FOREWORD

This volume is the thirty-eighth of the WADD Technical Report 61-72 series 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 1961 through December 1962, at the Advanced Materials Laboratory of National Carbon Company, Lawrenceburg, Tennessee, under the management of Mr. R. M. Bushong, Director of the Advanced Materials Project and of Mr. 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, Aeronautical Systems Division, Captain R. H. Wilson, L.J. Conlin, and W. P. Conrardy acting 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 Dislocation and Low Angle Grain Boundaries in Graphite Single Crystals, by R. Bacon and R. Sprague.

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

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Supplement - Evaluation of Graphite Materials in a Subscale Solid-Propellant Rocket Motor, by S. O. Johnson and R. B. Dull.

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Volume XXXV - Methods of Measuring Mechanical Properties of Graphite in the 20° to 2700°C Temperature Range, by M. B. Manofsky and R. B. Dull.

Volume XXXVI - Studies of the Quality of Petroleum Coke from a Pilot-Scale Delayed Coker, by C. F. Stout, M. Janes and J. A. Biehl.

Volume XXXVII - Studies of Graphite Deposited by Pyrolytic Processes, by P. H. Higgs, R. L. Finicle, R. J. Bobka, E. J. Seldin and K. J. Zeitsch.

ABSTRACT

This report describes the development, fabrication processes and physical properties of grade RVD graphite (formerly RT-0008), 18-inch diameter by 15-inch length, and an attempted scale-up of this grade to 33-inch diameter. Grade RVD graphite, an extra-fine-grain material formed by pressure curing, is nominally characterized by a density of 1.87 to 1.89 g/cc and flexural strengths of 4700 lbs/in^2 with the grain and 3100 lbs/in^2 across the grain. Nozzles made from RVD graphite, tested in a subscale rocket motor, exhibit a low erosion rate and high thermal shock resistance.

This report has been reviewed and is approved.

W. G. RAMKE
Chief, Ceramics and Graphite Branch
Metals and Ceramics Division
Air Force Materials Laboratory

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1. INTRODUCTION

The aerospace industry has a need for high temperature materials having high strength, low erosion rate, and thermal shock resistance. Some of these properties are manifested to varying degrees in graphites; grades ATJ and ZTA[1] in small sizes and grades RVA[2] and CFZ[3] in larger sizes. Although satisfactory for many applications, these graphites are limited in some of the more critical applications by sizes available and/or by desirable combinations of properties; e.g., erosion, thermal shock, and so forth.

Prior experience suggested that a finer-grain material than RVA, but similarly processed, should provide the desired lower erosion rate. The development of grade RVD was undertaken to evaluate this hypothesis. The basic difference between grades RVD and RVA, both of which are fabricated by a pressure curing process,[2] is that the former is composed of all-flour or fine filler materials while the latter contains a prescribed amount of particles sized to pass through a 20-mesh screen and be retained on a 35-mesh screen. Experience in carbon and graphite processing has shown that a blend containing fine filler materials produces a finished article which has high flexural strength and small-size pores but is difficult to process. In the process employed to produce grade RVA, blends containing sized particles rather than all flour in the filler material were used. A prior report[2] describes the development of the pressure curing process used in the fabrication of grade RVA graphite. Briefly, the technique involves the forming of a plug at 115 to 130°C from graphite-base blends containing a pitch-sulfur binder which is thermoplastic at these temperatures. After the plug is formed it is surrounded with a particle envelope in an insulated mold and the binder is thermoset by either induction or resistance heating, under mechanical pressure, to approximately 325°C. The particle envelope facilitates gas removal on heating and provides a choice of electrical resistivity for control of temperature distribution. Precompaction of the blend prevents migration of particles during the thermosetting operation and reduces sidewall friction with its consequent harmful effects.

The pressure curing technique has made it possible to produce grade RVD in 18-inch diameter and, based on the information herein reported, should permit scale-up to larger diameters. Physical property measurements and rocket motor test firings[4] indicate that grade RVD possesses a desirable combination of high strength, low erosion rate and good thermal shock resistance.

Manuscript released by the authors October 1963 for publication as an ASD Technical Documentary Report.

2. EIGHTEEN-INCH DIAMETER GRADE RVD GRAPHITE

2.1. Fabrication

Grade RVD graphite was originally made by the particle envelope technique in an 18-inch diameter by 15-inch length size. The procedure followed was to first make preliminary curing trials to establish optimum process conditions. A pilot lot of the same size was then processed based on these conditions to establish processing yields and determine physical properties. Finally some of the grade RVD was tested as a nozzle insert in a sub-scale solid fueled rocket motor, and the susceptibility of grade RVD to further impregnation was examined.

Eighteen preliminary trials utilizing the precompaction, particle envelope, direct resistance heating technique were made primarily to establish the optimum curing cycle for this grade. This curing cycle is defined as the fastest rate of temperature rise that can be tolerated in curing without cracking the piece either during curing or in the subsequent baking operation. In these trials, up to ten thermocouples per piece were used to measure rate of temperature rise and temperature gradient. The limiting parameter is actually temperature gradient since the uniformity of curing the binder is a function of this. For a given system the temperature gradient is largely determined by the rate of rise. Other process variables, including pressure and blend composition, had been studied in previous work and controlled operating conditions were already established. Curing pressure was 1000 lbs/in^2 and the standardized blend composition for grade RVD is shown in Table 1.

Table 1. Grade RVD Blend

Ingredient	Per Cent by Weight
Graphite Flour, 45 per cent through 200-mesh screen	64.6
Thermatomic Black, 100 per cent through 325-mesh screen	10.3
175°C-Melting-Point Coal Tar Pitch, 100 per cent through 35-mesh screen	20.9
Sulfur, 100 per cent through 35-mesh screen	4.2
Total	100.0

As a result of these exploratory trials a standard curing cycle was established at approximately three hours. This cycle is illustrated in Figure 1 where the curing temperature and compaction of the piece or slump is plotted against time.

