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STUDIES OF GRAPHITE FOR FUEL ELEMENTS

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Metallurgy and Ceramics

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STUDIES OF GRAPHITE FOR FUEL ELEMENTS

by

L. D. Loch
J. A. Slyh
W. H. Duckworth

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STUDIES OF GRAPHITE FOR FUEL ELEMENTS

by

L. D. Loch, J. A. Slyh, and W. H. Duckworth

Improved graphites for use in fuel elements were developed from artificial graphites and phenolic resins. These materials are particularly well suited for fuel-element preparation. The resins do not soften during baking, so bodies hold their shape and show good dimensional uniformity. The physical properties of graphite were obtained without heating at "graphitizing" temperatures, which would be detrimental to UO_2 or other inclusions of nuclear fuel. High densities and bending strengths, viz., 1.80 g/cm^3 and 15,000 psi, were obtained directly without the usual impregnation of the baked product with pitch and rebaking. At 2770 F, one of the experimental bodies had a tensile strength of 8250 psi as compared to 4700 psi for Type ECA, a commercial graphite of interest for fuel elements.

UO_2 -bearing bodies were prepared by using the improved graphites as matrices. The UO_2 was added during primary fabrication of the bodies by several different methods which produced a wide range of particle sizes. Consideration of the qualitative effects of UO_2 particle size and of some of the experimental results indicate that the use of UO_2 nodules between 100 microns and 800 microns in diameter may have three important advantages: (1) less fission damage to the graphite, (2) less diffusion and loss of uranium, and (3) better retention of fission products by the fuel element.

INTRODUCTION

For the high-temperature reactors of the future, refractory ceramics are among the most promising materials for fuel-element construction. Among the refractory ceramics, graphite has received considerable attention as a matrix material for high-temperature fuel elements.

Basically, graphite is one of the most attractive of the ceramic fuel-element materials. In addition to being a good moderator, it has a very high sublimation point, good strength at high temperatures, and excellent thermal-shock resistance. However, our knowledge of the behavior of graphite in its customary industrial roles is not nearly sufficient to appraise it as a fuel-element material. Much more must be learned about its behavior under the combined effects of radiation, high temperatures, and severe thermal stresses. Also, much can be done to develop special grades of graphite for use as fuel elements.

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The work described in this report is divided into two parts: the first part describes the development of improved graphite matrices for fuel elements, and the second deals with the studies of UO_2 -graphite bodies based on these improved matrices. The emphasis in Part II is on the effects of fuel-particle size. These effects are discussed qualitatively and some experimental observations of their importance are given.

PART I. DEVELOPMENT OF IMPROVED GRAPHITE MATRICES

The research on matrices was limited to those prepared from thermosetting resin binders and artificial graphite flours. For the proposed application, these materials have a number of advantages over the petroleum-coke flours and coal tar-pitch binders normally employed in industry for producing graphite products.

In particular, the thermosetting resin may be polymerized in a simple, low-temperature heat treatment and does not soften on reheating during the baking operation. This eliminates the extreme care needed in supporting pitch-bonded articles to prevent distortion during baking. Also, shrinkage of resin-bonded articles during baking is more uniform than shrinkage of pitch-bonded articles; thus, closer dimensional tolerances may be held. These characteristics should be of great advantage in producing shapes without expensive machining operations.

Through the use of artificial graphite as a filler, experimental bodies having essentially the properties of commercial artificial graphite were obtained by heating only to a temperature of 2500 F. Petroleum-coke bodies must be heated to 4500 F to be converted to graphite. This simplifies greatly the problem of retaining fuel additions such as UO_2 in the desired chemical form and in the desired position in the graphite structure.

Raw Materials

Graphite Flours

Two sources of graphite were employed. For most experiments, a commercial, artificial-graphite flour was used. This material, Grade No. 2301*, was nominally "minus 200 mesh", or less than 74 microns in particle size. The ash content was about 0.11 w/o. For a few experiments,

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graphite flour was prepared in the laboratory by milling chips of reactor-grade graphite (AGOT) to various particle sizes. Milling was done in a carbon-lined mill with carbon grinding balls.

Phenolic Resins

Three phenol-formaldehyde resins were used as binders. One was an alcohol solution, known as Grade BV1600*. It contained about 50 w/o resin solids and was reported to have an ash content, based upon the original solution, of about 0.008 w/o. The other resins were water emulsions, Grades 79L and 79LHS**, containing 65 and 85 w/o resin solids, respectively. Based on the resin content, the ash in these resins was about 1.3 w/o. Most of the ash consisted of sodium hydroxide, which volatilized during baking at 2500 F.

A phenol-furfural resin was used in small quantities. This was Durite S-3160***, containing 55 to 58 w/o of resin solids.

Compositions

Extruded Bodies

In the early work, the extruded bodies were prepared with 79L resin binder. From 51 to 66 parts by weight of resin per 100 parts of graphite flour were used. As the work progressed, a gradual conversion was made to 79LHS resin; 51.5 to 62 parts per 100 parts of graphite flour were used. Exact compositions are given when the specific bodies are discussed.

Molded Bodies

For the molded bodies, BV1600 resin was used in amounts ranging from 50 to 100 parts per 100 parts of graphite. In some instances, small additions of S-3160 resin were used with the BV1600 to increase the flowability of the batch. The amounts of such additions were from 2.5 to 10 parts of S-3160 per 100 parts of graphite.

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Preparation of Bodies

Mixing

The primary purpose of the mixing operation was to distribute the binder uniformly on the particles of filler. In addition, the mixing operation was employed, when necessary, to distill off volatile components of the binder and obtain the proper consistency for forming.

Five different mixers were used. These are described in Table 1. In all cases, whether for extrusion or for molding, the graphite powder and the resin were blended in a muller or tank-type mixer. Except when the mixer rolls were used, the mixture was brought to the proper consistency by continued mixing in the same unit. Batches which were to be finished on the mixer rolls were blended in a muller-type mixer before transfer to the rolls.

TABLE 1. MIXERS USED TO PREPARE MATERIALS FOR FORMING

Mixer	Type of Mixer and Blades	Manufacturer	Usual Batch Weight, g	Usual Mixing Time, hr
Lancaster, counter current	Muller	Posey Iron Works Lancaster, Pennsylvania	600	1-1/4
Simpson, intensive	Muller	National Engineering Co. Chicago, Illinois	6500	1
Day, 1/2 gal	Tank, fish-tail blades	J. H. Day Co. Cincinnati, Ohio	1500	3-1/2
Day, Mogul-type, 2-1/2 gal	Tank, flat masticator blades	Ditto	8000	2-1/2
Mixer rolls, 8-in. diameter x 12 in. long	Counter-rotating, cylinders chromium plated	Erie Engine and Manufac- turing Company Erie, Pennsylvania	1000	1/4

The proper mixing time for a batch was determined by experience, guided by measurements of the bulk density and strength of previous batches. Extrusion batches were quite plastic, with sufficient "body" to require a considerable pressure for extrusion without causing "drag" at the surfaces of the die. In contrast, a molding mix was worked until it became stiff and brittle. It then was pulverized in a muller-type mixer to pass a 100- or 200-mesh* sieve before molding.

*The U. S. Standard sieve series was employed throughout this work.

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Forming

Extrusion. A piston-type extrusion apparatus equipped for deairing the batch was used in all cases. The apparatus employed to form rods, 1 in. and 5/8 in. in diameter, consisted of a 5-in.-diameter cylinder, a tapered transition section with a 60-deg angle, and a nozzle of suitable diameter and length. Nozzles 3, 4-1/2, or 5 in. long were used to extrude 1-in. rods; a 4-in.-long nozzle was used for the 5/8-in. rods. A 3-in. cylinder and a die with a nozzle 1 in. long also were employed for the extrusion of certain 1/4-in. rods.

Preparatory to extrusion, the batch, in the form of lumps 1/2 in. or smaller in size, was sealed inside the cylinder. It was deaired for at least 10 min at an absolute pressure of 15 mm, or less, of mercury. The hydraulic pressure then was applied to the piston, which extruded the specimens vertically downward. The maximum total load on the 5-in. piston was about 10 tons.

Molding. The prepared molding powder was placed in a steel die and compressed at pressures ranging from 5 to 20 tons per sq in. Direct compression molding was used throughout.

For hot molding, the dies were insulated and were equipped with strip-type electrical heaters. Temperatures up to 350 F were obtained. The power source was a 110-v circuit through a 25-amp variable transformer.

Curing

Curing or polymerization of the resin binder was done in the usual manner. In some cases, however, very close control of this operation was necessary. Molded specimens were cured for 2 hr at 300 F in a Despatch* circulating-air oven. No difficulties were encountered in the curing of molded bodies.

The curing of extruded bodies usually was more critical. A uniform rate of curing throughout the cross section was necessary to avoid internal cracking and surface blistering. This condition could be approximated only when the rate of surface evaporation was small. The Despatch oven met these requirements sufficiently well only in cases of low to moderately high densities and/or small cross sections.

Extruded bodies having baked densities greater than 1.73 g/cm³ or cross sections larger than 1/4-in. diameter were cured in a special oven which was built at Battelle. This oven consisted of a light-gage metal

*Manufactured by the Despatch Oven Company, Minneapolis, Minnesota.

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shell with a tight-fitting door externally heated by means of strip heaters. The specimens were completely covered with a layer of powdered graphite before curing was begun. This protective layer and the sealed chamber sufficiently limited evaporation and polymerization at the surface to produce an even cure throughout the cross section.

Three different schedules were used for the various types of extruded specimens as shown in Table 2.

Gas Baking

All specimens were baked in a gas-fired furnace to carbonize the resin and to set the resultant binder carbon. The specimens were packed in graphite flour in a covered graphite crucible which in turn was packed in a clay-graphite crucible. The crucible lid was sealed on with a mixture of kaolin and silica. The temperature was raised gradually to 2500 F and held there for a period of 4 or 6 hr.

During baking, the critical temperature range (because of rapid loss of volatiles) was between 700 and 1300 F. The permissible rate of temperature increase through this range was governed by the size and density of the specimen. As in the case of curing, three different temperature schedules were used to accommodate specimens of varying sizes and densities. These schedules are listed in Table 3.

