GEL-ADDITION PROCESS
CHEMICAL STUDIES

— Final Report —

by

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Gel-Addition Process Chemical Studies
— Final Report —

R. V. Carlson

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Irradiation Testing

ABSTRACT

Babcock & Wilcox's Lynchburg Research Center has completed its work on the development of sol-gel and related processes for preparing (U,Pu)O₂ fast reactor fuels. This final report summarizes the technical achievements from July 1, 1966, to June 30, 1971. The program was sponsored by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3714.

The contract was established to further the development of processes for preparing particulate fast reactor fuels and to compare and evaluate the operational characteristics of particulate and pellet fuels in thermal and fast reactors. The chemistry of the B&W Gel-Addition Process, which involves the pickup of plutonium from aqueous solutions by urania gel microspheres, was investigated. The results from a large number of scouting experiments and from a statistically controlled parametric study indicate that this process is a promising means for the preparation of thermal reactor fuels. However, the results for fast reactor fuels are inconclusive.

ORNL precipitation-peptization processes for preparing UO₂ and PuO₂ sols were studied, and a pilot-plant scale system for preparing (U,Pu)O₂ sol-gel microspheres was designed and constructed. About 3.5 kg of (U,Pu)O₂ sol-gel microspheres and 12.5 kg of (U,Pu)O₂ co-precipitated powder, which was fabricated into pellets and shards, were

prepared for irradiation testing in the BAWTR and the EBR-II. A total of 91 fuel pins was assembled. Seventeen capsules—containing one sphere-pac, one vipac, and one pellet pin each—were irradiated in the BAWTR for from 8 hours to 55 days at linear heat ratings of 6, 10, 15, and 20 kW/ft. A 37-pin unencapsulated subassembly, shared with ORNL, is being irradiated in the EBR-II.

Examination of nine of the BAWTR capsules in B&W's hot cell facilities revealed no evidence of center melting in any of the pins. Coarse spheres could be seen next to the cladding in all of the sphere-pac pins examined. Central voids were seen in all pins operated at 10, 15, and 20 kW/ft, but not in those operated at 6 kW/ft. However, the central voids in the fuel operated at 15 kW/ft are somewhat larger than those in the fuel operated at 20 kW/ft.

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1. INTRODUCTION

1.1. Foreword

Fuels for potential fast breeder reactor application are being developed, characterized, and tested in many laboratories. The major effort is being directed toward mixed UO_2 - PuO_2 in two physical forms—pellets and particles. To date, pellet fuels have been studied far more thoroughly than have particulate fuels. However, many fuel pin failures and increases in pin diameter from fuel swelling seem to indicate that pellet oxide fuels may not achieve high enough burnups to make fast breeder reactors economically competitive with present thermal reactors. These pin failures may be caused by highly localized strains resulting from interaction of the fuel and the cladding. Although the solution to the problem of fuel pin integrity involves an understanding of all phases of the interactions of fuel, cladding, and coolant, reducing the stress applied to the cladding by the fuel would certainly be an important advancement.

In fuel rods containing particulate fuels, the concentration of voids per unit volume of fuel is at least 15%; the concentration for high-density pellets is normally between 7 and 10%. Since the average fuel temperature achieved in an LMFBR operation is not high enough to promote extensive sintering near the fuel-cladding interface, this zone of void space is essentially available for accommodation of swelling. Because of its potentially greater capacity to accommodate swelling, particulate fuel should exert lower strains on cladding than does pellet fuel. However, to date, sufficient data are not available to substantiate this potential advantage of particulate fuel. The Gel-Addition Contract between B&W and the USAEC was established to further the investigations of particulate nuclear fuels.

1.2. Contract Background

In 1962 Babcock & Wilcox initiated a pilot plant study¹ of $^{233}\text{UO}_2$ - ThO_2 recycle fuel preparation using the sol-gel flow sheet that Oak Ridge National Laboratory (ORNL) developed during its Kilorod Project.² The process begins with the preparation of a thorium aquasol to which aqueous uranyl nitrate is added. Drying a sol of the proper composition yields a mixed oxide gel that can be fired at temperatures near 1150°C in a reducing atmosphere to produce a UO_2 - ThO_2 solid solution of exceptionally high particle density and uniform composition.

During the pilot plant studies, it was discovered that a mixed gel could be prepared by contacting a single component solid (ThO_2) gel with uranyl nitrate solution, as well as by drying a mixed sol. It was immediately recognized that urania-plutonia and even pure urania reactor fuels could probably be prepared by analogous methods. Early in 1966 B&W applied for a series of patents on the process, now known as the B&W Gel-Addition Process.^{3,4,5}

In June of 1966 the USAEC entered into Contract AT(30-1)-3714 with B&W to investigate the chemistry of this process as it applied to urania-plutonia fuels for fast reactor application. The scope of this one-year contract was limited to initial chemical studies to demonstrate the feasibility of the process. Since these studies gave early indications of success, in February of 1967 the scope and period of performance were increased materially with the broader objective of optimizing the process for producing UO_2 - PuO_2 fuel materials containing about 20% $\text{Pu}/(\text{Pu}+\text{U})$.

1.3. Contract Organization

The work was divided into three phases: Phase I, bench scale studies; Phase II, investigation of unit operations in a scale-up of the process or processes developed in Phase I; Phase III, demonstration through pilot-plant operation that the process or processes provide an economical means of producing fast reactor ceramic fuel. In addition, Phases II and III included an irradiation testing program designed to compare gel-addition fuels with particulate fuels irradiated under other USAEC programs. Phase I and portions of Phase II were completed.

Because of the scope of work required, a formal project organization was established as shown in Figure 1-1. Responsibility for the various technical tasks changed over the 5-year contract period and are listed in chronological order. In addition to those listed in Figure 1-1, a large number of Lynchburg Research Center employees assisted in associated work.

Figure 1-1. Summary of Gel-Addition Contract Organization

1.4. Gel-Addition Studies

The first phase included bench-scale studies of the gel-addition process. The fundamental steps in this process are (1) contacting uranium oxide gel spheres with acidic aqueous solutions of plutonium, (2) pickup of a quantity of plutonium by the spheres, and (3) calcining the resultant material to $\text{UO}_2\text{-PuO}_2$. The gel-addition process has two primary potential advantages over other sol-gel processes: the fuel particles are prepared and sized without commitment of fissionable material and thus without regard to criticality problems; most scrap recycle involves only a single-component system and therefore eliminates the need for chemical separation.

The results from the gel-addition chemistry studies were consistent with the concept of urania gel being an inert, porous material on which plutonium, at least in the trivalent form, was absorbed and desorbed. Mixed oxide with sufficient plutonium content for thermal fuel was readily prepared. However, numerous technical problems were encountered in attempting to prepare mixed oxide with a plutonium content consistently in the region of interest for fast reactor fuels. Therefore, it was decided to utilize a mixed sol process for fuel preparation during Phase II. The fundamental steps in this process are (1) preparing separate UO_2 and PuO_2 sols, (2) blending the sols to obtain the desired Pu/U ratio, (3) forming mixed-gel microspheres, and (4) calcining to obtain $\text{UO}_2\text{-PuO}_2$.

1.5. Irradiation Testing

Late in Phase I the USAEC requested B&W to expand the irradiation testing program to cover the broader scope of qualifying particulate fuel for fast reactor use. A relatively complex program involving irradiations in thermal reactors, TREAT, and EBR-II was considered necessary to obtain data needed to qualify particulate fuel. The program was divided into six subtasks: (1) time required for in-pile restructuring, (2) sorbed gas release, (3) EBR-II tests, (4) thermal conductivity of restructured fuel, (5) sodium-fuel compatibility, and (6) transient tests. However, as a result of limited funds, only subtasks 1 and 3 were activated during this period of the contract.

The objective of the first subtask was to determine the effect of heat rate and time on the restructuring characteristics of sol-gel spheres and of angular particles prepared from coprecipitated UO_2 - PuO_2 powder. Each capsule prepared during this subtask contained at least one pin with high-density pellets and two pins with particulate fuel. Thus, data on particulate fuel could be compared directly with data on pellets of similar smeared densities.

The primary objective of the third subtask was to obtain data on the operational characteristics of particulate fuels irradiated in a fast reactor. The effect of heat rate and burnup on the overall performance of sol-gel spherical particles and of angular particles and pellets prepared from coprecipitated powder will be compared and evaluated. Twenty-eight unencapsulated pins will be irradiated in 18 positions of a 37-pin subassembly shared with ORNL. This subassembly was placed in the EBR-II in May 1971.

1.6. Contract Objectives

The primary objectives during FY-1967 were (1) to investigate the gel-addition process for preparing urania-plutonia fuels and (2) to determine whether this process was potentially applicable to fast reactor technology. As mentioned previously, the scope and period of the contract were increased substantially during the first year when early indications of success became evident.

For FY-1968 the primary objectives initially were (1) to continue investigating gel-addition chemistry and, if possible, to optimize the process for preparing fast reactor fuels on a bench scale, and (2) to prepare sufficient fuel and to load pins for initiating subtask 1 of the irradiation program in the Babcock & Wilcox Test Reactor (BAWTR). During the fiscal year it was decided to shift the primary fuel preparation studies from the gel-addition process to a mixed-sol process, and development of a pilot plant was initiated at that time.

For FY-1969 the primary objectives initially were (1) to complete the development and construction of a pilot plant for preparing at least 1 kg of UO_2 -20% PuO_2 per day by a mixed-sol process, (2) to prepare sufficient fuel pins to complete subtask 1 of the irradiation program, (3) to complete the irradiations scheduled under subtask 1, and (4) to

initiate subtask 2 of the irradiation program. However, after the first quarter, the contract schedule was radically changed at the request of the USAEC. Pilot plant construction and subtask 2 of the irradiation program were suspended, and the number of capsules to be irradiated under subtask 1 during FY-1969 was reduced from 17 to 7.

The primary objectives during FY-1970 were (1) to prepare fuel and fabricate fuel pins for the first subassembly to be irradiated in EBR-II under subtask 3 of the irradiation program, (2) to irradiate additional capsules scheduled under subtask 1, and (3) to initiate post-irradiation examination of the fuel pins irradiated in the BAWTR.

Before B&W could initiate the FY-1971 work, the USAEC stated that funding limitations would probably require suspending support for sol-gel development for several years beginning with FY-1972. Therefore, the gel-addition contract was renegotiated with a reduced scope of work to be completed by June 30, 1971. The primary objectives for FY-1971 were (1) to prepare sufficient fuel and fuel pins to complete the requirements for the EBR-II subassembly, (2) to continue post-irradiation examination of the capsules previously irradiated in the BAWTR consistent with the funds available, and (3) to close out all contract activities.

In general, the contract objectives were met. Details of the work performed in all technical areas of the program have been reported in Quarterly and Topical Reports.⁶⁻²⁵ Accomplishments made during the program are summarized in the remaining sections.