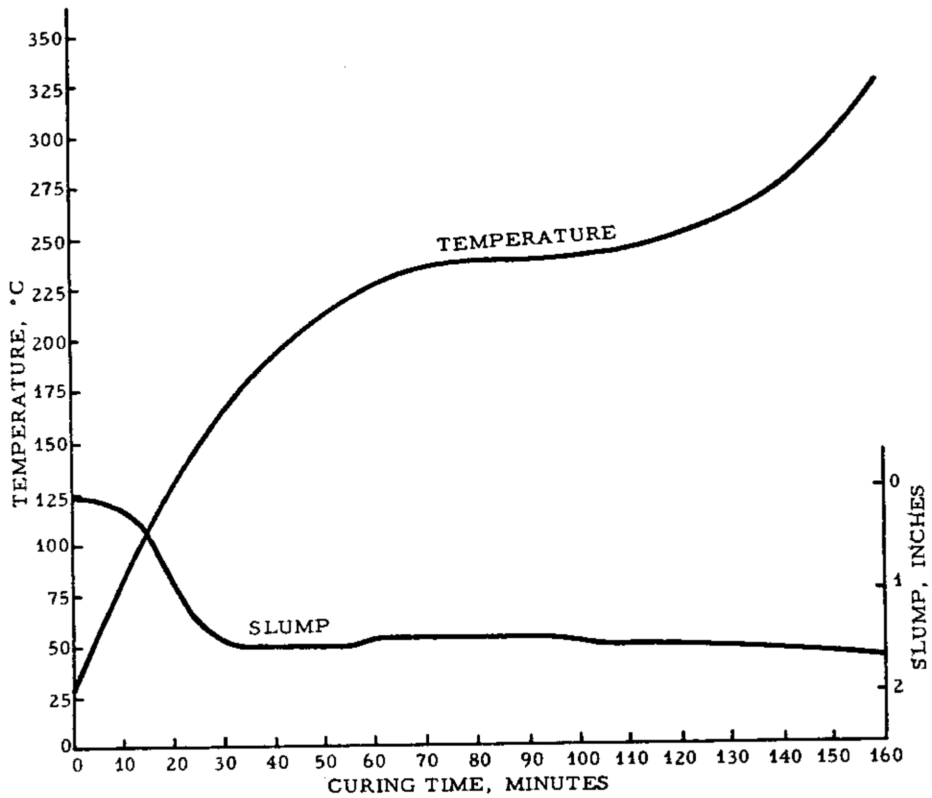

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Figure 1. Typical Heating and Slump Curve for Curing 18-Inch Diameter by 15-Inch Length Grade RVD Graphite

Curing of grade RVD requires about 50 per cent longer time than the coarser grained grade RVA. The slower rate for the RVD is necessary to allow escape of gases through the smaller diameter pore passages.

The electrical resistance of the precompacted RVD plug is about twice that of the grade RVA plug. With equivalent curing cycles this would normally require a higher resistivity particle envelope to prevent excessive heating at the periphery of the billet. In this case, however, excessive heating was eliminated by the longer heating cycle because of the greater heat losses through the mold. This permitted use of the same envelope material as for grade RVA.

The pieces made in these preliminary trials were not processed beyond the baking step since the results of varying the curing conditions can almost always be ascertained at this point.

Using the processing conditions established in these preliminary trials, a pilot lot comprising seventeen pieces of 18-inch diameter by 15-inch length grade RVD was fabricated. These pieces were carried through the entire process consisting of plugging, curing, baking, pitch impregnating, rebaking and graphitizing. Baking and rebaking were accomplished in a conventional gas fired furnace on a 15 day schedule. Graphitization was performed in an Acheson Furnace. Processing yields through graphitization for the 17 pieces were 80 per cent.

2.2. Physical Properties

Two 18-inch diameter blocks of grade RVD graphite were sampled for property characterization, and room temperature properties of RVD as well as those for grade RVA are presented in Table 2. All seventeen blocks had bulk apparent densities in this range. These data indicate the excellent uniformity of physical properties of grade RVD graphite within a piece and from piece to piece. The increased strengths obtained by use of an all-flour blend are also apparent. The cumulative pore volume versus pore diameter for grades RVD and RVA is plotted in Figure 2 and clearly shows the lower porosity of RVD graphite. Photomicrographs comparing the structure of grades RVD and RVA are presented in Figure 3.