Results of Fabrication Studies

Bulk Density and Modulus of Rupture

Systematic investigations were made of the effect of composition and of method of fabrication on bulk density and modulus of rupture. As the test specimens were regular in shape, it was convenient to compute bulk density directly from measurements of specimen weight and gross volume. The error in the resulting values of density is estimated to be less than 0.8 per cent.

Modulus of rupture was determined conventionally by supporting the specimen as a simple beam and applying a concentrated load at mid-span. The length of the span was 8 times the diameter (or depth) of the specimen. In the case of extruded bodies, the neutral axis coincided with the axis of extrusion. The neutral axis in molded bodies, of course, was parallel to the largest dimension of the specimen. Molded bodies were supported in such a way that the direction of loading, the neutral axis, and the direction of the applied molding force formed three mutually perpendicular axes.

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TABLE 2. HEATING SCHEDULES FOR CURING EXTRUDED SPECIMENS

Type of Specimen ^(a)	Oven Used ^(b)	Curing Schedule	
		Time, hr	Temperature, F
1/4-in. rods, low density	Despatch	15	180
		9	200
		15	220
		5	250
1/4-in. rods, high density; 5/8-in. and 1-in. rods and tubes, low density	Despatch	15	120
		9	150
			150
		15	200
		9	250
		15	300
5/8- and 1-in. rods and tubes, high density	Battelle	24	400
		40	150
		24	200
		9	250
		15	300
		30	400

(a) Low-density specimens are those with a baked density less than 1.73 g/cm³; high-density specimens have a baked density of 1.73 g/cm³ or greater.

(b) For description of ovens, see text.

TABLE 3. HEATING SCHEDULES FOR BAKING RESIN COKE-BONDED BODIES

Class of Specimen ^(a)	Baking Schedule		
	Temperature Range, F	Rate of Rise, deg F/hr	Soak Period, hr
1, 4-in. extruded rods, low density	400 - 800	50	4
	800 - 1300	40	
	1300 - 2500	150	
1/4-in. extruded rods, high density; all cold-molded bodies	400 - 600	30	6
	600 - 1300	15	
	1300 - 1900	35	
	1900 - 2500	150	
All 5/8- and 1-in. extruded rods and tubes; all hot- molded bodies	400 - 800	20	6
	800 - 1300	10	
	1300 - 1500	35	
	1500 - 2500	75	

(a) See Footnote (a), Table 2.

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Modulus of rupture was the maximum fiber stress at failure, calculated from standard formulas for simple beams. In general, the average was determined on 10 to 20 individual determinations.

Effect of Composition. Five extrusion batches were prepared on the mixer rolls, each from 400 g of 2301 graphite and sufficient 79LHS resin to obtain compositions from 20.0 to 24.8 w/o resin coke. Test rods were prepared by using the 1/4-in. die and the 3-in. cylinder. The results of this experiment are summarized in Figure 1. The strength was not greatly affected by changes in resin-coke content, but density appeared to decrease when more than about 23 w/o resin coke was used.

Effect of Particle Size of Filler. Machine cuttings of reactor-grade graphite were separated into the following U. S. Standard sieve fractions: minus 140 plus 200 mesh, minus 200 plus 325 mesh, and minus 325 mesh. Ten extruded bodies were prepared, one from each of the three particle sizes and seven from mixtures of the three sizes.

The batches, each consisting of 400 g of graphite and 236 g of 79L resin, were mixed for 2 hr in the Lancaster mixer. The material was extruded into rods, 1/4 in. in diameter, at a load of 3 to 6 tons. In this experiment, the batch was not deaired. The bulk densities and moduli of rupture of these specimens after baking at 2500 F are shown in Figure 2. The results demonstrate clearly that a blend of particles covering a wide range of sizes produces higher strength and density than does a mixture of particles of nearly uniform size. Mixture which contained a predominance of fine particles produced the highest densities and strengths. Similar observations have been made in studies of other ceramic materials.

No systematic study was made of the effect of particle size on the properties of molded bodies.

Effect of Mixing Methods. The bulk density and modulus of rupture show the efficiency of mixing, or the extent to which the graphite filler is "covered" by the resin binder. Mixing equipment may be rated for efficiency on the basis of these two properties. In Table 4, comparative results are shown for four different mixers in the preparation of an extrusion batch and for two different mixers in the preparation of a cold-molding batch.

Proper mixing of these graphite-resin formulations required a positive kneading action with considerable pressure on the mix to force the resin into all the available pores of the graphite filler. The fish-tail blades of the 1/2-gal Day mixer supplied very little kneading under a very low pressure. This mixer produced poor results. Both of the muller-type mixers supplied some kneading action under a moderate pressure,

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FIGURE 1. EFFECT OF COMPOSITION ON THE PROPERTIES OF EXTRUDED BODIES

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FIGURE 2. EFFECT OF PARTICLE SIZE OF THE FLOUR ON THE PROPERTIES OF EXTRUDED BODIES

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TABLE 4. COMPARATIVE EFFICIENCIES OF SEVERAL TYPES OF MIXERS

Mixer ^(a)	Mixing Period Required, hr	Properties of Bodies	
		Bulk Density, g/cm ³	Modulus of Rupture, psi
<u>Extrusion^(b)</u>			
1/2-gal Day	3-1/2	1.55	2,475
Lancaster	1-1/4	1.72	7,800
Simpson	1	1.71	9,700
Mixer rolls (pre- ceded by 1 hr in Simpson mixer)	1/4	1.78	16,600
<u>Cold Molding^(c)</u>			
Lancaster	1/2	1.56	5,180
Mixer rolls (pre- ceded by 1/2 hr in Lancaster mixer)	1/4	1.75	6,240

(a) See Table 1 for descriptions of these mixers.

(b) Specimens were rods, 1/4 in. in diameter.

(c) Specimens were bars, 5/16 by 5/16 by 3 in.

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and they gave satisfactory end results. The mixer rolls supplied very active kneading and shearing actions under rather high pressures. As a consequence, the rolls did an excellent mixing job in a relatively short time.

Effect of Deairing the Batch. A special extrusion batch was prepared to measure the effect of deairing the material prior to extrusion. A mixture of 400 g 2301 graphite and 236 g 79L resin was prepared in the Lancaster mixer. One half of this batch was extruded without deairing and the other half was evacuated to an absolute pressure of 24 mm mercury. The results are shown in Table 5.

As expected, deairing the mix prior to extrusion increased markedly the bulk density and the modulus of rupture of the baked specimens.

TABLE 5. EFFECT OF DEAIRING THE BATCH ON THE PROPERTIES OF EXTRUDED BODIES

	Bulk Density, g/cm ³	Modulus of Rupture, psi
Not deaired	1.40	1,770
Deaired to 24 mm mercury	1.58	6,500

Effect of Forming Pressure. The forming pressure used in extrusion is fixed within a narrow range by such factors as the binder content and the length of the die nozzle. Therefore, it was not possible to isolate the effect of forming pressure from the effects of these other parameters. Usual practice was to employ the maximum possible forming pressure that could be used without tearing the surface of the extruded column.

In general, the density and strength of a molded body increased with forming pressure up to a limiting pressure which was characteristic of the particular body. Typical curves for two cold-molded bodies are shown in Figure 3. These results were obtained with a batch consisting of 75 parts BV1600 per 100 parts 2301 graphite. After mixing for 1/2 hr in the Lancaster mixer and for 1/4 hr on the mixer rolls, the material was pulverized and screened to minus 100 plus 200 and minus 200-mesh sizes, respectively. Bodies were prepared from both particle sizes at pressures of 7-1/2, 10, and 15 tons per sq in.

Limitations of Resin Coke-Bonded Bodies

Certain limitations were found in the suitability of thermosetting resins as binders for artificial graphite. Internal stresses occur in such bodies because of uneven compaction during forming, nonuniform curing of the

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FIGURE 3. EFFECT OF MOLDING PRESSURE ON THE PROPERTIES OF COLD-MOLDED BODIES

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resin, and the anisotropic thermal expansion of the graphite crystallites during gas baking. The rigid structures of the cured resin and of the resin coke prevent the stress relaxation that takes place in pitch-bonded bodies during the early stages of baking. The tendency of dense resin coke-bonded bodies to crack and laminate during baking, and even during curing, placed practical limits on the amounts of resin that could be used, and prevented the preparation of bodies in very large cross sections. The latter may be only a minor disadvantage in that most fuel-element designs require thin cross sections.

Selection and Descriptions of Standard Bodies

Four types of resin coke-bonded graphites were evolved during the fabrication studies: extruded, dense extruded, cold molded, and hot molded. Each one represents a major variation in processing which resulted in a distinct level of quality, in terms of bulk density and strength. For the purpose of making further measurements of physical properties, an optimum composition and processing specification was selected for each of the four classes and designated as "standard". The compositions, processing techniques, densities, and strengths of these standard bodies are shown in Table 6.

Physical Properties of Standard Bodies

A number of determinations were made of tensile strength, modulus of elasticity, thermal conductivity, thermal expansion, and electrical resistivity. However, no attempt was made to measure all of these properties on each of the developed bodies.

Because graphite is anisotropic, it is necessary to specify the direction in which a given property is measured. The conventions which are used for molded and extruded bodies are shown in Figure 4. In both molded and extruded specimens, any preferred orientation of the c_0 axes of the crystallites will be in the transverse direction. Molded specimens have two parallel directions and they are identified as "major parallel" and "minor parallel", in the direction of the longer dimension and the shorter dimension, respectively.

Tensile Strength

The tensile-testing apparatus described by Adams and Nelson^{(1)*} was used to obtain tensile-strength data at temperatures up to 2750 F. Two modifications were made in the apparatus for this work. The specimen was redesigned. Figure 5 is a sketch of the specimen used. Also, the load was

*References on page 65.

