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ABSTRACT

THE FABRICATION OF THE GRAPHITE-URANIA FUEL
FOR THE TRANSIENT REACTOR TEST

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The two predominate methods of dispersing uranium in graphite are reviewed and evaluated. This study indicated that the most feasible method of dispersing uranium in graphite would be to fabricate a mixture of graphite and U_3O_8 bonded with a thermosetting resin. A commercial type graphite fabricated by Great Lakes Carbon Corporation had been developed through independent research, and this fabrication procedure was adapted for the manufacture of the TREAT fuel matrix.

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INTRODUCTION

The Transient Reactor Test (TREAT) was designed to safely generate a large thermal neutron flux field for a very short period of time. To generate this flux with the greatest margin of safety a non-metallic fuel system operating on a low loading was required, and based on existing technology a dispersion of highly enriched uranium oxide in a matrix of graphite appeared to be the most suitable fuel. In this type of fuel the graphite would serve primarily as a moderator. However, due to the high thermal conductivity of the graphite, it would also serve to dissipate the heat from the uranium oxide fuel particles as well as to raise the energy of the thermal neutrons. This would increase the probability of the neutrons leaking from the reactor, and would result in a large negative temperature coefficient.

The average operating temperature of the Transient Reactor was calculated to be 260°C, however it was estimated that hot spots in the fuel could in all probability cause temperatures as high as 400°C, and as the reactor was to be air cooled it was deemed necessary to protect the graphite from oxidation. Therefore, the graphite-urania fuel blocks were incased in Zircaloy-3. This not only protected the graphite from oxidation, but also served to contain the fission products.

PRELIMINARY CONSIDERATIONS AND PRIOR DEVELOPMENT

A review of the literature indicated that the development of graphite-urania bodies has been primarily by two methods (1) impregnation of fabricated graphite with a soluble uranium salt, and (2) the fabrication and graphitization of mixtures of graphite materials and uranium oxide. Impregnation of graphite appears to be a feasible process when the graphite pieces are immersed in an aqueous uranyl nitrate solution under vacuum¹. The graphite following the immersion is dried and then heated to convert the nitrate to the oxide. Variations of this process have been reported in which the uniformity of the dispersion and the rate at which it is formed have been improved. The more uniform urania dispersion in graphite was reported to be formed² when the impregnated graphite was treated with ammonia gas to form ammonium diuranate before the conversion to the oxide by heat, and the more rapid impregnation³ resulted when the graphite was immersed in a solution of uranyl nitrate in tertiary butyl alcohol. In this last procedure the alcohol solution is frozen into the graphite pores, and the alcohol is sublimed under vacuum. These procedures rely on the porosity of the graphite, and the uniformity of the uranium dispersion can only be as uniform as the pore structure of the graphite. Thus high density graphite usually has a non-continuous pore structure, and therefore, is the most difficult to impregnate as many pores are not accessible to the impregnating solution.

Some natural occurring graphites such as the Ceylon or Canadian graphites can be cold pressed without binders to densities as high as 2.2 g/cc⁴. Synthetic graphites cannot be cold pressed with any degree

of success as these materials appear to be in the form of thin plates which become aligned under pressure. Thus only thin disks can be molded without pressure cracking. These synthetic graphites are fabricated industrially by mixing them with thermoplastic resins such as petroleum or coal tar pitch⁵. The mixture is pressed or extruded at the softening point of the binder, and the ware formed is then baked at a temperature sufficient to dissociate the binder. The rate of heating must be carefully controlled in order to dissociate the binder without causing it to become sufficiently plastic which would result in distortion in the fabricated piece.

Thermosetting binders such as the phenolic resins have also been used as binders for the synthetic graphites⁶. These resins are mixed with the graphite and urania, molded, and the ware thus formed is heated to polymerize the resin. The use of the thermosetting resin appears to minimize distortion and volume changes during the baking operation. Baked ware fabricated from mixtures of synthetic graphite and either thermosetting or thermoplastic resin binders is in the form of graphite particles held together by a carbon matrix. This carbon may be converted to graphite by heating the ware to temperatures of 2000 to 2500°C.

DEVELOPMENT OF THE FUEL MATRIX

The literature review indicated that both the impregnation of formed graphite, and the fabrication of a synthetic graphite with a resin binder would produce a suitable material for the TREAT fuel, and both of these methods were investigated⁷. A rather porous graphite* was impregnated by immersion under vacuum in each of two solutions: (1) an alcohol-1 weight percent uranyl nitrate solution, and (2) an acetone-1 weight percent

* Great Lakes Carbon Corporation's type G.T. Graphite

uranyl nitrate solution. Following impregnation the samples were dried at 80°C and then heated to 1000°C to convert the nitrate to the oxide.

