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THE DEVELOPMENT AND EVALUATION OF GRAPHITE-
MATRIX FUEL COMPACTS FOR THE HTGR

By
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August 8, 1961

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DIVISION OF

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GA-2289

METALS, CERAMICS, AND MATERIALS

THE DEVELOPMENT AND EVALUATION OF GRAPHITE-MATRIX
FUEL COMPACTS FOR THE HTGR

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ABSTRACT

A summary of the development and evaluation of graphite-matrix fuel compacts for the High-temperature Gas-cooled Reactor (HTGR) is presented. These fuel compacts consist of thorium-uranium dicarbide particles dispersed in a high-density graphite matrix and are produced by a hot-pressing process. Detailed experimental studies of fuel-compact properties with relation to method of preparation, starting fuel materials, and fuel concentration showed that satisfactory fuel compacts containing up to 40 wt-% fuel (Th + U) could be prepared. Compacts prepared from thorium-uranium oxide, thorium-uranium silicide, and thorium-uranium dicarbide coated with pyrolytic carbon were subjected to radiation and fission-product-retention testing and other evaluations.

Typical properties of these graphite-matrix, dispersion-fuel compacts include graphite density, 1.90 to 1.95 g/cm³; crushing strength, 8500 psi; thermal conductivity at 2000°C, 0.07 cal/cm²-sec/°C/cm; and permeability, 2×10^{-3} cm²/sec. Extensive radiation testing showed these compacts to be dimensionally and structurally stable after burnups of 6.9×10^{19} fissions/cm³ (60% of HTGR design) at 1100°C to 1500°C. Compacts containing thorium-uranium dicarbide particles coated with pyrolytic carbon showed continuing fission-product holdup times of several hundred hours after a burnup of 5.4×10^{19} fissions/cm³ at 1500°C to 1900°C. Results of the radiation and fission-product-retention testing of compacts and fuel materials are discussed in detail.

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INTRODUCTION

The High-temperature Gas-cooled Reactor (HTGR) is a helium-cooled, graphite-moderated, solid-homogeneous fueled type of reactor in which the high-temperature potentialities of gas cooling with high power density are combined with a fuel capable of high burnup.^{(1,2,3)*} The HTGR prototype plant is being designed to produce 1000°F steam at 1450 psi and to have a net capacity of 40 Mw(e). Fuel temperatures and gas pressures for this prototype plant will be approximately the same as those required for larger plants.

The general arrangement of the reactor is shown in Fig. 1. The reactor core is made up of 855 cylindrical elements, approximately 40 of which are control rods, arranged in a closely packed equilateral triangular array. The coolant gas passes through the tricuspid-shaped passages formed by the cylindrical elements.

The fuel element (see Fig. 2) consists of a low-permeability graphite can containing the fuel compacts and a portion of both the top and bottom reflectors. The fuel element is encased in a concentric sleeve of low-permeability graphite that is joined to the graphite end reflector sections. The space between the graphite sleeve and the graphite can is purged by helium flowing through it. The helium then flows back down the element through the space between the fuel compacts and the graphite can, through the internal fission-product trap, and then to an external fission-product trapping system. The element is 12 ft long and 3.5 in. in diameter. The fuel compacts consist of fuel (U^{235}) and fertile material (Th^{232}) in the form of carbides dispersed in a graphite matrix. The composition of the fuel compacts is about 1 atom of U^{235} to 10 atoms of thorium to 700 atoms of carbon.

Carbides of uranium and thorium are employed for the fissile-fertile

* References are listed at the end of this report.

Fig. 1--Isometric view of the high-temperature, gas-cooled, graphite-moderated reactor

Fig. 2--The HTGR fuel element

phase because, at the operating temperature of the fuel, they are thermodynamically stable. Because of the high U^{235} burnup expected (approximately 0.6 fission per initial fissile atom for the 40-Mw(e) prototype to about 2 for larger plants), the fuel and fertile material are mixed to avoid a large change in power distribution during core burnout. In addition, mixing of fuel and fertile material results in a useful contribution to the prompt negative temperature coefficient from Doppler broadening of the thorium resonance.

The arrangement of fissile-fertile particles in a graphite matrix is most desirable when the mean distance between the particles is larger than the range of fission-fragment recoil. Most of the graphite matrix of the fuel compact is thus free from fission-fragment damage, and the remaining continuous web of undamaged matrix material retains many of its desirable preirradiation properties.

The HTGR fuel-compact development program, begun in the fall of 1957, is discussed in this report. Initially, the program was a modest effort in which several approaches were investigated. During the past two years, however, there has been a more intensive effort that has culminated in the warm-pressing process for the fabrication of fuel compacts. Detailed experimental studies of fuel-compact properties with relation to methods of preparation, starting fuel materials, and fuel concentration are reported. Also, scale-up studies are described in which full-sized HTGR fuel compacts were produced with pilot-scale equipment.

Fission-product retention, dimensional and structural stability under irradiation, thermal conductivity, and other properties of the fuel compacts have also been studied, and the results are reported herein. Also discussed are the preparation of thorium-uranium dicarbide particles coated with pyrolytic carbon and the incorporation of these coated particles into graphite-matrix fuel compacts.

FUEL-COMPACT DESIGN AND DEVELOPMENT

The performance requirements placed on the fuel compacts by the HTGR design are summarized as follows:

1. Spatial Fixation of Fuel. The fissile-fertile phases must remain fixed within the graphite matrix; i. e., they must not migrate or evaporate at the elevated operating temperature of the HTGR.
2. Transfer of Heat at Desired Temperatures. Good high-temperature thermal conductivity and thermal-stress resistance are required to accommodate the high HTGR power densities and to permit the removal of heat without undue thermal gradients.
3. Mechanical and Dimensional Stability. The fuel compacts must retain their integrity and remain dimensionally stable under prolonged high-temperature irradiation.
4. Retention of Fission Products. Fission products must be retained within the fuel compacts as long as possible to minimize the load on the fission-product trapping system.
5. Low Cost. Low fuel costs, of course, constitute an important requirement for all commercial power-reactor programs.

More specific compositional and operational parameters are summarized in Table 1.

Although graphite, among conventional fuel-element materials, offered the best combination of high-temperature physical, mechanical, thermal, and nuclear properties, it had two serious shortcomings for this application: (1) the porosity of graphite would readily permit the fission products to escape, and (2) there was no satisfactory method for incorporating the necessary thorium and uranium into a graphite fuel body. These were the principal problems to be solved in the HTGR fuel-element development program.

Table 1
HTGR FUEL-COMPACT PARAMETERS

Composition

Uranium (93% enriched), wt-%	2.1
Thorium, wt-%	21.0
Total metal, wt-%	23.1
Graphite, wt-%	76.9
C:Th:U atom ratio	725:10:1
C:metal atom ratio	66:1

Dimensions

Outside diameter, in.	2.250
Inside diameter, in.	1.500
Length, in.	4.50

Temperature

Maximum fuel-centerline temperature, °C . .	1,800
Median fuel-temperature in core, °C	1,350

Burnup (3-yr core life at 80% load factor)

Fissions per original fissile atom	0.63
Mw-days (t) per metric ton of U ²³⁵ + Th ²³² .	75,000
Fissions/cm ³	1.1 × 10 ²⁰
kw-hr/cm ³	1,000

Fuel-compact Development

Incorporation of uranium in graphite by impregnation with aqueous solutions results in uranium carbide particles of such extremely small size that fission-recoil damage to the surrounding graphite and fission-product release are unnecessarily high. The effect of fuel-particle size and fuel loading on the portion of graphite matrix subjected to fission-fragment damage may be seen in Fig. 3 (the curves were calculated for HTGR conditions from Harrison's data⁽⁴⁾). Matrix damage increases rapidly as the fuel-particle size drops below 100 μ .

Since discrete fuel particles of 100 μ or larger were required for the HTGR fuel compacts and since they had to be uniformly dispersed in the graphite matrix, the admixture approach was chosen for this work. Also, the size, dimension, and property requirements imposed on the fuel compacts

Fig. 3--Variation of matrix volume subject to fission-fragment damage with ThC₂-UC₂ concentration for various fuel-particle sizes

by the HTGR design indicated that a molding process would offer several advantages over an extrusion process--namely, higher density and hence (it was hoped) lower permeability, higher thermal conductivity, and greater strength; closer dimensional control; and better adaptability to short lengths. Solid-solution thorium dioxide-uranium dioxide, $(\text{Th,U})\text{O}_2$, fuel particles were selected for the initial work, and it was planned to convert them in situ to solid-solution thorium dicarbide-uranium dicarbide, $(\text{Th,U})\text{C}_2$, by suitable heat treatment of the molded graphite compacts.

During the first stage of the development program, $(\text{Th,U})\text{O}_2$ particles were mixed with graphite powder and pitch, compacted cold, and sintered at 2100°C to convert the oxides to carbides. This conventional ceramic technique did not yield satisfactory compacts; densities and strengths were low, dimensional control was poor, and sintering times had to be prolonged to avoid bubbling of the pitch. Studies with other binders and varying processing conditions yielded no worthwhile improvement, and this approach was abandoned in favor of hot-pressing techniques.

Hot-pressing, wherein the elevated temperature curing and bonding of the pitch takes place while the compact is tightly secured in a die to prevent expansion, not only produces denser and stronger bodies but also produces them more rapidly and with less binder. Furthermore, compaction in the die prevents distortion during carbonization of the binder and thereby permits the attainment of very close dimensional tolerances.

Fuel-compact Design

Previously, the fuel-compact design for the HTGR was similar to that shown in Fig. 4, a composite annular design wherein the fuel was dispersed in the ring and the burnable poison in the center rod. Recently, the process has been shifted toward ring compacts, as shown in Fig. 5. These rings, which are approximately 1-1/8 in. long, contain the fuel; they are slipped over a central rod, or spine, of graphite in the fuel element. Such an arrangement offers several advantages from a production viewpoint: speed and uniformity of production are improved; dimensional tolerances

Fig. 4--HTGR cylindrical fuel compact

Fig. 5--Ring compacts prepared by coated carbide process: (a) 3/8-in.-thick annulus, (b) 5/8-in.-thick annulus

are better; fuel and poison are not combined, thereby making the recovery of scrap easier; purge grooves are readily molded in during warm-pressing; and coated carbide particles are more readily accommodated. Both ends of the compact are bevelled to allow an unimpeded flow of the purge gas without the necessity of aligning the purge grooves.