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TABLE 6. PROCESSING CONDITIONS AND PROPERTIES OF STANDARD RESIN COKE-BONDED BODIES

Body Designation	Resin Addition		Mixing Procedure	Forming Conditions	Largest Shape Produced	Properties of Baked Body	
	Grade	Parts Per 100 Parts of 2301 Graphite				Bulk Density, g/cm ³	Modulus of Rupture, psi
Extruded	79LHS	62	1-1/2 hr in Lancaster or Simpson	2 to 3 tons on 3-in. cylinder, or 15 to 20 tons on 5-in. cylinder	1-in. diameter rod, solid cross section	1.68 to 1.71	8,500 to 11,000
Dense extruded	79LHS	62	1/2 hr in Lancaster or Simpson; 1/4 hr on mixer rolls	Ditto	5/8-in.-OD by 1/8-in.-ID tube ^(a)	1.77 to 1.83	13,000 to 16,500
Cold molded	BV1600	75	Ditto	5 to 15 tons per sq in.	1 by 1 by 7-in. bar	1.67 to 1.74	4,000 to 6,800
Hot molded	BV1600	50	"	5 to 15 tons per sq in. at 250 F	3/4 by 3/4 by 5-1/2-in. bar	1.78 to 1.83	5,000 to 6,700

(a) The presence of the axial hole permitted more even curing and baking. Thus, it was possible to produce sound tubular specimens although solid specimens of the same body contained cracks and laminations.

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FIGURE 4. CONVENTIONS USED IN RELATING THE ANISOTROPIC PROPERTIES OF GRAPHITE TO THE DIRECTION OF MEASUREMENT

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FIGURE 5. GRAPHITE TENSILE SPECIMEN

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measured with a Dillon dynamometer* rather than with a pressure gage. In testing, the specimens were stressed at a rate of 2000 psi per min.

The short-time tensile strength, in the parallel direction, of the standard extruded body between room temperature and 2770 F is shown in Table 7. These data are plotted in Figure 6 together with the data of North American Aviation⁽²⁾ on ECA graphite, the strongest of the commercial graphites whose strengths at high temperatures have been reported in the literature.

The tensile strength of the standard dense-extruded body was 8450 ± 163 psi at room temperature, on the basis of six measurements. It was necessary to make these tests on tubes, 5/8-in. OD by 1/8-in. ID, because solid specimens of this body invariably were cracked and laminated.

Tensile strengths of the molded bodies were not measured.

TABLE 7. SHORT-TIME TENSILE STRENGTH OF THE STANDARD EXTRUDED BODY, PARALLEL DIRECTION

Temperature, F	Average Tensile Strength, psi	Number of Tests	Standard Deviation	
			PSI	Per Cent
68	6900	6	228	3.3
935	6200	4	218	3.5
1520	5600	4	496	8.8
1620	6100	2 ^(a)	--	--
1850	6700	5	328	4.9
2325	7100	4	498	7.1
2530	7800	3	311	4.0
2770	8300	5	235	2.9

(a) Insufficient tests to calculate standard deviation.

Modulus of Elasticity

Measurements were made by a sonic or dynamic method, except for one determination in which static loading was employed.

The sonic method described by C. W. Andrews⁽³⁾ was used with modifications as to the choice of oscillation and receiving equipment. For measurements at elevated temperatures, the specimens were supported on asbestos threads and heated by means of a Nichrome-wound resistor furnace.

*Manufactured by the W. C. Dillon Company, Chicago, Illinois.

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FIGURE 6. TENSILE STRENGTHS OF GRAPHITE BODIES AT HIGH TEMPERATURES

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The single measurement of the static-loading modulus was made in a simple bend test at room temperatures; two-point loading was used. The specimen was a bar of the standard extruded body, 0.4 by 0.4 by 6 in. It was loaded on a 4-in. span and the maximum strain was measured with an SR-4, Type A-5 strain gage*. The stress-strain curve was nonlinear. At zero stress, the modulus was calculated to be 4.8×10^6 psi. It gradually decreased to 3.6×10^6 psi at a stress of 9000 psi. Rupture occurred at 10,300 psi.

The dynamic moduli of several bodies at room temperature are shown in Table 8. The cross linkages which remain after pyrolysis of the resin have a pronounced "stiffening" effect, as shown by the increase in modulus with increase in resin-coke content.

Measurements of the standard extruded and the standard dense-extruded bodies were extended to a temperature of 1600 F. In the range between room temperature and 1600 F the moduli remained constant within $\pm 0.1 \times 10^6$ psi.

Thermal Conductivity

The method of Van Dusen and Shelton⁽⁴⁾ was used to determine the thermal conductivity. This method consists of heating one end of a cylindrical specimen and measuring the temperature gradient along its length. The heat flow is calculated from the measured temperature gradient in a metal of known conductivity placed in series with the unknown material. The conduction path is protected by a heated and insulated guard tube. In this work, a specimen 0.6 in. in diameter by 6 in. long was used. The ends were electroplated with copper and tin. One end was soldered to the heater block and the other to the metal standard. Measurements were made up to 1050 F.

The thermal conductivities of three resin coke-bonded bodies are shown in Figure 7. Measurements were made either in the parallel or the major parallel direction. The "fine-grained" and "coarse-grained" molded bodies were prepared from AGOT flour, sized to minus 140 and minus 50 plus 140 mesh, respectively.

Thermal Expansion

Linear thermal expansion was measured with an interferometer**;
a mercury-vapor light source was used.

*Manufactured by the Baldwin-Lima-Hamilton Corporation, Philadelphia, Pennsylvania.

**A product of the Gaertner Scientific Corporation, Chicago, Illinois.

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TABLE 8. THE DYNAMIC MODULI OF ELASTICITY OF RESIN COKE-BONDED BODIES AT ROOM TEMPERATURE

Type	Description of Body		Modulus of Elasticity, million psi	Plane of Vibration	Specimen Shape	Specimen Size, in.
	Resin-Coke Content, w/o	Density, g/cm ³				
Standard extruded	24	1.67	6.5	Parallel with extrusion axis	Round	1/4
Standard dense extruded	20.7	1.77	6.7	Ditto	Round	1/4
Cold molded	13	1.63	2.1	Perpendicular to direction of molding force	Square	5/16
Cold molded	23	1.65	2.9	Ditto	Square	5/16
Standard hot molded	13	1.79	2.9	"	Square	3/4

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FIGURE 7. THERMAL CONDUCTIVITIES OF RESIN COKE-BONDED BODIES

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Expansion curves for two standard bodies were obtained over the range from 75 to 750 F. The results are given in Table 9 in the form of mean coefficients at four temperatures throughout the interval. The lower expansion of the extruded body compared to the molded body is a result of its higher resin-coke content. High preferred orientation probably accounts for the exceptionally low expansion of the extruded body in the parallel direction.

TABLE 9. LINEAR THERMAL EXPANSIONS OF RESIN COKE-BONDED BODIES

Body	Temperature (t), F	Mean Coefficient of Thermal Expansion Between 75 F and Temperature (t), 10^{-6} per deg F	
		Parallel	Transverse
Standard extruded	200	0.27	1.91
	400	0.33	1.89
	550	0.39	1.83
	750	0.44	1.88
Standard hot molded	200	1.25	2.63
	400	1.34	2.75
	550	1.44	2.80
	750	1.52	2.87

Electrical Resistivity

The specimens were clamped between two copper electrodes and connected in series with a known resistance. By measuring the voltage drop across the standard resistance and across the specimen, the resistance of the specimen was determined. Measurements were made on extruded rods, 1/4 in. in diameter by 4 in. long, and on bars, 5/16 by 5/16 by 3 in., both extruded and molded. The resistivities at room temperature of three standard bodies are shown in Table 10.

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TABLE 10. ELECTRICAL RESISTIVITIES OF RESIN COKE-BONDED BODIES

Body	Bulk Density, g/cm ³	Electrical Resistivity ^(a) , microhm-cm
Standard extruded	1.70	1300
Standard dense extruded	1.81	1000
Standard cold molded	1.68	1400

(a) All measurements were made in the parallel or the major parallel direction.

Graphitization of Resin Coke-Bonded Bodies

The unique physical properties of resin coke-bonded graphites, particularly their high strengths and low thermal expansions, are primarily the result of the highly cross-linked, three-dimensional structure of the resin cokes. As Franklin⁽⁵⁾ points out, the cross linkages and the extensive microporosity in such carbons hinder crystallite growth by preventing migration of the small graphite layer planes into parallel arrays. Resin cokes, therefore, are essentially nongraphitizing carbons. However, at very high temperatures the cross linkages begin to break down and a small amount of crystallite growth takes place.

X-ray measurements on resin cokes and physical-property measurements on resin coke-bonded graphites were made to determine the extent of graphitization at temperatures from 3800 to 4650 F. At these temperatures, the crystallite size and c_0 spacing of the resin cokes changed very little, but there were substantial changes in the physical properties of resin coke-bonded bodies. These changes would be important if such fuel-element bodies were subjected to these high temperatures during the purification step of their manufacture or during operation in a reactor.

Graphitization treatments were carried out in a horizontal carbon-resistor tube furnace in an atmosphere of purified argon. A radiation pyrometer was employed for continuous temperature recording and control, while an optical pyrometer served as the primary standard.

Crystallite Size and c_0 Spacing

Samples of resin coke were prepared from 79LHS and BV1600, and their X-ray parameters were determined after graphitizing at several different temperatures.

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All X-ray measurements were made with a 90 deg, 2 θ Norelco spectrometer by using copper K-alpha radiation. The c_0 lattice constant was determined by comparing the position of the (004) line with the pattern of an annealed tungsten standard, 15 w/o of which was added to the sample.

To determine crystallite dimensions C and A, line breadths at half-maximum intensity of the (002), (004), (001), and (hk) reflections were determined from charts driven by a 1/4-rpm Geiger-counter drive. The annealed tungsten gave suitable reflections for making instrument corrections according to the method of Jones⁽⁶⁾. The crystallite dimension C refers to the direction perpendicular to the layer planes, while the dimension A refers to the direction parallel with the planes. The formulas for calculating C and A are given in the Appendix.

The X-ray parameters of the resin cokes after heat treatment at different temperatures are shown in Figure 8. These results may be interpreted on the basis of Franklin's⁽⁵⁾ description of the graphitization process. Between 2000 F and 4250 F, crystallite growth consists primarily of increases in the A dimension at the expense of the "non-organized" carbon. Growth in the C direction is hindered by the rigid cross linking between neighboring nuclei of carbon and probably also by a random orientation of the crystallites. At 4500 and 4650 F, the cross linkages break down sufficiently to allow substantial growth in the C direction, but extensive development is still prevented by poor orientation. Even at these temperatures, the resin cokes show no trace of homogeneous development of the three-dimensional graphite structure. The progressive decrease in c_0 spacing between 2000 and 4500 F results chiefly from an increase in the perfection of the individual crystallites. In all cases, the c_0 lattice constant is considerably greater than 6.706 Å, the value for natural graphite.

