FOREWORD

This work was conducted by the National Carbon Company, a Division of Union Carbide Corporation, under USAF Contract AF 33(616)-6915. This contract was initiated under Project No. 7350 "Refractory Inorganic Non-Metallic Materials", Task No. 735002 "Graphite Materials Development"; Project No. 7381 "Materials Application", Task No. 738102 "Materials Preproduction Process Development"; and Project No. 7-817 "Process Development for Graphite Materials". The work was administrated under the direction of the AF Materials Laboratory, Research and Technology Division, with Captain R. H. Wilson, L. J. Conlon, and W. P. Conrardy acting as Project Engineers.

Work under this contract has been in progress since May 1, 1960. The work covered in this report was conducted by the Advanced Materials Laboratory of National Carbon Company, located at Lawrenceburg, Tennessee, under the direction of Mr. R. M. Bushong, Director of the Advanced Materials Project, and Mr. R. C. Stroup, Manager of the Advanced Materials Laboratory. This report covers work conducted from May, 1960, through August, 1962.

This is the twelfth of a series of volumes of WADD Technical Report 61-72, prepared to describe various phases of the work. The preceding volumes of this 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 Roger Bacon and Richard 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 Temperatures, by. E. J. Seldin.
Volume VII	High Density Recrystallized Graphite by Hot Forming, by E. A. Neel, A. A. Kellar, and K. J. Zeitsch.
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.

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

ABSTRACT

This report describes a method for producing graphite using a pressure curing process which was partially developed prior to initiation of this contract. The process is based on a thermosetting binder system and is employed to develop a reasonably uniform fine-grain graphite. Also presented are the contract supported investigations of the process variables associated with attempting to reach optimum properties and with scaling up to 30-inch diameter sizes. This graphite, designated "Grade RVA", is nominally characterized by a bulk density of 1.85 g/cc, room temperature with and against grain flexural strengths of 3700 and 2900 lbs/in^2 respectively, with and against grain elastic moduli of 1.7 and 1.3 million lbs/in^2 respectively, and variations in these properties of only one-half to one-third of those normally associated with quality industrial graphites such as grade ATJ. Future activities to further improve quality are also indicated.

This report has been reviewed and is approved.

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1. INTRODUCTION

The use of carbon and graphite materials in aerospace applications has indicated a great need for improving their physical properties. One of the greatest challenges is reducing the property variation not only within a piece but also from piece to piece and accomplishing this for relatively large sizes. This challenge is made even more urgent by the lack of adequate nondestructive inspection techniques for billets larger than 15-inch diameter. A reproducible graphite with improved uniformity will significantly affect performance reliability and minimum design allowables even if average properties are not improved.

The objective of this effort was to develop and scale up a process capable of producing fine-grain graphite in large sizes (e.g., solid cylinders 30-inch diameter x 40-inch length) possessing reasonably uniform physical properties. A process potentially capable of producing material meeting these requirements had been partially developed by National Carbon Company prior to contract support and considerable progress had been made toward perfecting fabrication techniques in an experimental facility at the Columbia, Tennessee plant.

The process for the fabrication of this type of improved graphite (designated grade RVA) is based on the use of a thermosetting binder system and the curing of this binder under pressure. The heat necessary to thermally set the binder is supplied by passing an electric current through the mix and heating resistively in as uniform a manner as possible. Successful development of such a processing method has resulted in the fabrication of grade RVA graphite in sizes up to 30-inch diameter by 40-inch length, having one-half to one-third the variation in physical properties normally associated with quality industrial graphites such as grade ATJ.

2. EARLY DEVELOPMENT STUDIES

Early in the development of the pressure curing process, it was recognized that the major problem was achieving an isothermal temperature distribution within the product during the curing cycle. Use of an electrically insulated mold created higher temperatures along the axis of the piece, which resulted in the binder being set more rapidly in this area than on the outside of the piece. Blocks which were baked after being cured in this manner invariably contained horizontal cracks extending 2 to 3 inches inward from the outside of the piece. On the other hand, when the mold is not electrically insulated, the majority of the current passes through the metallic mold walls. This results in higher temperatures at the periphery of the stock rather than at the axis. Pieces baked after curing in this manner contained a single horizontal flaw located near the geometric center and extending toward the periphery of the piece. Figure 1 shows this type of cracking.

The thermosetting of the binder during curing is accompanied by a volume shrinkage of the block. Therefore, both types of cracking described above are attributed to the fact that, with uneven heating, one portion of the block has thermoset, shrunk and become rigid while adjacent portions are still shrinking. If a crack does not appear during curing, it will almost always do so when the stresses are relieved during subsequent baking.

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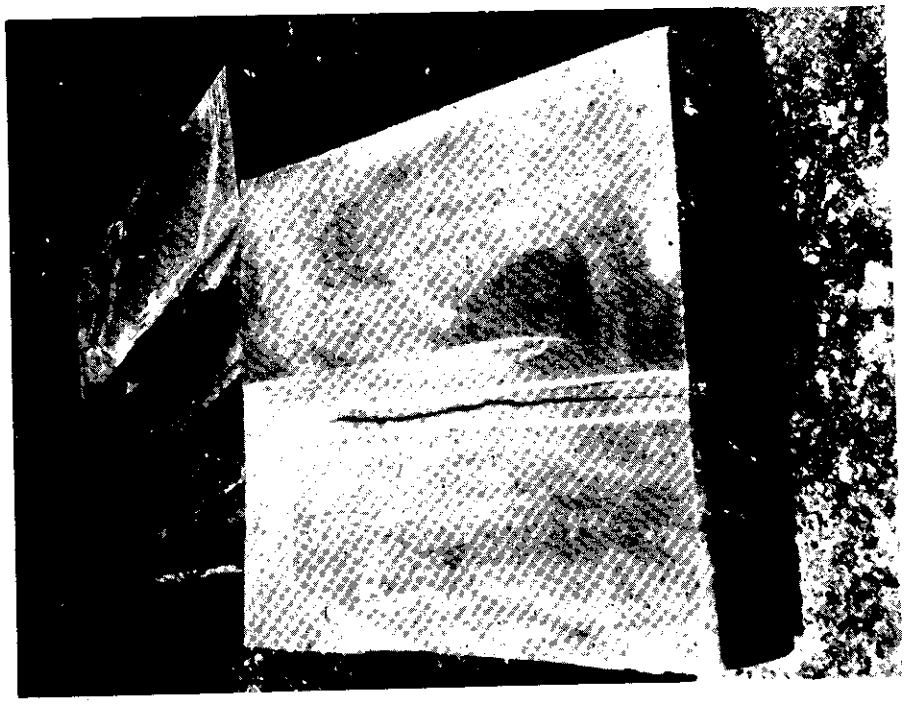

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Figure 1. Typical Cracking Caused by Pressure Curing in an Electrically Uninsulated Mold

What was obviously required was a type of mold in which enough heat was generated at any stage of the curing cycle to just balance the heat losses from the product at that stage. A step toward solving this problem was made prior to contract support. A controlled resistance mold, 30-inch I.D. by 69-inch length was developed which incorporated alternating layers, or rings, of conducting and insulating materials. This mold is shown in Figure 2. The laminated mold, however, had the primary disadvantage of being tied too closely to a given mix composition. The design of the ring laminates was dependent upon the resistivity of the mixes used and the size (diameter) of product desired. Although this laminated mold design was far superior to a simple conducting or nonconducting mold configuration, the heating of the piece was not as uniform as required and the process was still plagued with cracked material. The final product possessed physical properties inferior to the potential capabilities of the process.

3. RAW MATERIALS VS STRUCTURAL INTEGRITY

Initial development work on the process under this contract was aimed at up-grading the physical properties of the graphite. Since the strength of graphite is one of the most important properties, and since it is an excellent indication of the structural integrity of the body, means of increasing strength were first investigated. Raw materials were the initial items considered since it is well established that both filler and binder sources and sizings can have a large influence on the final graphite properties. Experiments were therefore conducted to determine (1) the optimum binder level for the mix composition used, (2) the effect of pitch fineness, and (3) the effect of the source of the graphite filler.

Previous development work established the filler blend which maximized the density of the uniformly blended dry ingredients. The composition of this filler is as follows:

Graphite particles through 20 on 35 mesh Tyler screens - 100 parts;

Thermatomic black, 100% through 325 mesh Tyler screen - 16 parts;

Graphite flour, 100% through 35 mesh Tyler screen - 100 parts.

