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Quarterly Progress
Report No. 9

August - October 1968

RESEARCH & DEVELOPMENT
DIVISION

NUCLEAR DEVELOPMENT
CENTER

Lynchburg, Virginia

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— Quarterly Progress Report No. 9 —

August - October 1968

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Prepared for
THE UNITED STATES ATOMIC ENERGY COMMISSION
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ABSTRACT

The development of the sol-gel process and related processes for preparing (U,Pu)O₂ fast reactor fuels has continued in Babcock & Wilcox's laboratories. Progress for the ninth quarter ending October 31, 1968, is reported. The program is sponsored by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3714.

Preparation of (U-20Pu)O₂ sol-gel spherical fuel in two size ranges for thermal reactor testing is complete. Two uranium enrichments—natural UO₂ and 20% enriched ²³⁵UO₂—were used to obtain material which will give two different in-pile heat rates at the same elemental compositions. The first irradiation capsule test is complete. The heat rate was 16.7 kW/ft, and the capsule received 9.3 EFPD. The capsule, which is cooling pending hot cell examination, is the first of a series designed to show differences in restructuring kinetics between pellets and vibratory compacted spheres and shards.

Equipment is installed for measuring particle crush strengths, water vapor contents and oxygen-to-metal ratios in fuels. UO₂ gel and oxide spheres have been examined on the B&W scanning electron microscope.

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1. INTRODUCTION

This is the ninth 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 August 1, 1968, to October 31, 1968.

In previous reports it was noted that emphasis of the program has shifted from the gel-addition process to the mixed sol approach developed at Oak Ridge National Laboratory. Both of these processes are in the sol-gel family, but different procedures are used for making mixed (U,Pu)O₂ spheres. In the gel-addition technique, UO₂ gel spheres are prepared first and then converted to mixed gel by soaking the spheres in aqueous plutonium solutions. In the mixed-sol approach, separate sols of UO₂ and PuO₂ are prepared and mixed in the appropriate ratio to give a mixed sol which is co-gelled and then fired to mixed oxide. All of the experimental work reported in the following sections relates to the latter process, since no gel-addition technique has been found that will give sufficient plutonium pickup for fast reactor fuel synthesis.

During this report period the program schedule was changed severely at the request of the Commission. At the start of the period, equipment for some of the unit operations leading to a sol-gel pilot plant was under construction and the fuel preparation schedule included material for fast-reactor exposure at EBR-II. The schedule slowdown resulted in a suspension of pilot plant development and a limitation of fuel preparation of materials for thermal reactor testing in the Babcock & Wilcox Test Reactor (BAWTR). A number of fuel preparation runs have been completed using laboratory scale equipment and are reported in section 2. The present status of the pilot plant equipment is also summarized briefly in the same section. The other sections summarize the fuel characterization and irradiation work in progress, as well as the analytical support for the program.

2. RESULTS AND CONCLUSIONS

2.1. Fuel Preparation

Laboratory scale preparation of spherical sol-gel (U,Pu)O₂ has been demonstrated for material at the 20% Pu/U+Pu level using both natural uranium and 20% enriched uranium. Spheres in two size fractions (<44 μ fines and 420-590 μ coarse) have been made for fabrication of irradiation specimens by Vipac techniques. The mixed oxides were made by direct admixture of the appropriate quadrivalent sols; during the sol preparation steps, differences in chemical behavior were noted between the reagent grade uranyl nitrate (Fisher Chemical Company) used to make the natural uranium sol and the 20% enriched uranyl nitrate used to make the enriched sols. The latter were more difficult to reduce from hexavalent to quadrivalent form and required a 20% reduction in uranium concentration for a quantitative yield of U(IV).

As a result of a schedule slowdown for the project, further work on pilot scale equipment has been postponed. The present laboratory scale apparatus can routinely produce up to 150 g/day of mixed oxides.