2. RESULTS AND CONCLUSIONS

2.1. Gel-Addition Chemistry

The results from early experiments indicated that urania gel spheres could sorb plutonium to a concentration of about 20% Pu/(Pu + U). However, these results were not reproducible and were probably clouded by a Pu(IV) hydrolysis reaction. The results of a test program designed to investigate the gel-addition variables under statistically controlled conditions led to the following proposed mechanisms for the interaction of aqueous plutonium solutions with urania gel:

- In solutions containing Pu(III), the urania gel behaves mainly like a porous, inert material into which the plutonium solution is absorbed and from which it can be washed with water.
- In solutions containing Pu(VI), a chemical reaction apparently occurs between the plutonium solution and the urania gel, and leads to a concentration of plutonium on the outer surface of the gel.
- In solutions containing Pu(IV), the urania gel behaves mainly like a porous, inert material, but—as opposed to Pu(III)—it is nearly impossible to wash the plutonium from the spheres with water.

The results from a series of experiments attempting to fix Pu(III) in urania gel were promising. At the conclusion of this work, it had been shown that $\text{UO}_2\text{-PuO}_2$ with a plutonium content sufficient for thermal fuels could be readily prepared by the gel-addition process. However, the applicability of this process for preparing fast reactor fuel is uncertain.

2.2. Fuel Preparation

About 3.5 kg of UO_2 -20% PuO_2 sol-gel microspheres and 12.5 kg of UO_2 -20% PuO_2 coprecipitated powder were prepared for the irradiation program. A modified ORNL formate process for preparing UO_2 sols and the ORNL precipitation-peptization process for preparing PuO_2 sols were generally quite reliable on a laboratory scale so long as reasonable care was taken to minimize marked deviations from the flow-sheets. Large gel microspheres (oxide diameters of 420 to 595 μ) were prepared by dehydrating mixed sol droplets, which were fluidized by a counter current flow of an organic desiccant in a tapered glass column. Small gel microspheres (oxide diameters $<44\mu$) were prepared by a stirred-pot technique. Both laboratory scale and pilot plant scale spheroidizing systems were built and operated successfully. The mixed oxide powder was prepared by continuous coprecipitation of ammonium diuranate-plutonium hydroxide from uranium-plutonium nitrate solutions in equipment having a capacity of over 2 kg/shift.

2.3. Fabrication of Irradiation Specimens

The irradiation program required UO_2 -20% PuO_2 fuel in three physical forms: microspheres, shards, and pellets. The pellets were fabricated from coprecipitated powder by a cold-press and sintering process, and the shards were fabricated by crushing slugs or pellets to the required size fractions.

A total of 91 fuel pins was loaded for the irradiation program—31 containing microspheres, 30 containing shards, and 30 containing pellets. The microspheres were loaded by the sphere-pac process, and the shards were loaded by the vipac process. Both processes are vibratory compaction techniques. Sphere-pac involves imparting significantly less energy to the fuel than does vipac—the shaker head is vibrated at about 60 Hz as compared with 200-5000 Hz for vipac. It was found the spheres could be loaded more rapidly and to a higher density if the vibration contained a lateral component rather than pure axial vibration. For vipac, it was found that the packing efficiency for the 13.5-inch fuel length required in the EBR-II pins was less than for the 4.5-inch fuel length in the BAWTR pins. Therefore, a sequential loading technique was used for loading shards into the EBR-II pins.

2.4. Irradiation Testing

A comprehensive program of irradiations in thermal reactors, TREAT, and EBR-II was developed to provide data needed to qualify particulate fuel for fast reactor use. However, USAEC funding limitations reduced the scope of the program to a series of irradiations in the BAWTR and a portion of an experimental subassembly in EBR-II.

The series in the BAWTR was designed to evaluate the effects of heat rate and time on the restructuring characteristics of sol-gel UO_2 - PuO_2 spheres and of angular particles and pellets prepared from coprecipitated UO_2 - PuO_2 powder. Sixteen capsules containing three pins each—one vipac, one sphere-pac, and one pellet—were irradiated in the thermal flux of the BAWTR for from 8 hours to 55 days at linear heat ratings ranging from 6 to 20 kW/ft. Nine of the capsules were disassembled in B&W's hot cell facilities, and the 27 fuel pins contained in these capsules were partially examined. Visual examinations and gamma scans revealed no failures, swelling, or other abnormalities in any of the pins. Preliminary metallographic examination of 22 of the pins revealed central voids in all pins operated at 10, 15, and 20 kW/ft, but not in those operated at 6 kW/ft. However, the central voids in the fuel operated at 15 kW/ft are somewhat larger than those in the fuel operated at 20 kW/ft. Coarse spheres were seen next to the cladding in all of the sphere-pac pins.

The EBR-II irradiation program was designed to compare and evaluate the effects of heat rate and burnup on the overall performance of pellets, spherical particles, and angular particles in a fast neutron flux. Twenty-eight unencapsulated pins are scheduled to be irradiated in EBR-II to burnups of from 25,000 to 100,000 MWd/tonne at 14 to 16 kW/ft as part of a 37-pin subassembly being shared with ORNL. The subassembly was inserted into the EBR-II in May 1971, but no results are available at this time.

3. GEL-ADDITION CHEMISTRY

3.1. Foreword

A series of scouting experiments at B&W's Lynchburg Research Center showed that thoria gels can sorb large quantities of uranium from aqueous uranyl nitrate; that is, hexavalent uranium in solution can associate in some way with quadrivalent thorium in oxide gel form to yield mixtures containing as much as 35% uranium. At the same time, other ions, such as Ra(II) and La(III), were apparently rejected or at least were not sorbed in quantities approaching the uranyl ion values. Moreover, little or no thorium appeared in the aqueous solution at the conclusion of the experiments. These facts suggested that urania-plutonia and even pure urania reactor fuels could be prepared by analagous methods and led to a series of patents^{3,4,5} now known as the B&W Gel-Addition Process. The fundamental steps in this process are (1) contacting uranium oxide gel spheres with acidic solutions of plutonium, (2) pickup of a quantity of plutonium by the spheres, and (3) calcining the resultant material to $\text{UO}_2\text{-PuO}_2$.

3.2. Feed Materials

Urania gel microspheres for the contacting experiments were obtained from three different sources—Nuclear Fuel Services (NFS), ORNL, and B&W's Lynchburg Research Center. The NFS material was used in preliminary work, the B&W material was used in most of the experiments, and the ORNL material was used in a series of experiments designed to determine the effect of gel history on the process. B&W used a modification of the ORNL formate process²⁶ to prepare UO_2 sol. The urania gel microspheres were prepared by both stirred-pot and column techniques.¹⁵

The plutonium for this program was obtained as quadrivalent nitrate solution, which was about 1 M Pu and 3-6 M nitric acid.

Experiments were conducted with trivalent, quadrivalent, and hexavalent plutonium. A number of reductants will reduce quadrivalent plutonium to the trivalent form, and hydroxylamine hydrochloride and hydrazine hydrate were used in this program.^{27,28} Two methods of producing hexavalent plutonium were used—oxidation of quadrivalent plutonium by sodium bismuthate,²⁷ and oxidation by reflux in dilute nitric acid.^{27,29}

3.3. Experimental Technique

Most of the plutonium solution-urania gel contacting experiments were conducted by one of two techniques. Early experiments utilized batch contacting, in which the solution and gel are placed in a container and gently agitated for a prescribed period of time. A photograph of such an experiment in progress is shown in Quarterly Progress Report No. 2.³⁰ Following the contacting, the spheres were recovered by decanting or filtering. Then, in many of the experiments, the spheres were washed with water, acetone, or ethanol. Finally, the spheres were dried in a vacuum oven and fired in a reducing atmosphere to $\text{UO}_2\text{-PuO}_2$.

Later in the program, contacting was performed by passing the solution through a bed of spheres. A wide variety of techniques was used to recycle solution and to pass fresh solution through the sphere beds. The final treatment for the contacted spheres was similar to that summarized for the batch contacting experiments.

3.4. Experimental Results

Several early experiments^{31,32} indicated that the urania gel spheres could sorb plutonium to a concentration of about 20% Pu/(Pu + U) from a weakly acidic quadrivalent plutonium nitrate solution. However, these results were not reproducible. One of the effects routinely observed during the contacting experiments was an increase in the pH of the solution. Quadrivalent plutonium will hydrolyze in solutions with an acidity of less than about 0.1 M and form a precipitate. Therefore, a hydrolysis reaction of this kind probably occurred in the early experiments, causing a portion of the precipitate to remain on the spheres when they were sampled for analysis.

The bench-scale experiments conducted during FY-1967⁶⁻¹⁰ indicated that the gel-addition process depends on several variables:

plutonium oxidation state, plutonium concentration, solution acidity, contact time, contact temperature, and sphere history.

A test program was conducted³³ to investigate these variables under statistically controlled conditions. The objectives were as follows:

1. To determine which variables significantly affect the plutonium sorption and to measure the magnitude of the effect.
2. To identify significant interactions between two or three variables and to measure the magnitude of the interactions.
3. To determine the optimum combination of the variables to maximize the amount of plutonium pickup.
4. To ascertain the reproducibility of the pickup process.

This test program was not designed to provide definitive evidence of the applicability of gel-addition as a process for preparing fast reactor fuel, but to identify significant trends in the gel-addition process as well as areas requiring additional experiments.

Owing to the large number of previous contacting experiments, it was relatively easy to select values for the variables of interest. The only restrictions were that the effect of each factor had to be tested at three different levels and that the intermediate value should be midway between the extremes. Since trends can be extrapolated, no attempt was made to test at the limits of experimental capability. The following test conditions were selected because they encompassed most of the experimentally accessible regions and were readily attainable:

Plutonium oxidation state	III, IV, and VI
Plutonium concentration, <u>M</u>	0.30, 0.60, and 0.90
Solution acidity (pH)	
Pu(III), Pu(VI)	0.5, 1.5, and 2.5
Pu(IV)	0.2, 0.5, and 0.8
Contact time, minutes	10, 125, and 240
Contact temperature, C	3, 30, and 57

To avoid biases caused by differences in urania sphere history, a homogeneous stock blend containing about 1.4 kg of gel spheres was prepared. For each contacting experiment, 5.0 g of the blend was sealed in a 125-ml serum bottle containing a nitrogen atmosphere and less than 0.1% oxygen. For each contacting test, 6.45 g of previously prepared plutonium solution was syringed into the serum bottle. As quickly as possible, the bottle was placed in either an ice bath or a heated sand bath on a thermovibrator (Precision Scientific Company, Chicago) and agitated gently for the desired test period. At the end of each run, the solution was decanted, and the spheres were rinsed once with 5 ml of demineralized water. The water rinse, which was performed by rapidly adding the water, swirling the bottle twice, and immediately decanting, removed most of the contact solution adhering to the surface of the spheres. The spheres were then dried in a vacuum oven and sieved on a 40-mesh screen. The entire +40 mesh split was submitted for uranium and plutonium analyses.

The technique of analysis of variance (at the 95% confidence level) was used to identify the variables that significantly affect plutonium pickup. The effect of each variable was first tested under the assumption that the interactions between two or more of the variables are negligible. Then, by testing all possible combinations of two variables, trend dependence on the interactions between two factors was identified.

