieces. The densities of the turned pieces A-9 and A-11 were high with the shorter piece, A-11, having the higher density.

b. Decreasing the thickness of the particle layers used on the top and bottom of the plugs during the curing operation resulted in a decrease of sidewall friction. This decrease in sidewall friction can be detected from the data showing the per cent increase in plug diameter (Table 9) with the lower sidewall friction producing the greater increase in diameter.

c. Pieces Nos. A-8 and A-10 were found to have vertical cracks in the cured state. The vertical cracks resulted from the application of too high a pressure in the initial stages of curing.

d. Piece A-9 was found to contain an internal crack after graphitizing to 2800°C. This crack is believed to be due to sidewall friction problems resulting from the extra length of this piece (61 inches). The shorter piece, A-11, (53 inches long), was found free of cracks in the graphitized state. The effect of sidewall friction can be seen in Figure 11 which is a plot of the density variations (from top to bottom) of piece A-11.

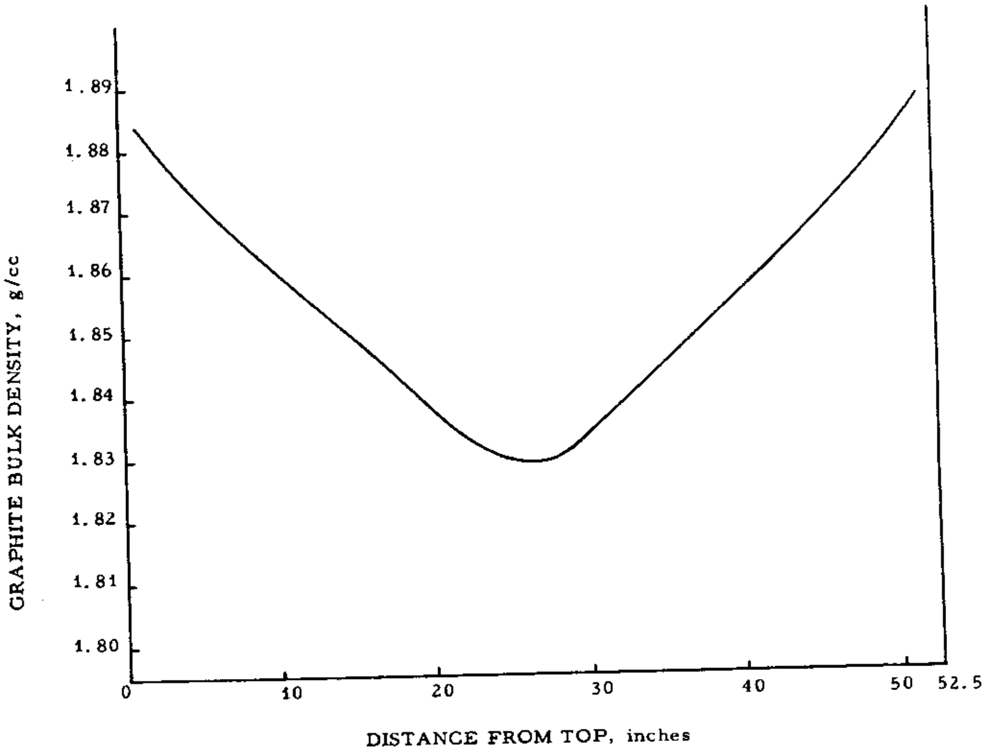

Figure 11. Bulk Density Along Outside of Piece A-11 Showing Effect of Sidewall Friction

The results of Series 2 indicated that with present processing methods (i.e., type of blend as well as forming and baking conditions) stock longer than 55 inches would be very difficult to process but that little difficulty should be encountered in processing lengths of about 45 inches. Consequently, a semi-production run of 45-inch long RVA was planned as the next step in the 1250 ton press trials.

3.3.3. Grade RVA Trials, Series 3, Semi-Production Trial in 1250 Ton Press

The objective of the semi-production run (see Tables 9 and 10, Series 3) was to determine if, and under what conditions, reproducible grade RVA graphite could be formed in 33-inch diameters by 45-inch lengths. Characterization of the material as to physical properties was also accomplished. In forming the 45-inch long sections, a 16-inch top ram extension and the previously mentioned 7-inch bottom ram extension were required to insure adequate ram travel on the 1250 ton press.

The precompacted plugs in trials A-17 and A-18 were removed from the mold after cooling for 5 hours but, because of the slow cooling rate obtained with the fiberglass liner (4 to 5°C per hour), the plugs were relatively soft which resulted in low density, cracked stock. Consequently, longer hold times, with or without pressure, were considered necessary to prevent these problems.