For much of the laboratory-scale development work, cylindrical compacts 1 in. in diameter by 1 to 2 in. long were studied. Numerous compacts of each design were produced, the process details of which are discussed in the following section.

PREPARATION OF COMPACTS BY HOT-PRESSING TECHNIQUES

The fuel compacts are prepared by mixing the fissile-fertile-phase particles with graphite and pitch and then hot-pressing the material to form a dense, strong compact. By using graphite powder for the filler and only a small amount (10 wt-%) of pitch binder, good thermal properties are obtained without taking the bodies to graphitizing temperatures. Also, the hot-press technique produces compacts of high density and good strength, and permits the use of substantially less binder than do conventional graphite fabricating techniques. (Only 10 wt-% pitch binder is required and after warm-pressing half of it remains, leaving a high-density matrix of 95% graphite and 5% carbon.)

Two types of hot-pressing procedures have been investigated:

1. Resistance Hot-pressing. This process combines the baking operation and the conversion of the oxide fuel to carbide in a single step. The mixture of fuel, graphite, and binder is compacted and heated to from 2100° to 2200° C by resistance heating with high currents. Since the compacts are internally heated, the dies may be strengthened by external, water-cooled metal jackets, and high compacting pressures can be used. There are, however, numerous problems associated with this process: (1) there is a lack of die materials with sufficient strength and chemical inertness (carbon and graphite are the most suitable, but they creep rapidly at these

temperatures); (2) there is difficulty in obtaining uniform and reproducible temperatures owing to current bypass and resistivity changes in the die materials; and (3) prolonged times are required to remove gases (primarily CO) from the compact while it is tightly confined in the die. This approach was therefore replaced by a two-step process.

2. Warm-pressing and Sintering. In this approach, the baking of the binder and the shaping of the compact are accomplished by pressing at 1000°C or below. The oxide fuel is then converted to the carbide form by heating the compact in a separate vacuum furnace. This basic process, termed the warm-press and sinter process, has been found to be the most suitable method for preparing HTGR fuel compacts.

Compact Materials

Graphite Flour. In order to obtain the desirable properties of a graphite matrix without the need of heat-treating the fuel bodies to graphitizing temperatures, graphite flour was selected instead of carbon or coke as the starting material for the matrix. Commercial graphite was ground to powder, sieved, and used for much of the initial work. Subsequently, National Carbon Company graphite powder (grade GP-38), a manufactured rather than a natural graphite, was selected because of its low ash and boron content, fine particle size, and availability. Natural graphites were tried in early work, but they produced compacts that were weaker in compression tests and more anisotropic than those made from synthetic graphites. The GP-38 used is 98% minus-200-mesh material with an average particle size (estimated) of less than $20\ \mu$.

Binder. Pitch, the traditional binder in the carbon and graphite industries, has proven satisfactory in making fuel bodies. The initial work was performed using pitch supplied by Portland Gas and Coke Company, Gasco No. 2387. The quality of this pitch was very satisfactory but the supply was not, so several other pitches were evaluated to select a successor. Melting points, purities, coking values, and solubilities were compared (see Table 2), and compacts prepared from each pitch were

Table 2

PROPERTIES OF PITCH SAMPLES EVALUATED FOR HTGR FUEL COMPACTS

Pitch Identification ^a	Melting Point ^b (°C)	Ash (wt-%)	Boron Content ^c (ppm)	Coking Value ^b (wt-%)	Solubility in Various Solvents (wt-%)				
					Triclene D	Methylethyl-ketone	Benzene	Quinoline ^b	Solv G
Barrett No. 1	71-74	0.044	<1/2	----	80	58	86	----	79
Barrett No. 2	93	0.16	<1/2	33.6	79	61	85.5	94.8	67
Barrett No. 3	100	0.12	<1/2	43.4	81	49	70.8	87.8	44
Barrett No. 4	157	0.042	3	44.6	61	36	73	94.7	12
Barrett No. 30	101	0.083	<1/2	55.8	51	73	72.1	87.1	NS ^d
Resin "C"	----	0.071	<1/2	----	96.5	87	83	----	NS
MP 112	112	0.12	ND ^e	58	70	70	66.2	88.7	NS
MP 130	~130	0.082	ND	----	77	68	68	----	43
MP 150	~150	0.11	ND	----	76	68	73	----	NS
MP 175	174	0.26	ND	66.7	64	53	39.5	84.1	NS
Gasco	105	0.05	ND	----	86	38	88	----	58

^aAll pitches were supplied by Plastics and Coal Chemicals Division, Allied Chemical Corporation, except Gasco pitch, which was supplied by Portland Gas and Coke Company.

^bValues reported by manufacturer.

^cSpectrographic determination.

^dNS indicates less than 10% solubility.

^eND indicates less than 2 ppm.

evaluated for density, crushing strength, and permeability (see Table 3). Barrett No. 30 medium pitch was selected as the binder, although several of the others would have been satisfactory.

Table 3
PROPERTIES OF COMPACTS PREPARED FROM
VARIOUS PITCH SAMPLES

Pitch	Density (g/cm ³)	Crushing Strength ^a (psi)		Helium Permeability ^b (cm ² /sec)	
		Transverse ^c	Longitudinal ^c	$\Delta P = 10 \text{ atm}$	$\Delta P = 1 \text{ atm}^d$
Barrett No. 1	1.95	9040	7830	12×10^{-2}	3×10^{-3}
Barrett No. 2	1.94	9130	7490	12×10^{-2}	3×10^{-3}
Barrett No. 3	1.95	8600	6740	17×10^{-2}	4.3×10^{-3}
Barrett No. 4	1.97	7450	7550	8.2×10^{-2}	2×10^{-3}
Barrett No. 30	1.97	8530	7420	8×10^{-2}	2×10^{-3}
Resin "C"	1.95	8410	6560	12×10^{-2}	3×10^{-3}
MP 112	1.98	9560	7310	4.5×10^{-2}	1.1×10^{-3}
MP 130	1.96	9200	7170	8.1×10^{-2}	2×10^{-3}
MP 150	1.97	9870	8060	4.5×10^{-2}	1.1×10^{-3}
MP 175	1.96	9650	7790	4.5×10^{-2}	1.1×10^{-3}
Gasco	1.96	8480	6800	13×10^{-2}	3.3×10^{-3}

^aDetermined on specimens 0.25 in. long and 0.25 in. in diameter.

^bDetermined on specimens 1.0 in. in diameter and 0.25 in. thick; helium flow was transverse to grain orientation.

^cDirection with reference to grain orientation.

^dCalculated from values at $\Delta P = 10 \text{ atm}$ by using experimentally determined conversion factor.

Other materials, including furfuryl alcohol, phenol-formaldehyde resin, and sucrose, were investigated as binders for the warm-press and sinter process. None produced compacts with as good physical properties as did pitch.

Plasticizer and Vehicle. To aid in granulating the fuel mixture, a plasticizer was incorporated in the mix. The plasticizer is ethyl cellulose, grade N-200, manufactured by the Hercules Powder Company.

A liquid phase is used to facilitate mixing and to aid in distributing the pitch. The two most promising vehicles were benzene and trichloroethylene because of their solvency for pitch and their fast evaporation rate. Trichloroethylene (Triclene D manufactured by E. I. Du Pont de Nemours and Company) was selected because of its lower toxicity and flammability.

Fuel. Solid-solution thorium-uranium dioxide, $(\text{Th}, \text{U})\text{O}_2$, thorium-uranium silicides, and solid-solution thorium-uranium dicarbide, $(\text{Th}, \text{U})\text{C}_2$, coated with pyrolytic carbon have been used as fuel feed materials in preparing compacts. These three fuels are discussed in later sections of this report.

Equipment

For cold-pressing three-segment dies (see Fig. 6) are used; tool steel is used for these dies and punches.

For warm-pressing graphite dies and punches are employed. (ATJ, manufactured by National Carbon Company, and HLM, manufactured by Great Lakes Carbon Company, are both satisfactory die and punch materials.) Two heating methods have been employed: (1) external heating by a resistance furnace or induction coil and (2) internal heating by passing heavy currents through the punches and compact. A typical warm-press unit for producing solid cylindrical compacts is shown in Fig. 7, and Fig. 8 illustrates a warm-press unit for producing annular compacts of the HTGR design. The graphite die is reinforced by an external, water-cooled steel jacket.

Vacuum furnaces of the type shown in Fig. 9 are used for sintering or heat-treating the warm-pressed compacts. The heating element is graphite.

Fig. 6--Cold-press die and punches used for making annular compacts

Fig. 7--Warm press used in making solid fuel compacts

Fig. 8--Warm press used in making annular fuel compacts

Fig. 9--High-temperature sintering furnace; shaded area is copper or brass, cross-hatched area is graphite

Mixing and Fuel Distribution

In the initial work on fuel compacts, graphite flour, powdered pitch, and fuel particles were mixed together dry in a twin-shell blender. Because of the large differences in particle size and density, segregation of the fuel was a problem. Quite a bit of care was necessary while unloading the blender and loading the dies to prevent jarring that might cause the heavy fuel particles to settle to the bottom of the mix.

To overcome the segregation problem, the mixture was granulated. A plasticizer was added to the mix to aid in the granulation; it also served as a lubricant to the mix during granulation and added strength to the mix after drying.

Uniformity of fuel distribution in the compacts was determined both qualitatively and quantitatively. Qualitative determination was made by radiographing whole fuel compacts and 1/8-in.- and 1/16-in.-thick slices from compacts. The different fuel-particle sizes can clearly be distinguished in Fig. 10. Quantitative determination of fuel distribution was made by chemical analysis of core samples cut from fuel compacts. The pieces were ignited to a constant weight of $\text{ThO}_2\text{-U}_3\text{O}_8$ and the analyses were reported in weight percent. Data on the chemical analyses of a typical compact cut into 24 equal pieces are given in Table 4. By selection of location and orientation, it was possible to obtain both longitudinal and transverse composition profiles.

