GEL-ADDITION PROCESS CHEMICAL STUDIES

— Quarterly Progress Report No. 17 —

August - October 1970

Compiled by

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Babcock & Wilcox
Research and Development Division
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— Quarterly Progress Report No. 17 —
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ABSTRACT

The development of a sol-gel process and related processes for preparing (U,Pu)O₂ fast reactor fuels has continued at Babcock & Wilcox's Lynchburg Research Center. Progress for the 17th quarter, ending October 31, 1970, is reported. The program is sponsored by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3714.

Eighteen fuel pins containing ²³⁵UO₂-20% PuO₂ in the form of pellets, shards, or sol-gel microspheres have passed final inspection for an unencapsulated bundle to be irradiated in the EBR-II. These pins are now ready for shipment.

Sufficient coprecipitated powder and sol-gel microspheres for the EBR-II reload pins have been prepared. Pellets and shards are being fabricated.

Nine capsules irradiated in the BAWTR were disassembled previously. Gas analyses and detailed metallographic examinations of the 27 fuel pins contained in these capsules are in progress in B&W's hot cell facilities.

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1. INTRODUCTION

This is the 17th progress report on a continuing program of experimental work on sol-gel and related methods for preparing mixed uranium-plutonium oxide fuels for fast reactor application. The program is sponsored by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3714. This report covers the period from August 1 to October 31, 1970.

The work program for the contract establishes several technical tasks, including fuel preparation and fabrication, reactor testing in both thermal and fast neutron fields, and analytical support. For FY-1971 the primary objectives are to (1) prepare 16 additional EBR-II pins containing fully enriched UO_2 -20% PuO_2 and (2) continue the post-irradiation examination of the BAWTR capsules consistent with the funds available.

The 16 EBR-II pins will include five pellet, five vipac, and six sphere-pac pins. These will provide sufficient pins for the scheduled reloading at 50,000 and 75,000 MWd/t burnup as well as two spares or archives with each fuel form. The fuel for these pins has been prepared, and the pellets and shards are being fabricated. Assembly of the pins is expected to be completed during the next quarter.

Nine of the 16 capsules irradiated in the BAWTR were disassembled in the B&W hot cell facilities during FY-1970. Gas analyses and detailed metallographic examination of the 27 pins contained in these capsules are in progress. The progress in all technical areas of the program is reviewed in the following sections.

2. RESULTS AND CONCLUSIONS

2.1. Fuel Preparation

Nearly 1700 g of coprecipitated $^{235}\text{UO}_2$ -20% PuO_2 powder was prepared in five batches with an average yield of 94%. Each batch of powder was within the $\text{Pu}/(\text{Pu} + \text{U})$ specification of $20.0 \pm 0.5\%$. The powder was blended into one lot and released for pellet and shard fabrication.

The results from a short series of scouting experiments indicated that previous problems in preparing UO_2 sol of suitable quality for sphere forming were primarily due to the urea-to-uranium mole ratio being too high during reduction. Six 300 g batches of $^{235}\text{UO}_2$ sol were prepared and found to be suitable feed for sphere forming.

In all, 371 g of rounded 420-595 μ spheres, 203 g of rounded 210-420 μ spheres, and 267 g of <37 μ spheres were prepared. The average yield was 97% for the fines and 42.5% for the coarse fractions. The primary factor limiting the yield of the rounded coarse product was a tendency for the spheres to dimple slightly. The spheres have been released for loading into EBR-II cladding.

2.2. Fuel Fabrication

About half of the UO_2 insulator pellets required for the EBR-II reload pins have been prepared. Sufficient $^{235}\text{UO}_2$ -20% PuO_2 pellets for the reload pins have been pressed, fired, centerless ground, washed, and dried. In addition, another lot of $^{235}\text{UO}_2$ -20% PuO_2 pellets has been pressed. After sintering, these pellets will be crushed into shards to be used as vipac feed. All the EBR-II reload pins are scheduled to be assembled during the next quarter.

2.3. Irradiation Testing

Gas analyses and detailed metallographic examinations of 27 fuel pins previously irradiated in the BAWTR are in progress in B&W's hot cell facilities.

Detailed nondestructive testing of the 21 EBR-II fuel pins previously assembled was completed. Three of the pins were rejected because of dimensional defects in the cladding. The 18 accepted pins include seven sphere-pac, six vipac, and five pellet pins, which are sufficient for the initial EBR-II bundle.

2.4. Analytical Support

A formal quality verification plan was written for the fuel being prepared in FY-1971. Difficulties in measuring the oxygen-to-metal ratio of coarse microspheres have been encountered frequently. The standard thermogravimetric technique often results in unusually low O/M values as well as poor reproducibility. It has been found that good results are obtained if the oxidation and reduction temperature is increased from 850 to 950C.

3. FUEL PREPARATION (R. V. Carlson)

The FY-1971 fuel order includes about 1200 g of coprecipitated powder and 600 g of sol-gel microspheres containing 20% PuO_2 in UO_2 enriched to 93% ^{235}U for the EBR-II irradiation tests. This fuel will be used to fabricate 16 pins. Most of these pins will be loaded in the EBR-II bundle during scheduled outages, and the remainder will serve as archive samples or as replacements for rejected pins.