Electrical Resistivity and Dimensional Shrinkage

The change in electrical resistivity and shrinkage of the standard dense-extruded body was determined for graphitizing temperatures of 4000, 4300, and 4500 F. The results are shown in Table 11. There was very little change as a result of heating at 4000 F, as would be expected from the X-ray diffraction results which showed little crystallite growth at this temperature.

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FIGURE 8. X-RAY PARAMETERS OF RESIN COKES AFTER HEATING AT GRAPHITIZING TEMPERATURES

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TABLE 11. DECREASE IN RESISTIVITY AND SHRINKAGE AT GRAPHITIZING TEMPERATURES

Standard Dense Extruded Body.

Heat Treatment	Ratio of Original to Final Resistivity, $\frac{\rho_o}{\rho}$	Shrinkage, per cent
4000 F for 4 hr	1.01	0.21
4300 F for 4 hr	1.08	0.43
4500 F for 2 hr	1.07	0.63

One experiment was made to determine the effect of metallic additions on the change in resistivity. According to Tomin⁽⁷⁾, silicon, titanium, and nickel are among those elements which accelerate graphitization. These elements were added to the standard extruded body as silicon carbide, titanium carbide, and nickel metal, respectively. The amounts of these additions and their effect on resistivity changes after heat treatment at 4000 F for 2 hr are shown in Table 12. These show that each of the metals was effective, to some degree, in producing a low-resistivity carbon at 4000 F. Without such additions, an equivalent change in resistivity was not obtained even at 4500 F, as shown in Table 11.

TABLE 12. DECREASE IN RESISTIVITY OF STANDARD EXTRUDED BODY WITH METAL ADDITIONS AFTER HEATING AT 4000 F

Addition	Amount of Addition, w/o of metal (before graphitizing)	Ratio of Original to Final Resistivity, $\frac{\rho_o}{\rho}$
Silicon	2.08	1.57
Titanium	1.95	1.25
Nickel	5.87	1.49
None	--	1.01 ^(a)

(a) Specimen heated for 4 hr; all others were heated for 2 hr.

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Other Properties

Changes in modulus of rupture, modulus of elasticity, thermal conductivity and thermal expansion were determined for graphitization at 4500 F for 2 hr. Table 13 shows the effect on these properties of partial breakdown of the cross linkages in the resin coke. Modulus of rupture and modulus of elasticity were decreased as a result of a reduction in the number of polar carbon-carbon bonds in the strength-giving resin-coke phase. The coefficient of thermal expansion increased upon removal of some of the cross linkages which suppressed the expansion of the crystallites in the resin coke. Similarly, Franklin⁽⁵⁾ noted that the thermal expansion of a coke prepared from a graphitizing coal was about twice that of a carbonized nongraphitizing coal and attributed this to the strength of the cross linking in the latter material. The increase in thermal conductivity of the resin coke-bonded bodies resulted from the decrease in grain-boundary scattering which accompanied crystallite growth in the resin coke.

Because the loss of strength at high temperatures is of particular interest, an additional experiment was made using a heat treatment at 4000 F for 4 hr. The modulus of rupture of the standard dense-extruded body decreased from 13,600 psi to 11,280 psi, in agreement with the X-ray results which showed some breakdown of the cross linkages at 4000 F.

TABLE 13. EFFECT OF HEAT TREATMENT AT 4500 F ON THE PROPERTIES OF RESIN COKE-BONDED BODIES

Body	Property	Value, Parallel or Major Parallel Direction	
		After Baking at 2500 F	After Reheating at 4500 F for 2 Hr
Standard extruded	Modulus of rupture, psi	7670	5700
Standard dense extruded	Modulus of elasticity, 10^6 psi	6.7	4.4
Standard extruded	Thermal-expansion coefficient at 100 F (α), 10^{-6} per deg F	0.27	0.36
Cold molded	Coefficient of thermal conductivity at 100 F, Btu/(hr)(ft)(F)	26.2	55.9

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PART II. STUDIES OF UO_2 -GRAPHITE BODIES

To evaluate resin coke-bonded graphite bodies as possible fuel elements and to investigate the importance of fuel-particle size, UO_2 particles of controlled sizes were added to the matrices described in Part I.

Several techniques were used for adding UO_2 , but in every case the addition was made during preparation of the original bodies rather than by impregnation. By using such methods, it was possible to obtain a wide selection of particle sizes and good control of the uranium distribution. Adding the uranium during primary fabrication also permitted the fabrication of high-density bodies. Porous bodies of relatively low bulk density are used when the uranium is added by impregnation.

Dispersions of fine UO_2 particles were obtained by adding uranyl nitrate or uranyl acetate to the base bodies and forming UO_2 in situ during subsequent heat treatment. Coarser additions were prepared directly from UO_2 and added to the graphite bodies.

The UO_2 as received from the producer consisted of relatively soft agglomerates with an ultimate particle size of less than 10 microns. Therefore, it had to be modified in order to produce a wider range of particle sizes. Methods for preparing durable particles by the addition of organic binders were studied in detail and the preparation of hard particles by sintering was investigated briefly.

The uranium content was held constant at 5 w/o. Reasonable variations from this composition are not expected to cause any processing difficulties.

Preparation of Experimental Bodies

Uranium-Bearing Raw Materials

Uranyl nitrate hexahydrate, $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was obtained from the Mallinckrodt Chemical Works, St. Louis, Missouri. Uranyl acetate dihydrate, $\text{UO}_2(\text{C}_2\text{H}_3\text{O}_2)_2 \cdot 2\text{H}_2\text{O}$, was obtained from the J. T. Baker Chemical Company, Phillipsburg, New Jersey.

UO_2 was supplied by the Mallinckrodt Chemical Works, St. Louis, Missouri. It contained 88.1 w/o uranium and had the following sieve analysis:

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<u>Size Range, U. S. Standard Sieve</u>	<u>w/o</u>
Plus 100	45
Minus 100 - plus 200	15
Minus 200 - plus 325	4
Minus 325	36

The material retained on the 100-mesh sieve consisted of relatively soft agglomerates of finer particles.

Uranyl Nitrate Addition

Preliminary Experiments. The first attempts to produce resin coke-bonded bodies bearing highly dispersed uranium consisted of adding a water solution of uranyl nitrate to graphite powder and blending the resin binder into the resulting wet mixture. The bodies produced by this method had three major faults: (1) low density, (2) structural weakness, and (3) nonuniform distribution of the uranium throughout the graphite.

Auxiliary experiments showed that the low density and strength were caused by a reaction between the uranyl nitrate and the alkali catalyst of the resin. Precipitation of the alkali, probably as sodium diuranate, reduced the pH of the system to the extent that the resin separated into two liquid phases. Proper polymerization to produce a resin with a satisfactory consistency and a high carbon yield then was impossible.

The poor uranium distribution was attributed to the use of a water-soluble phenolic resin and a water-soluble uranium compound in the same system. This combination permitted the uranyl nitrate to migrate during the curing treatment.

These faults were remedied satisfactorily by converting the uranyl nitrate to an insoluble compound before adding the resin.

Preferred Procedure. Preparation of the batch, preliminary to extrusion, was done entirely in the Mogul mixer referred to in Table 1. A water solution of uranyl nitrate was mixed uniformly with three-fifths of the 2301 graphite powder and then the uranyl nitrate was converted to ammonium uranyl carbonate* by the addition of a water solution of ammonium carbonate. The material was mixed further for 1/2 hr while cold, then mixing was continued while the material was dried at a temperature of 160 to 175 F. The drying temperature was held below 175 F to avoid decomposition of the ammonium salt.

*The composition of the product was not determined definitely. It was assumed to be ammonium uranyl carbonate, $2(\text{NH}_4)_2\text{CO}_3 \cdot \text{UO}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$, because of its appearance and its behavior.

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The material then was removed from the mixer and dried for 16 hr at 160 F. The resulting hard lumps were pulverized in a mortar and blended with the remainder of the graphite in the Mogul mixer. The resin then was added and the batch was brought to the proper consistency for extrusion by mixing for an additional 2 hr.

The most satisfactory batch, which was sufficient to produce twenty rods 1 in. in diameter by 12 in. long, contained:

5000 g 2301 graphite
 730 g uranyl nitrate hexahydrate (in 2000 cm³ of water)
 800 g ammonium carbonate (in 2000 cm³ of water)
 3100 g 79L resin.

The above batch* provides about twice as much ammonium carbonate as is necessary to convert all of the uranyl nitrate to ammonium uranyl carbonate. The large excess of this reagent reduced "clumping" of the uranium during the drying operation by keeping the ammonium uranyl carbonate in solution until drying had been nearly completed.

Use of Hydroxylamine. In several instances the uranium was kept in solution by the addition of hydroxylamine hydrochloride rather than with an excess of ammonium carbonate. The following batch was used in these tests:

400 g 2301 graphite
 56 g uranyl nitrate hexahydrate
 45 g hydroxylamine hydrochloride
 100 cm³ ammonium hydroxide (28 w/o NH₃)
 600 cm³ distilled water
 243 g 79L resin.

This batch was prepared in the 1/2-gal Day mixer (see Table 1) by adding a solution of the uranyl nitrate and the reagents to the graphite, heating the mixture to dryness, and adding the resin. The first set of 1/4-in. rods made in this way had good physical properties and excellent distribution of the uranium. However, after several unsuccessful attempts were made to duplicate these initial results, the work on this process was terminated.

Uranyl Acetate Addition

One experiment was made in which the uranium was added as a water solution of uranyl acetate. The following extrusion batch was prepared in the 1/2-gal Day mixer:

*This batch is calculated to give a body containing 5 ± 0.02 w/o uranium.

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34 g uranyl acetate
25 g ammonium acetate
1000 cm³ distilled water
310 g 2301 graphite
177 g 79L resin.

The uranyl acetate and ammonium acetate were dissolved in the water and the solution was mixed thoroughly with the graphite at room temperature. Mixing then was continued at 210 F to decompose the acetate and to dry the material. The ammonium acetate prevented decomposition of the uranyl acetate until most of the water had been removed. The nearly dry batch was placed in an oven and heated for 16 hr at 300 F. The batch then was pulverized, passed through a 200-mesh sieve, and blended with the resin in the Lancaster mixer. Sound specimens were produced, but the uranium inclusions were coarse and poorly distributed compared to those which were obtained with uranyl nitrate.