Process Variables

The effects of a number of variables on the properties of the graphite matrix were evaluated by preparing unfueled compacts and measuring the density and the crushing strength. The results are summarized as follows:

Mesh Size of Graphite Flour. Different ranges of mesh size of ground AGOT graphite flour were tested and material of minus-200 to minus-325 was found to produce the best compacts (see Fig. 11). Particles larger than minus-200 mesh produced weaker, less dense compacts, but with powder finer than minus-325 mesh, only a slight decrease in properties occurred.

<50 μ fuel
particles

110-250 μ
fuel particles

250-500 μ
fuel particles

1/16-in. -thick slices

1/8-in. -thick slices

Fig. 10--Radiographs of slices from fuel compacts showing uniform fuel distribution

Fig. 11--Variation of compact density and crushing strength with size of graphite flour

Table 4

RESULT OF IGNITION ANALYSIS FOR FUEL DISTRIBUTION

No. of Piece	ThO ₂ -U ₃ O ₈ (wt-%)	No. of Piece	ThO ₂ -U ₃ O ₈ (wt-%)
1	33.0	13	33.1
2	32.9	14	32.8
3	32.9	15	33.0
4	33.1	16	32.6
5	32.9	17	32.0
6	32.5	18	32.6
7	32.7	19	32.8
8	32.8	20	32.7
9	33.0	21	32.6
10	32.8	22	32.8
11	32.5	23	32.9
12	32.7	24	32.8

NOTE: Theoretical value was 32.3 wt-%;
average value was 32.8 wt-%.

Pitch Content. Strength and density of warm-pressed and sintered compacts increased rapidly with increasing pitch content to 10% by weight, and decreased after 15% (see Figs. 12 and 13).

Warm-pressing Variables

Graphite-pitch mixtures were pressed over the temperature range from room temperature to over 2200°C. Good strengths and densities were obtained above 600°C; the process was relatively insensitive to temperature above this minimum (see Figs. 14 and 15).

No significant effects on compact properties were observed as warm-pressing time at 750°C was varied up to 1 hr.

Compact properties are more dependent on pressure of warm-pressing than on temperature, as can be seen from Figs. 16 and 17. Cold-pressing at high pressures prior to warm-pressing also improves strength and density.

Fig. 12--Variation of density and crushing strength of compacts prepared from AGOT graphite flour with pitch content

Fig. 13--Variation of density and crushing strength of compacts prepared from GP-38 graphite flour with pitch content

Fig. 14--Variation of density and crushing strength of compacts prepared from AGOT graphite flour with warm-pressing temperature

Fig. 15--Variation of density and crushing strength of compacts prepared from GP-38 graphite flour with warm-pressing temperature

Fig. 16--Variation of compact density with cold- and warm-compacting pressures

Fig. 17--Density of compacts versus cold-compacting pressure and method of hot-pressing

Additives

Use of ethyl cellulose as a plasticizer in mixing and granulating has no deleterious effects on compact properties (see Fig. 18).

Thermax (a high-fired, finely divided carbon black) was added to AGOT-pitch mixtures to improve density and decrease permeability. However, as shown in Fig. 19, density and strength decreased with increasing Thermax additions.

SUMMARY OF HOT-PRESSING TECHNIQUES

Holding the compacts under pressure while the pitch binder carbonized (warm-pressing) produced high densities and strengths; this was accomplished at temperatures of 600°C and above. Increasing the pressure in this temperature range gave increased density and strength, but increasing the temperature or the time while holding the pressure constant gave no improvement in properties. The optimum pitch content was 10% to 15%.

FUEL-MATERIAL STUDIES

Thorium-Uranium Dioxide Fuel

During much of the fuel-development program, solid-solution thorium-uranium dioxide, $(\text{Th}, \text{U})\text{O}_2$, particles were used as the starting fuel material. It was therefore necessary to know (1) the temperature and time required for the in situ conversion of $(\text{Th}, \text{U})\text{O}_2$ to $(\text{Th}, \text{U})\text{C}_2$ and (2) the size and integrity of the converted carbide particles and their relationship to the graphite matrix.

In order to determine the minimum conditions necessary for conversion of the oxides to carbides, compacts prepared from $(\text{Th}, \text{U})\text{O}_2$, graphite, and pitch were sintered at temperatures from 1200° to 2200°C for varying times, and were then examined by X-ray diffraction. Strong oxide lines were present in the films of samples sintered between 1200° and 1800°C , and they were still present after 4 hr at 1800°C . Very weak monocarbide

Fig. 18--Variation of compact density and crushing strength with ethyl cellulose content

Fig. 19--Variation of compact density and crushing strength with Thermax concentration

lines were first detected at a sintering temperature of 1600°C , and mixed monocarbides and dicarbides were identified after heating at 2000°C . The minimum condition for complete conversion of $(\text{Th}, \text{U})\text{O}_2$ to $(\text{Th}, \text{U})\text{C}_2$ was found to be 2 hr at 2100°C .

The sensitivity of X-ray diffraction for identifying oxides in the presence of carbides was determined. $(\text{Th}, \text{U})\text{O}_2$ and $(\text{Th}, \text{U})\text{C}_2$ powders were physically mixed, and X-ray films of the powder were obtained. A photodensitometer trace was made on the films by scanning several distinct oxide and carbide lines; thus providing a relative measure of their intensities. The results are given in Table 5.

Table 5
X-RAY DIFFRACTION ANALYSIS OF MIXTURES
OF $(\text{Th}, \text{U})\text{O}_2$ - $(\text{Th}, \text{U})\text{C}_2$

Composition (wt-%)		Relative Line Intensities $\frac{I_{\text{carbide}, 25.1^{\circ}(20)}}{I_{\text{oxide}, 32.4^{\circ}(20)}}$	Remarks
$(\text{Th}, \text{U})\text{C}_2$	$(\text{Th}, \text{U})\text{O}_2$		
50	50	1.33	Strong oxide lines
75	25	1.65	Weak oxide lines
90	10	3.20	Oxide lines barely visible

It appears that X-ray films of powder cannot be used to detect $(\text{Th}, \text{U})\text{O}_2$ in the presence of $(\text{Th}, \text{U})\text{C}_2$ in the range 0 to 10 wt-%. The addition of the graphite matrix would further dilute the oxide; thus X-ray diffraction does not appear to be a good quantitative tool for measuring the conversion of oxides to carbides.

As another possible means of studying the in situ conversion of $(\text{Th}, \text{U})\text{O}_2$ to $(\text{Th}, \text{U})\text{C}_2$, electrical resistivity was measured as a function of sintering temperature on a compact containing $(\text{Th}, \text{U})\text{O}_2$ and on similar unfueled compacts. The results indicated that the oxide particles did not

influence the electrical resistivity of the compact. However, the electrical conductivity of the fueled compact started to improve significantly between 1800° and 2000°C, whereas that of the unfueled compact improved only slightly. After a 2000°C heat treatment, (Th,U)C₂ lines appeared on the X-ray diffraction pattern, indicating that the lowering of resistivity coincided with the conversion of the oxides to dicarbides.

Metallographic examination of sintered fuel compacts revealed that the (Th,U)C₂ particles retained the size and shape of the parent (Th,U)O₂ particles (see Figs. 20 and 21). A considerable portion of the graphite surrounding each particle was consumed by the conversion reaction

which left a void between the particles and the matrix, as can be seen in Fig. 21. No cracking or segregation of the particles was observed. However, the reverse reaction (hydrolysis) was found to cause disintegration of the carbide particles, which resulted in finely divided, amorphous oxide powders.

The variation of fuel-compact density with fuel loading for compacts prepared from oxides is shown in Fig. 22. Compacts containing over 40 wt-% metal (Th + U) were produced from (Th,U)O₂ by the warm-press and sinter technique. However, the strength of these compacts was found to decrease rapidly at loadings greater than 40 wt-% owing to the large graphite-matrix losses in the conversion reaction.

In preparing full-sized compacts by this process, it was necessary to pre-form the smaller units by cold-pressing and then to assemble the seven component pieces as shown in Fig. 23 before warm-pressing the assembly into an integral compact. The multicomponent arrangement was necessary to avoid dimensional distortion during fabrication.

Thorium-Uranium Silicide Fuel

Both oxides and carbides have disadvantages as fuel materials for

(75×)

Fig. 20--Photomicrograph of $(\text{Th,U})\text{O}_2$ fuel particles

(250×)

Fig. 21--Photomicrograph of $(\text{Th,U})\text{C}_2$ fuel particles formed by in situ conversion of $(\text{Th,U})\text{O}_2$ particles during fuel-compact fabrication; note voids between particles and graphite matrix

Fig. 22--Variation of fuel-compact density with metal (Th+U) content for compacts prepared from (Th,U)O₂

Fig. 23--Drawing of fuel compact prepared by converted-oxide process

compact fabrication. On the one hand, in situ conversion of $(\text{Th}, \text{U})\text{O}_2$ to $(\text{Th}, \text{U})\text{C}_2$ liberates two moles of carbon monoxide per mole of carbide and consumes four moles of carbon from the fuel compact matrix immediately adjacent to the fuel particles. This creates considerable porosity in the compacts and makes it difficult to obtain useful fission-gas retention. On the other hand, thorium-uranium carbide prepared by arc-melting is difficult to grind to $150\ \mu$ particles because of its hardness. Also, the extreme moisture reactivity of the ThC_2 in air makes it difficult to handle during its incorporation in the fuel compacts.

A search was made to find a fuel material that was stable in air, that was readily formed into particles, and that released no gases when converted to carbide in the compact. Thorium and uranium silicides appeared to meet all these criteria: they are fairly stable in air and are quite brittle, and furthermore, during the sintering of the fuel compact and the formation of carbides of thorium, uranium, and silicon no gaseous products should escape that would cause porosity in the compact. In addition, the metal-rich silicides of thorium and uranium (U_3Si , U_3Si_2 , and Th_3Si_2) are isomorphous (tetragonal crystal structure) and should form solid solutions.