3.1. Preparation of $^{235}\text{UO}_2$ -20% PuO_2 Coprecipitated Powder

Nearly 1700 g of powder containing 20% PuO_2 in fully enriched UO_2 was prepared during the quarter by continuous coprecipitation of ammonium diuranate-plutonium hydroxide from a uranium-plutonium nitrate solution. The process flowsheet was summarized previously.¹

Although the capacity of the continuous coprecipitation equipment is over 2 kg/shift, the fissile material mass limit of the glove box restricted the throughput to 315 g (on a metal basis) per run. The $\text{Pu}(\text{NO}_3)_4$ and $\text{UO}_2(\text{NO}_3)_2$ feed solutions were mixed on a weight basis from previously analyzed stock solutions. The compositions of these stock solutions are shown in Table 3-1. The pH was held at about 9.5 during precipitation to ensure homogeneity of the plutonium and uranium in the powder.^{2,3}

The data in Table 3-2 show that the weight loss averaged about 75% during drying and about 23% during calcining. The average yield was 94% as compared with 86 to 88% in previous campaigns.^{1,4} The higher yield was the result of not flushing the system with acid before each of the last three runs.

The plutonium content of each batch of calcined powder was measured before the acceptable powder was blended into one lot. The specification calls for a $\text{Pu}/(\text{Pu} + \text{U})$ of $20.0 \pm 0.5\%$. The data in Table 3-2 show that all batches were within these limits.

The five batches of calcined powder were ball-milled with tungsten carbide balls for about 6 hours until the powder would pass through a 200-mesh screen (74- μ openings). Finally, the powder was blended in a V-cone blender for 30 minutes to obtain a homogeneous feed for pellet and shard fabrication.

Table 3-1. Compositions of Stock Solutions for Coprecipitation

Plutonium Nitrate

Plutonium, mg/g soln	156.3 $\pm$ 1.2 ^(a)
Free acid, <u>M</u>	5.2
²³⁸ Pu, wt %	0.047 ^(b)
²³⁹ Pu, wt %	90.497 ^(b)
²⁴⁰ Pu, wt %	8.344 ^(b)
²⁴¹ Pu, wt %	1.033 ^(b)
²⁴² Pu, wt %	0.079 ^(b)

Uranyl Nitrate

Uranium, mg/g soln	220.2 $\pm$ 1.1 ^(a)
²³⁴ U, wt %	0.98 $\pm$ 0.01 ^(c)
²³⁵ U, wt %	92.77 $\pm$ 0.03 ^(c)
²³⁶ U, wt %	0.38 $\pm$ 0.01 ^(c)
²³⁸ U, wt %	5.88 $\pm$ 0.01 ^(c)

(a) Errors are for 95% confidence limits on the mean.

(b) Analysis performed on June 21, 1968.

(c) Analysis performed on December 10, 1970.

Table 3-2. Data From Preparation of Coprecipitated Powder

Batch No.	Weight of wet cake, g	Weight of dried cake, g	Weight of calcined product, g	Weight loss during drying, %	Weight loss during calcination, %	Pu/(Pu + U), % ^(a)	Yield, %
2-A-29	1753	398.5	314.16	77.3	21.2	19.90 ± 0.13	86.8
2-A-35	1524	413.4	310.87	72.9	24.1	19.66 ± 0.11	85.9
2-A-37	1714	482.5	365.38	71.8	23.5	19.84 ± 0.11	100.9 ^(b)
2-A-39	2124	485.6	362.51	77.1	24.8	19.73 ± 0.05	100.1 ^(b)
2-A-41	2013	455.2	346.57	77.4	23.0	19.97 ± 0.05	95.7 ^(b)

^(a)Errors are for 95% confidence limits on the mean.

^(b)System was not flushed with acid before run.

3.2. Preparation of ²³⁵UO₂-20% PuO₂ Sol-Gel Microspheres

Sufficient microspheres for the remaining EBR-II pins were prepared this quarter. In all, 371 g of rounded 420-595 μ spheres, 203 g of 210-420 μ spheres, and 267 g of <37 μ spheres are available for the sphere-pac pins.

3.2.1. Preparation of ²³⁵UO₂ Sol

Before preparing UO₂ sols containing fully enriched uranium, a short series of scouting experiments was performed using depleted uranium. These experiments were performed primarily to determine conditions for preparing UO₂ sols of better quality than were prepared in FY-1970.^{4,5} The reference process was the ORNL formate flowsheet.⁶

The results summarized in Table 3-3 indicate that stable UO₂ sols can be prepared at various but not all uranium and urea concentrations. Several other observations can be made from the data:

1. Comparing batches 176 and 177 with 178, it appears that the reduction time depends on the quantity of uranium being reduced even though a large excess of hydrogen was present during all three runs. However, this effect may be due to the mixing efficiency of the equipment.

2. Comparing batch 179 with 184, the reduction time is significantly less if the uranium concentration is lowered.

3. Comparing batch 182 with batches 183 and 184, the reduction time is less at a higher urea-to-uranium mole ratio.

4. The characteristics of batch 183 are very similar to those obtained last year^{4,5} with a urea-to-uranium mole ratio of 0.8 - 0.9 and a uranium concentration of 0.9 M. Therefore, to obtain a stable black sol, it appears that the urea-to-uranium mole ratio must be less than about 0.75 if the uranium concentration is less than 0.9 M. However, the data for batch 181 indicate that higher urea-to-uranium mole ratios can be tolerated if the uranium concentration is higher.