The results of over 150 contacting experiments are shown in Figures 3-1 to 3-3. Pickup mechanisms that are consistent with most of the data were proposed.³³ In solutions containing Pu(III), the urania gel behaves mainly like a porous, inert material into which the plutonium solution is absorbed and from which it can be washed by water. Therefore, the increase in pickup with increasing plutonium concentration is as expected. The slow increase in pickup with increasing length of contact may indicate that a slow chemical reaction between the plutonium and the urania gel is also taking place. However, since the pickup does not vary with temperature, perhaps a more reasonable explanation is that longer periods of time are required for the plutonium solutions to penetrate the smaller pores in the gel. Perhaps the increasing sphere attrition results in the closing of a number of pores, which prevents the plutonium from being washed out. Solubility product data indicate

that Pu(III) should be soluble at the pH values used in these experiments.³⁴ Hence, because of the washing technique and the possibility that the open sphere porosity depends on the contact conditions, it seems reasonable to assume that the washings were not conducted in a reproducible manner; therefore, the experimental error of 2.9%, determined from a number of duplicate contactings, can be attributed (in part) to the partial and irreproducible removal of plutonium by washing with water.

In solutions containing Pu(VI), a chemical reaction apparently occurs between the plutonium solution and the urania gel. The marked increase in pickup at higher contacting temperatures lends strong support to this proposal. In addition, alpha autoradiographic evidence is consistent with a reaction pickup mechanism.³⁵ This evidence shows that essentially all of the plutonium is concentrated in a shell around the outer surface of a urania-gel sphere. If Pu(VI) is being picked up by exchange with uranium or by chemi-adsorption at the surface, then an increase in plutonium content should be expected with increasing plutonium concentration, contact time, and temperature.

In solutions containing Pu(IV), the urania gel again apparently behaves mainly like a porous, inert material. In this case—as opposed to Pu(III)—it should be nearly impossible to wash the plutonium from the sphere with water because $\text{Pu}(\text{OH})_4$ is much less soluble in weak acid solutions than is $\text{Pu}(\text{OH})_3$, and the pH rises sufficiently during contact to convert nearly all the Pu(IV) to the even more water-insoluble polymeric form.³⁴ Hence, the experimental error of $\pm 1.2\%$ is much less for the Pu(IV) contact than for Pu(III). For the Pu(IV) experiments, the bulk of the error could be caused by the difficulty in preparing Pu(IV) solutions at pH values from 0.2 to 0.8 in an identical manner. This problem arises from the nonreproducible hydrolysis of Pu(IV) if the rate and method of pH adjustment are not carefully controlled. The slow increase in Pu(IV) pickup at longer contacting times and higher temperatures is not necessarily inconsistent with the proposed mechanism. The pH of a Pu(IV) contact solution increases very rapidly and thus produces large polymeric particles. Most of these particles are undoubtedly too large to enter the pores of the urania-gel spheres. However, over prolonged contact periods and at elevated temperatures, it is reasonable to expect a portion of the smaller particles to enter the spheres.

Based on the results of the statistically controlled experiments, a number of techniques for fixing Pu(III) in the spheres were tested. These include (1) oxidizing Pu(III) to Pu(IV) while the solution was in contact with spheres,^{33,36} (2) treating the urania spheres with gaseous ammonia before contacting with Pu(III), (3) treating the spheres with aqueous ammonia before contacting, (4) homogeneous increase of pH during contacting to precipitate the plutonium, and (5) contacting under vacuum.³⁶ Although these experiments produced some promising results, they could not be explored because of the limited time available for preparing fuel for the irradiation program.

Figure 3-1. Effects of Variables on Pu(III) Pickup

Figure 3-2. Effects of Variables on Pu(VI) Pickup

Figure 3-3. Effects of Variables on Pu(IV) Pickup

4. FUEL PREPARATION

4.1. Preparation of UO_2 - PuO_2 Sol-Gel Microspheres

About 3.5 kg of acceptable UO_2 -20% PuO_2 microspheres and 12.5 kg of UO_2 -20% PuO_2 coprecipitated powder were prepared for the gel-addition irradiation program. The ^{235}U content of the fuel ranged from depleted to fully enriched.

A detailed account of the techniques involved in preparing UO_2 - PuO_2 sol-gel microspheres is presented in BAW-3714-10.¹⁵ Therefore, the process is briefly summarized in the following paragraphs.

4.1.1. Preparation of UO_2 Sol

The UO_2 sol feed for the spheroidizing process was prepared by the modified ORNL formate process²⁶ as summarized in Figure 4-1. This flowsheet was found to be quite reliable on a laboratory scale provided that reasonable care is taken to minimize marked deviations from the stated conditions. The following items merit special attention when using this process:

1. The U(VI) must be reduced for the proper length of time; if the UNH solution is reduced either too long or too little, a stable sol cannot be prepared.

2. A good inert atmosphere must be maintained above the U(IV) during processing and storage. This is extremely critical before the sol is formed; sols in storage have been stable with U(IV) contents as low as 75%.³⁷⁻³⁹

3. The filter cake must be washed properly; improper washing caused rejection of a number of sol batches in early work.⁴⁰

When working with fully enriched uranium, it was necessary to increase the urea-to-uranium mole ratio to 0.6 in the solution being reduced in order to maintain tolerable reduction times.⁴¹ Also,

when the urea-to-uranium mole ratio was increased to 0.8 with fully enriched UNH solutions, the resultant sol was only semistable and therefore undesirable.^{42,43}

Sols were stored without difficulty when covered with an inert gas. Some UO_2 sols were stored for one year without noticeable deterioration.

Figure 4-1. B&W Flowsheet for Preparing UO_2 Sols

4.1.2. Preparation of PuO_2 Sol

The PuO_2 sols were prepared in batches using the ORNL precipitation-peptization flowsheet⁴⁴ as shown in Figure 4-2. This flowsheet is satisfactory for laboratory-scale amounts provided that the initial precipitation conditions are followed closely. If the free HNO_3 concentration is not $< 2 \text{ M}$ and the NH_4OH concentration is not $< 4 \text{ M}$, it is essentially impossible to form a stable PuO_2 sol.⁴⁵ The other critical step in the flowsheet is thermal denitration. If the nitrate-to-plutonium mole ratio is reduced to less than about 0.1, the solids cannot be resuspended.

Figure 4-2. Flowsheet for Preparing PuO_2 Sols

4.1.3. Sphere Formation

The basic process used to form the urania-plutonia microspheres involved (1) blending UO_2 and PuO_2 sols to obtain the desired Pu/U ratio, (2) dispersing aqueous sol droplets of controlled diameter into an organic desiccant, (3) fluidizing the droplets until enough water is removed to form rigid gel particles, and (4) firing the gel to the mixed oxide. However, different techniques were needed for the two sizes required. To prepare large microspheres (oxide diameters of 420 to 595 μ), a two-fluid nozzle was used to inject sol droplets into a tapered glass column; a counter-current flow of 2-ethyl-1-hexanol (2-EH) then fluidized the droplets until dry. To prepare small microspheres (oxide diameters $<44 \mu$), sol droplets were syringed into a pot and fluidized by stirring the 2-EH rapidly. Both laboratory-scale and pilot-plant scale systems⁴⁶ were used to form the microspheres.

Truly spherical particles cannot be prepared by injecting aqueous sol into pure 2-EH. Surfactants must be added to the 2-EH to prevent the sol droplets from clustering or from sticking to the walls of the column and to prevent the formation of gel particles with concave sides (often called cherry pitted) or irregular shapes (often called raisin shaped). Experience has shown that from 0.3 to 0.7 vol % Span-80 (Atlas Chemical Industries) will prevent clustering, sticking, or the formation of cherry-pitted particles, and that from 0.3 to 0.7 vol % Ethomeen S/15 (Armour Industries) will prevent the formation of raisin-shaped particles. A scouting experiment^{38,47} intended to determine optimum surfactant levels in 2-EH showed that the concentrations must be varied depending on the nature of the sol. Therefore, until the interactions involved in forming spherical particles with this type of system are better understood, a trial-and-error technique must be used to determine the quantities of surfactants for a given run. This involves selecting a surfactant level, preparing a few grams of microspheres, examining the spheres under a microscope, and then readjusting the surfactant concentrations until the desired product is obtained. The proper conditions can usually be found after three or four trial batches have been prepared.

After removing sufficient water from the sol droplets to form rigid gel particles, the spheres were removed from the 2-EH,

soaked in aqueous ammonia, rinsed with ethanol, and dried. They were then transferred to a box furnace for firing. The firing cycle was complicated because the carbon in the gel had to be oxidized without oxidizing the gel to a point that would cause the spheres to crack. In addition, unless the carbon is removed before excessive sintering occurs, a low-density product will result. After carbon removal, the metal must be reduced to obtain an O/M ratio of about 2.00. The following cycle was selected after a series of tests with UO_2 :⁴⁸

<u>Under CO_2 Atmosphere</u>	<u>Under N_2-6% H_2 Atmosphere</u>
Heat to 450C at 50 C/h	Heat to 1250C at 200 C/h
Heat to 600C at 25 C/h	Hold at 1250C for 4 h
Heat to 900C at 50 C/h	Cool to room temperature
Hold at 900C about 2 h	

After firing the mixed-gel microspheres, the oxide was screened to separate the desired sizes from the remainder of the product. The coarse sphere fraction was then passed over a roundometer (Wald Industries, Inc.) to separate the rounds from the non-rounds.

The preparation of UO_2 - PuO_2 microspheres containing depleted uranium, 20% enriched uranium, and fully enriched uranium is fully described in references 49 through 55.

4.2. Preparation of Coprecipitated Powder

The pellets and shards required for the irradiation program were fabricated from coprecipitated urania-plutonia powder. These mixed oxide powders were prepared by continuous coprecipitation of ammonium diuranate-plutonium hydroxide from uranium-plutonium nitrate solutions. The dried precipitates were converted to an acceptable feed for pelletizing by calcining and ball milling. Figure 4-3 summarizes the flow-sheet. The pH was held at about 9.5 during precipitation to ensure homogeneity of the plutonium and uranium in the powder.^{56,57}

The laboratory prepared a total of 2.6 kg of 20% PuO_2 in natural UO_2 ,⁵⁸ 1.3 kg of 20% PuO_2 in UO_2 enriched to 20% ^{235}U ,⁵⁸ and 8.5 kg of 20% PuO_2 in fully enriched UO_2 .^{42,59,60} Since several batches of this powder had a high aluminum content (~5000 ppm), the aluminum content

of all the feed solutions and the intermediate products was checked; the major source of the impurity was found to be the high-density alumina balls used in milling the calcined powder.⁴² This problem was solved by using tungsten carbide balls in subsequent processing.

The capacity of the continuous coprecipitation equipment is over 2 kg/shift. However, the throughput was restricted to less than 2 kg to ensure nuclear safety for this process by limiting the mass of fissile material permitted in the system. Thus, the throughput was limited to 315 g (on a metal basis) per shift when preparing the 20% PuO_2 in fully enriched UO_2 powder. As a result, material holdup in the large equipment reduced the average yield to about 90%.

Figure 4-3. Flowsheet for Precipitation of UO_2 -20% PuO_2 by Continuous Coprecipitation Process

5. FABRICATION OF IRRADIATION SPECIMENS

5.1. Foreword

Fuel in three physical forms—microspheres, shards, and pellets—was required for the irradiation program (see section 6). Fabrication of the microspheres is summarized in section 4.1. The shards and pellets were fabricated from coprecipitated powder by the techniques summarized below.