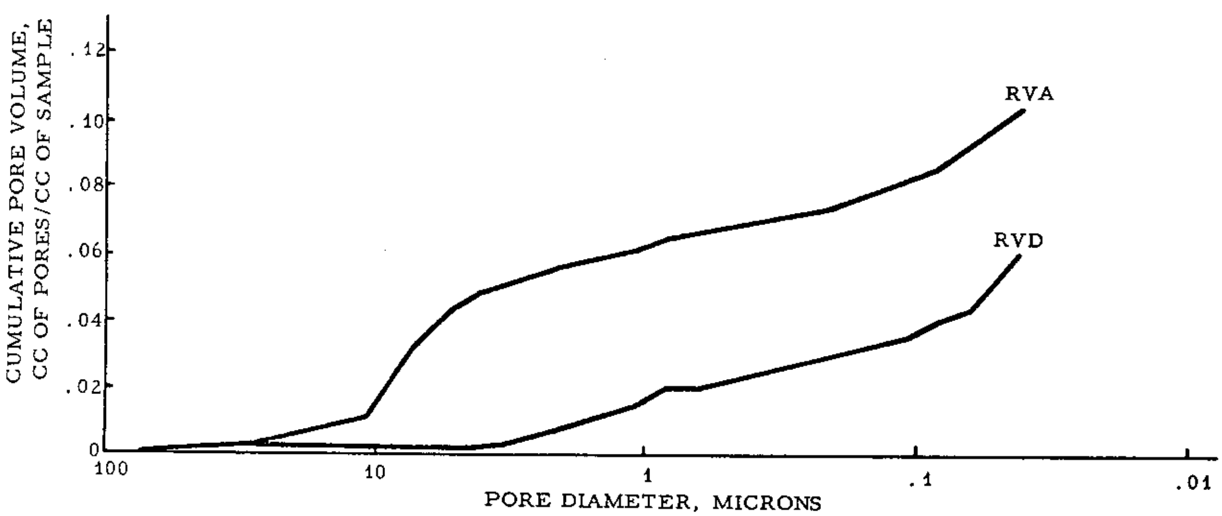
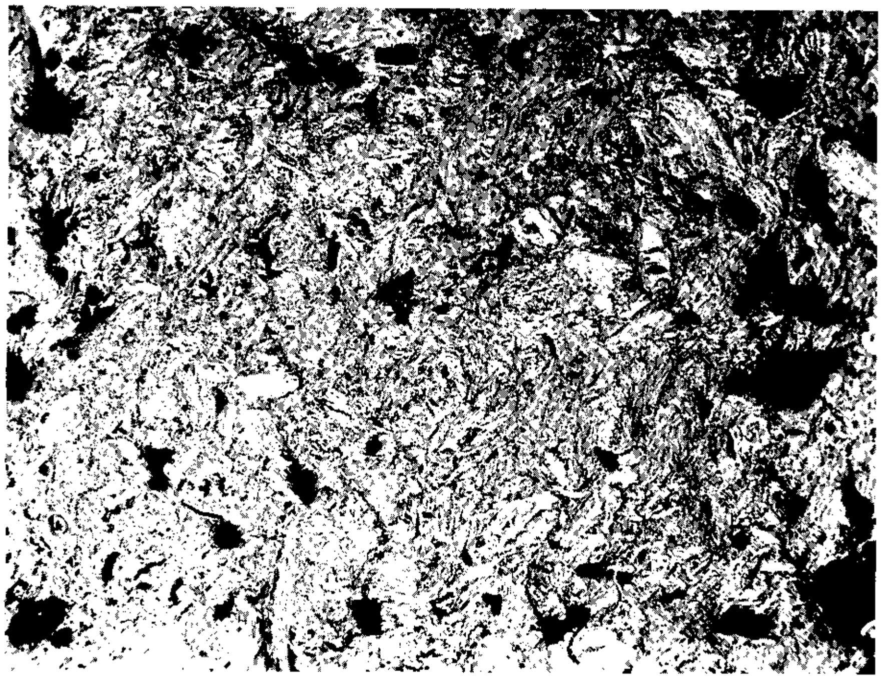


Figure 2. Pore Size Distribution, Mercury Porosimeter, Grades RVA and RVD Graphite



Grade RVD Graphite, 100 X

Grade RVA Graphite, 100 X

Figure 3. Photomicrographs of Grain Structure, Grades RVA and RVD Graphite

Table 2. Room Temperature Physical Properties, Grades RVD and RVA Graphite

Property	Grade RVD*									Grade RVA*		
	Block No. 199			Block No. 200			Block Nos. 199 and 200			Block Nos. A-19 A-20 and A-24		
	n***	Ave.	σ**	n	Ave.	σ	n	Ave.	σ	n	Ave.	σ
Bulk Density, g/cc												
w.g.	10	1.875	0.013	9	1.870	0.014	36	1.870	0.013	312	1.838	0.019
a.g.	9	1.872	0.013	8	1.863	0.005						
Electrical Resistivity, 10^{-4} ohm-cm												
w.g.	10	12.52	0.41	9	12.72	0.28	19	12.62	0.36	150	12.18	0.38
a.g.	9	21.72	0.97	8	21.54	0.47	17	21.64	0.76	162	15.73	0.96
Young's Modulus, 10^6 lbs/in^2												
w.g.	10	2.10	0.05	9	2.08	0.05	19	2.10	0.05	128	1.84	0.07
a.g.	9	1.13	0.05	8	1.11	0.04	17	1.12	0.05	162	1.30	0.09
Flexural Strength, lbs/in^2												
w.g.	10	4695	316	9	4718	420	19	4706	359	135	3800	321
a.g.	9	3154	271	8	3095	142	17	3127	216	121	2995	203
Compressive Strength, lbs/in^2												
w.g.	-	-	-	-	-	-	15	12,304	987	46	9960	1930
a.g.	-	-	-	-	-	-	14	11,816	1009	46	9000	2000
Room Temperature CTE, 20-100°C, 10^{-6}/°C												
w.g.	-	-	-	-	-	-	6	1.70	-	12	1.65	0.09
a.g.	-	-	-	-	-	-	6	3.43	-	12	2.77	0.07

* Grade RVD blocks were 18 inches in diameter by 15 inches in length; grade RVA blocks were 33 inches in diameter by 42 inches in length.
** σ = Standard deviation.
*** n = Number of samples.

2.3. Erosion Resistance

Table 3 shows the erosion rates of grades RVD, RVA, CFZ, and ZTA tested in a subscale solid-propellant rocket motor.[4] Grade RVD had next to the lowest erosion rate of the four graphite grades tested and did not crack from thermal shock. More nearly isotropic properties along with high strength in both directions were responsible for the better resistance to thermal shock of grade RVD compared to grade ZTA.

Table 3. Erosion Rates of Various Grades of Graphite in a Subscale Solid-Propellant Rocket Motor, 0.56-Inch Diameter Throat

Grade	Erosion Rate mils/sec Cured Propellant*	Chamber Pressure lbs/in^2	Erosion Rate mils/sec Uncured Propellant**	Chamber Pressure lbs/in^2
ZTA	0.25	960	1.76***	1015
RVD	0.37	930	1.87	1150
RVA	0.73	925	-	-
CFZ	0.52	950	-	-

* Cured Arcite-373 propellant, temperature 5600°F, omox ratio**** 1.00, one 60 second firing each.