Based on these data, it was concluded that a uranium concentration of about 0.8 M and a urea-to-uranium mole ratio of about 0.6 would result in a satisfactory reduction and would make possible the formation of stable UO_2 sol. The long reduction times (about 12 hours) can be tolerated and are about the same as observed previously under similar conditions.⁷

Table 3-3. Data From UO_2 Sol Preparation Experiments

Batch No.	Uranium reduced, g	Input U conc, <u>M</u>	Urea/ U_i mole ratio	Reduction time, h	Sol characteristics
176	150.1	1.26	0.50	9.0	Black; thixotropic after 12 wks
177	150.1	1.26	0.50	9.5	Black; stable after 15 wks
178	300.1	1.26	0.50	>24	No sol — reduction incomplete
179	300.1	1.26	0.66	>20	No sol — reduction incomplete
180	300.1	1.01	0.77	--	No sol — stirring rod broke during reduction
181	300.1	1.01	0.77	13.5	Black, stable after 14 wks
182	300.1	0.841	0.50	36	Black, stable after 13 wks
183	300.1	0.841	0.77	11.5	Grey, solids began separating out after about 2 wks, supernate stable after 12 wks
184	300.1	0.841	0.60	12.5	Black, stable after 11 wks

Table 3-4. Data From Preparation of $^{235}\text{UO}_2$ Sol

Batch No.	Uranium reduced, g	Input U conc, M	Urea/U, mole ratio	Reduction time, h
185	287.8	0.770	0.593	11.0
186	302.4	0.770	0.564	10.5
187	304.5	0.770	0.560	14.7 ^(a)
188	304.2	0.770	0.561	9.7
189	304.3	0.770	0.561	9.7
190	304.2	0.770	0.561	9.7

(a) H_2 flow was only 20% of normal for 10 hours.

Six fully enriched UO_2 sols were prepared under the conditions shown in Table 3-4. All runs yielded stable black sol with only a small amount of unsuspended solids. After allowing one week for settling, the stable sol was decanted.

3.2.2. Preparation of PuO_2 Sol

Sufficient PuO_2 sol for the FY-1971 fuel order was prepared during the past quarter.⁸

3.2.3. Preparation of (U, Pu) O_2 Microspheres

Because of the limited quantity of spheres required, the laboratory-scale spheroidizing system was used instead of the unit-operations-scale system. The operating procedure has been summarized previously.⁹ The PuO_2 sol feed and UO_2 sol feed were mixed on a weight basis from previously analyzed stock. The compositions of these stock sols are shown in Table 3-5.

About 370 g of coarse microspheres (420-595 μ diameter) and 270 g of fines (<37 μ diameter) are available for pin loading. In general, the preparation of this material was routine. However, during the first four runs, the yield was unusually low because of particle agglomeration in the spheroidizing column. This problem was traced to the effects of having (U, Pu) O_2 sol emulsified in the 2-ethyl-1-hexanol (2-EH) desiccant. During column operation, a small percentage (~5%)

of the sol droplets overflows into the 2-EH storage tank. Then, if the column inlet line is near the bottom of the tank, the sol is passed through the pump and emulsified. The problem was solved with a minor equipment modification.

Table 3-5. Compositions of Sol Feed for Sphere Forming

<u>Batch No.</u>	<u>UO₂ Sol</u>
	<u>U conc, mg/g sol^(a)</u>
185	242.0 ± 0.6
186	227.8 ± 0.4
187	206.4 ± 2.1
188	217.2 ± 0.2
189	226.8 ± 0.7
190	213.6 ± 0.2

<u>Batch No.</u>	<u>PuO₂ Sol</u>
	<u>Pu conc, mg/g sol^(a)</u>
39, 40	190.2 ± 0.2
41	131.1 ± 0.5
42	143.6 ± 0.2

(a) Errors are for 95% confidence limits on the mean.

Since several batches of ²³⁵UO₂ sol and PuO₂ sol were used, the surfactant levels had to be changed several times. The Span-80 (Atlas Chemical Industries) content was varied from 0.4 to 0.5 vol %, and the Ethomeen S/15 (Armour Industries) content was varied from 0.3 to 0.4 vol %.

The data from the sphere-forming runs are summarized in Tables 3-6 and 3-7. The average yield of fines was greater than previously observed.¹⁰ However, the yield of rounded coarse product was less than expected. The yield was reduced somewhat by the many

changes required in surfactant concentration. But the primary problem was that a large fraction of the coarse spheres was slightly dimpled. Although these were rejected on the roundometer, they would probably be a satisfactory feed for the sphere-pac process if they were required.

Table 3-6. Sphere Formation Data

<u>Coarse fraction</u>	<u>Average yield from all runs, %(a)</u>	<u>Yield from best run, %(a)</u>	<u>Yield from worst run, %(a)</u>
Rounded product (420 - 595 μ)	27.4	59.8 ^(b)	8.1 ^(c)
Rounded product (210 - 420 μ)	15.0	27.7 ^(b)	4.8 ^(c)
Nonround scrap	46.7	33.1 ^(c)	59.9 ^(b)
Offsize scrap	10.9	1.4 ^(c)	36.0 ^(b)
<u>Fine fraction</u>			
Product (<44 μ)	97.1	98.4 ^(b)	96.3 ^(c)
Offsize scrap	2.9	1.6 ^(c)	3.7 ^(b)

(a) All yields are calculated on the basis of recovered material.

(b) Highest yield obtained from any run.

(c) Lowest yield obtained from any run.