2.2. Oxide Characterization

Based on an earlier Oak Ridge system, equipment for measuring the crush strengths of sol-gel spheres has been designed and built in the B&W laboratories. Crush strengths of a series of ThO₂ sol-gel spheres prepared at Oak Ridge were measured at B&W and compared with the Oak Ridge results. Considerable scatter was noted in the crush strengths, and the mean mass required to crush a sphere was generally observed to be less (by 30-50%) than reported by Oak Ridge for each size range tested.

Equipment has been installed and internal procedures have been approved for x-ray diffraction studies of plutonium-bearing materials in the B&W laboratories.

Scanning electron photomicrographs of some randomly-selected UO_2 spherical gels and fired oxides have been made; these are believed to be the first ever made of sol-gel materials. The photographs show considerable microstructure detail and indicate that grain growth during sintering is slow.

2.3. Irradiation Testing

A stretchout in the project schedule has required postponement of fast reactor exposure of sol-gel materials beyond FY 1969. Thermal irradiations are proceeding at a reduced rate, and the first capsule of the thermal series intended to show the restructuring kinetics of the fuel was exposed for 9.6 EFPD in the BAWTR. The heat rate was 16.7 kW/ft and the exposure was completed during October; the capsule is cooling pending hot cell examination.

2.4. Analytical Support

Equipment has been installed for moisture determination in nuclear fuels and the operating procedure is now routine. The sample is heated to the temperature required to evolve the water (1000 C is the instrument maximum) which is trapped in a phosphorus pentoxide electrolytic cell; the water is determined coulometrically by integration of the current required to reconvert the generated phosphoric acid back to the oxide. After some modifications the instrument has been shown to give 99+% of the theoretical water content of citrate and tartrate standards. Secondary standards of chromatographic grade silica have been prepared and analyzed.

Oxygen-to-metal measurements are being run thermogravimetrically, and the method has been reduced to routine for pure uranium systems. Procedure checkout for mixed U-Pu systems is still in progress.

3. FUEL PREPARATION (R. N. Gurley)

3.1. Introduction

In the opening weeks of this report period the FY 1969 project schedule included construction and development of a sol-gel pilot plant. The decision had already been made to base pilot scale work on the Oak Ridge mixed sol approach. The fuel preparation schedule for FY 1969 included three classes of sol-gel fuel:

<u>Fuel</u>	<u>Purpose</u>
Nat UO_2 -20% PuO_2	Thermal exposure
20% enriched UO_2 -20% PuO_2	Thermal exposure
Fully enriched UO_2 -20% PuO_2	Fast exposure (EBR-II)

In addition, provision was made for mixed oxide pellets of the same composition to be made from mixed oxide powder prepared by coprecipitation methods and for angular particles to be made by crushing some of the pelletized material.

To make this material according to the schedule as it existed at the time and to provide for the development of pilot scale equipment, two unit-operations scale systems were under construction at the opening of this report period—a PuO_2 sol thermal denitrator and a spheroidizing system for making mixed oxide gel from input UO_2 and PuO_2 sols. Internal recovery of 2-ethyl-1-hexanol was planned for the spheroidization system.

A severe slowdown in the project schedule eliminated fast reactor testing and further pilot plant development from the FY 1969 schedule. Accordingly, work was terminated on both the thermal denitrator and the gelation system. They are on a standby basis pending reactivation

of pilot plant work. Preparation of fully enriched fuel was also dropped from the schedule. Preparation of natural U-20% Pu and 20% enriched U-20% Pu fuels continued.

A total of 2570 g of mixed-oxide powder containing natural uranium and 1288 g of mixed oxide containing 20% enriched uranium has been prepared by coprecipitation for pelletizing. The natural U-20% Pu sol-gel fuel order is complete, and preparation of 20% enriched U-20% PuO₂ sol-gel has been initiated.

3.2. Pilot Plant Equipment (R. N. Gurley)

Cold checkout and calibration of a thermal denitrator for use in the thermal denitration step of the plutonia sol process was completed in August. The equipment was scheduled to be placed in service in the PuO₂ sol system. However, owing to reduced funding in the Gel-Addition program, work on the thermal denitrator was discontinued.