The graphite filler was a mixture of AGR and AGX electrode graphite [1] milled to the desired particle size. In the normal process these materials were mixed with pitch and sulfur, charged to the mold, compressed, and cured. A high melting point (175°C) pitch was used to insure a high coking value and to minimize the amount of volatiles formed during the curing operation. Sulfur was used to plasticize and "polymerize" the pitch. The amount of sulfur necessary to complete polymerization was previously ascertained to be 20 weight per cent of the pitch. [2] The optimum forming pressure was determined to be 0.5 tsi. [3]

An additional processing variable, mixing technique, later was to prove extremely significant and was included in these experiments. The first mixing method was the same as employed in earlier work, i.e.,

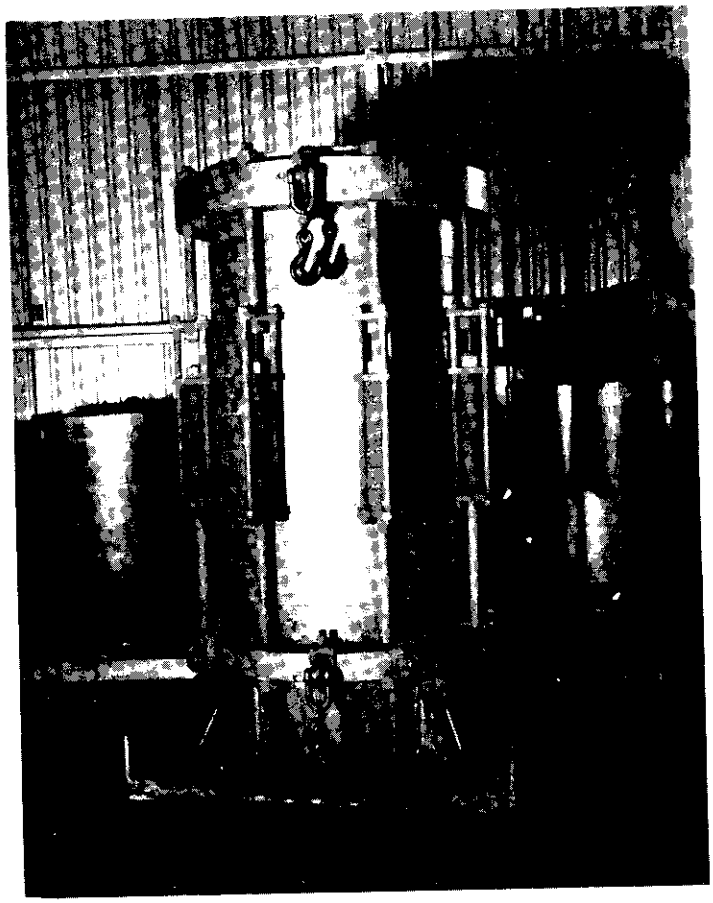

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Figure 2. Thirty-Inch Diameter Laminated Mold

the pitch and graphite particles were charged to a steam jacketed mixer at temperatures sufficient to yield a highly plastic mix. This is designated "hot mix". In the second method the pitch and graphite particles were mixed (or blended) cold. In the latter case, the pitch does not become plastic, and the resultant mix is referred to as "dry blend".

3.1. Optimum Binder Level

In order to determine the optimum binder level, it was first necessary to ensure reproducible forming conditions. This involved determining the mixing temperature at which the plasticizing action of the sulfur was a maximum and at which "mix balls" (which represent a concentration of binder) were eliminated. For these trials, hot mixing was employed to ensure a more uniform distribution of the binder and filler blend.

The plasticizing action of sulfur was investigated in the range of mixing temperatures from 135° to 155°C, the sulfur being added after the pitch-filler blend had reached final temperature. The mix was then hot molded in 3-inch diameter by 3-inch long cylinders at a pressure of 0.92 ton/in^2. For this experiment, the pitch level was maintained at 24 parts per hundred of the filler, by weight, and the sulfur level at 20 per cent by weight, of the pitch. In this series of experiments, it was observed that "mix balls" were prevalent throughout the range of investigated temperatures but that they could be virtually eliminated (up to 150°C mix temperature) by mixing under a slight mechanical pressure of 1.3 lbs/in^2. Table 1 lists the green bulk densities obtained from the various mixing temperatures both with and without pressure mixing. The values are plotted in Figure 3 and show that the plasticizing action of the sulfur is fairly uniform in the mix temperature range of 140° to 150°C and that application of mechanical pressure produces more uniform results. It was recognized in this series of experiments that the molding pressure (0.92 ton/in^2) was excessive, but was required to form plugs in the lower temperature ranges where very little plasticizing action of the binder and sulfur was observed.

Table 1. Determination of Maximum Plasticizing Temperature

Final Temperature of Mix Prior to Adding Sulfur and Molding - (°C)	Green Bulk Density	
	Pressure Mixed (g/cc)	Not Pressure Mixed (g/cc)
132	1.790	
135	1.800	1.725
140	1.800	1.740
141	1.795	
142	1.810	
146	1.760	1.725
148		1.690
150	1.815	1.740
154	1.795	1.750

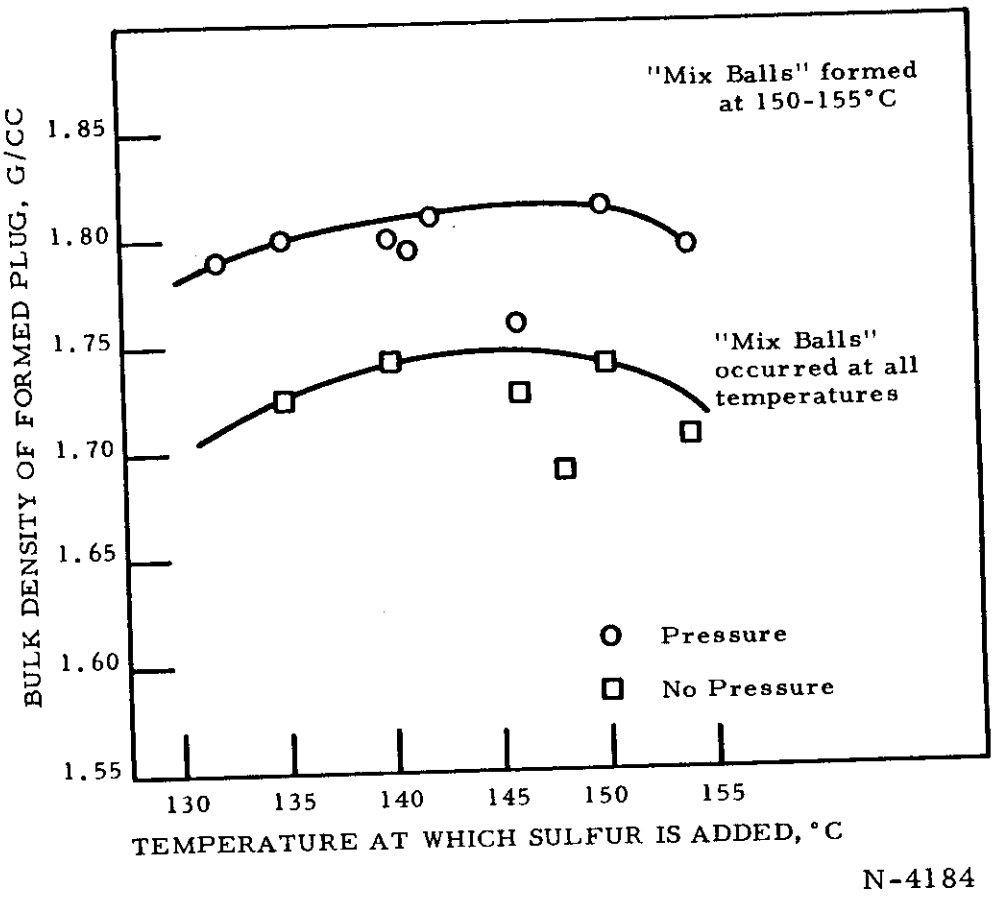

Figure 3. Green Bulk Density vs. Mix Temperature

Through a series of carefully controlled experiments, the quantity of binder necessary to fill the interstices between the particles of the blend was concluded to be between 24 and 27 parts of 175°C pitch per hundred parts of blend. The experiment performed was to mold plugs (three inch diameter) of hot-mixed blend containing regularly varied quantities of pitch ranging from 20 to 30 pph. These mixtures were plasticized with sulfur at a level of approximately 20 per cent of the binder, which was added when the mix reached a temperature of 140°C. Table 2 lists the green bulk densities and effective filler densities (the weight of the particles, flour, and black divided by the volume of the formed green article) for the indicated binder levels. At optimum effective filler density, the particles and flour are packed as closely together as possible under a given set of molding conditions. The values are plotted in Figure 4 and show that the optimum binder level is near 25 pph.