Table 3-7. Size Distribution of Spheres Prepared

<u>Coarse fraction, μ</u>	<u>Average from all runs, %</u>	<u>Run with highest yield of product, %</u>	<u>Run with lowest yield of product, %</u>
>710	2.5	0.0	2.9
595-710	1.8	0.0	1.5
500-595	12.4	11.3	4.7
420-500	34.5	77.9	19.2
350-420	23.1	6.5	29.5
210-350	19.1	2.9	28.7
149-210	4.5	1.1	8.3
125-149	0.6	0.25	1.8
105-125	0.4	0.08	1.7
<105	1.0	0.08	1.7
<u>Fine fraction, μ</u>			
>44	1.3	0.9	1.6
37-44	1.6	0.7	2.2
<37	97.1	98.4	96.3

Note: Data include rounds and nonrounds.

To comply with the quality verification program (see section 6.1.2), the plutonium content of the mixed sol for each sphere-forming run was measured. These data are shown in Table 3-8.

Table 3-8. Quality Verification Data for
Sol-Gel Microspheres

<u>Coarse Microspheres</u>	
<u>Batch No.</u>	<u>Pu/(Pu + U), %^(a)</u>
1	20.05 ± 0.18
2	21.58 ± 0.17 ^(b)
3	19.98 ± 0.13
4	19.91 ± 0.14
5	20.33 ± 0.08
6	19.89 ± 0.06
7	19.75 ± 0.07
8	19.90 ± 0.12
9	19.48 ± 0.18
10	19.07 ± 0.08
11	19.52 ± 0.05
12	18.86 ± 0.09
13	19.55 ± 0.08
<u>Fine Microspheres</u>	
1	19.52 ± 0.12
2	19.76 ± 0.14

(a) Errors are for 95% confidence limits on the mean.

(b) May be in error; spill occurred while preparing sample for analysis.

4. FUEL FABRICATION (A. H. Bremser)

4.1. Fabrication of UO_2 Insulator Pellets (A. H. Bremser, L. J. Ferrell, D. L. Fowler)

About 500 UO_2 insulator pellets are required for the EBR-II reload pins which are scheduled for assembly during FY-1971. The first batch has been pressed, sintered, and centerless ground to specification. The second batch was rejected because it became contaminated with molybdenum during sintering. Another batch of UO_2 pellets has been pressed and will be sintered and ground during the next quarter. The two batches will then be combined to form one lot.

4.2. Fabrication of EBR-II Fuel

4.2.1. (U,Pu) O_2 Powder Treatment (C. R. Sherman)

In order to produce a suitable feed for an automatic mechanical press, binder and lubricant were added to 1.5 kg of the calcined (U,Pu) O_2 powder. (See section 3.1.) The first step in the powder treatment was to split the lot into six 250-g batches. Then, 57 g of demineralized water and 0.75 g of stearic acid were added to each batch, and the mixture was blended for 15 minutes with a Hobart paddle-mixer. Next, 22.5 g of a solution containing 20 wt % Carbowax 20,000 in demineralized water was added, and the slurry was blended for an additional 15 minutes. The slurry was dried for 24 hours at about 100C under a flowing stream of dry N_2 -6% H_2 at a pressure of 5 to 7 inches of mercury (absolute). Finally, all batches were granulated and blended for 30 minutes in a V-cone blender to obtain one lot.

4.2.2. Fabrication of Fuel Pellets and Shards (A. H. Bremser, L. J. Ferrell, D. L. Fowler)

Sufficient pellets for three fuel pins, analytical samples, and archive samples were fabricated. The general flowsheet for preparing

pellets was described previously.¹¹ A portion of the prepared powder (see section 4.2.1) was prepressed and granulated several times to produce a feed that could be cold-pressed to about 45% theoretical density. This green density was required to obtain pellets (fabricated with available punch and die sets) that would meet both diameter and density specifications after sintering. After the binder was burned out of the green pellets, the pellets were sintered at 1650C under a flowing stream of N_2 -6% H_2 . All the fired pellets have been centerless ground to the specified diameter, washed, and dried.

The remainder of the prepared powder was pressed into pellets having a green density of about 40% theoretical. After sintering, these pellets will be crushed into shards to be used as vipac feed. Since the critical requirement for pellets to be fabricated into shards is the fired density rather than the diameter, no attempt was made to increase the green density by prepressing and granulating several times. These pellets will be fired and crushed into shards during the next quarter.

5. IRRADIATION TESTING (E. N. Harbinson)

5.1. Time Required for Inpile Restructuring (E. N. Harbinson, R. E. Womack)

The effects of heat rate and time on the restructuring characteristics of sol-gel $\text{UO}_2\text{-PuO}_2$ spheres and of angular particles and pellets prepared from coprecipitated $\text{UO}_2\text{-PuO}_2$ powder are being evaluated. Sixteen capsules containing three pins each—one vipac, one sphere-pac, and one pellet—have been irradiated for from 8 hours to 55 days at linear heat ratings of 6 to 20 kW/ft in the thermal flux of the BAWTR. The irradiation history for these 16 capsules was described previously.¹²

The post-irradiation examination of 27 fuel pins from nine previously disassembled capsules¹² is progressing in B&W's hot cell facilities. The gas analyses were delayed because of an equipment malfunction. However, the first fuel pin has been punctured for gas analysis, and detailed metallographic examination is under way. Hot cell examination of these 27 pins will continue during the next quarter.