Impregnation by this method appeared to produce a uniform dispersion of urania in the graphite. However, in each specimen a higher concentration of urania was in evidence on the surface of the graphite specimens as indicated by radiographs, and as the pore structure in the graphite was not uniform, it was difficult to maintain a uniform concentration of urania from specimen to specimen. For this reason the impregnation process was not deemed suitable for the production of a large number of graphite pieces as required by the TREAT reactor.

Fabrication of a graphite-uranium dispersion was initially attempted by molding a mixture of 79% carbon^{*}, 1% UO₂^{**} and 20% of a liquid thermosetting resin^{***}. The molded ware was heated slowly to 1000°C to decompose the resin and drive off the volatile materials. Following this baking the formed ware was graphitized by heating to 2500°C.

Specimens fabricated in this manner had relatively low densities (approximately 1.30 to 1.50 g/cc), and had developed several small cracks in the direction perpendicular to pressing. Radiographs of the specimens also indicated that much of the UO₂ was in the form of small agglomerates.

The apparent pressure cracking and low density was attributed primarily to the carbon, and as the baked samples had good mechanical strength, graphite flour^{****} was substituted for the carbon. This substitution would eliminate the need for graphitization and eliminate

* R. T. Vanderbilt Thermax
** Mallinckrodt Chemical Company
*** Bakelite Company - BKR-2600
**** Achasoa Grade Number 38

the danger of vaporizing urania at high temperatures. The formation of UO_2 agglomerates appeared to be characteristic of the finely divided UO_2 , and in order to achieve a more uniform uranium distribution, U_3O_8 which has a more discrete particle than UO_2 was used as a source of uranium.

Mixtures of graphite flour and 1% U_3O_8 were bonded with both thermosetting* and thermoplastic** resins. These mixtures were formed by pressing at a temperature of 110 to 140°C and a pressure of from 5000 to 10,000 psi. The ware formed was slowly heated to 1000°C (3°C per hour) to dissociate the resin, and following this baking several specimens were graphitized at 2500°C.

The molded pieces baked at 1000°C were found to have good mechanical strength, were free of uranium agglomerates as indicated by radiographic inspection, and were free of apparent pressure cracks. Using thermoplastic resins (petroleum pitch) a maximum density of 1.44 g/cc was obtained with a mixture of 70% graphite-uranium and 30% petroleum pitch. A peak density of 1.70 g/cc was obtained with the thermosetting resin with a mixture consisting of 70 graphite-uranium and 30% resin.

The results of these experiments indicated that a uniform dispersion of urania in graphite having a density of at least 1.60 g/cc could be fabricated by forming a mixture of 79% graphite flour, 1% U_3O_8 and 20% Thermosetting resin. A similar direct process such as this for fabricating graphite had through independent research been developed by Great Lakes Carbon Corporation, and this process appeared to be readily adaptable for fabricating the TREAT fuel.

* Buehler Company Code 1385 AB

** Socorg, Mobil Oil Company - Petroleum Pitch

In order to evaluate the Great Lakes process several samples were manufactured in which 1 weight percent U_3O_8 was dispersed in (1) a graphite base formulation baked, but not graphitized, and (2) a calcined coke base formulation which was baked and samples were graphitized at 1800° , 2150° and $2500^\circ C$. The coke base samples were found to have an average density of 1.74 g/cc when graphitized at $1800^\circ C$, 1.75 g/cc at $2150^\circ C$ and 1.75 g/cc at $2500^\circ C$. These samples were all mechanically sound and no agglomerates of uranium oxide were detectable by radiography. The graphite base samples were found to range in density from 1.68 g/cc to 1.73 g/cc . These samples were also found to be mechanically sound and free of uranium agglomerates.

The examination of these samples indicated the baked graphite material was suitable for the TREAT fuel and that the Great Lakes Carbon Corporation's process was readily adaptable to the manufacture of the graphite-urania dispersion. However, as Great Lakes Carbon Corporation lacked experience in coping with accountability procedures, criticality, and health hazards, the fuel fabrication was resolved as a joint enterprise of both Great Lakes Carbon Corporation and Argonne National Laboratory. Great Lakes also with their production knowledge indicated that a graphite block 8" in length could be formed to a dimensional tolerance which would make machining of the fuel unnecessary, and based on this information the fuel specifications as shown in Table 1 were established.