Equipment for spheroidizing UO₂-PuO₂ sols is nearly complete and has been tested partially with water. The apparatus is entirely housed in one large glove box unit (see Figures 3-1, 3-2, and 3-3). Input materials are UO₂ sol, PuO₂ sol, and the surfactants needed in the spheroidization columns. Products are UO₂-PuO₂ mixed gels of any desired U/Pu ratio. The gels are stripped of organics by steam which is generated and recovered internally in the box; provision is also made for spheroidizing solvent [2-ethyl-1-hexanol (2-EH)] recovery by azeotropic distillation. Wastes from the system include 2-EH still bottoms and unspheroidized fines carried out the top of the spheroidizing column. The entire unit has been placed in standby; remaining steps for its completion include testing with 2 EH and checkout of the 2-EH recovery and steam systems.

At the time the gelation unit was designed, removal of organics from the raw gel by steam stripping was believed to be the method of choice; subsequently, the designers have concluded that organic removal by combined aqueous ammonia and ethanol washes should be provided as an alternate.

Preparation of fuel for the current FY 1969 schedule has continued in the laboratory scale spheroidizing system shown in Figure 3-4.

Figure 3-1. Unit Operations Gelation System (bottom panel off)

Figure 3-2. Unit Operations Gelation System (bottom panel on)

Figure 3-3. Unit Operations Gelation System (access to glove ports depicted)

Figure 3-4. Laboratory Scale Gelation System (presently in service)

Figure 3-5. Flow Sheet for Precipitation of UO_2 -20% PuO_2 by Continuous Coprecipitation Process

3.3. Preparation of (U-20% Pu)O₂ Powder by Coprecipitation (R. V. Carlson)

A total of 1380 g of powder containing 20% PuO₂ in natural UO₂ and 1250 g of powder containing 20% PuO₂ in UO₂ enriched to 20% ²³⁵U is required for irradiation testing under the Gel-Addition contract. These mixed oxide powders have been prepared by continuous coprecipitation of ammonium diuranate-plutonium hydroxide from a uranium-plutonium nitrate solution. The dried precipitate was converted to sinterable powder by calcination and ball milling. Figure 3-5 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.^{1,2}

A total of 2570 g of 20% PuO₂ in natural UO₂ and 1288 g of 20% PuO₂ in UO₂ enriched to 20% ²³⁵U has been prepared for this program. The properties of the powder containing 20% PuO₂ in natural UO₂ have been discussed previously.^{3,4} In the preparation of powder containing 20% PuO₂ in UO₂ enriched to 20% ²³⁵U, the uranium enrichment of the uranyl nitrate feed was adjusted by blending solutions containing natural and fully enriched uranium. The analyses performed on these solutions are summarized in Table 3-1. The UO₂(NO₃)₂ and Pu(NO₃)₄ feed solutions were carefully analyzed and then weighed out to get a Pu/(Pu+U) ratio of 20.00 ± 0.14%. The confirming analyses of the two blended feed solutions used in the preparation of the enriched powder indicated that the first contained 20.2 ± 0.4% Pu/(U+Pu) and the second contained 20.3 ± 0.4% Pu/(U+Pu). No other data are available at this time.

3.4. Preparation of (U-20% Pu)O₂ Microspheres (R. V. Carlson)

A sufficient quantity of natural UO₂-20% PuO₂ microspheres for the Gel-Addition irradiation program has been prepared. In addition, preparation of the required amount of UO₂ (enriched to 20% ²³⁵U)-20% PuO₂ microspheres has been initiated.