A total of 91 fuel pins was loaded for the irradiation program: 30 containing pellets, 30 containing shards, and 31 containing microspheres. The particulate fuels were loaded by vibratory compaction techniques, which are commonly referred to as sphere-pac for microspheres and vipac for shards. The methods of loading fuel pins are also summarized below.

5.2. Fabrication of Pellets

Pellets for the irradiation program were prepared from coprecipitated powder by the standard cold-press and sinter technique. Pellets for the BAWTR pins were fabricated⁶¹ with a manually operated hydraulic press, which prepressed the powder into slugs at 40,000 to 60,000 psi. The slugs were hand-granulated through a 20-mesh screen to produce a free-flowing feed for final pressing at 40,000 psi. Pellets for the EBR-II pins were fabricated by adding binder and lubricant to the powder, granulating, and pressing on an automatic mechanical press.⁶²⁻⁶⁷

Pellets were densified by sintering in a high-temperature, cold-wall vacuum furnace. The pellets were then loaded into the furnace, which was evacuated to about 50 microns and backfilled with N_2 -6% H_2 . When backfilling was completed, a N_2 -6% H_2 flow rate of about 4 liters/minute was established while a positive pressure of about 2 psi was maintained within the furnace chamber.⁶¹ The precise firing cycle to

densify each batch of pellets to specification was determined by sinterability tests. In general, the temperature was raised to 1650C at 330 C/hour, held for one hour, and lowered to 800C at 330 C/hour. When a temperature of 800C was reached, the power was turned off and the furnace was allowed to cool to room temperature. The sintered pellets were removed, and geometric densities were determined. Pellets for the EBR-II irradiation subtask were then centerless ground to the specified diameter. Before loading, samples were taken for final acceptance.

5.3. Fabrication of Shards

The shard material for the irradiation program was obtained by selecting pellets fabricated according to the technique summarized in section 5.2 and crushing them to the required size fractions.⁶¹ These pellets were selected solely on the basis of the percentage of theoretical density of each individual pellet. The pellet density is important because the packed density must fall in the range of densities specified for the irradiation tests. This range can be determined from the equation,

$$\text{bulk density} = \text{packing efficiency} \times \text{particle density}.$$

For this work, the packing efficiency was assumed to be 88%.⁶⁸

Pellets with densities within the desired range were selected and crushed in a hardened steel mortar. The crushed pellets were separated into coarse size, 60 wt % - 12 + 16 mesh, followed by the intermediate size, 25 wt % - 100 + 140 mesh, and finally, the fine fraction, 15 wt % - 325 mesh. These size splits were selected on the basis of previous work.^{69,70,71}

5.4. Loading of Pellet Pins

Before loading the fuel, bottom end caps were welded in place on empty fuel pins, and the welds were helium-leak-checked. To protect the end of the pin from contamination during loading, 0.001-inch shim stock was rolled and inserted into the pin to a depth of about 3/8 inch. The pellets and internal hardware were loaded through this shim.

The shim stock protruding from the pin was then bent closed, and the pins were bagged from the glovebox and decontaminated. The loaded pins were then transferred to the alpha weld box for end cap insertion, back filling with helium or a helium-argon mixture, and fusion welding. After the pins were welded, they were helium-leak-checked and X-rayed for final acceptance.⁶¹ Pins for the EBR-II irradiations subtask underwent xenon tagging and additional nondestructive testing.⁷²

Loading data for the BAWTR pins are presented in a topical report,⁷³ and loading data for the EBR-II pins are summarized in several quarterly reports.^{64,65,67}

5.5. Loading of Vipac Pins

The vipac facility consists of the main glovebox, where fuel is loaded into the pin, and a contamination-prevention box, which is kept free of radioactivity. The open end of the empty pin is sealed into the bottom of a plastic bag with tape. The bag is then affixed to a glove port on the bottom of the main glovebox. The welded end of the pin is held at the end of an extension rod leading down through another plastic bag on a glove port in the bottom of the contamination-prevention box, and is finally attached to the head of an electromagnetic shaker located outside both boxes.

Once the pin was secured, the bottom insulator pellets were loaded. A funnel was placed in the end of the pin, and a pre-weighed quantity of shards sufficient to fill the pin to the specified height was introduced while the shaker head was vibrating. The funnel was removed and replaced by a push rod with a weight attached. The shaker head was vibrated at frequencies between 5000 and 200 Hz until the specified fuel height was achieved.⁶¹ The final steps in completing the pins were similar to those described for pellet pins.

It was difficult to load EBR-II pins to the desired fuel smeared density. The packing efficiency for the 13.5-inch fuel length required for the EBR-II pins was less than observed for the 4.5-inch fuel lengths for the BAWTR pins. Several attempts were made to increase the packing efficiency by varying both the particle size distribution of the shards and the packing technique. However, it appeared that the packing efficiency was limited by the ratio of the fuel length to the pin diameter.

In order to load the EBR-II pins at an energy low enough to eliminate the possibility of pin damage during loading, the shards were loaded sequentially in three 4.5-inch segments.⁶⁵

Loading data for the BAWTR pins are presented in a topical report,⁷² and data for the EBR-II pins are summarized in two quarterly reports.^{65,67}

5.6. Loading of Sphere-Pac Pins

A variety of vibrational frequencies and modes of input were tested for the vibratory compaction of microspheres. Although frequency seemed to have little effect on packed density, a frequency of about 60 Hz provided the best loading rate. Vibration methods that included a lateral component gave faster packing and higher densities than did pure axial vibration. Thus, a small Syntron vibrator was mounted on a 45-degree incline with the associated pin clamping device as designed by ORNL. The fuel cladding was placed in the vibrator clamping device, and centerless-ground insulator pellets were loaded into the tubing. A pre-weighed quantity of coarse microspheres (420-595 μ diameter) was poured into the pin, and a funnel, whose lower end was covered with a screen, was inserted into the tubing until it rested on top of the coarse bed. This assembly was vibrated for approximately 2 minutes at an axial acceleration of about 2 gs. Next, a pre-weighed quantity of fine microspheres (<44 μ diameter) was poured into the funnel, a follower rod was inserted, and the assembly was vibrated at an axial acceleration of about 7 gs until all the fine microspheres infiltrated the coarse bed.⁶¹ The final steps in completing the pins were similar to those described for pellet pins.

Loading data for the BAWTR pins are presented in a topical report,⁷² and data for the EBR-II pins are summarized in two quarterly reports.^{65,67}

6. IRRADIATION TESTING

6.1. Foreword

The initial irradiation program under this contract was designed to determine the performance of vibratory compacted gel-addition urania-plutonia under fast-reactor operating conditions. Irradiations were planned for both the BAWTR and the EBR-II.

The tentative BAWTR irradiation program was designed to determine the irradiation performance of gel-addition fuel and to compare it with coprecipitated powder fuel. Of the fuel and operational variables considered for evaluation in the irradiation program, six were selected:⁷³ impurity level, absorbed gas and fission gas release, thermal conductivity, high-burnup behavior, cyclic operation, and fuel-sodium compatibility.

Late in Phase I, the USAEC requested B&W to expand the irradiation program to cover the broader scope of qualifying particulate fuel for fast reactor use. Fuels in the form of spherical particles, such as those produced by a sol-gel process, and angular particles, such as those produced from crushed slugs or pellets, were included in the program.

6.2. Irradiation Program Description

A comprehensive program involving irradiations in thermal reactors, TREAT, and EBR-II was considered necessary to provide data to qualify particulate fuel. The program was divided into six subtasks:

1. Time Required for Inpile Restructuring.
2. Sorbed Gas Behavior.
3. EBR-II Tests.
4. Thermal Conductivity of Restructured Fuel.
5. Sodium-Fuel Compatibility.
6. Transient Tests.

The objectives of each of these subtasks⁷⁴ are identified below. Because some of the data required would become available from the national program, it was not possible to establish the scope of each subtask at the beginning of the program.

6.2.1. Time Required for Inpile Restructuring

The effect of heat rate and time on the restructuring characteristics of sol-gel spheres and of angular particles prepared from coprecipitated $\text{UO}_2\text{-PuO}_2$ was to be determined. Each capsule in this task contained at least one pin with high-density pellets and two pins with particulate fuel. Thus, the performance of particulate fuel could be compared directly with that of pellets of similar smeared densities.

6.2.2. Sorbed Gas Behavior

The rate of gas release from reactor-exposed particulate fuel was to be determined. Capsules were to be irradiated under static and cyclic power conditions at different heat rates. The pressures within the fuel pins were to be monitored continuously to determine the extent of the gas release and the approximate average fuel temperature at which the release occurred. Some of the irradiations were to be continued for about 30 days to determine whether the gases were reabsorbed by the fuel and/or cladding.

6.2.3. EBR-II Tests

The EBR-II irradiations were designed to obtain statistical data on fuel performance in a fast reactor. In this program, the overall irradiation performance of sol-gel spherical particles and of angular particles and pellets prepared from coprecipitated particles were to be compared and evaluated at two different heat rates.

6.2.4. Thermal Conductivity of Restructured Fuel

The thermal conductivity of restructured fuel was to be determined. The scope of this subtask was to be defined more clearly after a thorough review of the national program.

6.2.5. Sodium-Fuel Compatibility

This subtask was designed to determine the compatibility of particulate fuel with the sodium coolant. There are two potential types of fuel pin defects: those occurring during the initial startup when the sodium can infiltrate the as-fabricated powder, and those occurring after the fuel has been restructured.

The effect of sodium infiltration on sodium logging and sodium-fuel compatibility can be determined in static capsules. However, in a static capsule, it is difficult to assess fully the sodium-fuel compatibility after restructuring occurs because the flow rate of the coolant and the solubility of $\text{UO}_2\text{-PuO}_2$ in sodium can significantly affect the extent of the interaction. Hence, this subtask was designed to evaluate only the effect of the infiltration. The effect of the fuel rod failure late in life is best evaluated in an inpile sodium loop, but outpile studies on defected exposed fuel were expected to yield valuable data.

6.2.6. Transient Tests

Data were required to define the effects of transients on fuel movement in the fuel's as-fabricated and restructured conditions and to establish the allowable transients in each case. Also, transient testing of fuel during operation at temperature was required to define further the operational limitations. The required testing was to be established after the national program had been evaluated more thoroughly.

6.3. Time Required for Inpile Restructuring

Each capsule under this subtask included one pin of high-density pellets and two pins of particulate fuel. A fuel smeared density of about 82% theoretical was selected for all pins because this appeared to be about the maximum density that could be readily achieved for the sphere-pac pins. Thus, the restructuring characteristics of particulate fuels could be compared directly with those of pellets after inpile operation under nearly identical conditions.

Seventeen capsules were scheduled to be irradiated in the BAWTR. The design operational characteristics for each capsule are listed in Table 6-1. The linear heat rates listed represent minimum, average,

peak, and overpower peak conditions for oxide fuels operating in an LMFBR of current design. The irradiation behavior of spherical particles prepared by ORNL was compared with the behavior of spherical particles prepared by B&W to provide reference points for comparing data from the irradiation programs at the two sites.