Pieces Nos. A-28 and A-31 were formed for use in 30-inch diameter induction curing trials.(3) These two plugs were high in density and showed no evidence of cracking.

In the semi-production run, six pieces were formed from blends using standard graphite filler materials (pieces Nos. A-19 through A-24) and two from blends using controlled graphite filler (pieces Nos. A-26 and A-27). Five of the eight pieces were sawed in half for structure examination. Three of these pieces contained horizontal cracks (pieces Nos. A-19, A-21 and A-23) and the other two were without visible flaws (pieces Nos. A-20 and A-24). Pieces Nos. A-19, A-20 and A-24 were sampled for measurement of physical properties at room temperature which are shown in Table 12 with properties of standard 30-inch diameter by 40-inch length grade RVA formed previously included for comparison.

The data in Table 12 show that considerable variation in properties (high standard deviation) was obtained with the 33-inch diameter material. Density gradients within the three pieces of RVA, presented in Figures 12, 13 and 14, illustrate the large outside to inside density variation which exists in this material. The method of heating these pieces during curing (inside to outside heating), which causes higher temperatures at the center of the plug, as well as sidewall friction, should have resulted in higher densities along the axis rather than at the outside of the stock. The density gradients were likely caused by the fast heating rate used for curing the relatively impervious plugs since plugs of this type, when heated rapidly, must necessarily puff to facilitate gas removal. This puffing condition would be most pronounced in the center of the plugs and the lowest densities, therefore, would be expected in the center and highest densities would be expected at the corners of the plugs.

Table 12. Room Temperature Properties of 33-Inch Diameter by 45-Inch Length Grade RVA Graphite Formed in 1250 Ton Press

	33-inch diameter by 45-inch length grade RVA formed in 1250 ton press												Standard 30-inch diameter by 40-inch length grade RVA		
	Piece No. A-19			Piece No. A-20			Piece No. A-24			Pieces Nos. A-19, A-20, A-24					
Property	No. of Samples	Ave.	σ	No. of Samples	Ave.	σ	No. of Samples	Ave.	σ	No. of Samples	Ave.	σ	No. of Samples	Ave.	σ
Bulk Density, g/cc	81	1.83	0.019	114	1.84	0.021	117	1.84	0.016	312	1.838	0.019	200	1.85	0.01
Flexural Strength,* lbs/in^2															
w. g.	42	3770	303	49	3880	336	44	3735	301	135	3800	321	86	3640	240
a. g.	35	2870	176	44	3165	288	42	2925	276	121	2995	203	114	2900	165
Compressive Strength, lbs/in^2															
w. g.	15	9425	1160	15	10250	1235	16	10200	1425	46	9960	1930	--	--	--
a. g.	15	7730	1350	15	9790	1830	16	9450	2175	46	9000	2000	--	--	--
Specific Resistance, 10^{-4} ohm cm															
w. g.	45	12.25	0.39	49	12.34	0.35	55	12.08	0.34	150	12.18	0.38	86	12.00	0.30
a. g.	35	16.87	0.34	65	15.20	0.92	62	15.65	0.66	162	15.73	0.96	114	15.20	0.45
Young's Modulus, 10^6 lbs/in^2															
w. g.	45	1.81	0.04	44	1.83	0.05	39	1.88	0.07	128	1.84	0.07	86	1.69	0.04
a. g.	35	1.19	0.05	65	1.32	0.11	62	1.35	0.09	162	1.30	0.09	114	1.28	0.06
Room Temperature CTE, 10^{-6}/°C															
w. g.	4	1.64	--	4	1.76	--	4	1.56	--	12	1.65	0.09	--	--	--
a. g.	4	2.85	--	4	2.77	--	4	2.65	--	12	2.77	0.07	--	--	--

* 1¼-by 1¼- inch cross section - third point loading

Solutions to this puffing problem would be (a) to use a longer curing cycle, (b) to use a lower forming pressure and/or (c) to use a plug in which the permeability is controlled. Lowering the initial binder level to a point below that required to yield optimum packed density of the dry ingredients might provide the permeability needed to prevent puffing; however, some sacrifice in other properties would undoubtedly have to be made.