Table 2. Binder Level Series - Green Bulk Density and Effective Filler Density

Pitch Level (pph)	Green Bulk Density (g/cc)	Effective Filler Density (g/cc)
20	1.72	1.390
22	1.76	1.390
24	1.80	1.400
26	1.82	1.385
28	1.81	1.350
30	1.81	1.330

Molding conditions - 0.5 tsi pressure at 140°C

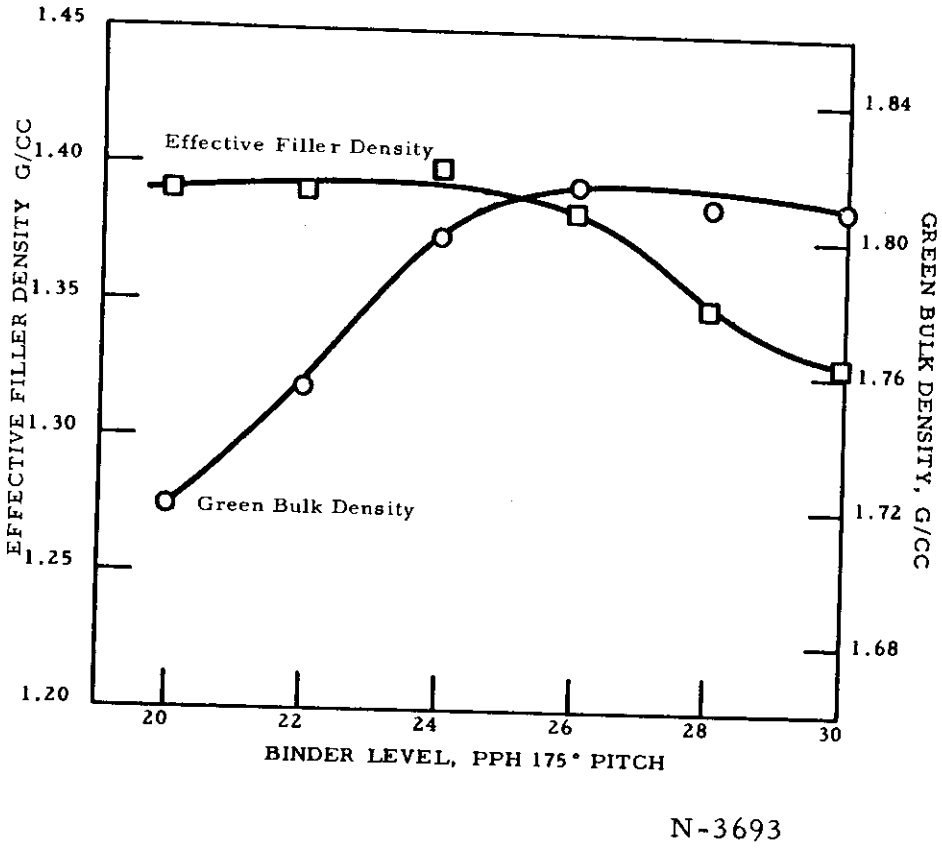

Figure 4. Binder Level vs. Green Bulk Density and Effective Filler Density

The green plugs were baked (750°C), graphitized (2800°C) and sampled for resistivity and flexural strength. As previously stated, strength is a good measure of structural integrity. The electrical resistivity is also a sensitive measure of the presence of microflaws. These data are tabulated in Table 3 and pictured graphically in Figures 5 and 6. From the graphs, it is evident that when the filler is bonded with 24 to 26 pph 175°C melting point pitch, density attains a maximum and electrical resistivity (processing flaws) a minimum.

Table 3. Binder Level Series - Baked and Graphitized Data

Pitch Level pph	Baked B.D. (g/cc)	Graphitized B.D. (g/cc)	Graphitized Resistivity (10^{-3} ohm-cm)	Graphitized Flexural Strength psi
20	1.660	1.650	1.75	1800
22	1.720	1.725	1.56	2542
24	1.780	1.780	1.52	2683
26	1.795	1.805	1.61	2159
28	1.795	1.805	1.60	2512
30	1.795	1.805	1.68	2545

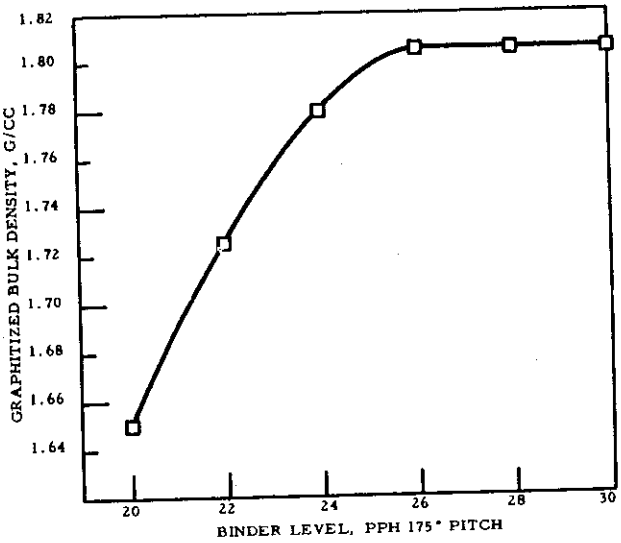

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Figure 5. Binder Level vs. Graphitized Bulk Density

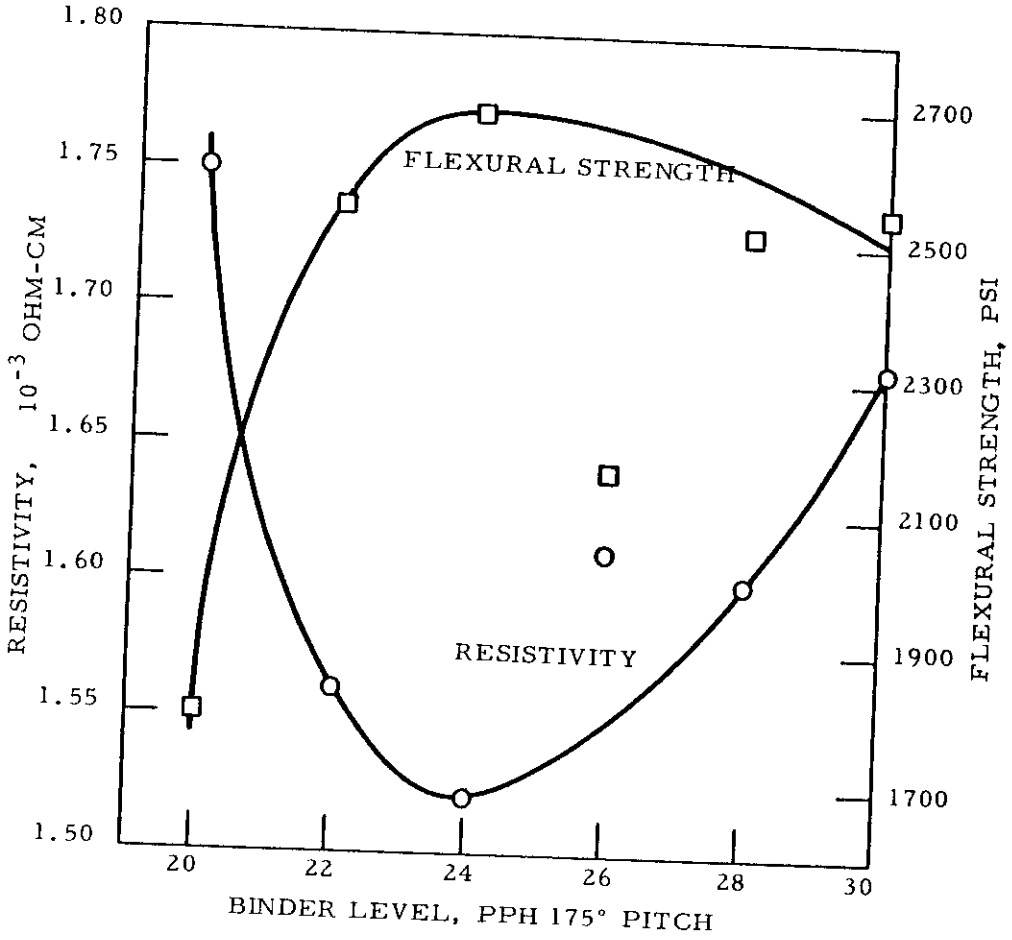

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Figure 6. Binder Level vs. Electrical Resistivity and Flexural Strength

3.2. Effect of Pitch Fineness Upon Structural Integrity

The effect of pitch fineness upon the density and strength of the product was evaluated.

The first phase of this work consisted of forming and curing 10-inch diameter material from blends and mixes differing only in the fineness of the milled 175°C melting point pitch, which was varied from 20 per cent to 100 per cent through 200 mesh in five regularly varied steps. The mixtures were charged to the mold both as dry blend and as hot mix, and three pieces were formed for each method of charging. After baking, pitch impregnation, and graphitization, seven samples were cut across the grain and six with the grain for determination of bulk density, resistivity, sonic modulus, and flexural strength. The latter property was determined on 1.25-inch square sections by the third-point loading technique. Table 4 lists the average values of these properties as a function of pitch fineness.

Table 4. Pitch Fineness Series

Pitch Fineness*		20	40	60	80	100
Hot Mix						
B.D., g/cc		1.846	1.857	1.863	1.853	1.854
Sonic Modulus (10^6 psi)	W	1.47	1.51	1.51	1.47	1.47
	A	1.16	1.23	1.22	1.13	1.06
Resistivity (10^{-4} ohm-cm)	W	11.40	11.68	11.95	11.27	11.39
	A	13.53	13.35	13.84	13.15	13.57
Flexural Strength (psi)	W	2257	2586	2418	2212	2349
	A	1432	1612	1432	1475	1083
Dry Blend						
B.D., g/cc		1.858	1.858	1.865	1.858	1.881
Sonic Modulus (10^6 psi)	W	1.57	1.56	1.56	1.53	1.64
	A	1.18	1.20	1.12	1.21	1.26
Resistivity (10^{-4} ohm-cm)	W	11.65	10.97	11.62	11.44	11.44
	A	14.63	13.66	13.98	13.76	13.83
Flexural Strength (psi)	W	3035	3074	2862	2723	3038
	A	1966	2409	1777	2009	2122

* Per cent through 200 mesh screen.