Table 6-1. Design Conditions for Time-for-Restructuring Irradiations

Average capsule heat rate, kW/ft	Irradiation time, days				
	<u>1</u>	<u>3</u>	<u>9</u>	<u>27</u>	<u>81</u>
20 ^(a)	X ^(b)	X	-- ^(c)	--	--
20	X	X	X	X	--
15	X	X	X	X	X
10	--	X	--	X	X
6	--	X	--	X	X

(a) These capsules contained pins with B&W and ORNL spherical particles; all other capsules contained spherical and angular particles prepared by B&W.

(b) Capsule planned.

(c) No capsule planned.

6.3.1. Capsule Design

The BAWTR capsules were designed to achieve the required linear fission heat rates listed in Table 6-1 while maintaining the surface temperature of the cladding at about 1200F regardless of the heat generation rate. As a result, four different capsules were designed, one for each of the required heat rates. A diagram of the 15 kW/ft capsule⁷⁵ is shown in Figure 6-1. Cross sections of the 6-, 10-, and 20-kW/ft capsules⁷⁶ are shown in Figure 6-2.

Because of uncertainties in the nuclear and thermal calculations, it was considered advisable to irradiate a calibration capsule. Therefore, a capsule was fabricated and irradiated for short

periods of time in various locations of the BAWTR.^{74,75} The results of these irradiations, which are summarized in Table 6-2, indicate that the capsule design parameters were satisfactory.

Table 6-2. Results of Calibration Capsule Irradiations^(a)

<u>Item</u>	<u>Calculated</u>	<u>Measured</u>
<u>Position C-5</u>		
NaK temperature, F	974 - 1055	1040 - 1070
Linear heat rate, kW/ft	16.7 - 17.9	16.2 - 18
<u>Position C-2</u>		
NaK temperature, F	930 - 955	930 - 970
Linear heat rate, kW/ft	15.0 - 16.2	13 - 16.4
<u>Position RL-1</u>		
NaK temperature, F	440 - 470	480 - 525
Linear heat rate, kW/ft	5.2 - 6.0	5 - 6.0 ^(b)

(a) Unperturbed Maxwellian average thermal flux in positions C-5, C-2, and RL-1 are 14.5×10^{13} , 12.4×10^{13} , and 4.9×10^{13} n/cm²/s, respectively.

(b) This value increases to about 7 kW/ft as calculated from the NaK temperature.

Figure 6-1. Diagram of 15 kW/ft
BAWTR Capsule

Figure 6-2. Cross Sections of BAWTR Capsule Designs

6.3.2. Irradiation Results

Fifteen of the 17 capsules scheduled for irradiation in the BAWTR were completed. Two capsules scheduled for 81-day irradiations, one at 10 kW/ft and the other at 15 kW/ft, were eliminated from the program because of funding limitations.

The operating conditions for the capsules irradiated are shown in Table 6-3. The analytical data for the fuel contained in these capsules are summarized in quarterly progress report No. 15,⁷⁷ and typical photomicrographs and alpha autoradiographs of the unirradiated fuel are shown in several quarterly reports.^{78,79,80} The type of fuel contained in each pin and the pins contained in each capsule are listed in Tables 6-4 and 6-5.

Fourteen of the 17 BAWTR capsules operated as expected. However, anomalous thermocouple readings were obtained from capsules GA-2, -9, and -12.⁸¹⁻⁸⁴ Capsule GA-2 was scheduled for a 27-day irradiation at 15 kW/ft, but its instrumentation indicated that the maximum linear fission heat rate was 10% greater than the design heat rate.^{81,82} Therefore, the exposure of GA-2 was terminated after about 15 days, and capsule GA-7 was irradiated for about 27 days instead of the scheduled nine days.

Capsule GA-9 and then capsule GA-12 were scheduled to be irradiated for 81 days at 6 kW/ft. However, erratic thermocouple readings were obtained from capsule GA-9 after five days' exposure⁸³ and from capsule GA-12 after 55 days' exposure.⁸⁴ It is not known whether the erratic readings were due to thermocouple failures, to electronic problems in the readout system, or to failed fuel pins. Although neutron radiographs indicated that the fuel train was still in the proper position and that none of the fuel pins had failed, it was decided to terminate the irradiation of these capsules.

Table 6-3. Operating Conditions for BAWTR Capsules

Capsule No.	Exposure time, days	Linear heat rate, kW/ft		NaK temperature, F	
		Design	Actual	Design	Actual
GA-2	15	15	15.3-16.7	1100	1080
GA-4	1	20	17.2-19.6	1150	965-1045
GA-5 ^(a)	30	20	17.5-19.0	1150	1065-1080
GA-6	11	20	17.0-20.0	1150	1060-1120
GA-7 ^(a)	30	15	13.5-16.5	1100	975-1180
GA-8 ^(b)	4	20	17.0-19.8	1150	1050-1140
GA-9 ^(c)	5	6	6.2-7.3	1040	1140-1225
GA-10 ^(d)	3.5	20	20.0-22.0	1150	1120-1160
GA-11	1	15	15.5-17.0	1100	1040-1060
GA-12 ^(e)	55	6	4.8-6.0	1040	1015-1025
GA-13 ^(b)	4	15	15.2-16.1	1100	1140-1170
GA-14 ^(b)	4	10	7.5-10.3	1080	950-1110
GA-15 ^(b)	4	6	5.0-6.5	1040	1140
GA-16 ^(d)	0.33	20	17.5-22.2	1150	1090-1200
GA-18 ^(a)	30	10	8.2-9.8	1080	975-1035
GA-19 ^(a)	30	6	7.0	1040	1190

- (a) Capsules GA-5, -7, -18, and -19 were irradiated simultaneously.
- (b) Capsules GA-8, -13, -14, and -15 were irradiated simultaneously.
- (c) Capsule GA-9 was to be irradiated for 81 days, but was removed after 5 days of operation because of indicated abnormal temperatures.
- (d) Capsules GA-10 and -16 contained pins with B&W and ORNL spherical particles.
- (e) Irradiation suspended after 55 days of operation because of indicated abnormal temperatures.

Table 6-4. Fuel Contained in BAWTR Pins

<u>Type of fuel</u>	<u>Pins prepared</u>
Depleted (U,Pu)O ₂ pellets	
Firing 1	C-16, C-17, C-42
Firing 2	C-1, C-3, C-102, C-103
Firing 4	C-10, C-19, C-109, C-110, C-114, C-117
20% ²³⁵ U-enriched (U,Pu)O ₂ pellets	
Firing 1	C-99, C-100
Firing 2	C-84, C-87, C-88, C-89, C-97
Depleted (U,Pu)O ₂ shards	
Firing 1	C-23, C-139
Firing 2	C-53, C-84A, C-126, C-128, C-129, C-137
Firing 4	C-31, C-34, C-75, C-83
20% ²³⁵ U-enriched (U,Pu)O ₂ shards	
Firing 1	C-45, C-59
Firing 2	C-43, C-49, C-58, C-64, C-65
Depleted B&W (U,Pu)O ₂ microspheres	C-24, C-68, C-69, C-73, C-74, C-78, C-80, C-132, C-141, C-146
20% ²³⁵ U-enriched B&W (U,Pu)O ₂ microspheres	C-46, C-51, C-82, C-125, C-134, C-138
ORNL (U,Pu)O ₂ microspheres	C-52, C-122

Table 6-5. Assembly Data for BAWTR Capsules

<u>Capsule numbers</u>	<u>Pin numbers</u>
GA-2	C-23, C-24, C-42
GA-4	C-49, C-51, C-100
GA-5	C-59, C-84, C-138
GA-6	C-45, C-97, C-134
GA-7	C-10, C-126, C-146
GA-8	C-43, C-82, C-99
GA-9	C-3, C-31, C-73
GA-10	C-46, C-88, C-122
GA-11	C-15, C-74, C-139
GA-12	C-53, C-68, C-110
GA-13	C-80, C-83, C-103
GA-14	C-34, C-78, C-102
GA-15	C-1, C-69, C-75
GA-16	C-52, C-87, C-125
GA-18	C-114, C-132, C-137
GA-19	C-19, C-84A, C-141

6.3.3. Post-Irradiation Examination

B&W modified its hot cell facility to accommodate the post-irradiation examination of $\text{UO}_2\text{-PuO}_2$ fuel pins irradiated in the BAWTR and EBR-II. An alpha-containment box was constructed for use within an existing hot cell. Quarterly Progress Report No. 10⁸⁵ contains a detailed description of the facility. Owing to funding limitations, only nine capsules were disassembled in B&W's hot cells. The remaining seven capsules have been transferred to ORNL. Table 6-6 describes the 27 pins examined at B&W and presents their irradiation histories. Visual examinations and gamma scans revealed no failures, swelling, or other abnormalities in these pins.

All of the pins were punctured under vacuum to collect the fission and sorbed gases released. The calculated percentage of fission gas release is shown in Table 6-7. The percentage of gas release is based on the quantity of xenon measured by gas chromatography or by mass spectrometry and on the burnup calculated from the data in Table 6-6. A fission gas yield of 0.22 xenon atoms per atom fissioned was assumed for these calculations. In general, the data show that less fission gas is released from pelletized fuel than from the particulate fuels. However, to draw other conclusions, the data must be analyzed further than the funding level permitted.

Twenty-two pins were sectioned in the transverse direction, and specimens were obtained for metallographic examination. These specimens were mounted and ground, and a few were polished. They have been transferred to ORNL for completion of the detailed metallography.

Photomicrographs of the sectioned pins are shown in Figures 6-3 to 6-24. Central voids are apparent in all pins operated at 10, 15, and 20 kW/ft, but not in those operated at 6 kW/ft. The data indicate that particulate fuels restructure so rapidly that their low initial thermal conductivity does not result in center melting when the linear heat rate is rapidly increased up to 20 kW/ft. Coarse spheres can be seen next to the cladding in all the sphere-pac pins examined. However, in the pins exposed at 15 and 20 kW/ft, a portion of the diameters of the coarse spheres in the outer row appears to have restructured.

The central voids for the pins operated at 15 kW/ft are somewhat larger than those for pins operated at 20 kW/ft. This anomalous restructuring was observed in all three fuel forms. Since the ^{235}U content had to be increased to 20% to achieve a linear heat rating of 20 kW/ft, it is believed that the flux depression factor for these capsules was larger than that for the other capsules that contained depleted uranium. This more severe flux depression resulted in a lower fuel center temperature, a reduced temperature gradient near the fuel's centerline, and a very steep temperature gradient near the outer surface. Detailed calculations to determine the temperature profile across the fuel surface and a more complete metallographic examination are required to determine whether the larger flux depression factor is a satisfactory explanation for the anomalous restructuring.

Table 6-6. Description of Irradiated Pins Examined

Capsule No.	Fuel pin No.	Fuel form	Design linear heat rate, kW/ft	Actual exposure time, days
GA-2	C-24	Sphere-pac	15	15
	C-23	Vipac	15	15
	C-42	Pellet	15	15
GA-4	C-51	Sphere-pac	20	1
	C-49	Vipac	20	1
	C-100	Pellet	20	1
GA-6	C-134	Sphere-pac	20	11
	C-45	Vipac	20	11
	C-97	Pellet	20	11
GA-8 ^(a)	C-82	Sphere-pac	20	4
	C-43	Vipac	20	4
	C-99	Pellet	20	4
GA-10	C-46	Sphere-pac	20	3.5
	C-122 ^(b)	Sphere-pac	20	3.5
	C-88	Pellet	20	3.5
GA-11	C-74	Sphere-pac	15	1
	C-139	Vipac	15	1
	C-15	Pellet	15	1
GA-13 ^(a)	C-80	Sphere-pac	15	4
	C-83	Vipac	15	4
	C-103	Pellet	15	4
GA-14 ^(a)	C-78	Sphere-pac	10	4
	C-34	Vipac	10	4
	C-102	Pellet	10	4
GA-15 ^(a)	C-69	Sphere-pac	6	4
	C-75	Vipac	6	4
	C-1	Pellet	6	4

^(a) Capsules GA-8, GA-13, GA-14, and GA-15 were irradiated simultaneously.