** Uncured Arcane-58 propellant, temperature 6000°F, omox ratio**** 1.20, one 30 second firing each.

*** Cracked by thermal shock.

**** Omox ratio = $\frac{O_2}{CO+Al_2O_3}$

2.4. Impregnation

An attempt was made to impregnate RVD graphite after graphitization to further improve its strength and hopefully obtain a further increase in its already excellent erosion resistance. A 5- by 5- by 5-inch block of grade RVD was pressure impregnated with coal tar pitch, rebaked in a pressure furnace at 750 lbs/in^2 to a temperature of 700°C and regraphitized. Examination of the regraphitized block showed that the pitch had penetrated to a depth of only one inch and impregnation attempts were discontinued.

3. SCALE-UP OF GRADE RVD GRAPHITE

3.1. Trials of 24-Inch Diameter

Two pieces of RVD graphite, 24 inches in diameter by 25 inches in length, were made for the initial scale-up trial. The same curing and processing procedures were used as in the 18-inch trials except that the stock was graphitized in an induction coil. Both 24-inch diameter blocks exhibited minor surface cracking during graphitization which was believed due to the faster heating rate employed in the induction graphitizing operation. One of the blocks was cut into samples for physical property measurement and the results are shown in Table 4. The properties are close to those obtained in the 18-inch size and reported in Table 2.

Table 4. Room Temperature Physical Properties, 24-Inch Diameter Grade RVD Graphite

Property	With Grain n		Across Grain n	
Bulk Density, g/cc	16	1.883	17	1.890
Young's Modulus, 10^6 lbs/in^2	16	2.200	17	1.017
Specific Resistance, 10^{-4} ohm-cm	16	11.23	17	21.43
Flexural Strength, lbs/in^2	16	5380	17	3276
Tensile Strength, lbs/in^2	10	4643	10	2770
CTE, 400-1000°C, 10^{-6}/°C	2	3.3	2	5.2

3.2. Trials of 33-Inch Diameter

The superior properties and performance of grade RVD in the smaller sizes indicated the desirability of scaling up this grade to the 30-inch diameter size. Equipment was available to permit trials for producing RVD in 30-inch diameter by 45-inch lengths. The forming of grade RVD in shorter lengths could not be attempted in these trials because press stroke limited the length to a minimum of 42 inches with this particular tooling (long molds) which had been designed for 72 inch product.

The procedures used in the 33-inch diameter RVD trials were generally the same as those used for the RVA trials;[5] i.e., the 1250-ton press and precompaction-particle envelope technique of curing. A total of nine RVD plugs, 33 inches in diameter by 45 inches in length, were precompacted and seven of these were cured. The precompaction and curing data for these trials are listed in Tables 5 and 6 while Figures 4 through 10 give a graphical representation of the temperature and slump versus time during the curing cycle.

Table 5. Precompaction Data for 33-Inch Diameter Grade RVD Graphite Trials in 1250-Ton Press

Piece	pph of Filler 175°C M. P. Pitch	Total Precompact Time, min.	Final Temp. °C	Per Cent Slump	Hold Time*, hrs.	Plugged Bulk Density, g/cc	General Appearance of Precompact
A-6	28	40	---	25**	0	1.68	O.K.
A-12	30	70	---	27	16	1.82	O.K.
A-13	30	60	119	24	14	1.73	O.K.
A-14	30	74	130	28	14	1.83	Horiz. cracked
A-15	30	74	127	27	12	1.79	O.K.
A-16	30	100	113	24	12	1.73	O.K.
A-25	30	50	120	28	14	1.82	Horiz. cracked
A-29	28	50	127	28	14	1.86	Horiz. cracked
A-30	28	50	128	28	14	1.85	O.K.

* Denotes time held under pressure; precompact left in mold overnight before ejection.
** Not fully compacted.

Table 6. Curing Data, 33-Inch Diameter Grade RVD Graphite, 1250-Ton Press

Piece	pph 175°C M.P. Pitch	Type of Envelope	Envelope Resistivity at 50 lbs/in² 10^{-4} ohm-cm	Total Curing Time, hrs.	Final Curing Temperatures* °C			Per Cent Slump	Hold Time, hrs.	Cured Bulk Density, g/cc
					Side	Top	Bottom			
A-12	30	0.03 to 0.06 Sized Coke	660	5.8	404	280	280	-	16.0	-
A-13	30	0.015 to 0.03 Sized Coke	790	7.8	347	289	262	11.5	14.0	1.80
A-14	30	80% Coke + 20% Fluid Coke	1190	6.7	311	275	336	3.9	16.5	1.75
A-16	30	80% Coke + 20% Fluid Coke	1190	6.0	335	220	229	9.0	17.0	1.80**
A-25	30	70% Coke + 30% Fluid Coke	1500	8.5	340	260	273	3.1	14.0	1.80
A-29	28	50% Coke + 50% Fluid Coke	2460	6.8	346	231	-	4.0	15.0	1.78
A-30	28	50% Coke + 50% Fluid Coke	2460	7.5	339	301	-	4.3	15.0	1.76

* See firing curves, Figures 4 through 10.
** Measured on turned-and-faced piece. All other pieces were not turned.