FABRICATION OF THE TREAT FUEL ELEMENT

Description

The TREAT fuel element is shown in Figure 1. The graphite-uranium section is four feet long and has a C to U^{235} ratio of approximately 10,000 to 1. This section is enclosed in Zircaloy-3 25 mils thick to protect the fuel from oxidation and to contain fission products. To simplify fueling operations, the top and bottom reflector sections are made integral with each fuel element. These reflectors are of ordinary graphite two feet in length, and are incased in 50 mil aluminum. These sections are united to each end of the fuel section, and the extremities are fitted with appropriate aluminum fittings for gripping the fuel element during handling operations, and to align the fuel elements in the reactor. The finished assembly is approximately 9 feet in length and weighs about 100 pounds. Special fuel elements similar in appearance are required for control rod guides (Figure 2), and to provide access slots to the core.

Fabrication of the Fuel Matrix

A flow sheet of the fuel matrix fabrication is shown in Figure 3. The enriched uranium oxide (U_3O_8) was weighed at ANL, and transported to GLC in batch size containers. The graphite, carbon, and pitch were weighed at GLC. These materials were hot mixed for one hour in a Muller type mixer. Following mixing the batch was cooled, transferred to a pulverizer, and crushed. The crushed material was weighed into tared containers with each container holding just enough material for one block. These containers were transferred to a preheated oven and heated

for one hour before the material was pressed into a block. The pressed block was deburred, weighed, loaded into a stainless steel baking crucible, and packed in graphite. Two of these crucibles (about 3 feet in diameter and 3 feet high) were loaded side by side in a baking furnace.

The pressed blocks, containing about 1.5% by weight of hydrogen due to the resin binder, when packed in graphite represent a better moderated mass than the final fuel blocks. It was, therefore, necessary from criticality considerations to limit each crucible to a 1000 pound charge of blocks, and to divide each crucible into quadrants with thermally black boron-stainless steel dividers.

The baking furnace was slowly heated to peak temperature of 950°C, and cooled in a cycle of two weeks. The blocks were removed and brushed clean of adhering packing material.

Inspection of the Fuel Blocks

Radiographs taken of 570 blocks selected so at least one block from each mixed batch was inspected revealed that 94.0% were free of any visible agglomerates, 3.7% had one agglomerate which was estimated to be less than 0.015" in diameter, 1.6% had two agglomerates estimated to be less than 0.15" in diameter, 0.1% (1 block) had three agglomerates of less than 0.15" size and the remaining 0.6% had four or more agglomerates of assorted sizes. The blocks in which four or more agglomerates were found were manufactured from consecutive batches, and at the time these blocks were manufactured the drive belt on the mixer was worn and slipping. It was also found that during the mixing the U_3O_8 was added to the top of the batch and the dust created in mixing had a tendency to stick to the

mixer top. The mixer was repaired, and to prevent the U_3O_8 from sticking to the mixer lid, the cover was cleaned after a short initial mixing period. The blocks from these batches, which incidently included the block in which three agglomerates were found, were rejected.

Fifty blocks picked at random were measured and the bulk densities calculated. These densities were found to range from 1.71 g/cc to 1.76 g/cc. The average density of the fifty blocks was calculated and found to be 1.73 g/cc. Chemical analyses of the fuel for uranium, iron and boron revealed the average composition of the fuel was 0.2% uranium, 0.06% iron, and 0.9 ppm boron.

Thermal Conductivity and Heat Capacity

The thermal conductivity and enthalpy of the graphite-uranium fuel was measured by Armour Research Foundation. The method for measuring the thermal conductivity consisted of measuring the radial heat flow and radial temperature drop in a vertical stack of disks⁹. These measurements were made in the temperature range of 150°-1950°F. After reaching the peak temperature of 1950°F the disks were held at this temperature for a period of 36 hours, and the thermal conductivity was again measured on the cooling cycle. These measurements were about 5% higher than the measurements made during heating as shown by Figure 4. It is not known, at this time, what caused this increase, however, this could have been caused by a loss of volatiles from undecomposed binder. The enthalpy of the graphite-uranium was measured in the temperature range of 387° to 1807°F¹⁰. These values are shown in Figure 5, and the specific heat as calculated is shown in Figure 6.