^(b) Fuel pin C-122 contained spherical sol-gel particles prepared by ORNL.

Table 6-7. Gas Released by Fuel in BAWTR Pins

<u>Capsule No.</u>	<u>Pin No.</u>	<u>Fuel form</u>	<u>Design linear heat rate, kW/ft</u>	<u>Gas release, %</u>
GA-2	C-23	Vipac	15	70 ^(a)
	C-42	Pellet	15	75 ^(a)
GA-4	C-51	Sphere-pac	20	76
	C-49	Vipac	20	33
GA-6	C-134	Sphere-pac	20	96
	C-45	Vipac	20	61
	C-97	Pellet	20	13
GA-8	C-82	Sphere-pac	20	51 ^(a)
GA-10	C-46	Sphere-pac	20	44 ^(a)
GA-11	C-74	Sphere-pac	15	41 ^(a)
	C-139	Vipac	15	33 ^(a)
GA-13	C-80	Sphere-pac	15	44
	C-83	Vipac	15	54
	C-103	Pellet	15	31
GA-14	C-102	Pellet	10	37
	C-78	Sphere-pac	10	48 ^(a)
GA-15	C-69	Sphere-pac	6	51
	C-75	Vipac	6	40
	C-1	Pellet	6	26

(a) Analysis by mass spectrometry; others by gas chromatography.

Table 6-7. Gas Released by Fuel in BAWTR Pins

<u>Capsule No.</u>	<u>Pin No.</u>	<u>Fuel form</u>	<u>Design linear heat rate, kW/ft</u>	<u>Gas release, %</u>
GA-2	C-23	Vipac	15	70 ^(a)
	C-42	Pellet	15	75 ^(a)
GA-4	C-51	Sphere-pac	20	76
	C-49	Vipac	20	33
GA-6	C-134	Sphere-pac	20	96
	C-45	Vipac	20	61
	C-97	Pellet	20	13
GA-8	C-82	Sphere-pac	20	51 ^(a)
GA-10	C-46	Sphere-pac	20	44 ^(a)
GA-11	C-74	Sphere-pac	15	41 ^(a)
	C-139	Vipac	15	33 ^(a)
GA-13	C-80	Sphere-pac	15	44
	C-83	Vipac	15	54
	C-103	Pellet	15	31
GA-14	C-102	Pellet	10	37
	C-78	Sphere-pac	10	48 ^(a)
GA-15	C-69	Sphere-pac	6	51
	C-75	Vipac	6	40
	C-1	Pellet	6	26

(a) Analysis by mass spectrometry; others by gas chromatography.

Figure 6-3. As-Ground Cross Section of Sphere-Pac Pin C-69
(Irradiated 4 days at 6 kW/ft)

Figure 6-4. As-Ground Cross Section of Sphere-Pac Pin C-78
(Irradiated 4 days at 10 kW/ft)

Figure 6-5. As-Ground Cross Section of Sphere-Pac Pin C-80
(Irradiated 4 days at 15 kW/ft)

Figure 6-6. As-Ground Cross Section of Sphere-Pac Pin C-74
(Irradiated 1 day at 15 kW/ft)

Figure 6-7. As-Ground Cross Section of Sphere-Pac Pin C-24
(Irradiated 9.6 days at 15 kW/ft)

Figure 6-8. As-Ground Cross Section of Sphere-Pac Pin C-46
(Irradiated 3.5 days at 20 kW/ft)

Figure 6-9. As-Ground Cross Section of Sphere-Pac Pin C-122
(Irradiated 3.5 days at 20 kW/ft)

Figure 6-10. Polished Cross Section of Sphere-Pac Pin C-82
(Irradiated 4 days at 20 kW/ft)

Figure 6-11. As-Ground Cross Section of Sphere-Pac Pin C-51
(Irradiated 1 day at 20 kW/ft)

Figure 6-12. As-Ground Cross Section of Vipac Pin C-75
(Irradiated 4 days at 6 kW/ft)

Figure 6-13. As-Ground Cross Section of Vipac Pin C-34
(Irradiated 4 days at 10 kW/ft)

Figure 6-14. As-Ground Cross Section of Vipac Pin C-83
(Irradiated 4 days at 15 kW/ft)

Figure 6-15. As-Ground Cross Section of Vipac Pin C-139
(Irradiated 1 day at 15 kW/ft)

Figure 6-16. As-Ground Cross Section of Vipac Pin C-23
(Irradiated 9.6 days at 15 kW/ft)

Figure 6-17. As-Ground Cross Section of Vipac Pin C-43
(Irradiated 4 days at 20 kW/ft)

Figure 6-18. As-Ground Cross Section of Pellet Pin C-1
(Irradiated 4 days at 6 kW/ft)

Figure 6-19. As-Ground Cross Section of Pellet Pin C-102
(Irradiated 4 days at 10 kW/ft)

Figure 6-20. As-Ground Cross Section of Pellet Pin C-103
(Irradiated 4 days at 15 kW/ft)

Figure 6-21. As-Ground Cross Section of
Pellet Pin C-15 (Irradiated
1 day at 15 kW/ft)

Figure 6-22. As-Ground Cross Section of Pellet Pin C-42
(Irradiated 9.6 days at 15 kW/ft)

Figure 6-24. As-Ground Cross Section of Pellet Pin C-99
(Irradiated 4 days at 20 kW/ft)

Figure 6-23. As-Ground Cross Section of Pellet Pin C-88
(Irradiated 3.5 days at 20 kW/ft)

6.4. EBR-II Tests

The EBR-II irradiation program was designed to provide data for comparing and evaluating the effects of heat rate and burnup on the overall performance of pellets, spherical particles, and angular particles. The initial program⁸⁶ included two 19-pin subassemblies and a total of 76 fuel pins. This program is summarized in Table 6-8, in which the numbers denote the number of pins to be irradiated at each set of conditions.

Because of funding limitations and the requirement of compatibility between the B&W and ORNL programs, the irradiation of a 19-pin encapsulated subassembly at 8-10 kW/ft was eliminated, and B&W was assigned 18 positions in an unencapsulated 37-pin subassembly to be shared with ORNL.⁸⁷ The B&W fuel pins proposed for this subassembly are described in Table 6-9, and both B&W and ORNL's pins are summarized in Table 6-10.

Table 6-8. Initial EBR-II Irradiation Program^(a)

Burnup, MWd/tonne	Linear heat rate, kW/ft					
	8-10			14-16		
	Angular particles	Spherical particles	Pellets	Angular particles	Spherical particles	Pellets
25,000	3	3	3	3	3	3
50,000	4	3	3	4	3	3
75,000	3	4	3	3	4	3
100,000	3	3	3	3	3	3

(a) Each position within the bundle will be used twice; for example, the pins removed at an exposure of 25,000 MWd/tonne will be replaced with pins that will be irradiated to an exposure of 100,000 MWd/tonne.

Table 6-9. Program for 18 B&W Positions in 37-Pin Unencapsulated EBR-II Subassembly

Position	Material	Bundle burnup, 10^3 MWd/tonne			
		0	25	50	75
1	Vipac	---Pin 1----- ---Pin 38---			
2	Vipac	---Pin 2----- ---Pin 39---			
3	Sphere-pac	---Pin 3----- ---Pin 40---			
4	Sphere-pac	---Pin 4----- ---Pin 41---			
5	Sphere-pac	---Pin 5----- ---Pin 42---			
6	Pellets	---Pin 6----- ---Pin 43---			
7	Pellets	---Pin 7----- ---Pin 44---			
8	Vipac	-----Pin 8----- -----Pin 45-----			
9	Sphere-pac	-----Pin 9----- -----Pin 46-----			
10	Pellet	-----Pin 10----- -----Pin 47-----			
11	Vipac	-----Pin 11-----			
12	Vipac	-----Pin 12-----			
13	Vipac	-----Pin 13-----			
14	Sphere-pac	-----Pin 14-----			
15	Sphere-pac	-----Pin 15-----			
16	Sphere-pac	-----Pin 16-----			
17	Pellet	-----Pin 17-----			
18	Pellet	-----Pin 18-----			

Pins removed, 10^3 MWd/tonne

Type of fuel	25	50	75	100	Total number
Vipac	2	2	2	3	9
Sphere-pac	3	2	3	3	11
Pellet	2	2	2	2	8

Table 6-10. Summary of B&W and ORNL Programs

Type of fuel	Pins removed, 10 ³ MWd/tonne				
	25	50	75	100	Total
Sphere-pac					
ORNL	2	10	2	5	19
B&W	3	2	3	3	11
Vipac					
B&W	2	2	2	3	9
Pellets					
ORNL	0	6	0	4	10
B&W	2	2	2	2	8

6.4.1. Fuel Pin Description

The designs of B&W and ORNL fuel pins are similar. Detailed features and dimensions of these pins are shown in Figure 6-25. Design values common to all the fuel pins are summarized as follows:

Fuel form	Sphere-pac, vipac, or sintered pellet
Fuel composition, wt %	80 UO ₂ -20 PuO ₂
Enrichment, wt %	92 ²³⁵ U in U
Fuel OD, in.	
Sphere-pac, vipac	0.218
Pellet	0.205
Fuel column length, in.	13.5
Avg fuel smear density, % theor	80 ± 2
Blanket material	Depleted UO ₂ pellets
Reflector material	Nickel
Spring material	302 SS
Plenum tube material	316 SS
End cap material	316 SS, ASTM-276-67 and ASTM-484-65
Cladding material	316 SS, ASTM A213, except tolerances
Cladding dimensions, OD/ID, in.	0.250/0.218
Gas volume (at RT), cm ³	
Sphere-pac, vipac	7.8
Pellet	8.2
Gas pressure (at RT), atm	1.1

Figure 6-25. B&W EBR-II Unencapsulated Fuel Pin

6.4.2. Fuel Material

The fuel is hypostoichiometric UO_2 -20% PuO_2 fabricated by three different processes: (1) sphere-pac pins containing sol-gel-derived microspheres, (2) vipac pins containing angular particles prepared from coprecipitated oxide powder, and (3) pellet pins containing sintered pellets prepared from coprecipitated oxide powder. For each form of fuel the UO_2 is fully enriched in ^{235}U . The blanket and insulator material in all the pins is depleted UO_2 pellets.