5.2. EBR-II Irradiations (E. N. Harbinson)

The primary objective of the EBR-II irradiations is to obtain data on the operational characteristics of particulate fuels irradiated in a fast reactor. The effects of heat rate and burnup on the overall performance of sol-gel spherical particles and of angular particles and pellets prepared from coprecipitated $\text{UO}_2\text{-20% PuO}_2$ powder will be compared and evaluated. Twenty-eight unencapsulated pins are scheduled to be irradiated in the EBR-II at 14 to 16 kW/ft as part of a 37-pin subassembly to be shared with ORNL.

After inspecting the 21 fuel pins described in the previous quarterly report,¹² three were rejected because of dimensional defects in the cladding. The remaining 18 are available for shipment. The

detailed fabrication history and the nondestructive testing of these fuel pins are described in the following paragraphs.

5.2.1. Fuel Pin Description

The B&W fuel pin is similar in design to the ORNL fuel pins, which will be irradiated in the same subassembly. Detailed features and dimensions of these pins are shown in Figure 5-1. The as-built data for each fuel pin are presented in Table 5-1. 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 %	93 ²³⁵ 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

DATE	REV. NO.	REVISION DESCRIPTION
4-8-70	1	GENERAL REVISION

BILL OF MATERIAL				
ITEM	DWG. NO.	DESCRIPTION	QUAN.	MAT'L
1	NDC 1730D	TOP END CAP	1	316 SST.
2	NDC 1730D	TUBE .250 ± .001 OD x .215 ± .001 ID x 37 ± LONG	1	316 SST
3	NDC 1730D	TUBE .187 ± .002 OD x .014 ± .001 WALL ID. 438 LONG	1	316 SST.
4	NDC 1730D	PLUG	1	316 SST.
5	NDC 1730D	SPRING	1	AS NOTED
6	NDC 1730D	ROD .212 ± .001 DIA x 2 $\frac{7}{32}$ LG.	1	NICKEL
7	NDC 1730D	PAD $\frac{7}{32}$ DIA. x $\frac{1}{16}$ THICK	2	FIBERFRAX
8	NDC 1730D	INSULATOR PELLET "K" DIA x $\frac{1}{4}$ LG.	4	DEFLECTG UO ₂
9	NDC 1730D	SPHERE-PAC, VIPAC OR PELLET FUEL	AS REQD	²³⁵ 10-20% MU) O ₂
10	NDC 1730D	BLANKET PELLETS "K" DIA x $\frac{1}{4}$ LG.	AS REQD	DEFLECTG UO ₂
11	NDC 1730D	WIRE .040 DIA. (TO BE INSTALLED BY ANL)	AS REQD	316 SST.
12	NDC 1730D	BOTTOM END CAP	1	316 SST.

① FULL PENETRATION PUSSION WELD
REQUIRED (1-T WITH $1\frac{1}{2}$ T LAND)

Table 5-1. As-Built Description of Babcock & Wilcox 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	Vi-pac	pellet	sphere-pac	pellet	pellet	pellet	Vi-Pac	sphere-pac	Vi-Pac	Vi-Pac	Vi-Pac	Vi-Pac	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
²³⁵ U/U, wt %	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68	92.68
(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	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.	0.210	0.210	0.211	0.211	0.210	0.210	0.211	0.210	0.211	0.210	0.210	0.210	0.210	0.210	0.211	0.210	0.210	0.211
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	2.2495	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.

5.2.2. 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 powders. For each form of fuel the UO_2 is fully enriched in ^{235}U . The isotopic composition of the fuels and complete characterization data for both the fuel and blanket material were presented previously.^{13,14} The blanket and insulator material in all the pins is depleted UO_2 pellets.

5.2.3. Cladding Tubing

5.2.3.1. Procurement Specifications

The cladding for these fuel pins is 316 stainless steel tubing with an OD of 0.250 ± 0.001 inch and a wall thickness of 0.016 ± 0.001 inch. The tubing, obtained from BNWL, is from the same lot as that used by ORNL for their fuel pin cladding. BNWL purchased this material from Carpenter Steel Company according to ASTM Specification A213 (except tolerances) and BNWL purchase order B9S-777-47372. All the tubing was fabricated from Carpenter Steel Co. heat number 87210. Results of independent chemical analyses performed by National Spectrographic Laboratories are presented in Table 5-2.

5.2.3.2. Inspection and Testing

Fabrication tolerances on the tubing were specified in the BNWL purchase order. The tubing was 100% ultrasonically inspected by Wolverine Tube to ensure that no tubes showing defects greater than the standard (0.001-inch deep $\times$ 0.030-inch long $\times$ 0.005-inch wide) would be accepted. Inside and outside diameters of all tubes were measured to a precision of ± 0.0001 inch with an air plug and air ring gage.

The microstructure of this material is shown in Figures 5-2 and 5-3. Results of room temperature tensile tests are presented in Table 5-3.