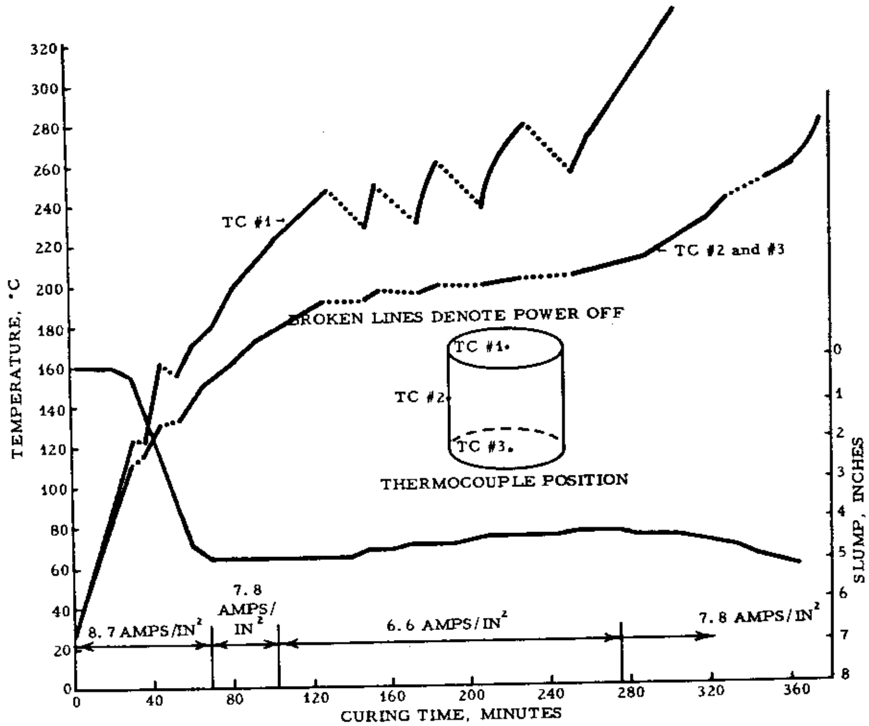


Figure 4. Curing Cycle for Grade RVD Graphite Plug No. A-12, Slump and Temperature Versus Time

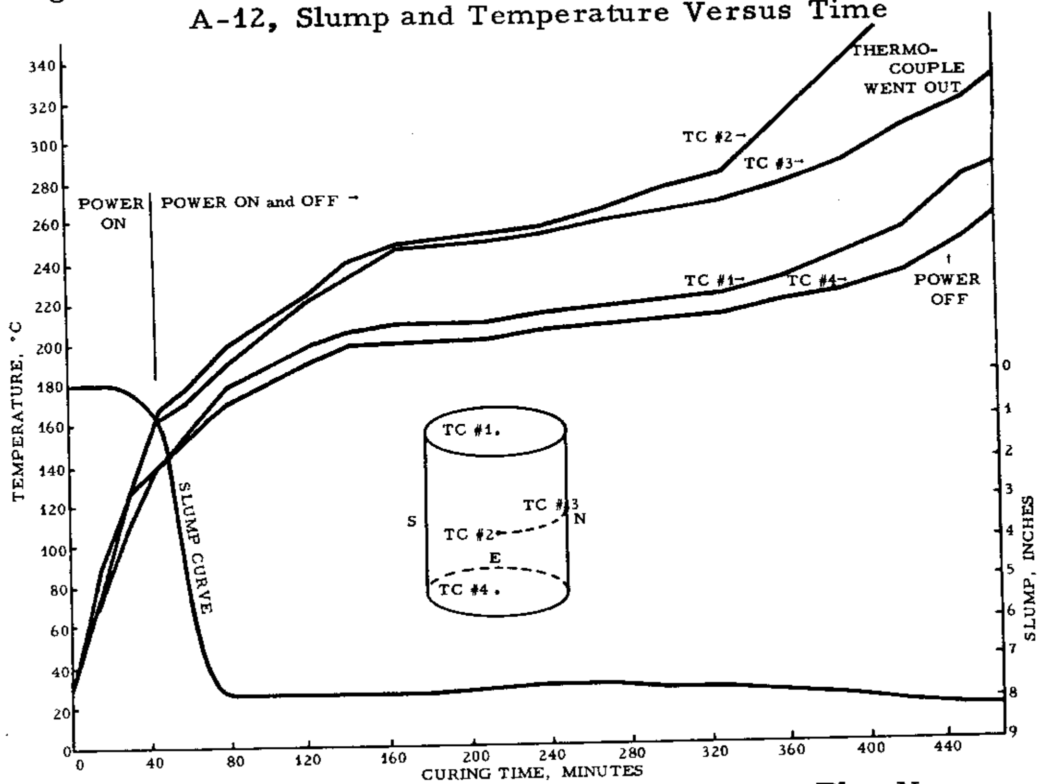


Figure 5. Curing Cycle for Grade RVD Graphite Plug No. A-13, Slump and Temperature Versus Time

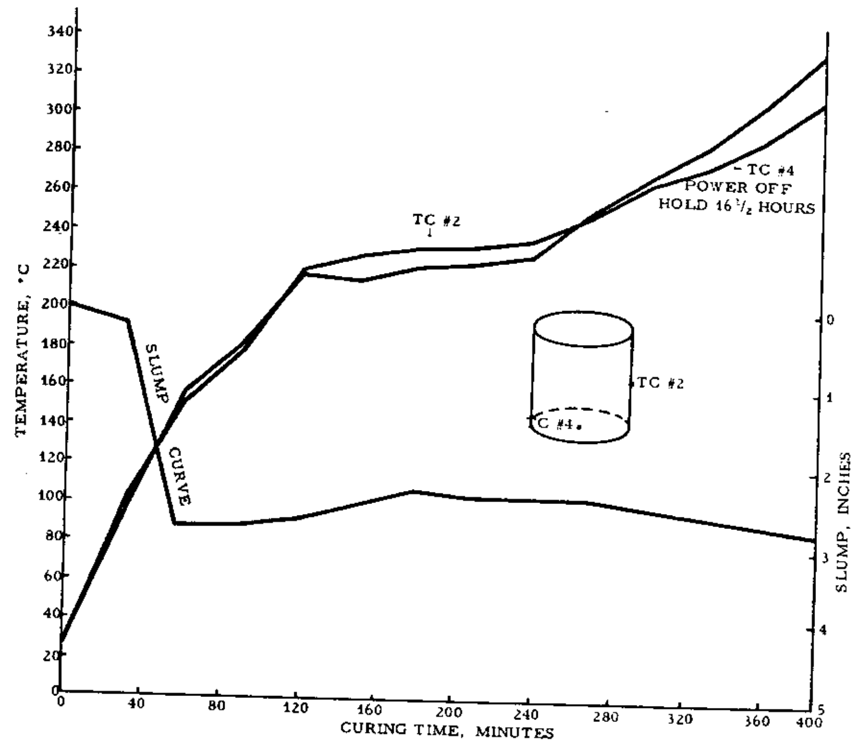


Figure 6. Curing Cycle for Grade RVD Graphite Plug No. A-14, Slump and Temperature Versus Time