3.4.1. Preparation of Natural UO₂ Sol

A total of 1337 g of uranium was converted into stable UO₂ sols using the ORNL formate flow sheet.⁵ The results from the analyses of the stock uranyl nitrate acid solution are summarized in Table 3-1, and the run data from the sol preparations are summarized

Table 3-1. Composition of Stock Uranyl Nitrate Solutions

Type of sample	²³⁵ U content, %	No. of analyses	Uranium, M ^(a)	Uranium concentration, mg/g solution ^(a)	Nitrate/uranium mole ratio ^(a)
Nat U for downgrading and powder prep	--	9	1.175 ± 0.009	201.6 ± 1.6	2.10 ± 0.03
Nat U for downgrading and sol prep	--	18	--	206.5 ± 0.8	--
Nat U for downgrading and sol prep	--	7	--	199.7 ± 0.9	--
Enriched U for downgrading	93.162	15	--	214.8 ± 0.8	--
Nat U for sol prep (#90 - 101)	--	9	1.27 ± 0.01	--	4.14 ± 0.05
Enriched U for sol prep (#102 - 108)	19.70	9	1.30 ± 0.01	--	4.21 ± 0.05
Enriched U for sol prep (#109 - 112)	NA ^(b)	9	1.293 ± 0.006	205.5 ± 1.1	4.25 ± 0.04
Enriched U for powder prep	19.70	9	--	207.4 ± 0.8	--

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

^(b)NA - not available.

in Table 3-2. The run data from the other natural UO_2 sols required for this sphere preparation campaign have been summarized previously.⁶

One of the five sol runs containing natural UO_2 (batch 98) resulted in a sol from which a large quantity of solid material slowly settled upon standing. This unstable sol was grey rather than the usual black. It is thought that the particle size in this run was too large to form a stable colloid, but the reason is not known.

Batches 87 - 96 are not listed in Table 3-2. Several of these were prepared under other projects, and the rest were test runs with new equipment. One important observation from these runs was that a Type-303 stainless steel stirring rod was severely corroded during the catalytic hydrogen reduction of U(VI) . Because of the impurities introduced from this corrosion, a number of runs were rejected and a glass stirring rod that was used previously was placed back in the system.

Table 3-2. Data From the Preparation of UO_2 Sols

Batch No.	^{235}U enrichment, %	Uranium reduced, g	Uranium concentration during reduction, M	Reduction time, hr
97	0.71	226.6	1.06	3.8
98 ^(a)	0.71	226.6	1.06	4.0
99	0.71	370.1	1.04	8.0
100	0.71	370.1	1.04	7.5
101	0.71	370.1	1.04	6.0
102	19.70	379.4	1.06	>32.0 ^(b)
103	19.70	379.4	1.06	>31.0 ^(b)
104	19.70	52.6	0.276	3.5
105	19.70	157.9	0.830	<5.0 ^(c)
106	19.70	210.1	0.830	4.2
107	19.70	252.0	0.826	3.5
108	19.70	227.6	0.826	3.5
109	NA ^(d)	249.9	0.822	3.5
110	NA	249.9	0.822	3.8
111	NA	249.9	0.822	3.8
112	NA	249.9	0.822	4.0

^(a) Sol was unstable.

^(b) U(VI) reduction was not quantitative.

^(c) Over-reduction occurred.

^(d) NA - not available.

Table 3-3. Summary of Batch Preparation of Pu(IV) Sols

Batch No.	Stock solution		Pu input, g	4 M NH_4OH , l	No. washes	Vol H_2O per wash, l	NO_3^-/Pu mole ratio to peptize	Baking time, hr	Final NO_3^-/Pu mole ratio	Yield of denitrated powder	Pu recovered as sol, % ^(a)
	Pu, g/l	H^+ , M									
22	56.2	1.0	99.5	2.5	5	1.5	1.87	0.2	0.15	112.6	96
23	56.2	1.0	99.5	2.5	5	1.5	1.87	0.3	0.15	76.5 ^(b)	65 ^(b)

^(a) Assuming denitrated powder is 85 wt % Pu.

^(b) Yield reduced because of in-box spill during processing.

3. 4. 2. Preparation of UO_2 Sol Enriched in ^{235}U

A total of 1742 g of uranium containing a nominal 20% ^{235}U was converted into stable UO_2 sols using the ORNL formate flow sheet.⁵ The results from the analyses of the stock uranyl nitrate acid solutions are summarized in Table 3-1, and the run data are summarized in Table 3-2.