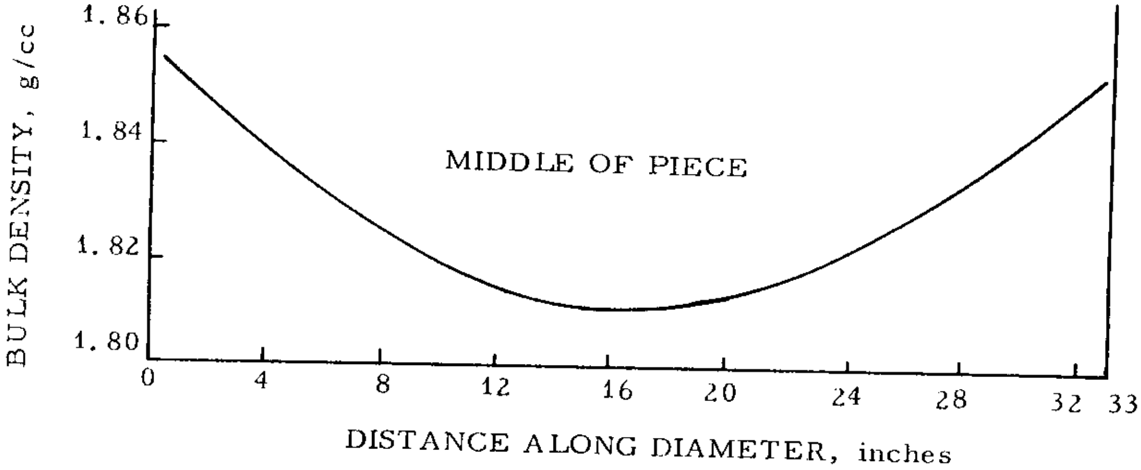

Figure 12. Density Gradient Along Diameter of Grade RVA Graphite, Piece No. A-19

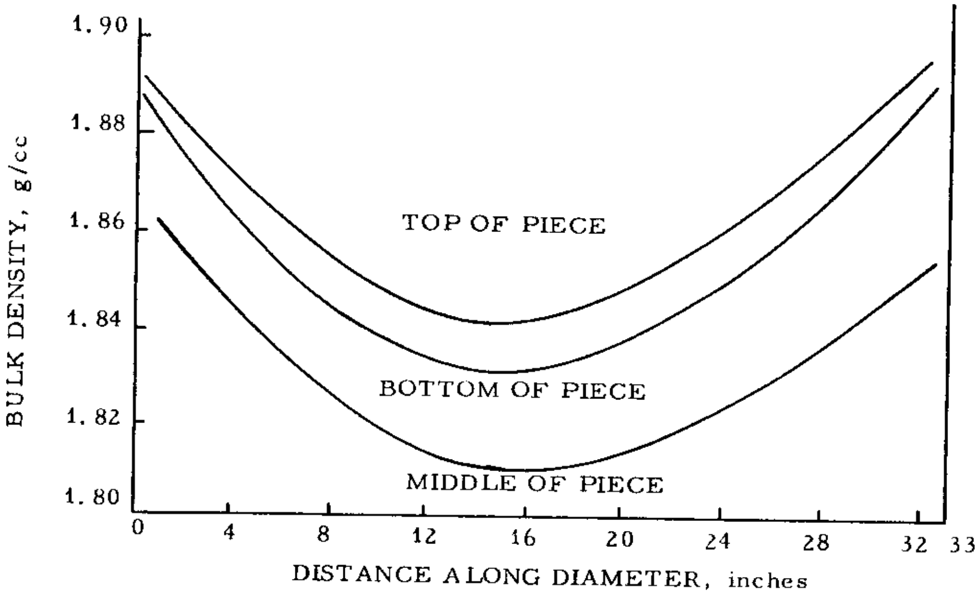

Figure 13. Density Gradients Along Diameter of Grade RVA Graphite, Piece No. A-20