UO₂-Powder Addition

All of the bodies which contained UO₂ powder were formed by extrusion. The first series contained UO₂ which had been crushed to pass a 325-mesh sieve. The UO₂ and graphite were blended in a muller-type mixer before adding the resin.

In the next tests, the minus 325-mesh UO₂ was ball milled in order to produce a more closely sized product. A 1-gal mill lined with abrasion-resistant carbon was used with 1-in.-diameter carbon balls as the grinding medium.

Two tests were made in which 200 g UO₂ was dry milled for 24 hr with 1800 g carbon balls. In one of these tests, the UO₂ was "cushioned" by an addition of 200 g 2301 graphite. The effect of wet milling for 24 hr also was determined. Here the mill charge consisted of 200 g UO₂, 200 g 2301 graphite, 500 cc water, and 1800 g 1-in. carbon balls.

In these tests on the ball milling of UO₂ there was very little contamination from the mill. However, the batches picked up carbon from the grinding balls at the rate of 1 to 2 g per hr.

A few experiments were made in which stock UO₂ was dry screened to obtain coarse particles which were added to extrusion bodies. This method appeared to be satisfactory up to a particle size of about 200 microns, but larger particles were broken down during the fabrication of specimens.

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UO₂-Nodule Addition

Preparation of Bonded Nodules. In general, the preparation of bonded particles or "nodules" of UO₂ consisted of the following steps: (1) add an organic binder, (2) form the mixture into a solid mass, (3) crush and screen to the desired size, and (4) wash out the undersize particles. This process basically is very simple, but considerable work was required to develop a technique which avoided excessive losses of uranium.

Choice of the binder was very important. Methyl and ethyl cellulose both were unsatisfactory because they are soluble in water. The prepared nodules disintegrated in the washing operation. Phenolic resins, such as BV1600, produced tough water-resistant nodules, but this binder hardened during processing to the extent that it was difficult to reprocess the off-size particles. Orange flake shellac was found to have the necessary toughness and water resistance. Because of its thermoplastic nature, it was possible to repress the fines and off-size particles so that substantially all of the original UO₂ was converted to nodules of the required sizes.

One process of preparing bonded nodules has been described at length in a previous report⁽⁸⁾. A mixture of 90 w/o UO₂ and 10 w/o shellac was pressed into small pellets which then were crushed and screened to produce nodules of the desired sizes. The fine particles were removed from the nodules by placing the sized material on an appropriate sieve and dipping the sieve in water for several hours. Washing was facilitated by a small addition of Aerosol OT wetting agent*.

A second method of nodulizing UO₂ lends itself more readily to large-scale preparations. This process consists of nodulizing a mixture of UO₂ and orange flake shellac in a Kitchen Aid mixer**. The shellac was dissolved in ethyl alcohol and added to the UO₂. Heat was supplied to the mixer bowl by a copper steam coil. Evaporation of the alcohol was begun with the mixer running at low speed. Gradually, the speed was increased as the mixture hardened. When the material had stiffened to a rubberlike mass, it was shattered into fine granules by running the mixer at its maximum speed. The material was sieved frequently on a 30-mesh sieve and the oversize particles were returned to the bowl. When all of the material passed the 30 sieve the nodules were sized and washed as in the pelleting method.

The nodules produced by this method were composed of 92 w/o UO₂ and 8 w/o shellac. They were more nearly spherical in shape than the nodules produced by the pelleting process but they had a somewhat lower bulk density. The distribution of particle sizes in a typical batch is shown by the following sieve analysis:

*A product of the American Cyanamid Company, New York, New York.

**A product of the Hobart Manufacturing Company, Troy, Ohio.

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<u>Size Range, U. S. Standard Sieve</u>	<u>w/o</u>
Minus 35 - plus 40	19
Minus 40 - plus 50	28
Minus 50 - plus 60	11
Minus 60 - plus 100	18
Minus 100 - plus 140	6
Minus 140	18

In production, of course, the aim probably would be to produce nodules in one rather narrow size range. If this method were used, the oversize and undersize particles would be returned to the mixer, resoftened with alcohol and the process would be repeated. The preparation of nodules in the mixer was not developed far enough to be suitable for enriched uranium. Some dusting occurred and use of the method without further development would result in prohibitive losses of uranium.

A third method of producing bonded nodules of uranium oxide was investigated briefly. This consisted of extruding a mixture of eight parts of UO_2 , two parts of 2301 graphite, and one part of BV1600 resin, by weight, through a plate which contained a number of small holes. After the resin had been cured, the formed rods, which were 0.130 in. in diameter, were converted into nodules by the methods which were described under the pelleting process. In washing these nodules, tannic acid was used as the wetting agent. This method of preparing bonded nodules is less promising than the other two because of inherent difficulties in controlling losses of uranium.

Addition of Bonded Nodules to Extruded Bodies. In preparing mixes for extrusion, some precautions were taken to avoid breakdown of the nodules. One technique was to mix the nodules and the graphite powder in the Simpson or Lancaster mixer and then add the resin. The mullers were not used until the mix had become plastic. Another method which was used to prevent breakdown of the nodules consisted of mixing the graphite powder and the resin in a muller-type mixer and blending the nodules into the plastic mass in a Day mixer or on the mixer rolls. The following batch was used to produce 30 specimens 5/8 in. in diameter by 12 in. long:

2970 g 2301 graphite
1840 g 79 LHS
250 g shellac-bonded UO_2 (8 w/o shellac).

Addition of Bonded Nodules to Molded Bodies. The addition of bonded nodules to molded bodies presented the problems of obtaining a homogeneous mixture of two nonplastic materials with widely different densities and of preserving homogeneity throughout the molding operation. Crushing of the nodules was no problem because a gentle mixing action was sufficient to blend the nodules with the molding powder.

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The following methods of blending the two components were studied: (1) blending by hand in a mortar, (2) rolling in a glass jar fitted with cardboard vanes, and (3) stirring the mixture in a beaker with a single-blade stirrer. The first two methods were very successful while the third one showed a tendency for the UO_2 to segregate at the bottom of the beaker.

When a homogeneous mixture had been obtained by one of the above methods, special precautions were taken to avoid segregation in the molding die. One method consisted of positioning the bottom plunger 1/4 in. below the top of the die for the first fill and lowering it in 1/4-in. increments for each subsequent fill.

Another means of preserving homogeneity was to wet the mixture so the UO_2 nodules would be held in place. Water was found to be unsatisfactory because it reduced the strength and density of the finished bodies. A petroleum ether fraction with a boiling range of 90 to 110 F was found to be very effective in amounts of 25 to 35 cm^3 per 100 g of molding powder. The wet mixture of nodules and molding powder was placed in the die cavity and compacted slightly by hand pressure. Before the final pressing, a light air blast was applied for 2 min to accelerate removal of the petroleum ether.

Hot-molded bars were prepared by using carbon tetrachloride to hold the nodules in place. The die cavity was filled with the wet mixture and the mixture was compacted by hand pressure. Two min at a molding temperature of 200 F were sufficient to evaporate the carbon tetrachloride before the final molding pressure was applied.

Sintered Nodules. Very hard nodules, which resisted breakdown even under severe processing conditions, were produced by pelleting the UO_2 , sintering the pellets under vacuum, and crushing them to the desired particle sizes.

The pellets were pressed in a steel die with a cavity 1 in. long and 1/8 in. in diameter. Minus 325-mesh oxide was used. It was pressed at a pressure of 2000 psi without the use of a binder or a lubricant.

For sintering, the pellets were placed on loose UO_2 in a beryllia crucible and heated to 3270 F in an evacuated induction furnace. The furnace was held at temperature for 1/2 hr under a vacuum of less than 10 microns of mercury.

The sintered pellets had a bulk density of 7.95 g/cm^3 . Because of their extreme hardness, processing the pellets to obtain nodules of controlled sizes was a difficult operation. The resulting nodules were of irregular shape, very angular and sometimes acicular. Because of these considerations, the shellac-bonding scheme was adopted for the preparation of radiation-test specimens.

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Further work on sintered nodules may be justified if very dense, tough nodules are needed.

Particle Size and Distribution of the UO_2 Additions

Microradiographs of thin sections were used to observe the particle size and distribution of UO_2 when it was added to graphite bodies by various methods. An X-ray plate was placed behind a slice of uranium-bearing graphite which was held in a lead sheet containing a suitable hole. This "sandwich" was positioned about 10 in. from the X-ray tube with the sample facing the tube. An X-ray tube with a fine focal spot was used at a voltage of 25 kv.

The samples were cut on a precision lathe to a thickness of four times the average diameter of the UO_2 particles, except that the minimum thickness was 0.010 in. In the case of coarse additions, the resulting slices were thin enough to make it unlikely that particles would be hidden behind each other. Also, this thickness was great enough so that relatively few particles were cut in two when the slices were prepared. The minimum thickness of 0.010 in. was used for UO_2 additions with particle sizes of 100 microns or less. This thickness was adequate down to an average particle size of about 25 microns but with smaller sizes it became difficult to distinguish individual particles.

For some purposes, radiographs of whole specimens, or of large segments of specimens, were made with a standard General Electric 140-kv industrial X-ray unit. When the specimen thickness was less than about ten times the average diameter of the UO_2 particles, such radiographs could be used to observe the general distribution of uranium in the graphite matrix.

Except for appropriate enlarging, the radiographs are shown in this report as they appeared on the original negative. That is, the white areas represent uranium and the black areas represent graphite.

Uranyl Nitrate Addition

Each of the three methods of adding uranyl nitrate to extruded graphite bodies produced a characteristic type of UO_2 dispersion. In every case the ultimate size of the UO_2 particles was between 1 and 3 microns. Distinct differences were noted, however, in the amount of "clumping" of the original particles and in the homogeneity of distribution of the UO_2 . Figure 9 shows the results of adding uranyl nitrate with and without chemical treatment. Chemical treatment eliminated clumping, although the use of

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100X

64315

100X

64316

No Chemical Treatment

100X

N3172

100X

N3171

Treatment With Hydroxylamine and Ammonium Carbonate

100X

N3168

100X

N3167

Treatment With Ammonium Carbonate Only

Field Near Center

Field Near Surface

FIGURE 9. EFFECT OF CHEMICAL TREATMENT OF URANYL NITRATE ON DISTRIBUTION OF THE UO_2

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ammonium carbonate alone produced a large number of "bare spots", or regions which appear to be entirely devoid of uranium. The most even distribution of the uranium was obtained by treatment with ammonium carbonate in the presence of hydroxylamine.