THERMAL OUTGASSING

Thermal outgassing studies of fired graphite fuel blocks indicate that appreciable quantities of noncondensable gases were evolved at temperatures up to 900°C. Although hydrocarbons, principally methane and ethane which were evolved at 600°C and a pressure of 5 to 6 mm of Hg were reabsorbed on cooling to room temperature, each block produced from 1100 to 1200 cc (STP) of CO and CO₂ which was not reabsorbed on cooling. Since no provision was made for removal of gas from the jacketed graphite fuel during reactor operation it was imperative that the blocks be thermally outgassed before being sealed in evacuated zirconium alloy cans. This was accomplished by heating all blocks for 12 hours at a temperature of 900°C in stainless steel tubes at a pressure of 25 microns or less. The blocks were cooled in vacuum to room temperature in the tubes before being transferred to the Zircaloy-3 cans.

DESCRIPTION OF ZIRCALOY-3 CANS AND METHOD OF FABRICATION

The Zircaloy-3 can material, 25 mils thick, was sheared and machined to $\begin{matrix} +.000 \\ -.005 \end{matrix}$ tolerances before forming into U shaped sections. These tolerances were necessary for proper fit of the zircaloy end caps for welding. Two U shaped sections, 50 inches long were heliarc welded with inert gas cover on both sides of the weld bead. The cans were cut to length and degreased prior to welding in the bottom end cap.

The Zircaloy-3 end cap material, 93 mils thick, was coated with a copper base paint and heated to 1200°F before forming in a die. The copper paint acted as a protective coating during heating as well as lubricant for forming. The caps were sand blasted and pickled before

machining to proper thickness. The top end cap carried a 3/8" O.D. x 11 inch evacuation tube which was heliarc welded in place under inert gas cover.

Four pieces of corrugated 25 mil Zircaloy-3 were spot welded together for a 1/4 inch thick spacer between the fuel and the ends of the zircaloy can. This spacer formed an air gap which acted as an insulator to protect the aluminum reflector cans from overheating during reactor operation.

Four 50 mil Zircaloy-3 tabs were spot welded to each end of the can after the end caps were in place. Each tab had three holes which permitted riveting the two-foot extruded aluminum cans to each end of the Zircaloy-3 fuel can.

In loading the bottom cap was welded into the can, a spacer added, and the can was filled with six graphite-uranium fuel blocks. The top end cap was welded in place completing the fuel subassembly.

FUEL ELEMENT EVACUATION AND SEALING

Loaded fuel cans were assembled on a vacuum manifold and evacuated through the 3/8" O.D. Zircaloy-3 tube. After evacuating the cans for a minimum of 12 hours to a pressure of less than 1 micron, all can and end cap welds were checked for leaks with a mass spectrometer helium leak detector. Leak tested cans were sealed by diffusion welding a 1/2" long section of the 3/8" diameter evacuation tube. All evacuation tube welds were pressured with 15 psi helium for 12 hours followed by a leak test. Tested cans were then ready for assembly into fuel elements.

DESCRIPTION OF FUEL ELEMENT ASSEMBLY

The Zircaloy-3 subassembly containing the graphite-uranium fuel, was attached to the aluminum end sections by means of the Zircaloy-3 tabs. The two end sections are 60 mil wall extruded aluminum tubes, 24 inches long and contain the graphite reflector. The cast aluminum top and bottom fittings are riveted to the aluminum cans completing the assembly.

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TABLE 1. FUEL MATRIX SPECIFICATIONS

Minimum Apparent Density	- 1.72 g/cc
Gross Section Dimensions	- 3.800 $\begin{smallmatrix} +0.020 \\ -0.000 \end{smallmatrix}$
Length of Block	- $8 \pm 1/8"$
Boron Content	- 1 pp Maximum
Iron Content	- 0.1% Maximum
Uranium Content	- 0.248% U_3O_8 (approximately 10,000 to 1 C to U^{235})
Uranium Enrichment	- 93.1%, U^{235}
Dispersion -325 mesh U_3O_8 with no measurable agglomerates.	
Baked stock not graphitized.

Figure 3 First Sheet of Block Fabrication

Figure 11. Thermal Conductivity of Graphite-Iron

Figure 5. Enthalpy of Graphite-Urania to a Datum of 80°F

55

102-4521

Figure 6. Specific Heat of Graphite-Urania

106 - 4524

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Fig. 1 - TREAT Fuel Element

Fig. 2 - Special TREAT Fuel Element

Fig. 1 - TREAT Fuel Element

Fig. 2 - Special TREAT Fuel Element