The density of pieces formed from hot mix tends to maximize when pitch fineness is in the range from 40 to 60 per cent through 200 mesh, while for pieces cured from dry blend, the highest density is achieved in

pieces made with the finer binders because of the better pitch distribution. The sonic moduli behave similarly, but the most significant feature of the data is the consistently higher strength values for the pieces made from dry blend over those made from hot mix regardless of pitch fineness. Table 5 lists the average flexural strengths together with the standard deviations of hot mixed versus dry blended material.

Table 5. Average and Standard Deviations of Flexural Strength for Experimental RVA Grade Graphite Made from Hot Mix and Dry Blend Materials

	Flexural Strength - psi					
	With Grain			Across Grain		
	N	Ave.	Standard Deviation	N	Ave.	Standard Deviation
Hot Mix	90	2364	355	105	1407	422
Dry Blend	90	2946	224	105	2056	391

The standard deviations were calculated on the total population of the samples, disregarding the pitch fineness used in the mix design. These values are therefore significant only in comparing the dry blend versus hot mix methods. The variation is less for the strength of pieces made by the dry blend technique. The more erratic strength values for the hot mixed RVA was due to small incipient flaws arising from prereaction in the mixer of the pitch with the sulfur. Figure 7 is a photograph of polished sections of samples of the two materials showing these flaws. None of the small cracks were evident in stock prepared from dry blend.

3.3. Effect of Graphite Filler Source vs. Structural Integrity

The second phase of this work entailed the forming of 10-inch diameter stock using graphite particles and flour prepared from cokes of widely different physical properties. Graphite was obtained from three sources. These sources were: (1) Grade CS (coke base) graphite made from a highly oriented coke; (2) grade CS graphite made from a less oriented coke; and (3) blended AGR and AGX graphite*. This experiment was designed to determine if the crystallinity of the coke used for the manufacture of the graphite filler would affect the final graphite properties. Normal processing was used, i.e., curing, baking to 800°C, pitch impregnating, and graphitizing to 2800°C. The finished stock was sampled for physical properties which are summarized in Table 6.

* AGR is a coke base graphite that is not impregnated before graphitization while AGX is pitch impregnated before graphitization.

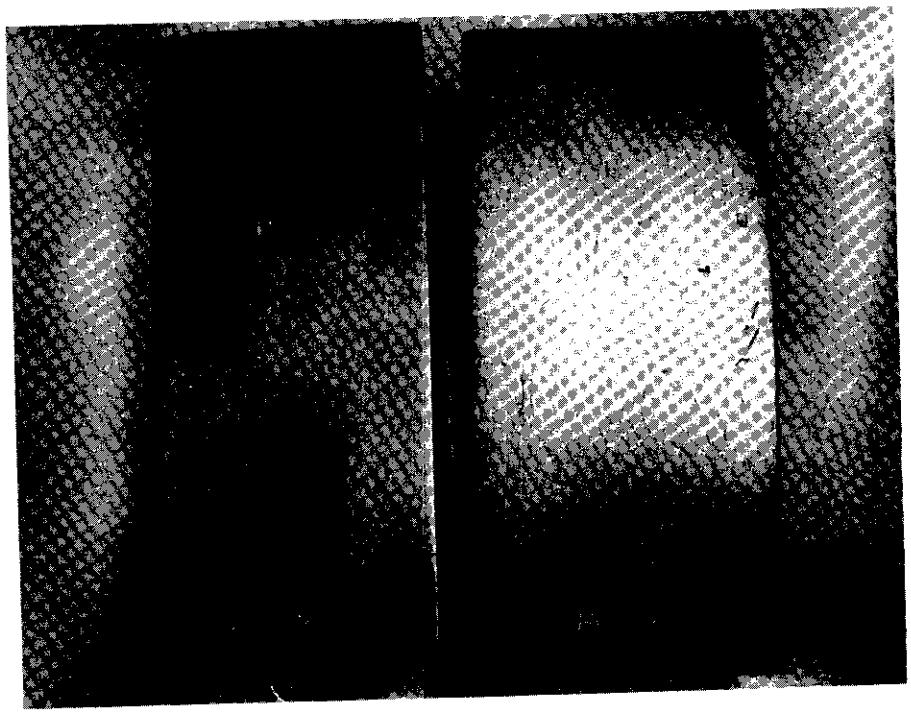

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Figure 7. Structure of Grade RVA Graphite, Hot Mixed vs. Dry Blend Method, Reduced 3X

Table 6. Effect of Graphite Source on Properties of Experimental Grade RVA Graphite

BO Source	Method	N W	N A	Graphite B.D. (g/cc)	Flexural Strength (psi) W	Flexural Strength (psi) A	Resistivity (10^{-4} ohm-cm) W	Resistivity (10^{-4} ohm-cm) A	Sonic Modulus (10^6 psi) W	Sonic Modulus (10^6 psi) A
CS (Highly Oriented Coke)	Dry	12	19	1.895	2660	2200	9.4	12.4	1.57	1.07
CS (Highly Oriented Coke)	Hot	18	18	1.892	2130	1330	10.1	12.3	1.42	1.00
CS (Less Oriented Coke)	Dry	14	19	1.886	2880	2530	10.4	12.4	1.56	1.26
CS (Less Oriented Coke)	Hot	16	19	1.886	2140	1450	10.8	12.3	1.40	1.14
Blended AGR and AGX	Dry	19	18	1.871	3040	2120	11.4	13.8	1.64	1.26
Blended AGR and AGX	Hot	19	18	1.854	2350	1080	11.4	13.6	1.47	1.09

As in the case of the pitch fineness series, the low strength of the hot mix material is attributable to incipient flaws in the stock arising from prereaction in the mixer of the pitch with the sulfur – even though the addition of the sulfur was delayed to the last five minutes of the mixing cycle. Differences in strength of stock prepared from the various coke sources do not appear to be critical, but trend toward higher values for the most poorly oriented cokes.

The differences in graphite density shown in Table 6 are readily explained by differences in coke density, and demonstrate that high density is not necessarily a desirable goal where maximum strengths are sought.

4. PARTICLE ENVELOPE CURING

Attention was next turned from raw materials to processing modifications as a means of improving the physical properties and structural uniformity of Grade RVA graphite. As stated earlier, the laminated mold design used for the pressure curing process had the primary disadvantage of being tied closely to a given mix composition, and different molds were required to match the different electrical resistances as compositions were changed. Serious problems had also been encountered with this mold design in gas removal during the curing operation, particularly with mix compositions requiring relatively high binder levels. An idea for a more flexible procedure was conceived, employing an electrically insulated mold lined with a porous electrically conducting envelope which completely surrounded the material to be cured. This system afforded two advantages -- first, the

heating pattern could be adjusted to any blend by changing the resistance of the porous envelope, and second, the porosity of the envelope facilitated gas removal.

4.1. Particle "Smokestack" Trials

The porous envelope concept was an outgrowth of problems encountered by National Carbon Company in producing an order of four graphite nozzle blanks 39-inch O.D., 24-inch thickness and varying inside diameters ranging from 14 inches to 23.5 inches. Decisions were made to:

1. Supply the order with pressure cured stock
2. Use the 41-inch diameter mold
3. Dry charge the mold with RVA blend with 26 pph binder
4. Cure the stock from the outside - in, i.e., cure in an electrically uninsulated mold

Since curing large sections of RVA stock in an uninsulated mold results in an undercured center and internal flaws after baking, it was felt that good stock could be produced for this order by boring prior to baking. Eleven such pieces were cured and baked, all of which cracked prior to or after baking. Visual observation showed that the well cured section of the stock was confined to a shell approximately 2-½ inches thick at the periphery of the stock. In no instance, either cured or baked, did the internal flaws penetrate the surface of the stock. Thus the problem resolved itself into a method of supplying heat to the center of the stock as well as venting the volatiles formed. One suggested method, shown in Figure 8, was to place coke particles next to the platens and to form a "smokestack" of calcined coke particles through the center of the curing piece. These particles would allow continuous venting from platen to platen and would provide a method of generating heat through the center of the stock. A 6-inch diameter stovepipe was used to position calcined coke particles in the center of the stock during loading. No difficulty was encountered in curing. Compaction versus curing time has been plotted as shown in Figure 9 for piece J-11, which was the best conventionally cured stock produced, and for pieces J-12 and J-13, which were cured with a "smokestack" of calcined coke particles. These curves show that pieces J-12 and J-13 cured with 50 per cent less expansion than did piece J-11. On the next five pieces of 40-inch stock cured and baked utilizing the "smokestack", two were O.K., two were salvable to 19-inch lengths, and one was scrap. These results were encouraging, considering the fact that all of the first eleven conventionally cured pieces were scrap. Thus, the contemplated advantages of a particle column to vent the volatiles were realized, although completely satisfactory results had not yet been attained.