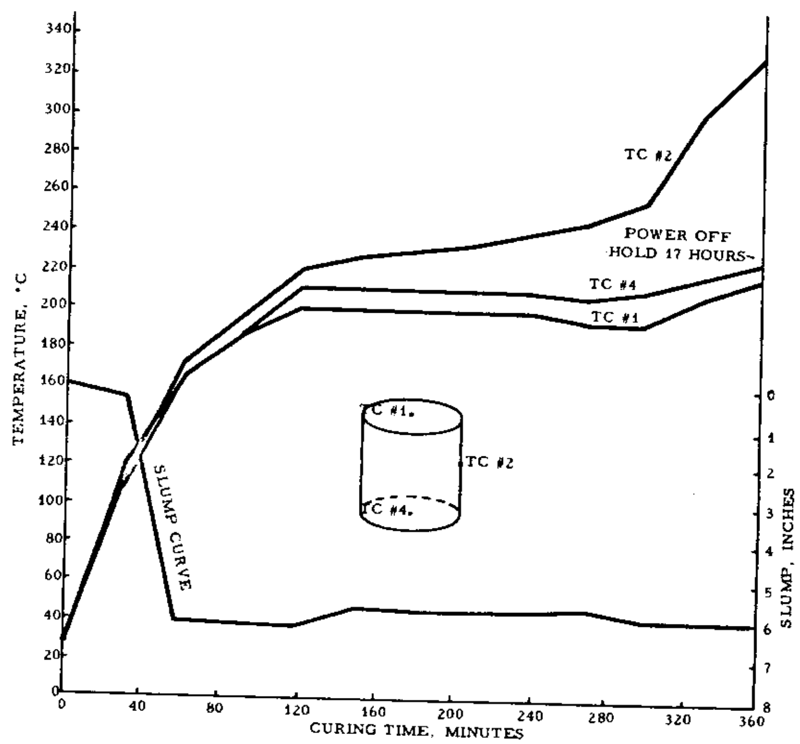


Figure 7. Curing Cycle for Grade RVD Graphite Plug No. A-16, Slump and Temperature Versus Time

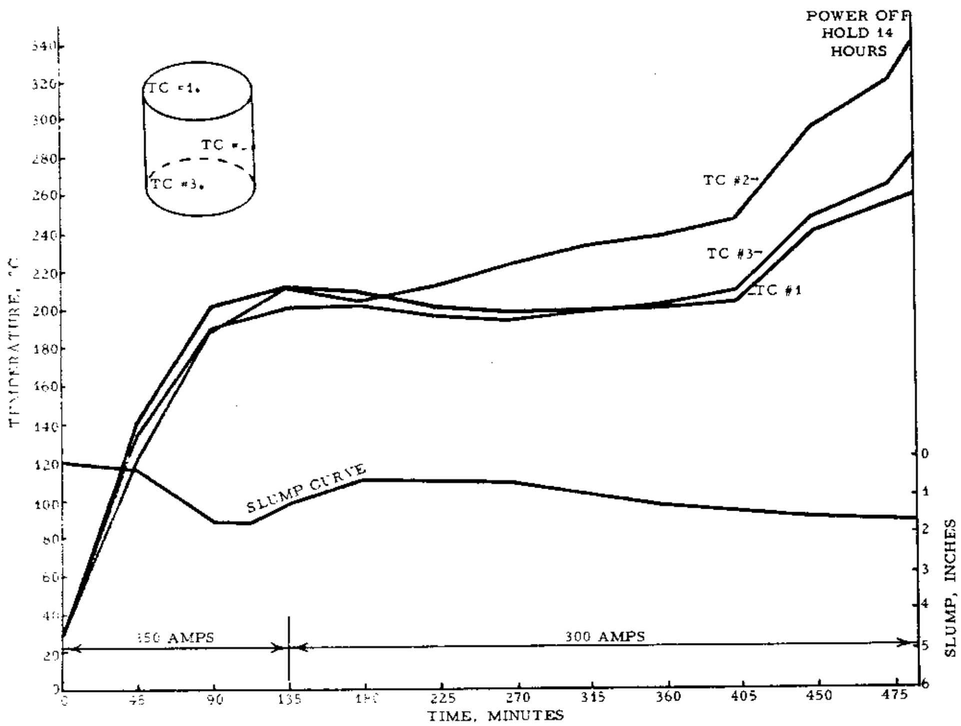


Figure 8. Curing Cycle for Grade RVD Graphite Plug No. A-25, Slump and Temperature Versus Time