In the first two runs (batches 102 and 103) with enriched uranium, the reduction of U(VI) was not quantitative even after allowing the reaction to proceed for over 30 hours. The real cause of this trouble is not known, but the problem was eliminated by diluting the input solution and reducing the total uranium mass in a batch. Once satisfactory conditions were found, sol preparation proceeded on a routine basis.

3. 4. 3. Preparation of PuO_2 Sol

About 160 g of plutonium were converted into stable PuO_2 sols using the ORNL precipitation-peptization flow sheet.⁷ The operating procedure has been previously reported,⁸ and the run data from these two batches are summarized in Table 3-3. No unusual problems were encountered with either run.

3. 4. 4. Sphere Formation (Natural UO_2 -20% PuO_2)

A photograph of the laboratory scale sphere-forming system is shown in Figure 3-4. The right-hand side of the glove box contains the sphere-forming column, and the left-hand side contains the equipment for making fines and for treating the gel spheres before sintering. The maximum capacity of this system is about 150 g oxide per 8-hour day. Several problems with this system have been discussed previously.⁸ The most serious was that the surfactant levels in the 2-ethyl-1-hexanol (2-EH) had to be adjusted frequently to obtain a spherical product. This was thought to be due to the changing properties of the sol resulting from oxidation while the UO_2 sol was stored in the air atmosphere of the plutonium glove box. During this campaign sufficient UO_2 sol for only one day's run was placed in the glove box each day. The remainder of the UO_2 sol was stored in an inert atmosphere glove box. A new problem encountered was extremely long column drying times

(up to 3 hours). This is probably due to the absorption of moisture from the very humid summer atmosphere into the 2-EH. (See reference 9 for a discussion of water pickup by 2-EH.) As a result of these difficulties, the operating procedure was changed several times, and the following are now standard:

For column prepared microspheres:

1. The surfactants (Span 80 and Ethomeen S/15) are pre-mixed in the 2-ethyl-1-hexanol to the desired concentrations.
2. The water concentration in 4 l of 2-EH is brought up to 0.4 vol %, and this organic is placed in the glove box storage tank.
3. Eight batches of mixed sol (50 ml each) are injected into the column through a two-fluid nozzle. (Fresh sol is mixed and introduced into the box each day.) After each batch of sol is injected, an additional 4 l of pre-mixed 2-EH containing 0.1 vol % H_2O are added to the storage tank. When the 16 l tank is filled, 12 l of 2-EH are pumped out to allow further addition of dry organic.
4. The total column residence time of the spheres is about 2 hours, at which time they drop through the throat. After all the spheres have dried in the column, they are soaked about 15 minutes in concentrated NH_4OH , washed with ethanol, and pre-dried with argon. Then they are dried overnight in a vacuum oven (150 C, 15" Hg) under nitrogen.

For the stirred-pot prepared spheres:

1. The surfactants are pre-mixed in the 2-EH to the desired levels, and the water concentration is brought up to 0.5 vol %.
2. About 4 l of the pre-mixed organic are added to the pot.
3. Next 75 ml of mixed sol are injected into the stirred organic, and stirring is continued for 20 minutes. After allowing the spheres to settle for 30 minutes, the bulk of the organic is pumped out of the pot. The remaining organic is decanted off the spheres.

4. The spheres are then soaked in concentrated NH_4OH for about 15 minutes, washed with ethanol, and pre-dried with argon. Finally, they are dried overnight in a vacuum oven (150 C, 15" Hg) under nitrogen.

Two separate batches of stock UO_2 sol were used in these runs. In each case the surfactant levels in the 2-EH required to make spherical particles remained constant once the appropriate concentrations were determined. With the first stock batch, the column was operated for four weeks with no change in surfactant levels.

3.4.5. Sphere Formation (UO_2 Enriched to 20% ^{235}U , 20% PuO_2)

The same procedure as summarized above has been used to prepare mixed PuO_2 - UO_2 spheres containing 20% ^{235}U . At the present time about 500 g of gel have been produced from this run.