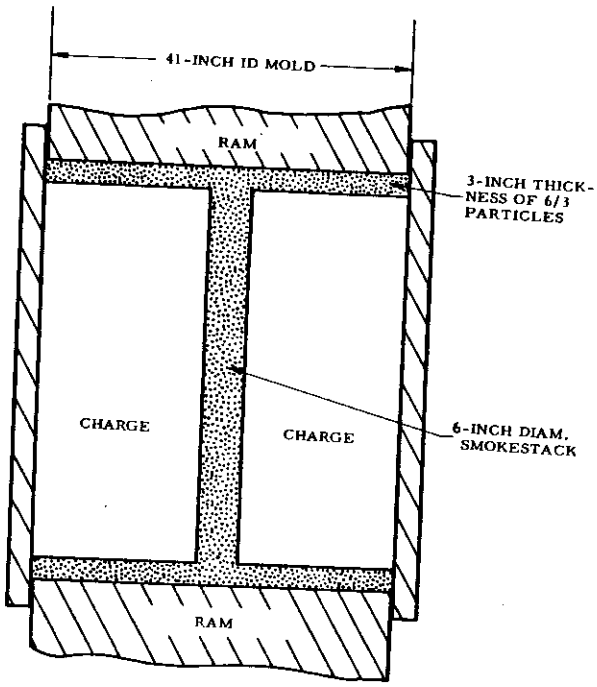

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Figure 8. "Smokestack" Curing

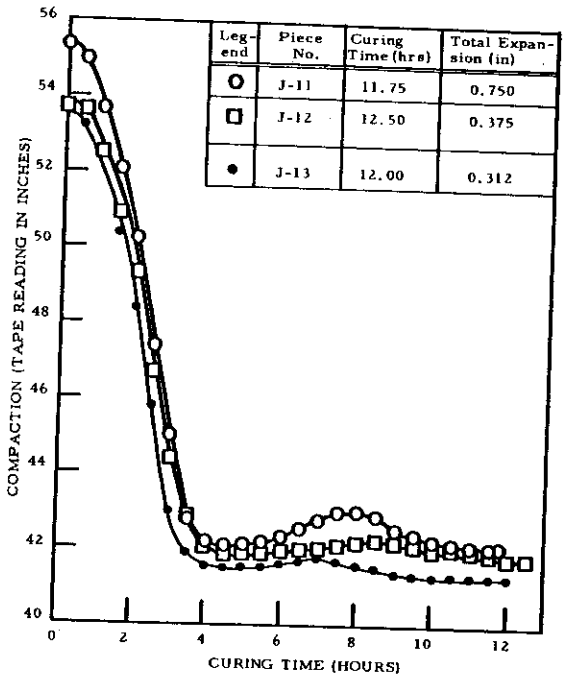

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Figure 9. Compaction vs. Curing Time

Because of the success obtained with the "smokestack", the next logical approach was the use of particles surrounding RVA mix to provide venting for solid sections.

4.2. Ten-Inch Diameter Envelope Trials

The initial experiments on the fabrication of graphite by the porous envelope technique were conducted on a small 50-ton capacity press equipped with a 10-inch diameter laminated mold. These initial trials consisted of pressure curing fine grain and very fine grain [4] dry blends containing 24 and 26 pph of pitch, respectively, in the 10-inch mold with a 1/4-inch layer of particles separating the blend from the mold wall. Prior to these experiments, the resistivities of various materials of different particle sizes were measured under a pressure of 1000 psi and compared with the resistivities of pressure cured blends. These resistivities are shown in Table 7. Table 8 lists the envelope materials together with the mix design and the baked density gradients. Two 10-inch diameter pieces, as shown in Table 8, were made with sand liners but only one of these survived the baking operation. All other pieces were flaw-free after baking.

Table 7. Resistivities of Possible Liner Materials at 1000 psi Pressure

Granular Material*		Resistivity at 1000 psi Pressure, ohm-cm
Calcined DK 3/1-1/2		0.085 ohm-cm
Calcined NA 3/1-1/2		0.082
Calcined AX 3/1-1/2		0.079
Calcined AX 6/3		0.060
BO 3/1-1/2		0.0093
BO 6/3		0.0055
DK 50 flour		0.084
BO 50 flour		0.013
BO 3/1-1/2 - 20%		0.058
DK 3/1-1/2 - 80%		
BO 3/1-1/2 - 40%		0.032
DK 3/1-1/2 - 60%		
BO 3/1-1/2 - 60%		0.019
DK 3/1-1/2 - 40%		
BO 3/1-1/2 - 80%		0.014
DK 3/1-1/2 - 20%		
Cured very fine grain blend	w.g.	0.071
	a.g.	0.081
Cured fine grain blend	w.g.	0.041
	a.g.	0.039

* 6/3 sizing is 100% through 0.06-inch opening, 100% retained on 0.03-inch opening 3/1-1/2 sizing is 100% through 0.03-inch opening, 100% retained on 0.015-inch opening AX, DK, AX refer to various calcined (1350° C) coke sources. BO is an all graphite material. w.g. = with grain; a.g. = across grain.

Table 8. Initial Forming Trials of Pressure Curing in a Porous Envelope

Trial No.	Mix Type[4]	Max. Mix Particle Size, Inch	Envelope Material	Baked Bulk Density - g/cc Outside	Inside	Average
1	Fine grain	0.03	NA-3/1-½	1.792	1.766	1.777
2	Fine grain	0.03	BO-3/1-½	1.795	1.775	1.782
3	Very fine grain	0.015	NA-3/1-½	1.766	1.746	1.755
4	Very fine grain	0.015	NA-3/1-½	1.786	1.730	1.751
5	Very fine grain	0.015	BO-3/1-½	1.807	1.779	1.791
6	Very fine grain	0.015	DK-3/1-½	1.796	1.758	1.774
7	Very fine grain	0.015	AX-3/1-½	1.776	1.755	1.762
8	Very fine grain	0.015	Sand	1.779	1.717	1.748
9	Very fine grain	0.015	Sand	1.789	1.723	1.751

The results of the 10-inch diameter trials were quite encouraging. It was determined that flaw-free stock could be processed and the resistivity of the liner could be controlled over a wide range. In addition, a reduction in curing time was indicated, because the volatiles were readily vented.

The 10-inch trials also point out that resistivity alone, cannot be used to determine the liner material for pressure curing as evidenced by flaw-free stock, which was produced with liners having different resistivities. Successful curing using various liner resistivities is due in part to the small cross-section of the stock, i.e., problems concerned with temperature gradients are less critical than in stock having larger cross-sections.

It has been the experience of the graphite industry that scale-up often introduces unanticipated problems. For these reasons, further experiments were shifted to 30-inch diameter sections.

4.3. Thirty-Inch Diameter Trials - Porous Liner Evaluation

A 41-inch diameter steel mold was lined (see Figure 7) with a castable refractory. An annular ring was welded to the bottom of the mold to support the liner and restrict the opening between platen and mold. A metal sleeve (approximately 31-inch I.D.) was fabricated to effect separation of the loose envelope and mix during the loading operation. As can be seen in Figure 10, the particles were not subjected to hydraulic pressure. Four exploratory trials were made (pieces X-1, X-2, X-3 and X-4) with minor variations in technique to determine the validity here of the earlier conclusions on the smaller size. Both "dry blend" and "hot mix" techniques were used. Piece X-3 was lost due to loss of hydraulic pressure; otherwise no difficulty was encountered during cure. After ejection, the stock presented an "hour glass" shape pictured in Figure 11, due to shifting of the loose envelope during removal of the sleeve and subsequent pressing.

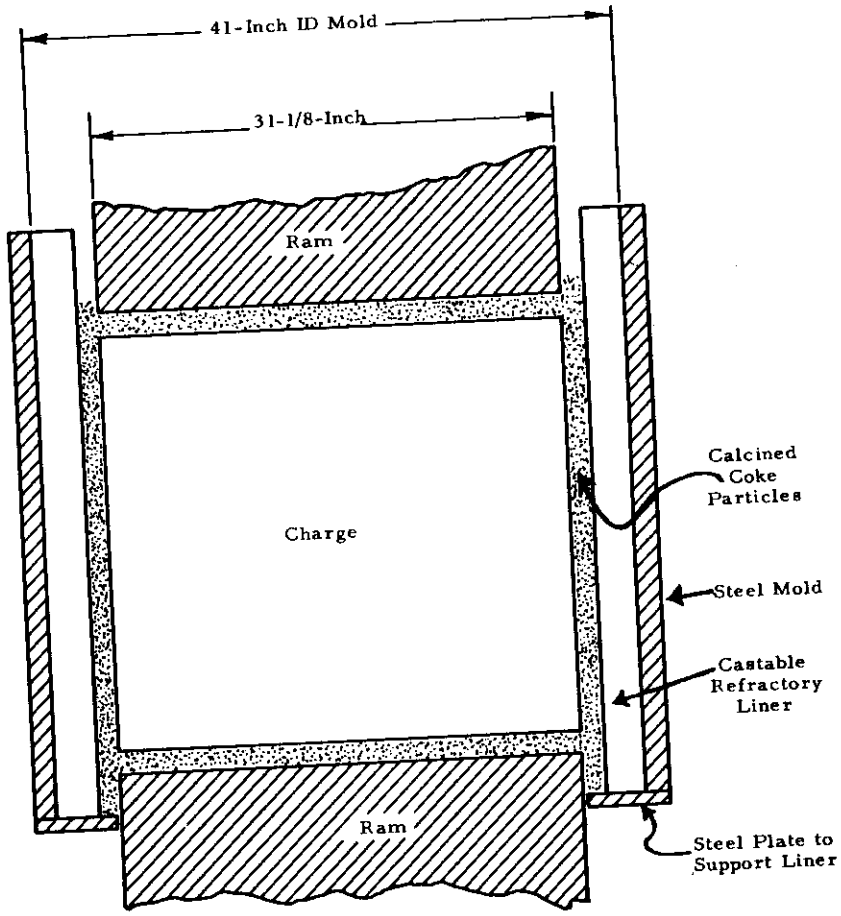

Figure 10. Particle Envelope Curing of 30-Inch Diameter Grade RVA Graphite in a 40-Inch Diameter Mold