Uranium silicides containing 7.4% to 18.5% silicon and thorium-uranium silicides containing 6.4% to 20% silicon and having a thorium-to-uranium ratio of 5:2 were prepared by arc-melting crystal bar thorium, high-purity uranium, and purified silicon. Each button was turned over and remelted several times to ensure homogeneity. These buttons were ground in a blender, using a tungsten carbide vial and ball to minimize contamination. (Uranium-silicon alloys containing 7.4% to 18.5% silicon were easily crushed, but U_3Si (3.8% silicon) was too malleable to be crushed to a powder.) These silicides, even though finely ground, appeared to be stable in air. Three mesh sizes of each composition were obtained for fuel-compact studies, and X-ray patterns were obtained on minus-300 mesh powder from each specimen. The X-ray diffraction results are summarized in Table 6.

X-ray diffraction was used to study the conversion of thorium-uranium

Table 6
X-RAY ANALYSES OF THORIUM-URANIUM SILICIDES
(Th:U = 5.2)

Silicon Content (%)	Results
6.4 } 7.4 } 10	Patterns appeared identical, revealing M_3Si_2 -type compound; no oxide
15	Mixture of M_3Si_2 - and MSi -type compounds; no oxide
20	MSi_2 -type compound, plus trace of another compound for which no comparison available (probably M_2Si_3 type)
	MSi_2 -type compound, trace of unidentified compound (probably MSi_3 -type); no oxide

NOTE: Visual comparisons were made with diffracted patterns of thorium silicides as recorded by Freeman, et al. (Ref. 5).

silicides to carbides. Fuel particle size, sintering time, and temperature were investigated. The thorium-uranium (5:2 atom ratio) silicides varied in composition from 6.4 to 20 wt-% Si. These compounds were crushed and sieved into three ranges of particle size (250 to 500 μ , 110 to 250 μ , and $\leq 50 \mu$) and were then mixed with graphite and pitch, and compacted. Compacts of each silicon composition and particle size were sintered at 2000°C for periods of 1 and 2 hr. The effects of the different variables were as follows:

1. Sintering for 2 hr at 2000°C was necessary for complete conversion of the thorium-uranium silicides to dicarbides for all silicon compositions, with the exception of the samples that contained the large silicide particles (250 to 500 μ). This indicates that the reaction process is probably diffusion controlled.
2. Each specimen still retained silicon carbide, which was detectable in the X-ray pattern. This implies that the vapor pressure of silicon over silicon carbide was not sufficient to cause complete

volatilization of the silicon from the specimens during the vacuum-sintering conversion process (see remarks on vapor pressure below).

The minimum conditions required for the complete conversion of silicide to carbide are compared below with the data previously reported for the conversion of oxide to carbide:

These data show that conversion of the silicide to the carbide is somewhat easier than the conversion of the oxide to the carbide.

Compacts prepared with silicides were slightly more dense than those prepared with oxides (this was expected since there is no evolution of carbon monoxide during the dicarbide formation). As the metal (Th + U) concentration of the compacts was increased from 0 to 35 wt-%, the densities of the oxide compacts increased from 1.9 to 2.6 g/cm³, whereas the densities of silicide compacts increased from 1.9 to 2.7 g/cm³ (see Fig. 24). All compacts were of good appearance.

The results of these experiments demonstrated that fuel compacts could be prepared with 0 to 40 wt-% metal (the range of fuel loadings in the HTGR) by using either oxides or silicides as starting materials.

A composition containing 7.4 wt-% silicon was chosen for irradiation study. This silicon content was high enough for easy grinding, yet not so high as to constitute a major addition to the fuel. Also, this composition appeared densest on metallographic examination. Figure 25 is a photomicrograph of the crushed alloy before sieving, Fig. 26 illustrates the structure of the alloy, and Fig. 27 shows the converted carbide particles in the graphite matrix.

Because of the possibility of vapor-phase migration of thorium, uranium, and silicon at high temperatures, the vapor pressures of the metals over their carbides in graphite were calculated from high-temperature free energy and metal vapor-pressure data. The results are

Fig. 24--Fuel-compact density versus metal (Th+U) content for compacts prepared from Th-U-Si

(100×)

Fig. 25--Photomicrograph of Th-U-Si (7.4% Si, Th:U = 5:2) arc melted and crushed (not etched)

(50×)

(250×)

Fig. 26--Photomicrographs of Th-U-Si (7.4% Si, Th:U = 5:2) prepared by arc melting (etched with HNO_3 , HF, H_2O)

(250×)

(250×)

Fig. 27--Photomicrographs of $\text{ThC}_2\text{-UC}_2\text{-SiC}$ fuel particles in a graphite-matrix fuel compact formed by in situ conversion of Th-U-Si particles (7.4% Si, Th:U = 5:2)

shown in Fig. 28. It can be seen that the vapor pressure of uranium over UC_2 is higher than that of thorium over ThC_2 , and that the vapor pressure of silicon over SiC is quite high. Hence, vapor-phase transport of silicon from silicide fuels might be expected at maximum HTGR operating temperatures. This expectation was confirmed by heating a compact containing silicide fuel at $1900^\circ C$ in vacuo. Over one-fourth of the silicon originally present was lost in 200 hr.

M. Bowman⁽⁶⁾ found that the vapor pressure of U over UC was lowered in UC-ZrC solid solutions. The data in Fig. 28 indicate that NbC might also be useful for lowering the vapor pressure. (Unfortunately, neither niobium nor zirconium produce friable alloys, when alloyed with thorium and uranium, as does silicon.) Therefore, various mixtures of silicon, zirconium, and niobium with thorium and uranium were prepared by arc-melting and were studied in order to produce a mixture of low volatility that would still retain the desirable processing properties of silicon.

Some vapor-pressure tests were made in order to check the volatility of silicon in these silicide fuels. Crushed mixtures of various compositions were heated in open-top graphite crucibles in vacuo at $2000^\circ C$, and weight losses were determined at temperature after 2 and 8 hr. The data (see Fig. 29) show that the rate of weight loss is reduced by a factor of three by the addition of 10 or 20 wt-% NbC or 10 wt-% ZrC. Vapor pressures of silicon at $2000^\circ C$ were calculated from the weight loss data shown in Fig. 29 and the results are listed in Table 7.

These data show that 10% Zr was the most effective in lowering the vapor pressure of silicon. The improvement, however, was not substantial enough; the vaporization rate of the silicon was too high for use in the HTGR (maximum predicted fuel temperature is $1800^\circ C$ and the expected fuel life is three years). Studies of silicide fuels were therefore discontinued.

Coated Carbide Fuel

$(Th, U)C_2$ is extremely reactive in air⁽⁷⁾ and fuel compacts containing unprotected $(Th, U)C_2$ disintegrate by hydrolysis after a few hours exposure

Fig. 28--Vapor pressure of silicon, uranium, zirconium, thorium, and niobium over their carbides

Fig. 29--Weight losses from arc-melted and crushed $\text{ThC}_2\text{-UC}_2\text{-SiC}$ fuel after heating at 2000°C in vacuo as a function of the addition of various amounts of ZrC and NbC

Table 7

VAPOR PRESSURES OF SILICON OVER VARIOUS CARBIDE
MIXTURES AT 2000°C

(Si = 7.4 wt-% of Th + U + Si)

<u>Composition</u>	<u>Vapor Pressure (atm)</u>
Th-U-Si	1.3×10^{-6}
ThC ₂ -UC ₂ -SiC	1.9×10^{-6}
ThC ₂ -UC ₂ -SiC-ZrC, 5% Zr	2.1×10^{-6}
ThC ₂ -UC ₂ -SiC-ZrC, 10% Zr	0.8×10^{-6}
ThC ₂ -UC ₂ -SiC-ZrC, 20% Zr	1.7×10^{-6}
ThC ₂ -UC ₂ -SiC-NbC, 5% Nb	2.0×10^{-6}
ThC ₂ -UC ₂ -SiC-NbC, 10% Nb	1.1×10^{-6}
ThC ₂ -UC ₂ -SiC-NbC, 20% Nb	1.2×10^{-6}
ThC ₂ -UC ₂ -SiC-NbC-ZrC, 5% Zr and 5% Nb . . .	1.9×10^{-6}

to laboratory air. Thus, fuel compacts produced by the in situ conversion of (Th, U)O₂ must be handled and stored in a dry, inert atmosphere. In order to overcome this problem, the use of carbon coatings on the individual (Th, U)C₂ particles was investigated.

Battelle Memorial Institute had developed a process for coating of fuel particles with pyrolytic carbon,⁽⁸⁾ and this work has been extended at General Atomic.⁽⁹⁾⁽¹⁰⁾ Testing of the coated carbides showed not only that the coatings rendered the fuel compacts inert to moisture, but that they also substantially improved fission-product retention. In addition, since no carbon is consumed from the matrix by a conversion reaction, the integrity of the fuel-particle-graphite-matrix interface was improved and the final sintering time and temperature for the compacts were reduced.

Coating of the particles is performed in a fluid-bed reactor (see Fig. 30) at 1400°C. Helium is the fluidizing gas and acetylene or methane furnish the carbon. Photomicrographs of coated particles are shown in Fig. 31.

Compacts with carbon-coated carbide particles are prepared by the warm-press and sinter process. Since cold-pressing tends to break the coatings on the particle, this step is eliminated. A comparison of the

Fig. 30--Schematic diagram of apparatus for the preparation of carbon-coated UC_2

(75×)

(250×)

Fig. 31--Photomicrographs of pyrolytic-carbon-coated $(\text{Th}, \text{U})\text{C}_2$ fuel particles; coating deposited from acetylene at 1400°C

process used with oxide fuel (converted oxide process) and that used with coated carbides (coated carbide process) is given in Fig. 32. Following warm-pressing, the compacts are given a stabilizing heat treatment to complete the removal of volatiles and to minimize dimensional changes resulting from subsequent thermal treatments. Typical dimensional changes resulting from heating the compacts after warm-pressing are shown in Fig. 33.