The most notable improvement in UO_2 distribution as a result of chemical treatment occurred at the surfaces of the specimens, as shown in Figure 9. The specimen prepared without chemical treatment shows a marked deficiency of uranium at the surface. A band of high uranium concentration extends inward from a point about 0.015 in. below the surface. The region of uranium deficiency at the surface is of variable thickness but it extends around the entire circumference of the specimen. Treatment of the uranyl nitrate with ammonium carbonate, with or without hydroxylamine, eliminated this condition.

These observations on uranium distribution show that for best results the uranium should remain in solution as long as possible during the drying operation but that it should be precipitated before adding the resin binder. The ammonium carbonate treatment was more effective in the presence of hydroxylamine because the uranium stayed in solution longer during drying. Precipitating the uranium at the end of the drying operation but before adding the resin prevented migration of the uranium during the curing operation.

Uranyl Acetate Addition

The type of uranium distribution which was obtained by the addition of uranyl acetate is shown in Figure 10. The particle size of the uranium is considerably greater than that produced with uranyl nitrate, and there was some tendency to form very large "clumps". The coarser size of these uranium inclusions may have been caused by precipitation of the uranium before drying had been completed.

UO_2 -Powder Addition

The uranium additions which were obtained with UO_2 powder are shown in Figure 11. These microradiographs of extruded bodies show that ball milling was very effective in reducing the size of the UO_2 particles to produce a more closely sized product. The use of a "cushion" of graphite powder increased the number of very fine particles but it did not decrease the maximum particle size. Wet milling in the carbon ball mill was unsatisfactory. The water evidently carried some of the UO_2 into the pores of the carbon mill and balls so that the final specimens contained 3.4 w/o uranium instead of the desired 5.0 w/o. This deficiency of uranium is clearly evident in Figure 11.

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100X

N1079

FIGURE 10. ADDITION OF URANYL ACETATE

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100X

N5465

Sieved Only

100X

62655

Ball-Milled Dry for 30 Hr

100X

62654

Ball-Milled Dry With Graphite "Cushion" for 30 Hr

100X

61692

Ball-Milled Wet for 24 Hr

FIGURE 11. ADDITIONS OF UO_2 POWDER, MINUS 325 MESH~~CONFIDENTIAL~~

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UO₂-Nodule Addition

Figure 12 shows that the bonding and washing operations were very effective in producing "clean" additions of UO₂. These bodies were prepared in muller-type mixers and there may have been some breakdown of the nodules during mixing. A washing period of 10 hr was adequate.

The problem of nodule breakdown was very troublesome in the preparation of extrusion batches. The results of two attempts to eliminate breakdown were examined by means of the radiographs. The bodies prepared in the Simpson mixer show a great deal of breakdown, even though the mullers were not used during the first 1/2 hr of mixing, that is, until the batch was plastic enough to cushion the nodules. Addition of nodules to the extrusion batch in the Mogul mixer prevented nodule breakdown. The small number of undersized particles in these specimens resulted from imperfect washing of the original nodules.

When bonded nodules were added to molded bodies there was no danger of nodule breakdown. The problem here was to obtain homogeneous distribution of the UO₂, because of the great difference in density between graphite and UO₂ and the nonplastic nature of the molding powder. The distribution of UO₂ nodules in molded bodies was observed by means of radiographs of 1/4 by 5/16 by 3-in. specimens. To simplify analysis of the radiographs, the specimens usually were cut into two or four smaller segments before making the radiographs.

When dry molding powder was used, charging the die in the usual manner resulted in poor distribution. Loading the die in 1/4-in. increments produced some improvement but the distribution was only fair. Wetting the molding powder to hold the nodules in place improved the distribution of the UO₂ still further.

Radiographs of hot-molded bodies in which carbon tetrachloride was used indicated that the distribution of the UO₂ was reasonably good. However the radiographs also showed that the nodules were flattened by the combined effects of heat and pressure on the thermoplastic shellac binder. This could be corrected by the use of resin-bonded nodules.

Radiographs were also made of molded bodies which contained two sizes of sintered UO₂ nodules. The nodules were screened dry and washed in water for 8 hr. The sintered nodules assumed a wide variety of shapes. The radiographs showed that most of the particles were angular and several were in the form of acicular "splinters". This is a natural result of crushing a hard and brittle material such as sintered UO₂.

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100X

UO₂ Powder,
Sieved Only

64025

100X

Bonded UO₂,
Sieved Only

65474

100X

Bonded UO₂, Sieved,
Washed 2 Hr

65476

100X

Bonded UO₂, Sieved,
Washed 10 Hr

N6086

FIGURE 12. EFFECT OF BONDING AND WASHING ON THE UNIFORMITY OF UO₂ ADDITIONS

Particle Size: Minus 140-Plus 200 Mesh

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Density and Strength of UO₂-Graphite
Bodies - Effect of UO₂-Particle Size

Bulk density, modulus of rupture, and tensile strength were measured by the same methods which were used for UO₂-free bodies. To compare densities on a uranium-free basis, an adjusted bulk density was obtained by multiplying the observed bulk density by the fractional carbon content of the body.

Uranyl Nitrate Addition

Chemical treatment of the uranyl nitrate additions improved the physical properties of the resulting bodies. A greater improvement was noted in 1-in. specimens than in 1/4-in. specimens. The effect of chemical treatment on the adjusted bulk density and the modulus of rupture of extruded specimens is shown in Figure 13. The matrix material of these specimens was not one of the standard bodies but an early composition of relatively low density and strength.

UO₂-Powder Addition

The addition of UO₂ powder to the standard extruded body had no observable effect on the adjusted bulk density and caused only a small decrease in the modulus of rupture. Three sets of 1-in.-diameter specimens were fabricated which consisted of the standard extruded body plus additions of unbonded UO₂ in the following sieve sizes: minus 100 plus 140, minus 140 plus 325, and minus 325. The three sets had adjusted bulk densities from 1.70 to 1.73 g/cm³ and moduli of rupture from 8000 to 8500 psi.

UO₂-Nodule Addition

Except for the coarsest nodules, additions of shellac-bonded UO₂ to extruded bodies did not change the modulus of rupture. The coarser nodules appeared to increase the adjusted bulk density of the graphite matrix, but this probably is not a real effect. Shown in Table 14 are the average densities and strengths of 5/8-in. specimens containing three different sizes of shellac-bonded nodules. The standard extruded body was the matrix material in these specimens.

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FIGURE 13. EFFECT OF CHEMICAL TREATMENT OF URANYL NITRATE ON THE PROPERTIES OF EXTRUDED BODIES

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TABLE 14. BULK DENSITIES AND MODULI OF RUPTURE OF STANDARD EXTRUDED BODIES^(a)
CONTAINING SHELLAC-BONDED UO₂ NODULES

Approximate Nodule Size, microns	Bulk Density, g/cm ³	Modulus of Rupture, psi
500	1.73 (adjusted)	8,700
300	1.75 (adjusted)	10,700
100	1.70 (adjusted)	10,500
No UO ₂	1.71	9,150

(a) Specimens were 5/8 in. in diameter.

In the case of cold-molded bodies, the addition of UO₂ nodules usually caused a significant decrease in the modulus of rupture. The bulk density of the matrix appeared to be affected slightly but in a nonuniform manner. Variables such as composition of the matrix, molding pressure, and other processing conditions obscured the effect of the nodules. The data on strength reduction, which are shown in Table 15, indicate that the loss of strength increased with the size of the nodules. Sintered nodules caused only a slight reduction in strength.

TABLE 15. MODULI OF RUPTURE OF COLD-MOLDED BODIES^(a)
CONTAINING THREE TYPES OF UO₂ NODULE

Type of Nodules	Approximate Nodule Size, microns	Modulus of Rupture, psi	Loss in Strength, per cent of UO ₂ - free strength
Extruded UO ₂ -graphite mixture, BV1600 bonded	500	3100	45
	300	3760	33
Pressed, shellac bonded	500	3560	27
	300	4240	13
Dry pressed and sintered	500	4785	5
	300	4600	8
	60	5040	0

(a) Specimens were 5/16 by 5/16 by 3 in.

The standard extruded body was selected as the matrix material for the fabrication of tensile specimens containing nodules of UO₂. Three sizes of shellac-bonded nodules were prepared in the Kitchen Aid by the hot-mixing method, and added to the extrusion batches in the Simpson mixer. The specimens were baked at 2500 F but not graphitized. Tensile strengths

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of these specimens up to a temperature of 2550 F are shown in Figure 14. The curves were drawn somewhat arbitrarily, inasmuch as the number of specimens was too small to obtain a reliable statistical average.

Graphitization of UO₂-Graphite
Bodies - Effect of UO₂-Particle Size

Electrical Resistivity

Standard extruded bodies which contained UO₂ particles of three different average sizes were heated at 4000 F for 4 hr and at 4500 F for 2 hr. The resulting changes in electrical resistivity are compared with those of the UO₂-free standard extruded body in Table 16. These results show that uranium promotes the graphitization of resin cokes and that it is most effective in the form of fine particles when it can permeate the graphite freely.

TABLE 16. ELECTRICAL-RESISTIVITY CHANGES IN UO₂-GRAPHITE BODIES
HEATED AT 4000 AND 4500 F

Type of UO ₂ Addition	Ratio of Original to Final Resistivity, $\frac{\rho_0}{\rho}$	
	Heated at 4000 F for 4 Hr	Heated at 4500 F for 2 Hr
Uranyl nitrate, 1-micron diameter (approx.)	1.65	2.66
UO ₂ , 20-micron-diameter nodules (approx.)	1.31	1.58
UO ₂ , 500-micron-diameter nodules (approx.)	1.17	1.34
No UO ₂ addition	1.01	1.07

Conversion of UO₂ to Uranium Carbides

The fine-particle dispersions of UO₂ which were obtained from uranyl nitrate were converted completely to uranium carbide at graphitizing temperatures. The results of X-ray diffraction studies on such specimens after baking to 2500 F and after "graphitizing" at 4500 F are shown in Table 17.