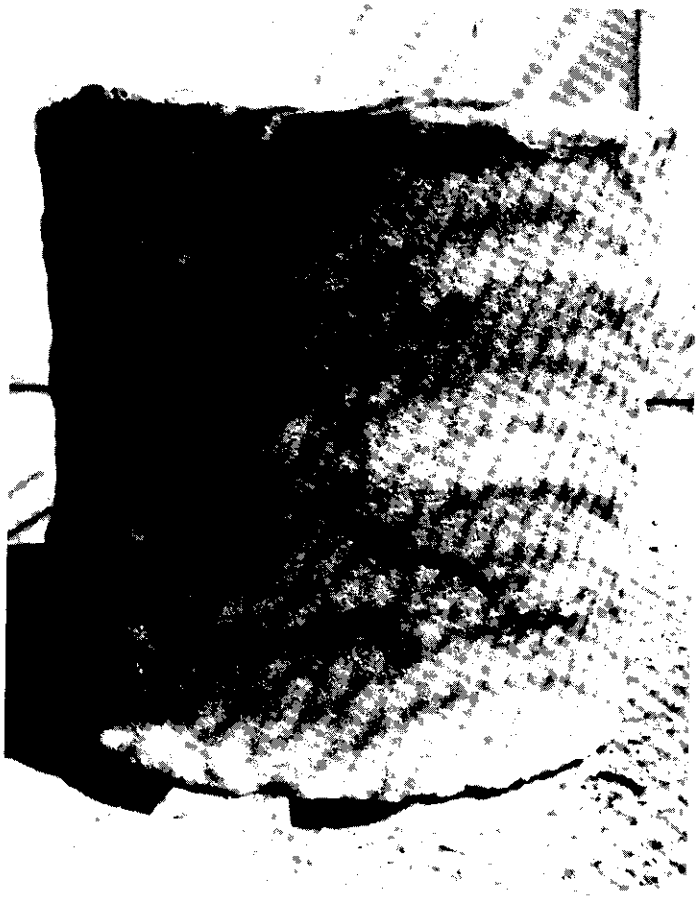

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Figure 11. Piece X-1, Showing Irregular Configuration Caused by Shifting of the Envelope

In every case, evidence of extreme particle interpenetration between the envelope and the mix was observed. This necessitated turning to the diameters indicated in Table 9. This table also contains a summary of all the particle envelope trials. Curing temperature uniformity was the best observed thus far in RVA development. After subjecting X-1, X-2 and X-4 to complete processing, i.e., baking (750°C), pitch impregnation, and graphitization to 2800°C, all were visually flaw-free. The intended variable in these first four trials was the composition of the particle envelope. However, a meaningful evaluation could not be made because of extensive migration of particles into the piece. Both 100 per cent graphite and 100 per cent calcined (1400°C) coke particles produced flaw-free stock. The 6/3 (through 0.06-inch opening and retained on 0.03-inch opening) coke particles appear to be most advantageous from the standpoint of shorter curing time, as indicated by the curing times listed for X-1 and X-2 in Table 9.

Physical properties were determined on two of the pieces -- one made from hot mix (X-4), the other from dry blend (X-2). These results are summarized in Table 10. The data in Table 10 show that the physical properties of both types of RVA graphites display a high degree of uniformity. It is also significant that the physical properties of the dry blended material are again somewhat superior to those of the hot mixed material.

Penetration of particles from the envelope into the mix occurred primarily when the separating sleeve was pulled from the mold. As one would expect, this intermixing occurred almost exclusively in the bottom portion of the stock. Figure 12 pictures a typical example of this effect. Additional trials were conducted in which the sleeve was vibrated, greased (pieces X-11 and X-12), and tapered with no apparent success. Experiments on the 350-ton press have shown that this intermixing can be eliminated if provisions are made to withdraw the separating sleeve uniformly. This problem arose on the 30-inch trials because of insufficient daylight in the press which necessitated removal of the sleeve by a fork truck and cable slings. Sufficient daylight existed on the 350-ton press to permit smooth removal of the sleeve by attaching it to the upper platen. Five pieces of experimental RVA stock 18-inch diameter by 15-inch length have been formed on the 350-ton press using this technique, and have been successfully processed through baking without visible flaws of any kind. Unfortunately, the press limitations on normal production scale equipment would generally prohibit this approach. Due to the fill ratio of the blend (2.6 inches of blend necessary to produce 1 inch of cured product), fabrication of a press having the necessary "daylight" to produce 30-inch diameter x 40-inch length RVA, would be extremely expensive.

4.4. Thirty-Inch Diameter Trials - Use of a Precompact Plus a Porous Liner

The problem discussed immediately above, namely that of intermixing of envelope and stock, made it mandatory to find an alternative technique which would permit substantial scaling to larger sizes. The most obvious alternative was to preform the body before insertion into the complex envelope curing procedure. The following sections discuss the two alternative approaches to a solution of this problem.

Table 9. Summary of Particle Envelope Trials

Pc. No.	ppn 175° Pitch	Blend Type	Curing Time (hrs.)	Precompacted Plug Dia. (in.)	Precompacted Plug Lgth. (in.)	Precompacted Plug Wt. (lbs.)	Precompacted Plug B.D. (g/cc)	Total Slump on Curing (Per Cent of Plug Length)	After Curing, Turning and Sawing Dia. (in.)	After Curing, Turning and Sawing Lgth. (in.)	After Curing, Turning and Sawing Wt. (lbs.)	After Curing, Turning and Sawing B.D. (g/cc)	After Baking Dia. (in.)	After Baking Lgth. (in.)	After Baking Wt. (lbs.)	After Baking B.D. (g/cc)	After Baking and Turning Dia. (in.)	After Baking and Turning Lgth. (in.)	After Baking and Turning Wt. (lbs.)	After Baking and Turning B.D. (g/cc)	After Graphitization Dia. (in.)	After Graphitization Lgth. (in.)	After Graphitization Wt. (lbs.)	After Graphitization B.D. (g/cc)	Comments
X-1	26	Dry	4.50	Not plugged.				-----	24.0	27.9	837	1.840	----	----	----	----	Not turned after bake.				23.62	27.67	821	1.88	X-1 was baked, pitch impregnated rebaked and graphitized.
X-2	26	Dry	6.25	Not plugged.				-----	27.9	28.3	1138	1.830	27.65	28.26	1100	1.805	Not turned after bake.				27.35	28.0	1110	1.870	Visually flaw-free, sampled for room temperature properties.
X-3	26	Dry	Blew	Pc. lost after 2.25 hrs. due to hydraulic failure.																					
X-4	24	Hot	5.25	Not plugged.				-----	27.4	31.4	1213	1.820	27.22	31.5	1196	1.805	Not turned after bake.								Scrapped.
X-5	24	Hot	Blew																						
X-6	24	Hot	6.25	----	----	----	-----	-----	31.68	31.37	1626	1.825	31.43	31.31	1580	1.81	29.03	31.31	1352	1.820	27.05	31.25	1202	1.850	Visually flaw-free, sampled for room temperature properties.
X-7	24	Hot	6.50	----	----	----	-----	-----	31.67	35.25	1804	1.805	31.38	35.20	1760	1.80	30.22	35.20	1638	1.800	28.76	31.25	1360	1.860	One bad cross-crack in top one-third of piece which did not turn out
X-8	24	Hot	6.25	31.38	43.37	2172	1.800	8.23	31.96	37.19	1945	1.815	31.66	37.12	1890	1.795	30.36	37.12	1738	1.795	29.95	35.0	1645	1.850	One bad cross-crack in top one-third of piece which did not turn out.
X-9	24	Hot	6.00	31.38	39.60	2004	1.825	7.40	31.38	33.87	1745	1.810	31.27	33.87	1705	1.810	30.28	33.87	1570	1.790	30.04	36.87	1756	1.865	One bad cross-crack in top one-third of piece which did not turn out.
X-10	24	Hot	5.50	31.38	46.12	2302	1.805	9.07	31.47	39.85	2015	1.800	31.18	39.75	1958	1.790	30.18	39.75	1835	1.790	29.92	33.50	1569	1.865	One bad cross-crack in top one-third of piece.
X-11	26	Dry	5.00	Not plugged.				-----	30.23	Ends not sawed.			29.97	32.00	1462	1.800					29.80	39.37	1842	1.875	Several cross-cracks in top one-third of piece did not turn out.
X-12	26	Dry	4.00	Not plugged-coke migration so bad that piece was ejected in two pieces. Not processed further.																					Visually flaw-free except for one coke inclusion 8" from bottom, scrapped.
X-13	24	Hot	5.00	31.38	47.5	2362	1.795	8.29	31.57	42.25	2142	1.800	31.30	42.15	2086	1.776	Not turned after bake.				29.6	31.75	1489	1.89	Scrapped.
X-14	24	Hot	5.50	31.38	46.88	2332	1.790	6.00	31.63	42.10	2130	1.795	31.35	42.3	2076	1.77	30.45	42.3	1960	1.77					Badly cracked after bake, cracks concentrated in top one-third of piece.
X-15	24	Hot	5.25	31.38	41.00	2018	1.775	8.05	31.61	35.25	----	----	31.32	35.35	1744	1.79	30.2	35.35	1614	1.775	30.9	41.75	2104	1.87	Inverted after plugging and cured in 41" mold, badly cracked.
X-16	24	Dry	5.75	31.38	41.50	2035	1.77	8.85	31.05	35.00	1692	1.775	30.78	34.75	1654	1.78	Not turned after bake. See Table 10								Entire mixer load discharged at once to prevent overheating of mix, badly cracked.
X-17	24	Dry	5.5	31.38	37.65	1932	1.850	6.65	31.46	35.50	1780	1.795	30.04	35.25	1728	1.78	Not turned after bake.								Visually flaw-free; plugged by resistance heating in 30" mold.
																									Visually flaw-free; plugged by resistance heating in 30" mold.