3.4.6. Sintering and Classification of Natural UO_2 , 20% PuO_2 Spheres

The dried gel was handled as five batches. Each batch was fired according to the following schedule:

Under CO_2 atmosphere:

Heat to 450 C at 50 C/hr
Heat to 600 C at 25 C/hr
Heat to 900 C at 50 C/hr
Hold at 900 C about 2 hr

Under N_2 -6% H_2 atmosphere:

Heat to 1250 C at 200 C/hr
Hold at 1250 C for 4 hr
Cool to room temperature

The final classification of the large spheres included screening and separation of the non-rounds. Only the 420 - 590 μ material was accepted, and this was passed over a roundometer five times. The fine spheres were screened, and only the material that was less than 44 μ in diameter was accepted. The quantity of material recovered from each batch is summarized in Table 3-4.

A total of 31% of the input plutonium and uranium was recovered as usable material. This includes all losses incurred during shake-down and start-up of the system, column operation, sizing, and rounding.

Table 3-4. Sol-Gel Material Recovered From Sintering Runs

<u>Batch</u>	<u>420 - 590μ rounded product, g</u>	<u>Coarse product waste, g^(a)</u>	<u><44μ product, g</u>
1	65.7	151.3	--
2	38	84	91
3	189	134	147
4	326.3	221.8	163.0
5	<u>25.0</u>	<u>97</u>	<u>61.0</u>
Total	644	688	462

(a) All off-sized material and material rejected from the roundometer are included in the waste.

3.5. Conclusion

It has been demonstrated that up to 150 g of mixed $\text{UO}_2\text{-PuO}_2$ sol-gel microspheres can be prepared in an 8-hour day on a routine basis with the laboratory system (see Figure 3-4). However, owing to the inherent deficiencies in this system, the total process efficiency is quite low. An improved performance would be expected with the unit operations system (see Figures 3-1, 3-2, and 3-3) if it were completed because of better control of the atmosphere, moisture content, feed rates, and injection system.

It has been demonstrated that with a given stock batch of sol, the necessary column conditions to prepare acceptable microspheres remain constant.

4. OXIDE CHARACTERIZATION (J. M. Kerr)

4.1. Materials Characterization

4.1.1. Particle Crush Strength

An apparatus has been designed and built at B&W for the empirical measurement of crush strengths of sol-gel spheres. The apparatus is based on an Oak Ridge instrument and is illustrated in Figure 4-1. Briefly, it consists of an O'Haus triple beam balance with a leverage factor of 2.6:1. Weight is added by adding water from a reservoir through a solenoid valve operated from a switch outside the glove box. Individual spheres are placed between two high-density alumina plates, and the crush point is detected through a contact microphone attached to the top plate. When the crushing noise is detected (by either loudspeakers or earphones, depending on the size of particle), the solenoid valve is closed and the amount of water in the container is related by the leverage factor to the weight necessary to crush the particle.

Table 4-1 shows the crush strength values observed for some thorium spheres prepared at Oak Ridge and measured both at Oak Ridge and in the B&W laboratories.

Table 4-1. ThO₂ Spherical Particle Crush Strengths

Particle designation (ORNL)	CSS 20/30	CSS 35/40	CSS 50/60	CSS 70/80	CSS 140/200
Particle size					
(Avg)	650 μ	450 μ	280 μ	200 μ	90 μ
(Range)	590-840 μ	420-500 μ	250-297 μ	177-210 μ	74-105 μ
ORNL crush strength (avg)	3300 g	1800 g	1000 g	600 g	270-400 g
B&W crush strength (avg)	2400 g	1600 g	700 g	560 g	200 g
One standard deviation	366 g	409 g	127 g	253 g	68 g