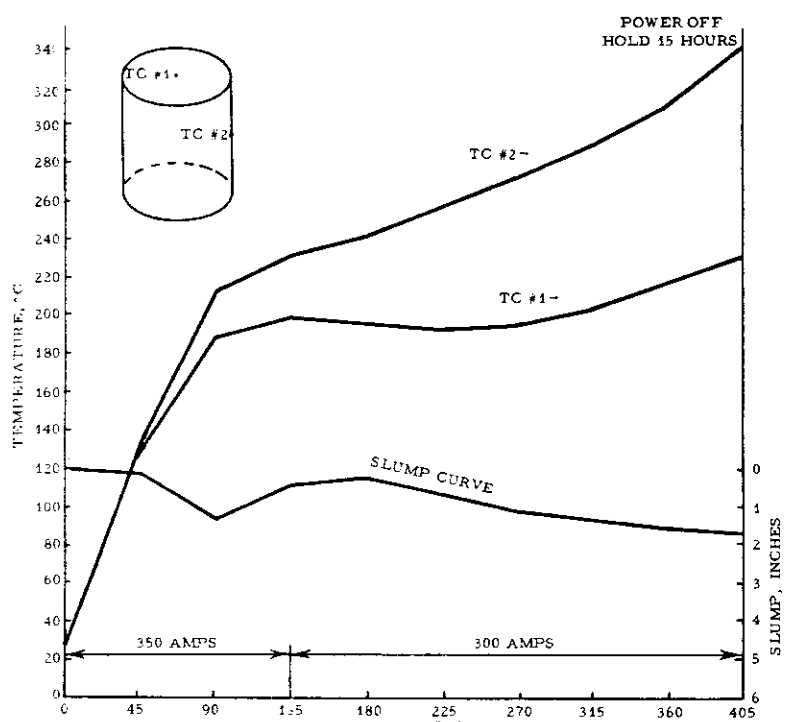


Figure 9. Curing Cycle for Grade RVD Graphite Plug No. A-29, Slump and Temperature Versus Time

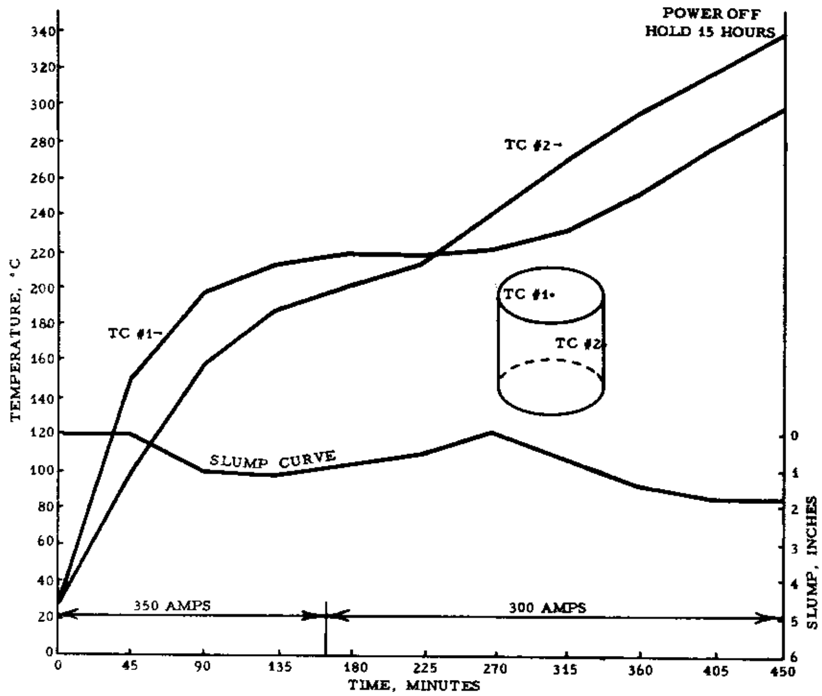


Figure 10. Curing Cycle for Grade RVD Graphite Plug No. A-30, Slump and Temperature Versus Time

Some difficulty was encountered in removing the precompacted RVD plugs from the mold. A force of 150 tons was necessary to eject the RVD plugs as compared to 75 tons for RVA and this resulted in cracking three of the nine plugs. Some of the cracked blocks were cured to check heating characteristics of different envelope materials.

Full compaction was not obtained in Trial No. A-6 due to the lack of adequate press stroke and the result was a block having low bulk density (1.68 g/cc). The relatively low densities of Piece Nos. A-13 and A-16 are believed to be the result of inadequate heating. The high resistivity of the RVD plug coupled with the excellent thermal insulating properties of the 33-inch diameter mold diverted the majority of the current to the envelope during the resistance heating cycle. It was therefore necessary to use envelopes with higher electrical resistivity to obtain uniform temperature distribution. The envelope resistivities were varied as shown in Figure 11 by using different combinations of AX petroleum coke and calcined fluid coke particles. However, the use of fluid coke increased sidewall friction problems and did not satisfactorily improve curing temperature uniformity. (See envelope type, resistivities and final curing temperatures in Table 6.) Only one piece of RVD, No. A-16, was flaw free in the cured state and this piece cracked on subsequent baking to 750°C yielding a salvable length of only 22 inches. The rest of the 33-inch diameter pieces were discarded after curing.