The particle envelope consisted of coke particles for all pieces except X-2 which used graphite particles; sizing was 6/3 (through 0.06-inch opening and retained on 0.03-inch opening.

Table 10. Physical Properties of Experimental RVA Grade Graphites

	Experimental RVA									
	X-2 (Dry Blend)					X-4 (140°C Hot Mixed)				
	N	Max.	Min.	Ave.	σ	N	Max.	Min.	Ave.	σ
Bulk Density, g/cc	56	1.90	1.88	1.87	0.014	56	1.91	1.86	1.87	0.014
Specific Resistance (μ-ohm-cm)										
w.g.	22	1204	1089	1149	27	23	1136	1071	1108	19
a.g.	34	1566	1331	1454	72	33	1382	1228	1279	21
Flexural Strength, psi*										
w.g.	22	4205	3636	3990	171	22	3779	2434	3143	352
a.g.	34	3456	2512	3143	185	33	3438	2507	2925	295
Young's Modulus (10^6 psi)										
w.g.	22	1.84	1.62	1.73	0.05	23	1.76	1.47	1.61	0.11
a.g.	34	1.41	1.22	1.32	0.04	33	1.50	1.27	1.39	0.08
Permeability, millidarcys										
w.g.	2	0.68	0.66	0.67	----	2	0.70	0.28	0.49	----
a.g.	2	0.59	0.56	0.57	----	2	0.55	0.10	0.32	----

* Samples were 1-1/4 x 1-1/4 x 5 Inches, Third Point Loading Used.

w.g. = with grain; a.g. = across grain; σ = standard deviation.

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Figure 12. Typical Particle Migration Showing Coke Inclusions in the Bottom as Cured -- Arrow Points to Region of Inclusions

4.4.1. Hot Mixed Precompacts

The first method of eliminating particle intermixing was to hot mix the blend below the pitch-sulfur reaction temperature and form a precompact, the so-called plug. This semirigid plug could then be loaded into an insulated mold, surrounded with the envelope, and cured with minimum intermixing. To explore this technique, several plugs were formed in a 10-inch diameter mold, turned to 9.5-inch diameter, and cured using coke particles around the plug. No curing problems were encountered and the cured stock was sectioned and found to be visually flaw-free. Trials were then initiated using the 31-inch diameter mold to form the plugs. After cooling, the plugs were stripped and loaded into the 41-inch diameter mold for curing under pressure.

These completely cured bodies were found to have remarkably clean separation from the envelope and did not exhibit an "hour glass" or any other irregular configuration (see Figure 13).

Moreover, all stock was turned and faced after curing and the envelope particle penetration was found not to exceed 1/8 inch. Temperature uniformity was excellent. Maximum temperature differential encountered during the cure of this piece was 12°C.

Detailed inspection of the baked pieces (X-6, 7, 8, 9, 10 and 13) in the above experiment revealed light jagged cross cracks which obviously could not be attributed to temperature differentials. The most illuminating observation concerning these cracks was the fact that the pieces showed expansion at the location of each crack, indicating that this area of the piece had not thermoset during the curing operation. The reason for this loss of thermosetting action was tentatively attributed to a lack of sulfur arising from inadequate mixing. Confirmation of this hypothesis was obtained by a run in which a piece was prepared by insufficient mixing between the time when sulfur was charged to the mixer and the mix was discharged into the mold. This piece exhibited cracks after baking which were even more pronounced and were raised in a manner which indicated lack of thermosetting action.

It was evident at this point from all prior experience with RVA processing that hot-mixing had always compounded the problems of producing flaw-free material. This can be unequivocally attributed to premature polymerization due to lack of local temperature control and nonuniform sulfur distribution associated with hot mixing for relatively short times.

Physical properties were determined on piece X-10 made by the hot-mixing-precompact method just described and were compared to the properties of piece X-11 made from dry blend using the sleeve separation technique described earlier. These properties are summarized in Table 11. The results of strength measurements confirm those already reported (see Table 10) in that the piece made from dry blend (piece X-11) is significantly stronger in both directions. Of equal importance are the lower standard deviations of the strength indicating the higher degree of strength uniformity attainable by avoiding hot-mixing. The photographs shown in Figure 14 are