Photomicrographs of compacts with pyrolytic-carbon-coated $(\text{Th}, \text{U})\text{C}_2$ fuel particles are shown in Figs. 34 and 35. The improved contact between particle and matrix may be noted by comparison with Fig. 21. Typical full-sized compacts are shown in Figs. 36 and 37.

A coating thickness equivalent to several recoil ranges is desirable to keep a large portion of the coating relatively free from the intense fission-fragment damage that the carbon receives immediately adjacent to the carbide particle. Thick coatings are also more resistant to stresses developed by fission-gas pressure within the particle. However, if thick coatings are used on small fuel particles, the coated particles occupy a large volume for a small amount of fuel. Since it is desirable to maintain a continuous matrix of warm-pressed graphite around the fuel particles, the coated particles should not occupy over 30 vol-% of the compact. Hence, for HTGR loadings (refer to Table 1) a carbide-particle size greater than $200\ \mu$ is required. This permits the use of $50\ \mu$ carbon coatings.

PROPERTIES OF WARM-PRESSED AND SINTERED GRAPHITE-MATRIX FUEL COMPACTS

A number of physical and thermal properties have been determined for the graphite-matrix fuel compacts prepared by the warm-press and sinter process described in the previous sections. Also, fairly extensive irradiation and fission-product-retention testing has been conducted with this material. Some typical properties are summarized in Table 8. Discussions of the test programs and results are presented in the following sections.

Fig. 32--Fuel-compact fabrication processes

Fig. 33--Weight and dimensional changes resulting from sintering of warm-pressed, annular fuel compacts at various temperatures for 2 hr

Fig. 34--Sectioned fuel compact containing carbon-coated (Th, U)C₂ fuel particles; 1-in. -diameter compact was split by chisel (upper right-hand edge); particles adhered to broken surfaces and did not pull out or break

(250×)

Fig. 35--Pyrolytic-carbon-coated (Th, U) C_2 particle
in graphite matrix; note good bond between particle
and matrix

Fig. 36--Annular fuel compacts containing carbon-coated $(\text{Th}, \text{U})\text{C}_2$ fuel particles; compacts are 2.25 in. in outside diameter

Fig. 37--Annular fuel compact containing carbon-coated $(\text{Th, U})\text{C}_2$ particles;
compact is 2.25 in. in outside diameter

Table 8
TYPICAL PROPERTIES OF GRAPHITE-MATRIX
FUEL COMPACTS

Graphite density	1.90-1.95 g/cm ³
Crushing strength*	
Transverse	8500 psi
Longitudinal	7500 psi
Thermal expansion* to 1000°C	
Transverse	$7.5 \times 10^{-6}/^{\circ}\text{C}$
Longitudinal	$2.25 \times 10^{-6}/^{\circ}\text{C}$
Thermal conductivity at 2000°C,	
radial	0.3 w/(cm ²)(°C/cm)
	0.07 cal/(cm ²)(sec)(°C/cm)
Electrical resistivity	3.5×10^{-3} ohm-cm
Permeability (He at 1 atm)	2×10^{-3} cm ² /sec
Pore structure	<1% of porosity due to pores >1 μ in diameter
Radiation stability	<0.1% contraction after - 6×10^{19} fissions/cm ³ at 1100°-1500°C

*Direction with reference to grain orientation.

Density

As discussed in "Preparation of Compacts by Hot-pressing Techniques," the density of the unfueled graphite matrix may be varied by varying the processing conditions (see Figs. 13, 15, 16, and 17). Values of 1.90 to 1.95 g/cm³ are generally obtained, although densities of > 2.0 g/cm³ have been produced. Variations of density with fuel loading are shown in Figs. 22 and 24.

Strength

Crushing strengths were determined by using machined rods whose length-to-diameter ratio was approximately one. Figures 12, 13, 14, and 15 illustrate the variations in strength with processing conditions. Typical crushing-strength values obtained on 1/4-in. -diameter by 1/4-in. -long samples are 8500 psi transverse (perpendicular to grain orientation and

parallel to direction of pressing) and 7500 psi longitudinal. Values about 1000 psi lower were obtained on 1-in. -diameter specimens.

Thermal Expansion

Coefficients of thermal expansion were determined in vacuo with an optical dilatometer over the range from room temperature to 700° and 1000°C. Specimens 5/32 in. in diameter by 1 in. or 2 in. long were used. Values for the unfueled graphite matrix gave an isotropy ratio of 3.3; the expansion is greatest in the direction of pressing. Fuel-particle size ($<50\ \mu$ to $500\ \mu$) and fuel loading (0 to 22 wt-% Th + U) had little if any effect on the thermal expansion.

Thermal Conductivity

Heat must be transferred radially from the fuel compacts, and since graphite is anisotropic, it was desirable to measure thermal conductivity in the radial direction. A simple apparatus (see Fig. 38) was used to obtain reasonably good data on laboratory-scale (1-in. -diameter by 2-in. -long) fuel compacts. The method⁽¹¹⁾ is based on the resistance heating of the rod-shaped specimen by the longitudinal passage of large currents. Heat is generated uniformly in the sample and is lost from the surface by radiation, resulting in an axial temperature gradient from the center to the outer surface. This temperature gradient is inversely proportional to the thermal conductivity of the material. A graphite sample of known thermal conductivity is used as a reference.

Fueled and unfueled graphite-matrix compacts were found to have thermal conductivities between 0.07 and 0.08 cal/(cm²)(sec)(°C/cm) over the temperature range from 1400° to 2000°C. The final heat-treat temperature (in the range from 1400° to 2100°C) of the compact had little if any effect on the thermal conductivity.

Thermal Stress and Shock Resistance

Of the many severe thermal-cycle stress and shock tests that these

Fig. 38--Electric (resistance) heating apparatus for measuring thermal conductivity of graphite specimens

compacts have been subjected to, none has caused failure (cracking, spalling, etc.). In this respect, the compacts are similar to a high-density, petroleum-coke base, pitch-bonded graphite. Compacts have been heated both directly (by resistance) and indirectly (in a furnace) to temperatures as high as 2600°C. In several instances compacts were repeatedly heated from room temperature to 2600°C in less than 1 min without failure.

Electrical Resistivity

The room-temperature electrical resistivity of the unfueled compacts is $3.5 \pm 0.1 \times 10^{-3}$ ohm-cm; it is insensitive to the final heat-treat temperature of the compact over the range 1400°C to 2150°C. Prolonged heating at 2150°C, however, reduces the resistivity by one-third, and the addition of (Th,U)C₂ fuel to the compacts had a similar effect.

Permeability

Pressure-decay techniques were used to measure the helium permeability of the fuel compacts. Figure 39 shows the variation in permeability with compact density. Since low permeability was a desirable attribute (to increase fission-product retention), high compact densities were desirable.

Porosimetry

Pore spectrums were determined with an hydraulic, mercury-intrusion porosimeter. Curves of the differential accessible volume, $dV(r)/dr$, expressed as a percent of the sample bulk volume per micron, are shown in Figs. 40 and 41. The long tail at high pore radii found with most commercial graphites⁽¹²⁾ is noticeably lacking with the warm-pressed and sintered graphite fuel matrix. This tight, uniform pore structure has been found ideally suited for impregnation treatments to further reduce permeability. The effects on the pore spectrums of additions of ethyl cellulose may also be seen in Figs. 40 and 41. The uniform structure revealed by the porosimetry data is visually confirmed in Fig. 42, which shows the graphite fuel matrix.

Fig. 39--Permeability versus density of graphite-matrix material for the HTGR fuel compacts

Fig. 40--Pore spectrum of warm-pressed and sintered graphite fuel matrix

Fig. 41--Pore spectrum of warm-pressed and sintered graphite fuel matrix containing 1% ethyl cellulose

Fig. 42--Photomicrograph of warm-pressed and sintered graphite fuel matrix

FISSION-PRODUCT RETENTION

Fission-product control in the HTGR⁽²⁾ starts in the fuel compacts, where roughly one-half of the fission products formed can be expected to remain fixed, either because they are nonvolatile or because they form stable, nonvolatile carbides. The principal elements of this group are Y, Zr, Nb, Mo, Tc, Ru, Rh, Pd, La, Ce, Pr, Nd, and Pm. The remaining fission products will diffuse more or less rapidly out of the fuel compact, depending on their volatility, and if not otherwise controlled, they would enter the primary coolant stream. The control method proposed for the HTGR avoids this problem by providing an impervious graphite containment around the fuel compacts, and the interspace between the compacts and the container will be continuously scavenged by a small fraction ($\sim 0.1\%$) of the primary coolant flow, which will enter by way of a controlled in-leak. This helium purge stream will carry the fission products to an external fission-product trapping system, the purified helium being returned to the primary circuit. The principal advantage of this system over a bypass system is that the chemically reactive or condensable fission products are not allowed to plate out in the primary circuit before reaching the trap. In addition, the trap receives the fission products relatively undiluted, and thus trapping difficulties are decreased.

The fuel compacts should retain or hold up the fission products as long as possible to allow the large energy release of the short half-life fission products to be given up in the element rather than in the trap, where it would result in a cooling problem. Testing of fuel compacts for fission-product retention has therefore been an important part of the HTGR fuel-development program; these testing techniques and results have been described in previous reports.⁽¹³⁻¹⁶⁾

Briefly, the testing method is as follows: Fuel materials (particles, coated particles, or compacts) are subjected to irradiation of short duration in the General Atomic TRIGA reactor to produce trace levels of fission products. The samples are then placed in a high-temperature graphite-tube

furnace. Helium flows over the sample and through a system of traps where Xe^{133} is collected and counted.

In general, a relative method of determining the xenon fraction remaining in the compact, as a function of time, was used. Thus, at the end of a test at a given temperature the compact was brought to a high temperature (usually 2200°C) and all of the xenon activity was driven out. The experimental method was to accumulate the Xe^{133} carried from the compact by the helium stream (flow rate approximately $300\text{ cm}^3/\text{min}$) on an activated charcoal trap held at liquid-nitrogen temperature. The fraction released at any time was based on the final activity collected.