Figure 5-2. Microstructure of EBR-II Fuel Cladding

Figure 5-3. Typical End Closure Weld for EBR-II Fuel Pin

Table 5-2. Alloy Composition of Cladding and End Plug Material

Element	316 SS cladding comp, wt %		316 SS end plug comp, wt %	
	Specification limits	Independent analysis(a)	Specification limits	Independent analysis(a)
Carbon	0.04 to 0.06	0.054	0.08 max	0.048
Manganese	1.00 to 2.00	1.51	1.00 to 2.00	1.30
Phosphorus	0.03 max	0.013	0.03 max	0.013
Sulfur	0.03 max	0.006	0.03 max	0.006
Silicon	0.75 max	0.46	0.75 max	0.45
Nickel	12.0 to 14.0	13.29	12.0 to 14.0	13.18
Chromium	16.0 to 18.0	16.81	16.0 to 18.0	16.70
Molybdenum	2.00 to 3.00	2.46	2.00 to 3.00	2.49
Copper	0.20 max	0.07	0.50 max	0.04
Boron	0.0010 max	0.0006	0.002 max	0.0006
Nitrogen	0.02 to 0.03	0.0074	0.06 max	0.0072
Cobalt	--	0.045	--	0.026
Iron	Balance	Balance	Balance	Balance

(a) Analyzed by National Spectrographic Laboratories, Inc.

Table 5-3. Cladding Material Tensile Test Data

Tube No.	Temperature	Yield strength 0.2% offset, psi	Ultimate strength, psi	Total elongation, %
16	RT	37,500	88,900	56
35	RT	35,700	84,100	59
53	RT	36,300	85,500	57

Note: Tensile tests were performed by B&W's Lynchburg Research Center.

All tests were performed on tubing from Carpenter Steel Company, mill release numbers 83594, 83613, and 83619.

Table 5-4. Alloy Composition of Nickel Reflector, Plenum Spring, and Plenum Tube

Element	Nickel reflector, wt % ^(a)	302 SS plenum spring, wt % ^(a)	316 SS plenum tube, wt % ^(a)
Carbon	0.048	0.065	0.065
Manganese	0.21	0.95	1.51
Sulfur	0.008	0.020	0.007
Phosphorus	--	0.018	0.012
Silicon	0.016	0.95	0.48
Nickel	99.4	7.83	13.47
Molybdenum	--	--	2.47
Chromium	--	17.94	16.73
Copper	0.032	--	0.06
Cobalt	0.060	--	0.048
Iron	0.20	Remainder	Remainder
Boron	--	--	0.0005
Nitrogen	--	--	0.010

^(a)Analyzed by National Spectrographic Laboratories, Inc.

Table 5-5. Composition of Fiberfrax^(a)

Element or compound	wt %
Si as SiO ₂ ^(b)	48.3
Al as Al ₂ O ₃ ^(b)	50.2
Fe as Fe ₂ O ₃	0.3
Cu as Cu ₂ O	<0.1
B as B ₂ O ₃	1.2

^(a)Analyzed by B&W's Alliance Research Center.

^(b)Wet chemical analysis.

Note: All the elements are reported as the oxides. This does not necessarily imply their presence as such. The elements Ti, Mg, Ni, Cr, Mo, V, Co, Mn, Zn, Pb, Sn, and Zr were not detected in this sample. The limit of detectability for these elements by the semiquantitative technique is approximately 0.05%.

5.2.4. End Fittings

End caps for the fuel pins were made from 316 stainless steel bar stock obtained from BNWL. BNWL purchased this material from Crucible Steel Company according to ASTM Specifications A-276-67 and A-484-65 and to BNWL purchase order B9S-777-47376. Results of independent chemical analyses performed by National Spectrographic Laboratories are presented in Table 5-2.

5.2.5. Reflector, Spring, and Plenum Tube

The bar stock for the nickel reflector was obtained from BNWL, who purchased it according to ASTM Specification B-160061 and BNWL purchase order B9S-777-47368. Independent chemical analyses are presented in Table 5-4.

The 302 stainless steel plenum springs were obtained from BNWL, who purchased them according to the specifications in BNWL purchase order B9S-777-55818. Independent chemical analyses are presented in Table 5-4.

BNWL supplied the 316 stainless steel plenum tubing, which was purchased from Carpenter Steel Company according to ASTM Specification A-269 and BNWL purchase order B9S-777-47370. Independent chemical analyses are presented in Table 5-4.

5.2.6. Fiberfrax Pad

Chemical analyses of the Fiberfrax material used for the top and bottom pad are presented in Table 5-5.

5.2.7. Fuel Pin Assembly and Quality Control

Before the pins were assembled, all metallic components were inspected, and the bottom end caps were welded to the clad tube. After welding, each bottom closure weld was helium-leak-tested. The leak-test results are presented in Table 5-6. Each bottom closure weld was radiographed in accordance with the Guide for Irradiation Experiments in EBR-II.¹⁵ Any closure weld that did not meet the weld acceptance criteria was rejected. Room-temperature burst tests were performed on closure welds using the standard welding procedure and cladding and end caps from the lots above; all welds failed outside the weld

and heat-affected zones. Oversized welds were polished to size before being radiographed and helium-leak-tested.

After the bottom closure weld was established as acceptable, the fuel and internal hardware were loaded into each fuel pin. The top end cap was welded in place after a mixture of helium plus 1 cc of xenon was introduced into the fuel pin.¹² The gas mixture was at 1.1 atmosphere pressure (at room temperature). All closure welds met the acceptance criteria.