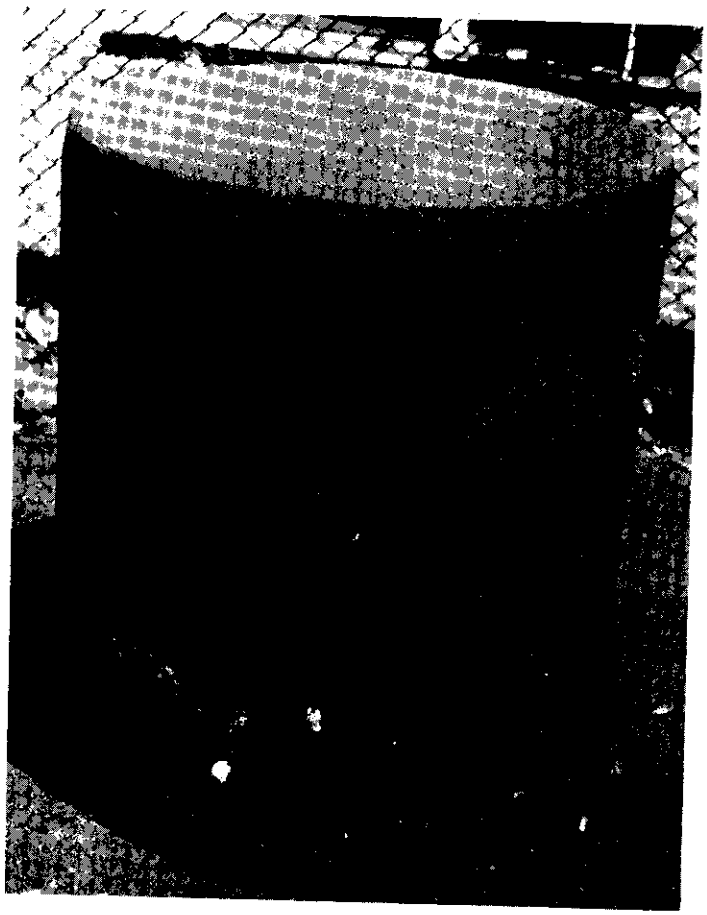

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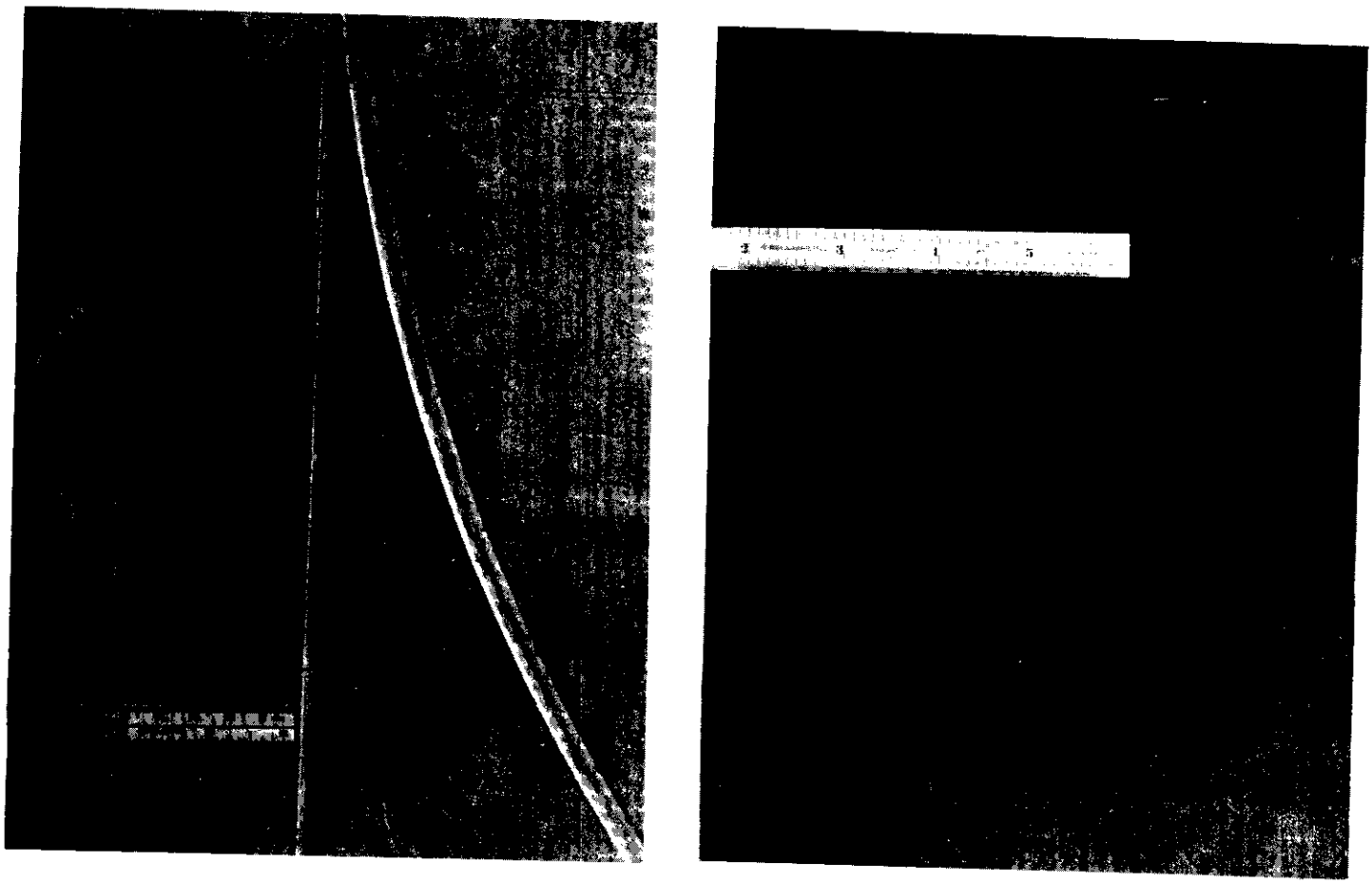
Figure 13. Piece X-6, Indicating Well-Defined Surface Typical of Minimal Envelope Intermixing With Preformed Compact

Table 11. Physical Properties of Experimental RVA Grade Graphite Fabricated by Hot Mix-Precompact Technique vs. Dry Blend-Sleeve Technique

	Piece X-10 (Precompacted Hot Mix)					Piece X-11 (Dry Blend-Sleeve Technique)				
	N	Max.	Min.	Ave.	σ	N	Max.	Min.	Ave.	σ
Bulk Density, g/cc	108	1.886	1.831	1.854	0.011	66	1.865	1.801	1.837	0.016
Flexural Strength, psi*										
w.g.	54	3278	2214	2705	246	46	3750	2800	3320	203
a.g.	54	3269	1039	2072	619	20	3079	2214	2687	281
Young's Modulus (10^6 psi)										
w.g.	54	1.613	1.450	1.518	0.039	46	1.904	1.418	1.583	0.079
a.g.	54	1.473	1.149	1.306	0.090	20	1.347	1.234	1.277	0.025
Specific Resistance, (μ-ohm-cm)										
w.g.	54	1272	1130	1205	37	46	1211	903	1096	58
a.g.	54	1453	1264	1305	43	20	1476	1308	1367	48

* Samples 1-1/4 x 1-1/4 x 5 Inches, Third Point Loading Used.

w.g. = with grain; a.g. = across grain; σ = standard deviation.



Hot Mix

Dry Blend

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Figure 14. Structure of Experimental Grade RVA Graphite, Hot-Mixed Precompaction (Piece X-10) vs. Dry Blend-Sleeve Technique (Piece X-11)

close-up views of pieces X-10 and X-11 showing the incipient flaws in the hot mixed piece X-10 to which the low transverse strength and high standard deviation are attributed. Such flaws are not apparent in piece X-11.

Whatever the advantages of precompacting had been, they have obviously not overcome the inherent weaknesses of hot mixing. Hence an equivalent method of handling dry mixing had to be sought.

4.4.2. Dry Blend Precompacts

The next logical step was to precompact dry blend by resistance heating. Two precompacts (pieces X-16 and X-17) were made by charging dry blend into a 30-inch mold and heating electrically. This method produced compacts of comparable rigidity to those formed from the hot mix. The dry blend compacts were charged and cured in the 41-inch diameter mold utilizing a particle envelope technique identical to that described above. After processing, i.e., (baking to 750°C, pitch impregnation, and graphitization), both pieces were flaw-free. Piece X-17 was extensively sampled. The physical properties of pieces X-17 are compared with those of standard grade ATJ graphite in Table 12. These data show the average physical properties of dry blend-precompacted grade RVA to be close to those of grade ATJ graphite, but with a piece-to-piece variation in strength and bulk density not more than one-third that of ATJ. Electrical resistance and Young's modulus are also much more uniform for RVA graphite.

Table 12. Physical Properties of Grade RVA Graphite Produced by the Dry Blend - Precompact Technique and Grade ATJ Graphite

	Grade RVA, Piece X-17			Grade ATJ	
	N	Ave.	σ	Ave.	σ
Bulk Density, g/cc	106	1.844	0.007	1.73	0.036
Specific Resistance(μ-ohm-cm)					
w.g.*	46	1204	31	1100	168
a.g.**	60	1536	36	1450	145
Flexural Strength, psi					
w.g.	46	3701	212	1410	773
a.g.	60	2878	160	3580	484
Young's Modulus (10^6 psi)					
w.g.	46	1.69	0.03	1.45	0.17
a.g.	60	1.26	0.04	1.15	0.09
Permeability, millidarcys					
w.g.	6	6.08	-----	20	13
a.g.	6	5.88	-----	15	9

* w.g. – with grain

** a.g. – across grain

A piece of 30-inch diameter x 40-inch length grade RVA graphite, which was later produced on factory equipment utilizing the dry blend compact and particle envelope curing technique was extensively sampled for physical properties and the data are presented in Table 13. Table 13 also repeats the data on laboratory-fabricated piece X-17 to indicate the reproducibility.

Table 13. Room Temperature Physical Properties of RVA Grade Graphite Fabricated by the Dry Blend-Precompact-Envelope Technique

	Stock Fabricated by Development Laboratory (Piece X-17)			Stock Produced by the Factory (Piece L-2)		
	N	Ave.	σ	N	Ave.	σ
Bulk Density, g/cc	106	1.844	0.007	94	1.853	0.008
Specific Resistance(μ-ohm-cm)						
w.g.*	46	1204	31	40	1191	27
a.g.**	60	1536	36	54	1493	42
Flexural Strength, psi						
w.g.	46	3701	212	40	3574	256
a.g.	60	2878	160	54	2933	170
Young's Modulus (10^6psi)						
w.g.	46	1.69	0.03	40	1.675	0.05
a.g.	60	1.26	0.04	54	1.313	0.06
Permeability, millidarcys						
w.g.	6	6.08		6	2.00	-----
a.g.	6	5.88		6	1.60	-----

* w.g. – with grain

** a.g. – across grain

It can be concluded that no degradation of properties was realized when grade RVA was produced on production equipment. The small differences in standard deviation strongly indicate that the excellent properties of grade RVA can be maintained up to 30-inch diameter.

5. CONCLUSIONS

The development of grade RVA graphite, a premium quality graphite capable of large scale-up has been one of the primary objectives of the contract program. The success of this project permits several important conclusions to be drawn relevant to the fabrication technology of large graphite shapes:

1) The feasibility of producing graphite shapes up to at least 30-inch diameter has been demonstrated.

2) Specifically, grade RVA graphite has been produced on a semiproduction scale, with physical strength and bulk density showing remarkably good uniformity and reproducibility.

3) The use of sulfur in plasticizing the mix and lowering the polymerization temperature facilitates the provision of thermoset bodies sufficiently strong to withstand subsequent baking stresses even in large sizes.

4) The technique of the "particle envelope" permits attainment of nearly isothermal curing environment essential to dependable processing.

5) This technique also permits rapid and easy venting of volatile material generated.

6. RECOMMENDATIONS

1. Graphites produced from an all flour filler blend generally have superior properties to graphites incorporating particles, but can be processed only in small sizes. It is felt that the use of the pressure curing particle envelope technique with all flour blends may permit processing of sizes heretofore impossible. Work along these lines is scheduled and will be pursued.

2. RVA grade graphite, as produced by the particle envelope technique, will be completely characterized up to a temperature of 2700°C.

3. Fine grain speciality stock is generally difficult to produce in sizes having a diameter-to-length ratio of less than one. RVA grade can be produced with a diameter-to-length ratio of 0.75. The possibility that the particle envelope technique will permit RVA to be produced in even longer sizes is being investigated.

4. The work covered in this report indicated that a controlled graphite filler source could have a marked effect on the final properties of RVA grade. Consequently, a program is under way investigating sources of graphite filler materials.

The results of the above work will be covered in a later report.

7. REFERENCES

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