Zumwalt and Anderson⁽¹⁷⁾ have found that the xenon release from uncoated carbide fuel particles in a typical dispersion fuel element is similar to the krypton release, which fits the equation

$$\text{Fraction released} = 1 - \frac{6}{\pi^2} \sum_n \frac{1}{n^2} \exp(-n^2 \pi^2 t/\delta),$$

where

$$\log \delta (\text{hr}) = \frac{16.1 \times 10^3}{T(^{\circ}\text{K})} - 6.12.$$

This expression has been used to calculate $t_{1/2}$ (time to lose 50% of the xenon) at several temperatures (see Table 9).

Table 9

Xe^{133} LOSS FROM FUEL COMPACTS
WITH UNCOATED FUEL PARTICLES

$T(^{\circ}\text{C})$	$t_{1/2}$
1090	670 days
1370	6.0 days
1650	5.4 hr
1930	29 min
2200	5 min
2480	1 min

Compacts containing pyrolytic-carbon-coated $(\text{Th}, \text{U})\text{C}_2$ particles have shown remarkably improved xenon retention. The initial release curve for an early compact tested at 1700°C showed a fast component (1.8% of Xe^{133}) with a characteristic diffusion time of 0.88 hr and a slow component for the balance of the Xe^{133} with a diffusion time of 3.3×10^4 hr. The release at 2200°C was characterized by a single component of 2.5×10^3 hr. Furthermore, it proved difficult to get the balance of the xenon activity out of the sample, so a series of thermal-cycling "shock" treatments with a 2600°C maximum temperature was performed. Relatively fast release was observed at room temperature following several of the 2600°C treatments. It is believed that the severe heating and cooling may have opened up the pyrolytic carbon sheath around the carbide particles. From the slope of the release curves, the characteristic release times ($t_{1/2}$) at 1700° and 2200°C were estimated to be 35 days and 10 days, respectively.

A xenon-release curve for one of the first compacts prepared with pyrolytic-carbon-coated fuel particles is compared in Fig. 43 with a typical curve for compacts with uncoated particles. Recent tests with pyrolytic-carbon-coated $(\text{Th}, \text{U})\text{C}_2$ fuel particles that were not in a compact have shown no detectable xenon release during 48 hr at 1700°C (upper curve in Fig. 43).

Fission-product-release testing on more highly irradiated fuel compacts is reported below in "Irradiation Studies."

IRRADIATION STUDIES

The physical characteristics of representative fuel compacts in a radiation field have been studied by means of two types of irradiation capsule: (1) the GA-308 series capsules (see Fig. 44), in which as many as six compacts in tandem may be irradiated simultaneously, and (2) the GA-309 series capsules (see Fig. 45) which are used for the study of the release of gaseous fission products from the fuel compacts during irradiation. The high temperatures produced in the compacts by fission heating are controlled by the variation in thermal conductivity of a binary gas

Fig. 43--Release of Xe^{133} from compacts with coated and uncoated fuel particles at indicated test temperatures

Fig. 44--GA-308 series irradiation capsule

Fig. 45--GA-309 series irradiation capsule

mixture in a control annulus located between the test specimen and the capsule coolant. (18)

During the irradiation studies described here, the combined fuel (U^{235}) and fertile (Th) contents of the test compacts were made to correspond to HTGR design loadings. In order to accelerate burnup and obtain high fuel-compact temperatures, additional fuel was substituted for a portion of the thorium, but the carbon-to-metal (Th + U) ratio was kept consistent with HTGR design. This seemed to be a safe expedient, since ThC_2 and UC_2 form a solid-solution system, and substitution of one for the other should lead to no unforeseen difficulties. A burnup equal to 60% of the HTGR design life of 3 years was obtained in a 4-month irradiation in the GETR.

The test conditions are listed in Tables 10 and 11, and the results of several irradiation tests, discussed below, are summarized in Tables 12 through 15. All the fuel compacts were prepared by the warm-press and sinter process previously described.

Table 10
FUEL-COMPACT COMPOSITIONS AND DIMENSIONS
FOR GA-308 CAPSULE IRRADIATIONS

	GA-308-2	GA-308-3	GA-308-4
Composition			
Uranium (93% enriched), wt-%	3.1	6.5	6.0
Thorium, wt-%	7.25	15.5	14.4
Silicon, wt-%	----	----	1.6
Total metal, wt-%	10.3	22.0	22.0
Graphite, wt-%	89.7	78.0	78.0
C:Th:U, atom ratio	570:2.4:1	240:2.4:1	255:2.4:1
C:Th+U, atom ratio	175:1	67.1	74:1
C:Th+U+Si, atom ratio	----	----	45:1
Dimensions			
Outside diameter, in.	1.00	1.00	1.00
Inside diameter, in.	----	0.50	0.50
Length, in.	1.10	1.78	1.78

Table 11

BURNUPS AND TEMPERATURES OF IRRADIATIONS FOR
GA-308 AND GA-309 CAPSULE IRRADIATIONS

	GA-308-2	GA-308-3	GA-308-4	GA-309-4, -5 and -6*
Temp. at compact centerline, °C	1,050-1,200	1,150-1,480	1,090-1,480	1,500-1,900
Burnup† U ²³⁵ , %	16.7	18	18	17
Fissions/cm ³	4.25 × 10 ¹⁹	6.9 × 10 ¹⁹	6.0 × 10 ¹⁹	5.4 × 10 ¹⁹
MwD/T	48,000	51,000	51,000	50,000
kw-hr/cm ³	210	600	600	500

* To May 1, 1961.

† Design burnup for HTGR is 1.1×10^{20} fissions/cm³.

Irradiation Test of Capsule GA-308-2

The fuel compacts for the irradiation of Capsule GA-308-2 were right circular cylinders 1.00 in. in diameter by 1.10 in. long. Solid-solution (Th, U)C₂ fuel particles 110 to 250 μ in diameter were formed by the in situ conversion of (Th, U)O₂. The fuel content was 3 wt-% U²³⁵; the thorium content was 7 wt-%.

During irradiation, the temperature of the graphite cans containing the fuel compacts varied from 775° to 830°C in the region of highest flux. The fuel-compact temperatures were estimated to be 275°C higher than the temperature of the cans. The maximum calculated burnup was 16.7% of U²³⁵, or 48,000 Mw-days/ton, which is equivalent to 4.25×10^{19} fissions/cm³.

When the capsule was disassembled, it was noted that the appearance of all the fuel bodies was excellent (see Fig. 46). The dimensional measurements of the fuel bodies, which checked against the preirradiation values, are given in Table 12.

Compact No. 4

Compact No. 5

Compact No. 6

Fig. 46--Compacts from capsule GA-308-2 after irradiation to 4.25×10^{19} fissions/cm³ at 1050° to 1200°C

Table 12
 DIMENSIONAL CHANGES OF FUEL COMPACTS
 FROM IRRADIATION OF CAPSULE GA-308-2

Compact	Av. Temp. of Graphite Can (°C)	Fuel-body Centerline Temp., Calc. (°C)	Dimensional Changes (%)	
			ΔD	ΔL
4	820	1200	-0.2	0
5	830	1200	-0.1	-0.1
6	775	1050	0	0

Irradiation Test of Capsule GA-308-3

The fuel compacts in the irradiation test of Capsule GA-308-3 differed in three major respects from those tested in the previous irradiation. First, these compacts were of an annular design (in order to correspond more closely to the configuration of the HTGR compact); second, the metal (Th + U) loading was increased from 10 to 22 wt-% (6.5% U, 15.5% Th), corresponding to the increased fuel concentration in the HTGR occasioned by the change to annular fuel compacts; third, three different particle sizes of fuel material were used to permit comparison of radiation effects as a function of fuel-particle size. The sizes of the particles were $<50 \mu$, 110 to 250μ , and 250 to 500μ . Six compacts were tested, two with each size of fuel particle. The compacts were made from solid-solution (Th,U)O₂ particles that were converted in situ to (Th,U)C₂ during compact fabrication. Each compact was 1.00 in. in outside diameter, 0.50 in. in inside diameter, and 1.75 in. long, and a graphite rod was inserted in the center of each compact to simulate the unfueled region in the HTGR fuel compact.

During irradiation, the temperature of the compacts ranged from 650° to 925°C; the burnup reached was 18% of the U²³⁵, 6.9×10^{19} fission/cm³, or 600 kw-hr/cm³. The dimensional changes and other pertinent data are recorded in Table 13.

The postirradiation appearance of the six fuel bodies was good. A typical fuel compact before irradiation is shown in Fig. 47, and Fig. 48

Fig. 47--Fuel compact of the type prepared for the irradiation of capsule GA-308-3

Compact No. 3; fuel particles $<50 \mu$

Compact No. 2; fuel particles $110-250 \mu$

Compact No. 6; fuel particles $250-500 \mu$

Fig. 48--Fuel compacts from capsule GA-308-3 after irradiation to 6.9×10^{19} fissions/cm³ at 1150° to 1480° C; surface pips are due to partial hydrolysis of carbide fuel during hot-cell examination

Table 13

DIMENSIONAL CHANGES OF FUEL COMPACTS
FROM IRRADIATION OF CAPSULE GA-308-3

Compact	Fuel-particle Size (μ)	Av. Temp. of Graphite Can ($^{\circ}\text{C}$)	Fuel-body Centerline Temp., Calc. ($^{\circ}\text{C}$)	Dimensional Changes (%)	
				ΔD	ΔL
1	250-500	650-760	1200	0	+0.2
2	110-250	730-840	1300	-0.2	+0.2
3	<50	840-900	1400	-1.7	+2.2
4	<50	900-925	1480	-2.2	+3.0
5	110-250	760-840	1200	-0.3	<-0.1
6	250-500	700-790	1150	0	<+0.1

shows the irradiated compacts. (The speckled surfaces on the irradiated compacts are a result of partial hydrolysis of the particles near the surface of the compact due to exposure to air during hot-cell examination.) After irradiation the compacts had approximately the same appearance as before irradiation; no spalling or cracking was evident on any of the six compacts in this capsule.