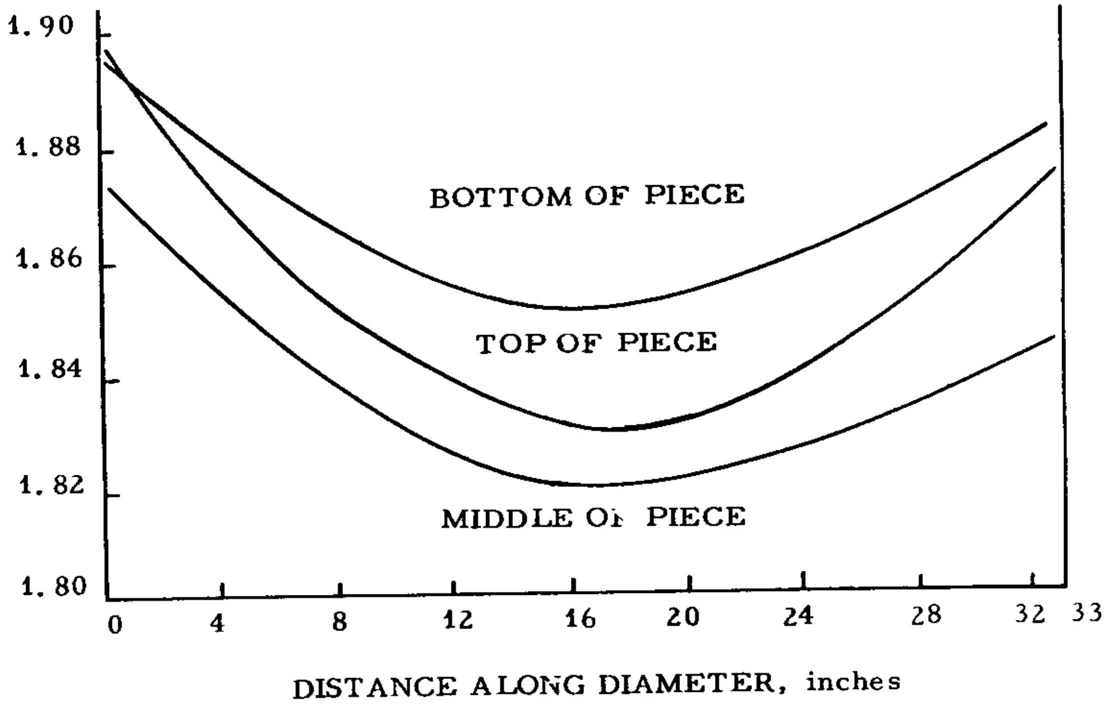

Figure 14. Density Gradients Along Diameter of Grade RVA Graphite, Piece No. A-24

4. CONCLUSIONS

The following conclusions are drawn from the trials on grade RVA graphite reported herein:

1) Graphite filler material with high porosity and high surface area imparts high strength to grade RVA graphite.

2) Graphite filler material with high kerosene apparent density imparts high bulk density to grade RVA graphite.

3) Prebaking a graphite filler material (e.g., extruded coke base rods) to 750°C before graphitizing to 2800°C is necessary to control property variations in the filler and subsequently, in the finished graphite article.

4) Grade RVA graphite, 33 inches in diameter, will be difficult to process in lengths greater than 45 inches unless a basic change in blend composition or processing procedure is found which will minimize the problems of sidewall friction and gas removal.

5. RECOMMENDATIONS

5.1. Sources of Graphite Filler Material

The large effect of the surface area, porosity and kerosene apparent density of the filler material on the room temperature density and strength of grade RVA shows that considerable improvement in RVA graphite is possible if these properties are carefully controlled. Further experimentation in this area might, therefore, be warranted. Some of the variables in the extrusion of graphite fillers which might be studied are as follows:

1) The effect of coke type on thermal and other properties of graphite filler materials.

2) The effect of coke flour fineness and coke particle size on the pore distribution in fillers.

3) The effect of oil level in the blends on the porosity of graphite fillers.

4) The effect of binder level on the kerosene apparent density of filler materials. Increased amount of pitch coke in graphite is expected to decrease the kerosene apparent density.

5) The effect of pitch type on the kerosene apparent density of graphite sources. Different pitch types will yield different amounts of pitch coke.

6) The effect of hot molding versus extrusion on the amount of binder required to process graphite filler materials.

5.2. Large Diameter Grade RVA Graphite

The results of the 1250 ton press semi-production runs were encouraging in that grade RVA graphite, 33 inches in diameter by 45 inches in length, was successfully processed without visible flaws. Overall processing success was marginal, however, and a reasonable scrap rate was not obtained (37.5 per cent scrap rate). Additional development work on improving the processability of grade RVA is necessary in the forming of larger sizes (e.g., 58-inch diameter). Improvements in processability might be accomplished by the following methods:

1) Changes in the basic blend composition for RVA graphite

can be made which will minimize the heating rate or gas removal problems. Three of the variables which should be studied in conjunction with firing rate are:

a. Particle to flour ratio: Increasing the amount of particles in RVA blend will increase the overall size of the pores in RVA and thus reduce the gas removal problem.

b. Binder level: Decreasing the initial binder level will increase the overall porosity of RVA. The degradation of properties obtained with this approach could be overcome by impregnation.

c. Graphite filler source: Using a porous filler material will result in an increase in overall porosity and strength of RVA (see Section 3 of this report). The increase in porosity would facilitate gas removal during the curing operation.

2. An envelope which minimizes sidewall friction can be used in place of the presently used coke particles. Possible substitutes for the coke particles are graphite particles; combination of graphite and coke particles; or a flour envelope made up of either coke or graphite flours or a combination of the two. Firing rates would have to be adjusted to the type of envelope used.

6. LIST OF REFERENCES

1. Waters, C. W. and E. L. Piper, WADD Technical Report 61-72, Volume XII, "Improved Large Diameter Fine Grain Graphite for Aerospace Applications".

2. WADD Technical Report 61-72, Volume XLII, Summary Technical Report, Appendix V, "Induction Heating for Pressure Curing".