The fuel was prepared in two separate campaigns, one in FY-1970 and one in FY-1971. Analytical data for both campaigns are summarized in quarterly reports.^{88,89,90}

6.4.3. Fuel Pin Assembly

Details on the procurement and inspection of the cladding tubing, end fittings, reflectors, springs, plenum tubes, and Fiberfrax are presented in quarterly report BAW-3714-19.⁹¹ After the bottom end caps were welded to the clad tubes, oversized welds were polished to size and each weld was helium-leak-tested. These results for the FY-1971 pins are shown in Table 6-11. Each bottom closure weld was radiographed in accordance with the Guide for Irradiation Experiments in EBR-II.⁹²

After the bottom closure weld was established as acceptable, the fuel and the internal hardware were loaded into each fuel pin. The top end cap was welded in place after a mixture of helium and 1 cc of xenon was introduced into the fuel pin.⁹³ The gas mixture was at 1.1 atmospheric pressure (at room temperature). All closure welds met the acceptance criteria. The as-built data for each FY-1970 and FY-1971 fuel pin are presented in Tables 6-12 and 6-13.

Table 6-11. Helium Leak Test Results

Fuel pin No.	Test date	Bottom closure welds		Test date	Top closure welds	
		System sensitivity, $10^{-10} \text{ cm}^3/\text{s}$	Measured leak rate, $10^{-10} \text{ cm}^3/\text{s}$		System sensitivity, $10^{-10} \text{ cm}^3/\text{s}$	Measured leak rate, $10^{-10} \text{ cm}^3/\text{s}$
D-34	10/29/70	2.2	<2.2	6/9/71	1.39	<1.39
D-35	10/29/70	2.2	<2.2	6/10/71	1.53	<1.53
D-36	10/29/70	2.2	<2.2	6/10/71	1.53	<1.53
D-37	10/29/70	2.2	<2.2	6/9/71	1.79	<1.79
D-38	10/29/70	2.2	<2.2	6/8/71	2.03	<2.03
D-39	10/29/70	2.2	<2.2	6/10/71	1.53	<1.53
D-40	10/29/70	2.2	<2.2	6/9/71	1.79	<1.79
D-41	10/29/70	2.2	<2.2	6/8/71	2.03	<2.03
D-42	10/29/70	2.2	<2.2	6/9/71	1.79	<1.79
D-43	10/29/70	2.2	<2.2	6/9/71	1.39	<1.39
D-44	10/29/70	2.2	<2.2	6/10/71	1.53	<1.53
D-50	10/29/70	2.2	<2.2	6/9/71	1.79	<1.79
D-51	10/29/70	2.2	<2.2	6/8/71	2.03	<2.03
D-52	10/29/70	2.2	<2.2	6/9/71	1.39	<1.39
D-53	10/29/70	2.2	<2.2	6/9/71	1.79	<1.79
D-54	10/29/70	2.2	<2.2	6/9/71	1.79	<1.79

Table 6-12. As-Built Description of
FY-1970 B&W-EBR-II
Fuel Pins

Fuel Pin Identification No.:	D-2	D-4	D-5	D-9	D-10	D-12	D-14	D-17	D-18	D-19	D-20	D-21	D-22	D-25	D-27	D-29	D-30	D-31
Fuel	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂
Fabrication	Sphere-pac	Pellet	Vipac	Pellet	Sphere-pac	Pellet	Pellet	Pellet	Vipac	Sphere-pac	Vipac	Vipac	Vipac	Vipac	Sphere-pac	Sphere-pac	Sphere-pac	Sphere-pac
Pu/(U+Pu), wt %	19.96	20.20	20.10	20.20	19.96	20.20	20.20	20.20	20.10	19.96	20.10	20.10	20.10	20.10	19.96	19.95	19.96	19.96
235U/U, wt %	90.77	87.14	92.11	87.14	90.77	87.14	87.14	87.14	92.11	90.77	92.11	92.11	92.11	92.11	90.77	90.77	90.77	90.77
(239Pu+241Pu)/Pu, wt %	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53
Fuel length, in.	13.55	13.458	13.518	13.494	13.51	13.483	13.458	13.457	13.541	13.55	13.490	13.482	13.554	13.501	13.49	13.48	13.55	13.53
Fuel diameter, in.	0.218	0.205	0.218	0.205	0.218	0.205	0.205	0.205	0.218	0.218	0.218	0.218	0.218	0.218	0.218	0.218	0.218	0.218
Fuel weight, g	71.19	74.82	70.98	75.01	71.10	75.00	74.74	74.76	71.07	71.14	70.58	70.66	71.00	68.96	71.19	70.87	71.20	71.17
Fuel smear density, % theor	78.26	82.50	78.18	82.78	78.40	82.73	82.92	82.79	78.15	78.21	77.90	78.03	77.99	76.05	78.61	78.32	78.28	78.36
Distance from top of fuel column to top of tube, in.	17-5/16	17-5/8	17-7/16	17-19/32	17-3/8	17-5/8	17-19/32	17-9/16	17-3/8	17-9/32	17-15/32	17-13/32	17-11/32	17-15/32	17-3/8	17-3/8	17-11/32	17-3/8
Blanket material	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂
Fabrication	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet
Length, in.	6.104	6.059	5.965	6.059	6.058	6.060	6.060	6.060	6.058	6.047	6.049	6.058	6.044	6.056	6.053	6.058	6.056	6.043
Diameter, in.	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214
Weight, g	36.96	37.055	36.993	37.054	37.18	37.082	37.144	37.164	37.149	36.97	37.230	37.034	36.93	37.100	37.17	37.07	37.16	37.15
Length of bottom Fiberfrax pad, in.	1/4	1/16	1/4	1/16	1/4	1/16	1/16	1/16	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4	1/4
Bottom insulators	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂
Fabrication	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets
Length, in.	0.508	0.507	0.506	0.501	0.486	0.490	0.501	0.499	0.500	0.500	0.505	0.496	0.499	0.482	0.500	0.514	0.499	0.501
Diameter, in.	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214
Weight, g	3.056	3.095	3.046	3.116	3.000	2.982	3.113	3.086	3.078	3.100	3.074	3.058	3.096	3.002	3.084	3.040	3.112	3.109
Top insulators	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂
Fabrication	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets	Pellets
Length, in.	0.495	0.501	0.494	0.500	0.508	0.505	0.502	0.496	0.504	0.500	0.494	0.500	0.509	0.496	0.509	0.507	0.510	0.499
Diameter, in.	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214
Weight, gm	3.017	3.095	3.043	3.078	3.067	3.104	3.100	3.076	3.063	3.106	3.054	3.114	3.074	3.084	3.063	3.088	3.130	3.083
Length of top Fiberfrax pad, in.	3/32	1/16	1/16	1/16	3/32	1/16	1/16	1/16	1/16	3/32	1/16	1/16	1/16	1/16	3/32	3/32	3/32	3/32
Nickel reflector																		
Length, in.	2.221	2.221	2.218	2.219	2.219	2.220	2.218	2.220	2.220	2.219	2.221	2.221	2.221	2.220	2.221	2.220	2.222	2.221
Diameter, in.	0.200	0.200	0.201	0.201	0.200	0.200	0.201	0.200	0.201	0.200	0.200	0.200	0.200	0.200	0.201	0.200	0.200	0.201
Weight, g	10.18	10.17	10.20	10.20	10.19	10.20	10.18	10.19	10.20	10.18	10.18	10.19	10.19	10.18	10.20	10.18	10.20	10.20
Spring																		
Free length, in.	4.500	4.475	4.500	4.525	4.525	4.525	4.500	4.525	4.500	4.475	4.525	4.475	4.450	4.500	4.500	4.525	4.500	4.500
Diameter, in.	0.208	0.209	0.208	0.207	0.209	0.207	0.206	0.204	0.208	0.208	0.207	0.209	0.207	0.208	0.209	0.207	0.208	0.207
Weight, g	3.30	3.28	3.24	3.27	3.31	3.29	3.23	3.21	3.23	3.20	3.29	3.25	3.24	3.26	3.30	3.27	3.27	3.24
Plenum tube																		
Length, in.	10.497	10.497	10.505	10.496	10.499	10.501	10.500	10.498	10.503	10.500	10.497	10.497	10.499	10.500	10.497	10.498	10.501	10.497
Diameter, in.	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187
Weight, g	11.23	11.29	11.26	11.23	11.30	11.27	11.24	11.24	11.27	11.26	11.23	11.25	11.26	11.23	11.23	11.25	11.26	11.26
Clad tube-type 316 SS																		
Length, in.	37.866	37.862	37.863	37.864	37.859	37.864	37.863	37.862	37.863	37.863	37.865	37.864	37.864	37.864	37.865	37.865	37.865	37.864
Maximum deviation from nominal 0.250 in. OD, in.	-0.0004	-0.0006	-0.0006	-0.0009	-0.0008	-0.0007	-0.001	-0.0005	-0.0005	-0.0002	-0.0006	-0.0005	-0.0005	-0.0006	-0.0003	-0.0009	-0.0005	-0.0005
Maximum deviation from nominal 0.218 in. ID, in.	+0.0003	+0.0004	+0.0004	-0.0003	+0.0006	-0.0008	-0.0003	-0.0003	+0.0002	+0.0008	+0.0002	+0.0009	+0.0005	+0.0003	+0.0007	+0.0002	+0.0005	+0.0008
Minimum wall thickness, in.	0.0155	0.0152	0.0150	0.0150	0.0151	0.0150	0.0152	0.0151	0.0154	0.0151	0.0151	0.0150	0.0151	0.015	0.002	0.0155	0.0152	0.0152
Fuel pin																		
Length, in.	39.978	39.967	39.979	39.972	39.957	39.967	39.959	39.971	39.976	39.965	39.965	39.974	39.977	39.964	39.976	39.983	39.977	39.972
Maximum OD, in.	0.2497	0.2495	0.2497	0.2502	0.2497	0.2500	0.2500	0.2506	0.2496	0.2502	0.2500	0.2500	0.2500	0.2495	0.2502	0.2497	0.2500	0.2495
Minimum OD, in.	0.2491	0.2490	0.2490	0.2492	0.2491	0.2494	0.2485	0.2491	0.2491	0.2490	0.2490	0.2493	0.2492	0.2487	0.2492	0.2490	0.2492	0.2480
Straightness, TIR, in.(a)	0.0025	0.003	0.007	0.004	0.005	0.004	0.005	0.005	0.0035	0.0025	0.0055	0.0065	0.003	0.005	0.002	0.002	0.003	0.005
Total weight of fuel pin, g	211.0	214.1	208.8	214.8	210.2	214.7	214.1	214.5	210.7	210.2	210.0	209.6	209.9	208.3	210.9	210.5	211.2	210.6
Smearable alpha activity, dpm/100 cm ²	29	<10	<10	<10	<10	<10	25	<10	17	41	<10	<10	25	<10	<10	<10	17	17

(a) Total indicator reading.