It will be noted that while the diametral change in these compacts was one of contraction, the longitudinal dimension of the bodies increased. Furthermore, the largest variations occurred in compacts with fuel particles smaller than 50 μ . These changes are characteristic of neutron radiation effects on unfueled graphite. However, the effect of small fuel particles is much larger than would be expected for pile-grade graphite under equivalent neutron exposure. This indicates a contribution from fission recoils, as one would expect. The smallest particle size that will produce acceptable dimensional stability in the fuel bodies lies apparently somewhere between 50 and 100 μ .

Irradiation Test of Capsule GA-308-4

The fuel compacts for the irradiation of Capsule GA-308-4 differed in one respect from the GA-308-3 compacts; they were prepared from thorium-

uranium silicide (7.4 wt-% Si) fuel rather than thorium-uranium oxide. The thorium and uranium were converted to dicarbides and the silicon to SiC in situ during fuel-compact fabrication. Dimensions, fuel loadings, and fuel-particle size were the same as for the GA-308-3 test.

During irradiation, the centerline temperatures of these compacts ranged from 1090° to 1480°C, as determined by melt wires placed in the graphite core of each compact. Burnup was 6.0×10^{19} fissions/cm³, 18% of the U²³⁵, or 51,000 kw-hr/cm³. Dimensional changes are summarized in Table 14.

Table 14
DIMENSIONAL CHANGES OF FUEL COMPACTS
FROM IRRADIATION OF CAPSULE GA-308-4

Compact	Fuel-particle Size (μ)	Av. Temp. of Graphite Can (°C)	Fuel-body Centerline Temp., Calc. (°C)	Dimensional Changes (%)	
				ΔD	ΔL
1	<50	650-760	1090*	-0.9	+3.0
2	250-500	700-790	1290	0	+0.3
3	<50	790-870	1370	-0.8	+0.8
4	110-250	870-925	1480†	-0.1	<+0.1
5	250-500	790-840	1230	0	+0.1
6	110-250	730-815	1175	0	+0.1

* Measured.

† Determined by melt wire.

The appearance of these bodies was good, although surface roughening was noted on one fuel body. The exact cause of this condition is not known. The general appearance of the fuel compacts before irradiation was similar to that shown in Fig. 47. Except for the surface roughening of compact No. 3 and a crack in compact No. 5, the condition of the remaining compacts (see Fig. 49) in this capsule is comparable to that before irradiation.

The dimensional changes, again, indicate the importance of particle

Compact No. 1; fuel particles $<50 \mu$

Compact No. 6; fuel particles $110-250 \mu$

Compact No. 2; fuel particles $250-500 \mu$

Fig. 49--Fuel compacts from capsule GA-308-4 after irradiation to 6×10^{19} fissions/cm³ at 1090° to 1480°C; surface pips are due to partial hydrolysis of carbide fuel during hot-cell examination

size. In this capsule one of the fuel bodies containing small particles was placed in a cold region and another in a hot region. In both cases there was a maximum contraction, indicating that the fission-recoil effect is rather insensitive in this temperature range.

The data obtained from these capsule irradiations indicate that, in general, these graphite matrix compacts are acceptable from the point of view of dimensional stability and physical integrity at metal loadings up to 22 wt-%. The dimensional stability can be affected by fuel-particle size, although it seems to be somewhat insensitive to temperature. The burnups for these capsules are 60% of that expected for the HTGR fuel. The starting material, whether oxide or silicide, performed satisfactorily.

Irradiation Test of Capsule GA-309

The irradiation test of Capsule GA-309 was designed to measure the in-pile, steady-state release of fission products from fuel compacts at elevated temperatures. In this experiment, three capsules of the type shown in Fig. 45 are irradiated in the same test hole in the reactor. From time to time the capsules are purged with helium; the released fission-product gases are then allowed to accumulate for 24 hr and the capsule is again purged with helium. This last purge is sampled, aliquoted, and analyzed using gamma-spectrometric techniques. The disintegration rates of the fission-product nuclides Xe^{138} , Kr^{87} , $\text{Kr}^{85\text{m}}$, Xe^{135} , Xe^{133} , and Kr^{85} at sampling time are determined by using their known decay schemes and half lives and the known gamma-counting efficiency of the scintillation detector of the spectrometer. Fission rates for the fuel specimens are calculated from their known U^{235} content, from the reactor power, and from flux as a function of reactor power and control-rod-bank setting at the position of the given capsule. The fractional steady-state release of nuclide i (F_i) is given by*

$$F_i = \frac{R_i / y_i (1 - e^{-\lambda_i t})}{R_f},$$

*See Ref. 16, p. 154.

where R_f = corrected fission rate (f/s),

R_i = disintegration rates of nuclide i at sampling time in entire purge sample (d/s),

λ_i = decay constant for i ,

y_i = fractional fission yield of i ,

t = accumulation time (usually about 24 hr).

Graphite compacts containing pyrolytic-carbon-coated (Th,U)C₂ particles were used for the GA-309-4, -5, and -6 group of irradiations. Since each capsule was designed for the same power generation (4500 w), the fuel loadings were different for each compact to compensate for the axial-flux distribution in the reactor. Table 15 gives the fuel loadings and dimensions of these compacts.

Table 15
FUEL LOADINGS AND COMPACT DIMENSIONS
FOR CAPSULES GA-309-4, -5, AND -6

	GA-309-4	GA-309-5	GA-309-6
Composition			
Uranium (93% enriched), wt-%	7.6	5.5	6.7
Thorium, wt-%	17.4	12.5	15.3
Total metal, wt-%	25.0	18.0	22.0
Graphite, wt-%	75.0	82.0	78.0
C:Th:U, atom ratio	194:2.3:1	292:2.3:1	228:2.3:1
C:metal, atom ratio	59:1	88:1	69:1
Dimensions			
Outside diameter, in.	1.00	1.00	1.00
Inside diameter, in.	0.50	0.50	0.50
Length, in.	1.78	1.78	1.78

The coated carbide fuel used for these compacts was some of the first material produced, and particle densities were low and coatings thin (Fig. 50). The size of the carbide particles was 105 to 250 μ , and the pyrolytic-carbon coating was 30 μ thick. The fuel compacts (Fig. 51), which

(75x)

(250x)

Fig. 50--Pyrolytic-carbon-coated $(\text{Th,U})\text{C}_2$ fuel particles prepared for GA-309-4, -5, and -6 capsule irradiations; coatings deposited from acetylene at 1400°C

Fig. 51--Fuel compacts containing pyrolytic-carbon-coated $(\text{Th}, \text{U})\text{C}_2$ fuel particles typical of those prepared for the GA-309-4, -5, and -6 and GA-309-7, -8, and -9 capsule irradiations

were annular and were of the same dimensions as the GA-308-3 and -4 compacts, were produced by the warm-press and sinter process.

The GA-309-4, -5, and -6 purge capsules began operating in the GETR in November, 1960, and by the end of April, 1961, they had achieved about 50% of the HTGR burnup. Tables 16, 17, and 18 give the percentage of steady-state release ($F_i \times 100$) of the xenon and krypton isotopes as determined at various times since startup. The total number of megawatt-days of reactor power logged as irradiation time up to the time of sampling is listed along with the date of removal from the reactor and the estimated fuel-body temperature at the time the sample was accumulated.

The data show an indication of increasing F_i with increasing fuel-body temperature; also, F_i shows some tendency to increase with increasing megawatt-days (MwD) of exposure in the reactor. The results indicate that the pyrolytic-carbon-coated fuel particles were largely intact and had a long characteristic diffusion time, $\gg 5$ days. However, it appears that 1% to 3% of the particles in the GA-309-5 and GA-309-6 fuel compacts ($< 1\%$ in the case of GA-309-4) were broken open and showed a steady-state krypton and xenon release behavior something like that of uncoated carbide particles. Sample series 23, 24, and 25 represent the first of a number of tests designed to determine the variation of F_i with fuel-compact temperature.

Capsules GA-309-7, -8, and -9 have been prepared and irradiation testing was begun in May, 1961. Two of these capsules contain compacts made with denser fuel particles with thick (50 to 60 μ) pyrolytic-carbon coatings (see Figs. 52 and 53). The third capsule contains the same fuel particles but with thin (10 to 15 μ) coatings (Fig. 54) to simulate possible end-of-life conditions.

High-burnup Irradiation Test of Capsule GA-113

In order to investigate end-of-life fission-gas pressure conditions inside coated fuel particles, compacts containing a small number of coated particles, of the type used for the irradiation test of capsules GA-309-4,

Table 16
KRYPTON AND XENON RELEASE DATA FOR CAPSULE GA-309-4

Sample Series	Date Removed From GETR	Irradiation Time* (MwD)	Fuel-compact Temp. (°C)	Steady-state Release (%)						
				Xe ¹³⁸ (17m)	Kr ⁸⁷ (78m)	Kr ⁸⁸ (2.8h)	Kr ^{85m} (4.4h)	Xe ¹³⁵ (9.1h)	Xe ¹³³ (5.3d)	Kr ⁸⁵ (10.3y)
8	11/22/60	191	960	----	0.002	0.004	0.006	0.0011	0.017	0.29
11	12/9/60	518	1650	----	0.09	0.07	0.30	0.005	0.041	2.1
12A	1/12/60	764	1471	----	0.13	0.15	0.23	0.015	0.12	----
14	1/18/61	944	1588	≤0.06	0.10	0.19	0.26	0.028	0.28	2.4
17	1/25/61	1111	1427	0.027	0.057	0.094	0.12	0.009	0.078	----
20	2/1/61	1321	1535	----	0.09	0.15	0.23	0.014	0.20	1.9
23	3/23/61	1495	----	----	0.13	0.10	0.20	0.015	0.028	----