Table 5-6. Helium Leak Test Results

Fuel pin No.	Test date	<u>Bottom Closure Welds</u>	
		System sensitivity, $\text{cm}^3/\text{s} \times 10^{10}$	Measured leak rate, $\text{cm}^3/\text{s} \times 10^{10}$
D-2	May 5, 1970	4.7	<4.7
D-4	April 6, 1970	5.1	<5.1
D-5	May 5, 1970	4.7	9.2
D-6	April 6, 1970	5.1	<5.1
D-9	April 6, 1970	5.1	<5.1
D-10	May 5, 1970	4.7	<4.7
D-12	April 6, 1970	5.1	<5.1
D-14	April 6, 1970	5.1	<5.1
D-16	April 6, 1970	5.1	7.6
D-17	April 6, 1970	5.1	<5.1
D-18	May 5, 1970	4.7	<4.7
D-19	May 5, 1970	4.7	<4.7
D-20	May 5, 1970	4.7	4.7
D-21	April 6, 1970	5.1	<5.1
D-22	May 5, 1970	4.7	<4.7
D-24	May 5, 1970	4.7	<4.7
D-25	May 5, 1970	4.7	<4.7
D-27	June 25, 1970	2.1	<2.1
D-29	June 25, 1970	2.1	<2.1
D-30	June 25, 1970	2.1	<2.1
D-31	June 25, 1970	2.1	<2.1
<u>Welded Fuel Pin (both end plugs welded in place)</u>			
<u>Group No.</u>			
1(a)	July 21, 1970	9.3	<9.3
2(b)	July 21, 1970	9.3	<9.3
3(c)	July 21, 1970	9.3	<9.3

(a) Pin numbers D-4, D-6, D-9, D-12, D-14, D-16, and D-17 were in group 1.

(b) Pin numbers D-5, D-18, D-20, D-21, D-22, D-24, and D-25 were in group 2.

(c) Pin numbers D-2, D-10, D-19, D-27, D-29, D-30, and D-31 were in group 3.

6. ANALYTICAL SUPPORT (R. H. Dodd)

6.1. Quality Verification (R. V. Carlson, R. H. Dodd)

A formal quality verification plan for the fuel being prepared in FY-1971 was written and approved by the USAEC. The procedures in MIL-STD-414¹⁶ are followed to ensure representative sampling of pellet lots, and the procedures given by Jones¹⁷ are followed to ensure representative sampling of sphere and shard lots. The acceptance criteria are based on the finished fuel specifications. The basic quality verification program is summarized in the following paragraphs.

6.1.1. Preparation of Coprecipitated (U,Pu)O₂ Powder

The Pu(NO₃)₃ and UO₂(NO₃)₂ feed solutions are each blended into a single lot and analyzed on a weight basis. The input solutions for each coprecipitation run are then measured by weight. A grab sample is removed from each batch of powder and analyzed for Pu/(Pu + U). To be accepted, a batch must have an average Pu/(Pu + U) content between 19.5 and 20.5%. (See Table 3-2.) All batches are blended to form a single lot of powder as feed for pellet and shard fabrication.

6.1.2. Preparation of Sol-Gel (U,Pu)O₂ Microspheres

Each batch of UO₂ sol and PuO₂ sol is analyzed on a weight basis. (See Table 3-5.) The input sols for each sphere-forming run are then measured by weight. A grab sample is removed from each batch of mixed sol and analyzed for Pu/(Pu + U). To be accepted, a batch must have an average Pu/(Pu + U) content between 19.5 and 20.5%. (See Table 3-8.) The microsphere batches that pass this acceptance criterion may be blended into larger batches and fired to (U,Pu)O₂. A grab sample is removed from each firing batch and analyzed for O/M ratio. To be accepted, the O/M ratio must be between 1.96 and 1.99.

All acceptable batches of microspheres are blended into two lots—one containing the coarse fraction and one containing the fine fraction. Eight 3- to 4-g grab samples (a total of at least 30 g) are taken from each lot for final characterization.

6.1.3. Fabrication of (U,Pu)O₂ Pellets

All of the pellets are pressed from a blended lot of fully enriched UO₂-20% PuO₂ powder and fired as one lot. Fired pellets are centerless ground to 0.206 ± 0.001 inch diameter. After grinding, the length and the weight of each pellet are measured. To be accepted, these parameters must lie in the acceptable density band on the Pellet Density Nomograph.¹⁶ At least 20 pellets are selected from the pellet lot for final characterization.

6.1.4. Fabrication of (U,Pu)O₂ Shards

All of the pellet feed material is pressed from a blended lot of fully enriched UO₂-20% PuO₂ powder and fired as one lot. The densities of 80 pellets are measured to determine the average. To be accepted, the average density must be $93 \pm 2\%$ of theoretical. The pellets are then crushed and separated into three size fractions. At least 10 g of material is selected from at least four random locations in each of the three size fractions to form a master sample for final characterization.

6.1.5. Fabrication of UO₂ Blanket and Insulator Pellets

All of the pellets are pressed from one lot of UO₂ powder and fired as several batches. The densities of 50 pellets from each firing batch are measured to determine the average density. To be accepted, the average density must be $93 \pm 2\%$ theoretical. The pellets from acceptable batches are combined to form one lot. All the pellets are then centerless ground to 0.214 ± 0.002 inch. At least 20 pellets are selected from the lot for final characterization. The remaining pellets are assembled into 7-inch stacks, and the average density of each stack is measured. To be accepted for loading into a pin, the average density of a stack must be $93 \pm 2\%$ of theoretical.