Table 6-13. As-Built Description of FY-1971 B&W-EBR-II Fuel Pins

Fuel Pin Identification No.:	D-34	D-35	D-36	D-37	D-38	D-39	D-40	D-41	D-42	D-43	D-44	D-50	D-51	D-52	D-53	D-54
Fuel	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂	(U,Pu)O ₂
Fabrication	Vipac	Sphere-pac	Sphere-pac	Vipac	Pellet	Sphere-pac	Vipac	Pellet	Pellet	Sphere-pac	Sphere-pac	Pellet	Pellet	Sphere-pac	Vipac	Vipac
Pu/(Pu+U), wt %	19.69	19.68	19.68	19.69	19.67	19.68	19.69	19.67	19.67	19.68	19.68	19.67	19.67	19.68	19.69	19.69
²³⁵ U/U, wt %	91.37	92.59	92.59	91.37	89.76	92.59	91.37	89.76	89.76	92.59	92.59	89.76	89.76	92.59	91.37	91.37
(²³⁹ Pu+ ²⁴¹ Pu)/Pu, wt %	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53	91.53
Fuel length, in.	13.59	13.52	13.55	13.52	13.44	13.59	13.53	13.53	13.50	13.49	13.46	13.51	13.45	13.56	13.59	13.42
Fuel diameter, in.	0.218	0.218	0.218	0.218	0.205	0.218	0.218	0.205	0.205	0.218	0.218	0.205	0.205	0.218	0.218	0.218
Fuel weight, g	70.89	71.11	71.19	70.76	76.43	71.19	70.89	74.90	75.04	71.19	71.19	75.37	76.59	71.19	70.89	70.89
Fuel smear density, % theor	77.71	78.35	78.26	77.96	84.71	78.03	78.05	82.45	82.80	78.61	78.78	83.10	84.82	78.20	77.71	78.69
Distance from top of fuel column to top of tube, in.	17-17/32	17-19/32	17-9/16	17-5/8	17-9/32	17-1/2	17-19/32	17-17/32	17-5/32	17-1/2	17-19/32	17-1/8	17-7/32	17-17/32	17-11/32	17-11/16
Blanket material	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂
Fabrication	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet
Length, in.	5.93	5.93	6.03	5.91	5.92	5.93	5.95	5.92	5.90	6.08	6.02	5.91	5.90	6.03	6.10	5.95
Diameter, in.	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214
Weight, g	35.20	35.14	36.85	34.83	35.15	35.14	35.31	36.54	34.79	36.54	36.85	34.78	35.26	37.22	36.20	35.23
Length of bottom Fiberfrax pad, in.	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	3/32	1/16	1/16	1/16	1/16	1/16	1/16
Bottom insulators	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂
Fabrication	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet
Length, in.	0.501	0.501	0.500	0.501	0.500	0.501	0.502	0.500	0.502	0.500	0.500	0.502	0.503	0.500	0.500	0.501
Diameter, in.	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214
Weight, g	3.00	3.10	3.11	3.10	3.04	3.06	2.99	3.06	3.11	2.98	3.11	3.03	3.06	3.10	3.01	3.05
Top insulators	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂	UO ₂
Fabrication	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet	Pellet
Length, in.	0.500	0.501	0.500	0.502	0.502	0.501	0.502	0.501	0.500	0.502	0.500	0.502	0.500	0.500	0.500	0.500
Diameter, in.	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214	0.214
Weight, g	3.11	3.04	3.02	3.05	3.02	3.04	3.07	3.04	2.95	3.08	3.11	3.08	2.94	3.10	3.01	3.10
Length of top Fiberfrax pad, in.	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16	1/16
Nickel reflector																
Length, in.	2.220	2.220	2.218	2.220	2.222	2.221	2.219	2.221	2.220	2.220	2.215	2.220	2.218	2.218	2.218	2.218
Diameter, in.	0.200	0.200	0.201	0.201	0.200	0.200	0.201	0.200	0.200	0.201	0.201	0.200	0.200	0.200	0.201	0.200
Spring																
Free length, in.	4.500	4.500	4.500	4.500	4.500	4.500	4.550	4.500	4.525	4.525	4.500	4.525	4.525	4.525	4.500	4.500
Diameter, in.	0.207	0.207	0.208	0.209	0.209	0.209	0.206	0.208	0.209	0.209	0.208	0.208	0.208	0.204	0.208	0.208
Pneum tube																
Length, in. (±.005)	10.500	10.500	10.500	10.500	10.500	10.500	10.500	10.500	10.500	10.500	10.500	10.500	10.500	10.500	10.500	10.500
Diameter, in. (±.001)	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187	0.187
Clad tube-type 316 SS																
Length, in.	37.880	37.880	37.892	37.892	37.900	37.887	37.900	37.893	37.879	37.901	37.893	37.882	37.887	37.895	37.898	37.889
Maximum deviation from nominal 0.250 in. OD, in.	-0.0007	-0.0005	-0.0007	-0.0006	-0.0005	-0.0007	-0.0007	-0.0005	-0.0007	-0.0008	-0.0006	-0.0007	-0.0005	-0.0007	-0.0008	-0.0007
Maximum deviation from nominal 0.218 in. I.D., in.	+0.0004	+0.0005	+0.0001	+0.0001	+0.0002	+0.0003	+0.0001	+0.0005	+0.0005	+0.0002	+0.0004	+0.0002	+0.0002	0.0000	+0.0002	+0.0002
Minimum wall thickness, in.	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015	0.015
Fuel pin																
Length, in.	40.007	39.992	40.004	40.003	40.018	39.998	40.013	40.003	39.989	40.002	40.006	39.995	39.985	40.001	40.012	40.002
Maximum OD, in.	0.2500	0.2498	0.2498	0.2500	0.2502	0.2496	0.2502	0.2503	0.2500	0.2500	0.2498	0.2500	0.2508	0.2502	0.2498	0.2498
Minimum OD, in.	0.2496	0.2495	0.2493	0.2495	0.2495	0.2493	0.2495	0.2495	0.2494	0.2495	0.2493	0.2494	0.2496	0.2496	0.2494	0.2494
Straightness, TIR, in. (a)	0.005	0.008	0.002	0.004	0.003	0.002	0.007	0.002	0.003	0.008	0.002	0.007	0.012	0.009	0.005	0.002
Total weight of fuel pin, g	208.7	208.7	211.0	207.8	214.3	208.9	209.3	212.2	212.2	210.4	210.4	212.7	214.4	211.0	209.6	208.3
Smearable alpha activity, <10 dpm/100 cm ²	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10

(a) Total indicator reading.

7. ANALYTICAL SUPPORT

7.1. Foreword

As in any experimental program, this program required good analytical support in order to produce meaningful results. The analytical Chemistry, Nuclear Ceramics, and Nuclear Metallurgy groups of B&W's Lynchburg Research Center and, occasionally, other B&W divisions and outside service laboratories provided analytical support. The analytical data for the fuel prepared are presented in several quarterly reports.^{77,88,89,90}

7.2. Analytical Techniques

Many analytical techniques were required to support the gel-addition studies. Most of the techniques were tested during two inter-laboratory comparison programs,^{94,95} and the results showed that B&W's techniques compare favorably with those of others in the nuclear industry. Most of the methods are summarized briefly in the following paragraphs.

7.2.1. Plutonium and Uranium

The plutonium and uranium contents of various feed solutions, intermediates in fuel preparation, and final products were determined by controlled-potential coulometry.^{96,97,98} The oxidation state of uranium was generally determined by controlled-potential coulometry. The oxidation state of plutonium was determined by either spectrophotometry⁹⁹ or controlled-potential coulometry. The isotopic distribution of uranium was measured by mass spectrometric techniques.

7.2.2. Oxygen Stoichiometry

The O/M atom ratios of intermediates in fuel preparation and final products were generally determined by microthermogravimetry.¹⁰⁰⁻¹⁰³ Occasionally this technique led to poor precision and

below-average O/M values for samples of coarse (U,Pu)O₂ microspheres. It was concluded from a study¹⁰⁴ of this problem that close attention to the reduction time during analysis will indicate whether or not the measurement conditions are satisfactory. It was recommended that we obtain a thermogram during each O/M measurement and compare it with a reference "ideal" thermogram.

7.2.3. Moisture

The moisture content of the fuels was determined with a modified CEC Type-321 AMA Solids Moisture Analyzer.^{103,105,106} No widely accepted standard method is available for determining the moisture content of nuclear fuels. As would be expected, the total moisture determined depends on storage and handling conditions, such as humidity. In addition, the temperature at which the analysis is performed can be an important variable in the method used.¹⁰⁸ Therefore, B&W attempted to minimize the difference between the moisture content of the fuel in a sealed pin and the measured moisture content.

7.2.4. Density

The tap density of powders was determined with a Numinco Model JEL ST2 tap density machine,¹⁰⁷ and the density of pellets was calculated from the weight-to-volume ratio of the sample.¹⁰⁴ Several liquid pycnometric techniques were tested for measuring the density of coarse microsphere samples. However, the reproducibility of these methods was poor, and the results did not compare favorably with estimates based on ceramographic examinations. Therefore, the particle density of the coarse fraction microspheres was determined by a vibratory compaction technique.^{107,108} This technique involves placing the sample in a tube having a diameter more than 10 times that of the maximum spherical particle, vibrating the tube until the spheres are packed in a minimum volume, determining the packed-bed volume, and, finally, calculating the particle density assuming that particles of single size are present. Ayer has shown theoretically that 100%-dense perfect spheres of the same size will fill 63.5% of the packed-bed volume.¹⁰⁹ However, experimental data indicate that only 62.5% of the packed-bed volume is filled by 100%-dense spherical particles of a single diameter.⁷¹ No

attempt was made to determine the density of the spheres with diameters below 44 microns because this fraction contains such a wide range of particle sizes that reasonably accurate results are impossible.

7.2.5. Sorbed Gas

The sorbed gas content of the fuel material was measured by placing a sample in a closed system under a high vacuum, heating to 1600C, measuring the pressure change, and calculating from the pressure change the volume of gas evolved.¹¹⁰

7.2.6. Carbon

The carbon content of the fuel material was determined with a modified LECO Low Carbon Analyzer.¹¹¹ Here, the carbon is separated from the nuclear fuel material by burning in an oxygen atmosphere, and the evolved CO₂ is measured with a gas chromatograph.

7.2.7. Nitrogen

Nitrogen was separated from the fuel material with a modified Kjeldahl technique, and the content was determined by constant-current coulometric titration.

7.2.8. Halogens

The halogens were separated from the fuel material by pyrohydrolysis and determined with ion selective electrodes.¹¹²

7.2.9. Trace Metallic Impurities

The trace metallic impurities were determined with a Bausch and Lomb Dual Grating Spectrograph by a d-c arc, carrier distillation method.

7.2.10. Ceramography and Alpha Autoradiography

Samples of all the fuel materials were examined microscopically to determine the microstructure and other features before irradiation. The samples were prepared for examination by mounting in room-temperature-setting resin, grinding on a lap, and polishing with 0.5-micron diamond paste on nylon cloth in a vibratory polisher.¹¹³⁻¹¹⁵

Alpha autoradiographs were prepared by placing cellulose-nitrate-covered glass slides face-down on the ceramographic mount with

aluminum foil as a filter between the specimen and the cellulose nitrate.^{116,117} After about 15 minutes' exposure, the cellulose nitrate slides were treated with NaOH.

7.3. Quality Verification

To ensure that the fuel prepared during FY-1970 and FY-1971 was within the specifications normally proposed for fast reactor fuels, the USAEC required quality verification programs. Several quality verification programs for the preparation of nuclear fuels are available. However, to provide programs that were compatible with the scope and funding restrictions of this contract, B&W prepared its own programs^{118,119} and had them approved by the USAEC. The procedures given in MIL-STD-414¹²⁰ were followed to ensure representative sampling of pellet lots, and Jones' procedures¹²¹ were followed to ensure representative sampling of sphere and shard lots.

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