* 1400 MwD is equivalent to ~9% U²³⁵ burnup, or 26,000 MwD/T, or 280 kw-hr/cm³

Table 17
KRYPTON AND XENON RELEASE DATA FOR CAPSULE GA-309-5

Sample Series	Date Removed From GETR	Irradiation Time* (MwD)	Fuel-compact Temp. (°C)	Steady-state Release (%)						
				Xe ¹³⁸ (17m)	Kr ⁸⁷ (78m)	Kr ⁸⁸ (2.8h)	Kr ^{85m} (4.4h)	Xe ¹³⁵ (9.1h)	Xe ¹³³ (5.3d)	Kr ⁸⁵ (10.3y)
8	11/22/60	191	1524	----	0.11	0.19	0.35	0.028	0.14	1.0
10	12/8/60	494	1702	----	0.39	0.65	0.94	0.0049	0.78	7.2
13	1/13/61	794	1760	----	0.37	0.49	0.76	0.047	0.53	---
15	1/19/61	974	1799	----	0.79	0.62	0.92	0.072	0.79	---
18	1/26/61	1141	1904	0.68	0.56	0.58	0.80	0.073	1.17	25
21	2/2/61	1351	1751	----	0.11	0.19	0.36	0.016	0.27	5.4
24	3/24/61	1525	----	----	0.27	0.31	0.70	0.027	0.18	---

* 1400 MwD is equivalent to ~9% U²³⁵ burnup, or 26,000 MwD/T, or 280 kw-hr/cm³

Table 18
KRYPTON AND XENON RELEASE DATA FOR CAPSULE GA-309-6

Sample Series	Date Removed From GETR	Irradiation Time* (MwD)	Fuel-compact Temp. (°C)	Steady-state Release (%)						
				Xe ¹³⁸ (17m)	Kr ⁸⁷ (78m)	Kr ⁸⁸ (2.8h)	Kr ^{85m} (4.4h)	Xe ¹³⁵ (9.1h)	Xe ¹³³ (5.3d)	Kr ⁸⁵ (10.3y)
8	11/22/60	191	1549	----	----	0.12	0.18	0.010	0.17	0.75
9	12/7/60	470	1865	----	0.28	0.37	0.51	0.031	0.64	7.0
16	1/20/61	1004	1616	----	0.63	0.54	0.93	0.19	0.87	20
19	1/27/61	1171	1746	----	1.4	1.8	2.7	0.16	2.2	----
22	2/3/61	1381	1750†	0.34	0.8	1.2	2.5	0.13	2.3	----
25	3/25/61	1555	----	----	0.22	0.36	0.66	0.027	0.137	----

* 1400 MwD is equivalent to ~9% U²³⁵ burnup, or 26,000 MwD/T, or 280 kw-hr/cm³

† Estimated.

(75×)

(200×)

Fig. 52--Pyrolytic-carbon-coated $(\text{Th,U})\text{C}_2$ fuel particles prepared for irradiation of capsule GA-309-9; coating was deposited from acetylene at 1400°C

Fig. 53--Pyrolytic-carbon-coated $(\text{Th}, \text{U})\text{C}_2$ fuel particle typical of those prepared for irradiation of capsule GA-309-8; coating was deposited from methane at 1400°C

Fig. 54--Thinly coated $(\text{Th}, \text{U})\text{C}_2$ fuel particles prepared for irradiation of capsule GA-309-7; $10\text{-}\mu$ coating deposited from acetylene at 1400°C

-5, and -6 (see Fig. 50), were prepared and subjected to a full burnup irradiation at ambient temperature ($<100^{\circ}\text{C}$). The particles were then heated to high temperature in order to generate pressure within the particles, and the fission-gas release was studied.

A compact containing 1 mg of U^{235} was irradiated in the GETR for one cycle. The sample was placed in the highest thermal-flux (2×10^{14} neutrons/ $\text{cm}^2\text{-sec}$) region of the reactor. A total of 3.5×10^{20} nvt was received by the sample, giving a burnup of 20.5% U^{235} . The compact was allowed to cool for one month, and was then heated to 1000°C for 1.5 hr in the fission-product testing furnace. A helium purge over the compact swept the released Xe^{133} and Kr^{85} into remote liquid-nitrogen-cooled charcoal traps, where the gases were monitored. The amount of Xe^{133} released was 0.42%. The temperature was then raised to 1700°C and maintained for 2.79 days. The quantity of Xe^{133} released was 17.8%. The release of Kr^{85} was evaluated in the same manner, giving a release value of 18%. To reduce the error in evaluating the fractional release based on the calculated burnup, the compact was thermal-cycled ten times to 2600°C for complete removal of Xe^{133} and Kr^{85} .

In order to compare the release of a high-burnup compact with that of unirradiated material, an identical control compact containing 10 mg U^{235} was irradiated in the General Atomic TRIGA reactor to 10^{13} fissions. This compact was then heated to 1700°C for 40 hr, and the Xe^{133} release was determined to be 0.5%.

These results indicate that a majority of the coated particles were still intact after the equivalent of a 100% HTGR burnup (3-yr fuel life). The release curve for Xe^{133} was similar to that observed for a compact with uncoated particles, which is apparently the behavior that may be expected from particles whose coatings have broken open.

Additional tests of this type are in progress. Various $(\text{Th}, \text{U})\text{C}_2$ particles with varying coating thicknesses are being investigated.

OTHER COMPACT STUDIES

Additives

Metals that form stable carbides and have low neutron-absorption cross sections were added to the graphite-pitch mixture and hot-pressed at about 2000°C. By reacting with the graphite during hot-pressing, the metals might act as sintering aids to produce denser compacts, to strengthen the compacts through formation of a network of carbides, and to decrease porosity, thereby giving greater fission-product retentivity.

Silicon, niobium, and zirconium in concentrations from 1 to 40 wt-% were studied; the results are shown in Table 19 and Fig. 55. Densities

Table 19

PROPERTIES OF COMPACTS PREPARED WITH SILICON, NIOBIUM, AND ZIRCONIUM ADDITIVES*

Additive	Concentration (wt-%)	Density (g/cm ³)	Crushing Strength (psi)		Permeability
			Transverse	Longitudinal	
Silicon	1	1.86	6,900	4,900	4.3×10^{-3}
	5	1.91	5,950	6,200	3.8
	10	1.97	3,900	5,400	3.5
	20	2.00	6,000	10,000	2.5
	20	1.95	8,400	5,150	7.3
	30	1.98	----	----	----
	40	1.90	----	----	----
Niobium	1	1.89	5,300	8,000	7.3×10^{-3}
	5	2.00	5,900	5,500	4.8
	10	2.07	3,350	4,500	6.6
	20	2.25	3,200	2,700	8.4
Zirconium	1	1.89	2,800	2,950	7.0×10^{-3}
	5	1.97	4,500	3,500	12.2
	10	2.04	3,300	4,000	13.5
	20	2.21	2,200	2,900	11.1
None	--	1.94	5,400	6,000	5.0×10^{-3}

* Metal powders added to a mixture of No. 28 graphite and pitch mixture; cold-compacted at 50,000 psi and hot-pressed at 4,500 psi at ~2000°C; compacts 1 in. in diameter by 2 in. long.

Fig. 55--Variation of compact density with concentration of metallic additive

lower than those found in control compacts with no additives were noted as the content of each metal reached 1%. The density of the silicon-containing compacts (assuming SiC formation) continued to decrease with increasing silicon content, but compacts containing zirconium remained about constant at 84% of theoretical density. Only niobium gave an increase in theoretical density beyond a 1% concentration, but even this metal did not permit the test compact to regain the density of the compacts without additives.

Strength and permeability data showed considerable scatter, though in two cases with silicon and one with niobium a considerable increase in compact strength was obtained. Three silicon-containing compacts showed slight decreases in permeability.

Graphite-matrix Control-rod Bodies

B_4C dispersed in graphite has been selected as the control material for the HTGR, and the boron concentration required is predicted to be in the range of 20 to 40 wt-%.

The warm-press and sinter process developed for fuel-compact fabrication was successfully adapted to the preparation of B_4C -graphite fuel bodies, and compacts containing up to 44 wt-% boron were produced. Boron loadings and atom ratios are given in Table 20 for 1-in. -diameter compacts that were warm-pressed at 800°C and sintered at 1400°C. Similar compacts were heated in vacuo for 2 hr at 2000°C with no detectable loss of boron.

Table 20
BORON LOADINGS AND ATOM RATIOS
OF B_4C -GRAPHITE COMPACTS

Boron Loading (wt-%)	Compact Density (g/cm ³)	Boron Loading (g/cm ³)	B_4C : Graphite Atom Ratio
20	1.84	0.37	3.6
30	1.81	0.55	2.1
40	1.75	0.70	1.35

The variation in density with boron content is shown in Fig. 56. Density decreases with increasing boron content, particularly after the boron content exceeds 20%. The annular compacts are less dense than solid ones as a result of friction on the additional die surface during pressing, but higher pressures can be used to compensate for this.

Crushing strength versus boron content is shown in Fig. 57. The exceptionally high strength of the 20%- and 30%-boron materials is not understood at present, and further studies are in order. (The point shown at 20% boron concentration in Fig. 57 is an average of five determinations; the points at 0%, 30%, and 44% boron concentration are the average of two to four determinations each; and the point at 40% boron concentration is a single determination.) If boron carbide really contributes to the strength of the graphite body, this would be an interesting subject to pursue. At this point, one may conclude that the strength of the fuel matrix graphite is not impaired by boron loading up to 30 wt-%. Beyond this concentration, however, there appears to be a definite decrease in strength.

Four sets of compacts are currently undergoing irradiation testing in the GA-310-5 capsule series. Each capsule contains a set of three compacts, the compacts consisting of 20, 30, and 40 wt-% boron, respectively. The first two capsules are being irradiated for two cycles in the core of the GETR (equivalent to about one-third the exposure lifetime of an HTGR control rod); one at 700°F and one at 1200°F. The second two capsules are being irradiated at the same temperatures, but for six cycles (100% exposure).

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Fig. 56--Density versus boron content for B_4C -graphite control-rod compacts prepared by the warm-press and sinter process

Fig. 57- -Crushing strength versus boron content for B_4C -graphite control-rod compacts prepared by the warm-press and sinter process

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