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FIGURE 14. TENSILE STRENGTHS OF STANDARD EXTRUDED BODIES CONTAINING UO_2 NODULES

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TABLE 17. IDENTIFICATION OF URANIUM COMPOUNDS IN BODIES
PREPARED WITH URANYL NITRATE^(a)

Heat Treatment	Compounds	Relative Intensity ^(b)
Baked to 2500 F in gas-fired furnace, 6-hr soak	UO ₂ U ₂ N ₃ ^(c)	Medium strong Medium strong
Heated at 4500 F for 2 hr in carbon-resistor furnace, argon atmosphere	UC ₂ UC ^(c)	Medium strong Medium faint

(a) Samples were prepared by crushing in a mortar under carbon tetrachloride.

(b) Compared to graphite as "very strong".

(c) Lattice constants of these phases were not identical to the accepted values for U₂N₃ and UC, respectively.

The results in Table 17 are consistent with the reported data on the reaction between UO₂ and carbon. In an electric vacuum furnace Greenwood⁽⁹⁾ found the first evidence of reaction at 2710 F. Heusler⁽¹⁰⁾ determined the equilibrium carbon monoxide pressures for the reaction in the temperature range between 2700 F and 3270 F. He obtained values of 18 mm mercury at 2700 F and 1 atm at 3270 F. The appearance of a phase with the approximate composition U₂N₃ during baking at 2500 F may have been the result of reaction between UC₂ and the nearly pure nitrogen atmosphere in the graphite-filled baking crucible.⁽¹¹⁾ The formation of some UC₂ at this temperature is likely because extrapolation of Heusler's data gives an equilibrium CO pressure of 3 mm mercury at 2500 F. The extremely small particle size of the UO₂ obtained with uranyl nitrate would allow the reaction to proceed to completion unhindered by any diffusional processes.

The effect of increased particle size on the conversion of UO₂ to uranium carbides was determined by heating special bodies which contained 20 w/o uranium as shellac-bonded nodules. The extent of conversion at 4000 and 4500 F, as a function of nodule size, is shown in Table 18.

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TABLE 18. CONVERSION OF SHELLAC-BONDED UO_2 NODULES TO UC_2 AT GRAPHITIZING TEMPERATURES

Approximate Nodule Size ^(b) , microns	Relative Intensity ^(a)			
	Heated at 4000 F for 4 Hr		Heated at 4500 F for 2 Hr	
	UO_2	UC_2	UO_2	UC_2
20	Not detected	Strong	Not detected	Strong
100	Not detected	Strong	Very faint	Strong
300	Faint	Strong	Medium faint	Strong
500	Faint	Strong	Medium strong	Medium strong

(a) Compared to graphite as "very strong".

(b) Samples were prepared by crushing in a mortar under carbon tetrachloride.

These data indicate that in the case of large nodules the over-all reaction rate of the reaction $\text{UO}_2 + 4\text{C} = \text{UC}_2 + 2\text{CO}$ is determined by a diffusional process rather than by the rate of the homogeneous reaction. As a result, chemical equilibrium is not attained rapidly, even at very high temperatures. Diffusion of a gas through a porous solid is much more rapid than diffusion in solids. Thus, it seems likely that the rate-controlling step is diffusion of carbon to the reaction site rather than diffusion of CO from the reaction site. The important process could be either diffusion of carbon atoms through the graphite structure or through a "skin" of UC_2 which may form on the surface of the nodules.

Effects of Fuel-Particle Size on Fuel-Element Performance

Fuel-particle size has a direct bearing on several aspects of fuel-element performance outside of the realm of physical properties. These matters have to do with the internal geometry of the fuel-moderator composite and the influence of this geometry on fission-product damage, diffusion and loss of uranium, retention of fission products, and the ability of the fuel element to discharge the heat of fission. This section contains qualitative discussions of these particle-size effects and some pertinent data on UO_2 -graphite bodies.

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Fission-Product Damage to Graphite

The effects of radiation damage to graphite are well known. Fast-neutron damage is not expected to be a problem in high-temperature reactors because of simultaneous annealing. Fission-product damage, on the other hand, persists at high temperatures, as shown by in-pile thermal-conductivity measurements on uranium-impregnated graphites. These measurements have been summarized by Durand, Klein, and Nykiel⁽¹²⁾, as shown in Figure 15. The results obtained by Durand, et al., are more optimistic than the earlier results of L. P. Hunter⁽¹³⁾.

Hunter⁽¹³⁾ irradiated specimens containing minus 200-mesh UO_2 in addition to the uranium-impregnated graphite. He found that the increase in thermal resistivity was much less in the bodies which contained the UO_2 additions than in the uranium-impregnated graphite. This was attributed to the fact that the UO_2 particles in the former case were large enough to absorb an appreciable fraction of the fission products originating within them.

Theoretical treatments of this particle-size effect have been given by F. E. Faris⁽¹⁴⁾ and by R. J. Harrison⁽¹⁵⁾. Faris predicted that when the fuel particles were about 300 microns in diameter, fission damage would be less than 5 per cent of that in the homogeneous case. Harrison calculated that this condition would be attained at a diameter of 100 microns. As Harrison⁽¹⁶⁾ has pointed out, however, Faris did not consider the fact that, if the percentage of fuel is held constant and particle size is increased, the point soon is reached at which only a fraction of the total moderator volume is subjected to fission damage at all. This occurs when the average spacing between particles becomes much larger than the range of the fission products. Harrison's calculations provide for this effect and it accounts for most of the discrepancy between his results and those of Faris.

Hunter's observation has been verified experimentally and extended to larger particle sizes in cooperative work by Battelle and Oak Ridge National Laboratory. Standard cold-molded specimens which contained enriched UO_2 nodules of four different average sizes were prepared at Battelle by techniques described in this report. The specimens were irradiated at 180 F for a period of four weeks in the X-10 reactor at ORNL. R. H. Kernohan⁽¹⁷⁾ measured their thermal and electrical resistivities before and after irradiation and also studied the effect of annealing on the electrical resistivity. Kernohan's measurements of the changes in electrical and thermal resistivity are shown in Table 19. In the bodies with coarse nodules, the combined effect of fission-product damage and fast-neutron damage was about equal to the fast-neutron damage in the UO_2 -free bodies. This shows that damage in the bodies with coarse nodules was caused primarily by fast neutrons. On the other hand, most of the damage in the bodies with 16-micron nodules was caused by fission products.

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FIGURE 15. IN-PILE THERMAL-CONDUCTIVITY MEASUREMENTS ON URANIUM-IMPREGNATED GRAPHITE

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TABLE 19. RADIATION DAMAGE TO ELECTRICAL AND THERMAL RESISTIVITIES OF UO₂-GRAPHITE BODIES AS FUNCTIONS OF NODULE SIZE

Approximate Nodule Size, microns	Increase in Resistivity ^(a) , per cent of unirradiated value	
	Electrical	Thermal
No UO ₂	27.5	11
586	21.2	9
334	21.1	13
94	28.1	13
16	83.0	50

(a) Increases shown are average values for three specimens.

The effect of UO₂-particle size on the relative importance of fission-product and neutron damage is shown very clearly by the annealing data⁽¹⁷⁾ given in Figure 16. Four of the irradiated specimens were step-annealed in 25 C intervals between 150 and 425 C. The specimens were heated for 1 hr at each temperature, cooled to 20 C to measure electrical resistivity, and then heated to the next temperature. The UO₂-free body and the bodies with coarse nodules show the low-temperature annealing characteristic of fast-neutron damage. Most of the original damage in the body with 16-micron nodules remains after heating at 425 C, showing that it was caused primarily by fission products.

Diffusion and Loss of Uranium

Other problems in the use of uranium-graphite fuel elements at high temperatures are the diffusion and volatilization (loss) of uranium. The problem of uranium loss already has been studied on uranium-impregnated graphite. Investigators at Argonne National Laboratory estimated⁽¹⁸⁾ that the problem of uranium loss would limit the operating temperature of impregnated fuel elements to 2600 F. Measurements at North American Aviation of the diffusion of uranium through graphite showed⁽¹⁹⁾ that impregnated fuel elements could be operated for only 1000 hr at 3600 F.

In work at Battelle, UO₂-graphite specimens that were prepared by the addition of uranyl nitrate lost uranium when they were heated to graphitizing temperatures. Weight losses on 1/4-in.-diameter extruded specimens are shown in Table 20.

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Note: ρ_0 is the resistivity before irradiation

FIGURE 16. RADIATION-DAMAGE ANNEALING IN UO_2 -GRAPHITE BODIES

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TABLE 20. URANIUM LOSS IN BODIES PREPARED WITH URANYL NITRATE

Heat Treatment in Addition to Gas Bake	Uranium Content, w/o
None	6.24
4000 F for 4 hr	5.70
4500 F for 2 hr	4.92

Radiographs of the specimens referred to in Table 20 showed a deficiency of uranium near the surface of the specimens that were heated at high temperatures. The distribution of the uranium suggests that it migrated towards the surface and volatilized, probably as uranium vapor.

Additions of UO_2 powder migrated rapidly at graphitizing temperatures. The radiographs in Figure 17 show the results of heat treatments at 4000 F and at 4500 F for 2 hr. The UO_2 particles in these specimens originally were between 2 and 100 microns in size. At these high temperatures, the uranium migrated and coalesced to form larger clumps which at 4500 F reached a size of about 250 microns.

No loss of uranium was observed during the heat treatment of bodies which contained UO_2 powder. There was, in fact, a small increase in the percentage of uranium in such specimens. For example, two batches which after baking contained 4.9 and 5.1 w/o uranium, respectively, contained 5.0 and 5.2 w/o uranium, respectively, after heat treatment at 4500 F for 2 hr. The increases resulted from weight lost by the graphite matrix. Uranium-free bodies of similar matrix composition showed weight losses of about 2 per cent during the same heat treatment.

Molded bodies containing shellac-bonded UO_2 nodules of three different sizes were subjected to a graphitizing treatment of 2 hr at 4500 F. The nodules are shown before and after graphitization in Figure 18. Those which originally were about 100 microns in diameter were obliterated completely. Those with average sizes of 340 and 580 microns are still clearly defined, although a substantial amount of uranium migration is evident.