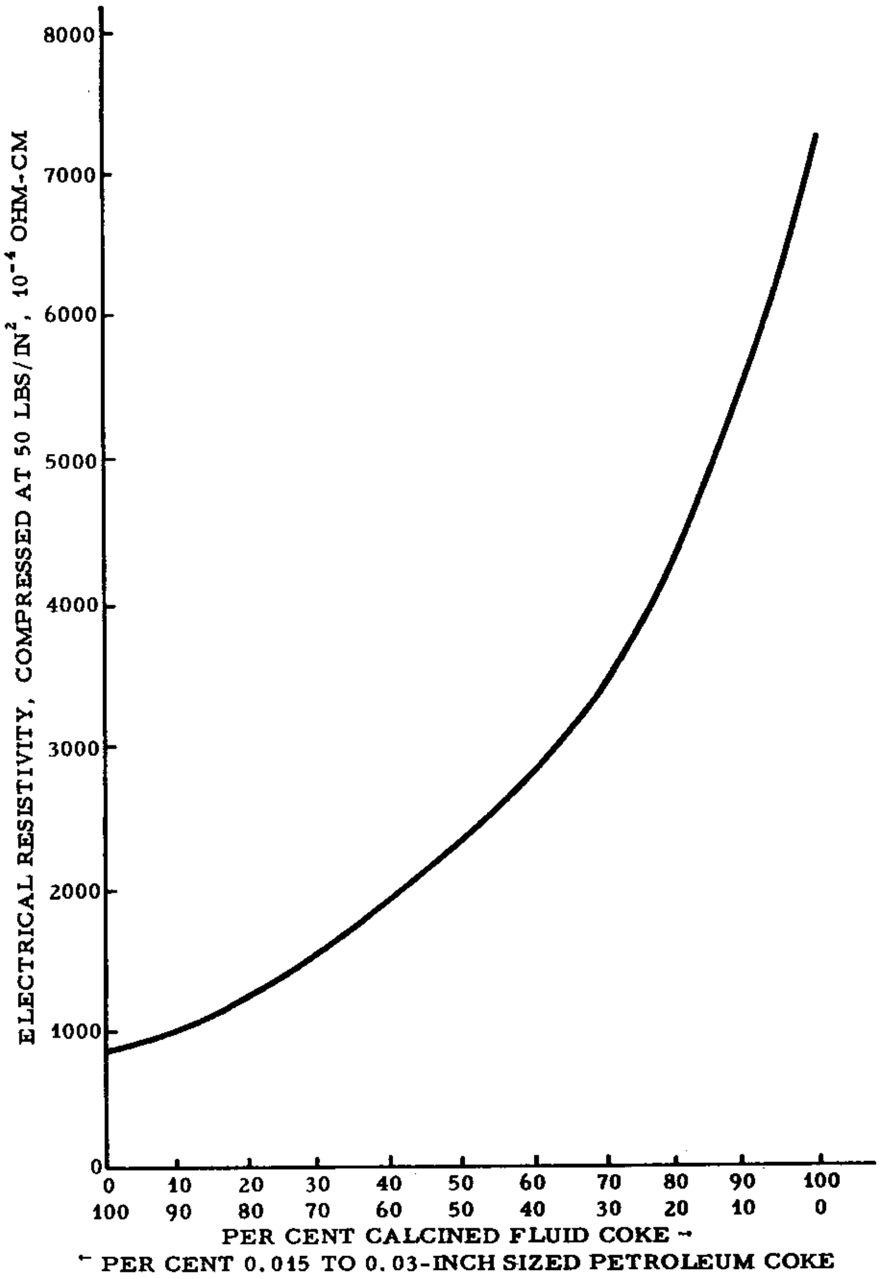


Figure 11. Electrical Resistivity of Combinations of 0.015-Inch to 0.03-Inch Sized Petroleum Coke and Calcined Fluid Coke

It must be concluded from this consistently poor experience that the fabrication of 33-inch diameter by 45-inch length grade RVD by the direct resistance heating method for curing is impractical. Prior experience in scaling up the diameter and length of molded graphite indicates that if the stock cracks during processing, the longest salvable length is often a guide to the length which can be processed without cracking. In this case a 22-inch length was salvaged after baking and processed successfully on through graphitization. It is estimated therefore that 33-inch diameter by 20 - 24-inch length grade RVD could be readily processed by this method, assuming properly designed tooling (short molds) was provided. It is further believed that modification of the techniques described in this report could very well lead to a successful extension in length of the piece. The two main problems are side wall friction and non-uniform heating in the curing operation. Induction heating has shown a tendency toward improvement in both of these areas. In induction heating the function of the particle envelope is primarily that of a chimney to facilitate gas escape. The current penetration and therefore the thermal balance can be regulated by other methods and it is not necessary to match the resistances of the envelope and the stock. With this extra latitude, it should be possible to develop an envelope material that would significantly reduce side wall friction in the curing operation.

4. SUMMARY

The results of the work described in this report demonstrates the feasibility of a process for fabricating RVD graphite in sizes up to 18 inches in diameter by 15 inches in length. Further, the work indicates a high probability of successfully scaling the process up to 30 inches in diameter by 20 to 30 inches in length. Extension of the length may be possible by the use of induction heating methods and modification of the curing technique described herein. The following specific conclusions and recommendations may be cited.

4.1. CONCLUSIONS

1) Grade RVD is nominally characterized by a bulk density of 1.87 g/cc and with- and across-grain flexural strengths of 4700 and 3100 lbs/in^2 respectively.

2) Grade RVD graphite, as tested in a subscale rocket motor, shows a better thermal shock resistance and only slightly higher erosion rate than ZTA graphite.

4.2. RECOMMENDATIONS

The excellent performance of grade RVD graphite in subscale rocket nozzle tests and the high density and strength and thermal shock resistance of this material justify further development study. Two areas of development should be considered.

1) Scale-up of grade RVD graphite to 33 inches in diameter by 22 to 30 inches in length should be attempted to verify the processability of these sizes indicated by the 1250-ton press trials.

2) The use of a finer-grain blend than grade RVD blend or the use of improved impregnants with grade RVD might result in a graphite with an erosion resistance equalling or surpassing that of grade ZTA, while retaining the thermal shock resistance exhibited by grade RVD. Further development studies in these directions might therefore be beneficial in obtaining a graphite grade suitable for the most critical rocket nozzle applications.

5. LIST OF REFERENCES

1. WADD Technical Report 61-72, Volume VII, "High Density Recrystallized Graphite by Hot-Forming," E. A. Neel, A. A. Kellar and K. J. Zeitsch.

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

3. WADD Technical Report 61-72, Volume XXXI, "High Performance Graphite by Liquid Impregnation," C. E. Waylett, M. A. Spring and M. B. Carter.

4. WADD Technical Report 61-72, Volume XXIX, "Evaluation of Graphite Materials in a Subscale Solid-Propellant Rocket Motor," D. C. Hiler and R. B. Dull.

5. WADD Technical Report 61-72, Supplement to Volume XII, "Development of an Improved Large-Diameter Fine-Grain Graphite for Aerospace Applications," R. L. Racicot and C. W. Waters.