6.2. Oxygen-to-Metal Ratio Analysis (R. H. Dodd, D. H. Schmitt, R. V. Carlson)

B&W uses a microthermogravimetric technique¹⁹ to measure the oxygen-to-metal ratio (O/M) of nuclear fuel materials. This procedure, adapted from a method developed by W. L. Lyon,²⁰ is based on (1) oxidation or reduction of the oxide depending on the type of sample (UO_2 , PuO_2 , or mixed oxide), and (2) measurement of the weight changes accompanying these reactions as indicated by an electrobalance. For a mixed oxide, the sample is dried in an argon atmosphere at 110C (if moisture has to be removed), oxidized in air at 850C, and then reduced to stoichiometric $(\text{U}, \text{Pu})\text{O}_2$ in a N_2 -6% H_2 atmosphere at 850C.

B&W used this method in two round-robin programs^{21,22} and obtained satisfactory O/M values for urania-plutonia pellets. In the current program, satisfactory results have been obtained for pellets, shards, and fine microspheres. However, difficulties have been encountered with coarse microspheres—the precision is often poor, and the indicated O/M values are often lower than would be expected for the conditions under which the microspheres are calcined. The data for samples A and B in Table 6-1 are representative of results obtained for coarse microspheres calcined at about 1200C in N_2 -6% H_2 . The oxidation and reduction temperature during the analyses was 850C for both samples.

A typical thermogram for a urania-plutonia pellet sample is shown in Figure 6-1. The reduction time for a sample is normally 5 to 6 minutes. However, reduction times of 30 minutes or longer are generally observed for coarse microspheres. Since pellet samples are crushed to increase the reaction rates during analyses, this technique was applied to several coarse microsphere samples. As indicated in Table 6-1, however, the O/M values obtained after such treatment are always hyperstoichiometric. Since a pellet is more easily crushed than is a sample of spheres, it is possible that when spheres are crushed, sufficient heat is generated to oxidize the sample.

The 850C reduction temperature specified in B&W's procedure was selected on the basis of an experiment in which the apparent oxygen stoichiometry of urania-plutonia pellets was determined at reduction temperatures between 700 and 1000C.¹⁹ This experiment was repeated

with a sample of coarse microspheres. A comparison of data from the two experiments (Figure 6-2) indicates that the optimum reduction temperature for coarse microspheres is higher than for pellets. At 950C the reduction time is about 5 to 6 minutes, and the probability of forming a hypostoichiometric oxide is small. Therefore, a reduction temperature of 950C is now used at B&W in measuring the O/M of coarse microsphere samples. The data for sample C (coarse microspheres calcined at about 1125C in N_2 -6% H_2) are representative of the results obtained under these conditions.

Table 6-1. Oxygen-to-Metal Results
for Coarse Microspheres

Sample treatment	Apparent O/M, atom ratio		
	Sample A ^(a)	Sample B ^(a)	Sample C ^(b)
None	1.976	1.920	1.988
	1.966	1.947	1.988
	1.968	1.948	1.993
	1.976	1.959	1.985
	--	1.971	--
	--	1.978	--
Crushed before analysis	2.002	2.019	--
	2.003	2.018	--
	--	2.024	--

(a) Analyzed at oxidation and reduction temperature of 850C.

(b) Analyzed at oxidation and reduction temperature of 950C.

Figure 6-1. Typical Thermogram of Urania-Plutonia Sample

Figure 6-2. Effect of Reduction Temperature on Oxygen-to-Metal Ratios

It is not clear why a higher reduction temperature is required for the O/M measurement of coarse microspheres. To obtain a measured O/M value less than 2,000, the final weight of the material being analyzed must be greater than the initial sample weight. (See the formula in Figure 6-1.) If there is incomplete reduction of the hyperstoichiometric oxide (formed during the oxidation cycle) to the stoichiometric oxide, the weight of the final product is too large. Therefore, the apparent O/M will be less than the actual O/M. This factor, as well as the difference in reduction times, indicates that the need for a higher reduction temperature is related to some characteristic that inhibits reduction of the hyperstoichiometric oxide.

Ceramographic examinations of coarse microspheres with a density of about 95% theoretical have indicated that the microspheres generally contain a high-density core surrounded by a higher-density shell. The shell might retard the rate at which the reduction gas gains access to the core of a sphere. This would lead to long reduction times and perhaps to incomplete reduction. At a higher reduction temperature, several factors could improve the reduction behavior. For example, the diffusion rate of the reducing gas through the shell would be increased, the reduction rate would be increased, and the possibility of the shell cracking would be increased, so that the reducing gas would have more rapid access to the internal porosity of a sphere.

This explanation is consistent with the observed behavior of the various materials tested. Difficulties are not always encountered with coarse microspheres. This could be related to the fact that some batches have surface cracks that could provide access to the internal porosity. Pellets and shards are crushed before analysis, so that a high density shell, if present, would not be expected to affect their behavior. Since fine microspheres have diameters that are a factor of about 10 less than those of coarse microspheres, the effects of a high-density shell would not be expected to be nearly so noticeable.

Whether or not our explanation for the difficulties encountered in measuring the O/M of coarse microspheres is correct, we believe that the potential difficulties must be carefully considered to ensure that valid results are obtained. We feel that close attention to the reduction time will indicate whether the reduction temperature is high enough.

We have always obtained good precision and reasonable results with a reduction time of 5 to 6 minutes. If it is not possible or desirable to obtain a thermogram with each O/M measurement, then the technique must be standardized periodically with standards or well-characterized materials that are truly representative of the samples being used.

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