In further experiments, bodies which contained the two coarser sizes were heated at 4300 F for 4 hr. Radiographs revealed only minor migration of these coarse nodules at this temperature. However, the X-ray method is insensitive to low uranium concentrations. Quantitative measurements have shown that under these conditions penetration of uranium into the

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As Baked

100X

63474

Heated at 4000 F for 2 Hr

100X

62641

Heated at 4500 F for 2 Hr

100X

63473

FIGURE 17. EFFECT OF HEAT TREATMENT
ON DISTRIBUTION OF URANIUM
ADDED AS UO_2 POWDER

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10X

10X

100-Micron Nodules

10X

10X

340-Micron Nodules

10X

10X

580-Micron Nodules

As Baked

Heated at 4500 F for 2 Hr

FIGURE 18. EFFECT OF HEAT TREATMENT AT 4500 F ON DISTRIBUTION OF URANIUM ADDED AS UO_2 NODULES

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graphite will be negligible, but that a small amount of uranium will diffuse through the pores in the graphite.

Retention of Fission Products

The question of whether fission products will be retained by a fuel element at high temperatures is a very important design consideration. In some reactors which have been proposed, the coolant system would be thoroughly shielded and fission products would diffuse continuously through the fuel element into the coolant. S. Siegel⁽²⁰⁾ and Faris⁽¹⁴⁾ have suggested that such a self-decontamination process would result in high neutron economy and would simplify reprocessing of the unspent fuel. However, this type of arrangement probably will be practical only in stationary power or power-breeder reactors. In many cases, extra shielding about the coolant system and facilities for decontaminating the coolant are prohibitively cumbersome. This is particularly true for naval and aircraft reactors. Most of the solid-fuel reactors which have been built or proposed have some provision for keeping fission products in the fuel element. The MTR and the STR, for example, depend upon claddings of aluminum and zirconium, respectively, to prevent the fission products from entering the coolant.

It seems very likely that the use of large fuel particles will ease the problem of fission-product retention in a porous matrix material such as graphite. With large fuel particles, most of the fission products would be stopped in the fuel itself. Judging from the experiments of C. A. Smith and C. T. Young⁽²¹⁾, diffusion of the fission fragments through dense uranium oxide or carbide would be much slower than through porous graphite. Thus, with larger fuel particles, fission-fragment retention would depend primarily on the rates of diffusion through uranium oxide or carbide. Plans have been made to measure diffusion rates from coarse particles, using some of the UO₂-graphite specimens which were irradiated during the studies on fission-fragment damage.

Ability to Discharge the Fission Heat

If the uranium oxide or carbide is incorporated in the graphite in relatively large particles, the fuel itself will reach a higher steady-state temperature, for the same specific power, than if it is dispersed homogeneously throughout the conducting matrix. Both the temperatures of the fuel and the internal thermal stresses in the graphite will increase with the size of the fuel particles.

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The magnitudes of these effects of finite particle size were estimated by calculating the temperature drop for steady-state conduction through an isotropic spherical shell of graphite enclosing a spherical fuel particle. The outer radius of the spherical shell was taken equal to one-half the average distance between particles. The details of the calculation are given in the Appendix and the results are shown in Table 21. Estimated temperature drops are given for selected values of the fuel-particle diameter, the specific power, and the temperature at the outer surface of the spherical graphite shell.

TABLE 21. ESTIMATED TEMPERATURE DROPS IN SPHERICAL SHELLS OF GRAPHITE ENCLOSING SPHERICAL FUEL PARTICLES

Particle Diameter, microns	Temperature Drop ($t_a - t_o$), F								
	Specific Power, kw/cm ³ of fuel element								
	0.5			1.0			5		
	t_o , F			t_o , F			t_o , F		
	1800	2500	3400	1800	2500	3400	1800	2500	3400
200	1	4	8	4	8	16	20	38	72
500	14	22	45	25	49	90	135	260	510
1000	52	97	210	110	200	400	700	1530	>4000 ^(a)

(a) This result is approximate because t_a is above the temperature at which accurate thermal-conductivity data are available.

The results in Table 21 indicate that the permissible fuel temperature and thermal stresses may limit the maximum size of fuel particle that can be used at a given specific power. At the present time, however, the deleterious effects of high temperatures and thermal stresses on uranium-bearing graphite bodies are not sufficiently known to assign even tentative limits of fuel-particle size.

The problem of transferring the heat of fission from the graphite matrix to the coolant has not been considered here. Although this may be influenced somewhat by the size of the fuel particles, it has been excluded from the present discussion because it depends so greatly on fuel-element design and on the coolant employed.

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APPENDIX

Calculation of the Temperature Drop in
the Vicinity of a Fuel Nodule

This calculation was made to estimate the effect of nodule diameter and power density on the steady-state temperature of a fuel nodule and on the temperature drop in the graphite surrounding the nodule. The physical system which was considered is shown in Figure A-1. It may be described as follows: A spherical nodule of nuclear fuel, A, is generating heat at a constant rate. The heat is flowing radially through a spherical shell of graphite, B, which surrounds A. The outer radius of B is taken as one-half the average distance between the centers of adjacent nodules in an idealized fuel element which has the nodules arranged in a perfect cubic lattice. In such a system the temperature distribution about Nodule A will be independent of the presence of other nodules in the system.

In calculating the numerical results shown in Table A-1, the fractional volume of fuel in the fuel element was assumed to be 0.017. This is about what one would obtain in a fuel element containing 5 w/o uranium.

Thermal-Conductivity Data for Graphite

The most reliable data on the thermal conductivity of graphite to very high temperatures probably are those of Powell and Schofield*, who measured the conductivity of Acheson electrode graphite up to 2700 C, evidently in the transverse direction. Their values of the conductivity at six different temperatures after conversion to $w/(cm)(C)$, are shown in Table A-1 as taken from Powell and Schofield's curve and converted to more convenient units for this purpose.

TABLE A-1. THERMAL CONDUCTIVITY OF GRAPHITE

Temperature, C	Thermal Conductivity (k), $w/(cm)(C)$
1000	0.549
1250	0.392
1500	0.276
1750	0.196
2000	0.144
2250	0.125

*Powell, R. W., and Schofield, F. H., "The Thermal and Electrical Conductivities of Carbon and Graphite to High Temperatures", Proc. Phys. Soc. (London), 51, 153 (1939).

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FIGURE A-I. IDEALIZED DISTRIBUTION OF FUEL NODULES IN GRAPHITE MATRIX

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It was found that these data could be represented closely by the equation $k = k_0 \theta^n$, where θ is the temperature in degrees K, $n = -2.38$ and $k_0 = 1.445 \times 10^7 \text{ w/(cm)(K)}$. This equation is accurate within 5 per cent of the observed values in the temperature range between 1300 and 2500 K.

Simplifying Assumptions

- (1) A spherical fuel nodule, A, with $0 \leq r < a$ is surrounded by the concentric spherical shell of graphite, B, with $a < r < L$.
 $L = 1/2N^{1/3}$, where N is the number of nodules per unit volume of fuel element.
- (2) Heat is generated in A at the constant uniform rate Q , per unit volume.
- (3) Temperature = θa for $0 \leq r \leq a$ at all times.
- (4) Heat flow in B is radial and temperature = θ_0 at $r = L$ for all times.
- (5) Thermal conductivity, k , is isotropic in B and depends on temperature only, according to the equation $k = k_0 \theta^n$.

General Solution of the Heat-Flow Equation

$$\text{Heat balance for hollow sphere } a < r < L: \frac{Qa^3}{3r^2} = k \frac{d\theta}{dr} \quad (A-1)$$

$$\text{Substituting for } k: \frac{Qa^3}{3r^2} = k\theta^n \frac{d\theta}{dr} \quad (A-2)$$

$$\text{Integrating: } \frac{Qa^3}{3} \int_L^a \frac{dr}{r^2} = -k \int_{\theta_0}^{\theta a} \theta^n d\theta \quad (A-3)$$

$$\frac{Qa}{3k} \left[\frac{1}{a} - \frac{1}{L} \right] = \frac{1}{n+1} \left[\theta_a^{n+1} - \theta_0^{n+1} \right]$$

$$\text{But } \frac{1}{L} = 2N^{1/3} = 2 \left[\frac{3v'}{4\pi a^3} \right]^{1/3} \quad (A-4)$$

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where $v' =$ fractional volume of fuel in the fuel element.

Then:
$$\frac{Qa^2}{3k} \left[1 - 1.24 v'^{1/3} \right] = \frac{1}{n+1} \left[\theta_a^{n+1} - \theta_o^{n+1} \right] \quad (A-5)$$

Numerical Solutions for Particular Cases

Nomenclature and Units

$\theta =$ temperature, degrees K

$P = Qv' =$ power developed per unit volume of fuel element, w/cm³

$v' = 0.017 =$ fractional volume of fuel in the fuel element

$k = k_o \theta^n =$ thermal conductivity of graphite, w/(cm)(K)

For $1300 < \theta < 2500$, $n = 2.38$,

$k_o = 1.445 \times 10^7$ w/(cm)(K)

$d =$ nodule diameter, cm

Substituting in (A-5):

$$\frac{Pd^2}{12kv'} \left[1 - 1.24 v'^{1/3} \right] = \frac{1}{n+1} \left[\theta_a^{n+1} - \theta_L^{n+1} \right]$$

$$\frac{Pd^2 (0.681)(1.38)}{(12)(1.445 \times 10^7)(0.017)} = \theta_L^{-1.38} - \theta_a^{-1.38},$$

produces the working equation

$$\theta_L^{-1.38} - \theta_a^{-1.38} = 3.178 \times 10^{-7} Pd^2 \quad (A-6)$$

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Calculation of Crystallite Dimension in Resin Cokes

The crystallite dimension C and A in a well-developed graphite are determined from the line breadths at half-maximum intensity of the (002)

and the (110) reflections, respectively. The equation is: $C \text{ or } A = \frac{0.89\lambda}{B \cos \theta}$,

where B is the breadth at half intensity in radians, corrected by the method of Jones*. In the case of resin cokes, which do not show the completely resolved graphite pattern but only the (002) and (hk) reflections, the equation of Warren** is used to determine A:

$$A = \frac{1.84\lambda}{B \cos \theta},$$

where B is the breadth at half intensity of the (hk) reflection.

LDL:JAS:WHD:pt/jj

*Jones, W. F., "The Measurement of Particle Size by the X-ray Method", Proc. Roy. Soc. (London), 166A, 16 to 43 (1938).

**Warren, B. E., "X-Ray Diffraction in Random Layer Lattices", Phys. Rev., 59, 693 (1941).

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