Figure 4-1. Schematic Diagram of B&W Particle Crush Strength Apparatus

① Triple Beam Balance	⑦ Hot Pressed Al_2O_3 Plate	
② Filling Bottle for H_2O	⑧ Contact Microphone	
③ Reservoir for H_2O	⑨ Solenoid Switch	
④ Solenoid Shut-off Valve	⑩ Amplifier	} external to glove box
⑤ Hot Pressed Al_2O_3 Plate	⑪ Loud-speaker	
⑥ Spherical Fuel Particle	⑫ Earphones	

It should be noted that the standard deviation from average observed at B&W is very large; the reliability of small numbers of crush strength values is therefore questionable. Figure 4-2 is a plot of the crush strength data. The lengths of the bars through the B&W data points indicate ± 1 standard deviation. B&W values generally fall below ORNL values, and the most significant departure is at the small sizes and large sizes. On a semilog plot, neither set of data falls in a straight line. Judging from the raw data and the calculated standard deviation, particle crush strength data are valid only for comparative purposes and even then, large numbers of particles must be run to get a meaningful average value.

Figure 4-2. ThO₂ Particle Crush Strength Vs
Average Particle Size

4.1.2. Plutonium X-Ray

Detailed operating procedures for using the X-ray equipment with plutonium-bearing materials have received internal approval.

4.1.3. Scanning Electron Photomicrography

Samples of UO_2 gel and fired oxide spheres were sent to B&W's Alliance Research Center for preliminary examination with a scanning electron microscope which was installed there early in 1968. This instrument is of particular interest because of its extreme depth of field at high magnification. Figures 4-3 through 4-6 show the results obtained at various magnifications. These pictures exceeded our expectation that scanning electron microscopy will be useful in delineating the microstructure of nuclear fuels. There are obvious differences between the structure of the gel and oxide sphere as well as between the surface and interior of the oxide sphere. It appears that the oxide spheres are themselves made up of small spheroidal crystallites or grains, yet with appreciable porosity remaining between the grains. It also appears that the grain growth that occurred during sintering was quite slow. This work was carried out at ARC by L. W. Sarver of the Metallurgy and Welding Section.

4.2. Fuel Fabrication Studies

The schedule stretchout discussed previously in this report (section 1) resulted in some changes in vibratory compaction objectives for FY 1969. A packed density in the range of $85 \pm 1\%$ of theoretical is considered achievable by spherical fuels, but the experimental evidence indicates that three size fractions are required. Because of funding limitations, development of spheroidizing methods that will yield three size fractions has been postponed beyond FY 1969; hence, current studies in this area are restricted to densities in the range $81 \pm 1\%$ TD, which are achievable with two size fractions. Therefore, all fuel materials for reactor exposure will be prepared in this smeared density range so that microstructure changes on Vipac shards and spheres and on pellets can be compared on the basis of equal smeared densities.

For FY 1969 the only fabrication studies planned are those required to fabricate the irradiation specimens. The work will be completed in the next quarter (ending January 31, 1969).

Figure 4-3. Scanning Electron Micrographs of UO_2 Gel Sphere Surface

100X

3000X

10,000X

Figure 4-4. Scanning Electron Micrographs of UO_2 Gel Sphere Surface

100X

3000X

10,000X

Figure 4-5. Scanning Electron Micrographs of UO_2 Sphere Surface (A) and Fracture Surface (B)

100X

10,000X

10,000X

Figure 4-6. Scanning Electron Micrographs of UO_2 Oxide Sphere Surface, Illustrating the Difference Between Natural Surface and Fracture Surface Grain Structure

100X

3000X

10,000X

5. IRRADIATION TESTING (C. J. Baroch)

5.1. Introduction

The irradiation task of this program, as described in a previous quarterly report,¹⁰ is divided into three subtasks:

1. Time Required for In-Pile Restructuring.
2. Sorbed Gas Behavior.
3. EBR-II Irradiations.

The scope and progress on each of these subtasks are described below.

5.2. Time Required for In-Pile Restructuring

In this subtask, the effect of heat rate and time on the restructuring characteristics of sol-gel $\text{UO}_2\text{-PuO}_2$ spheres and on angular particles and pellets prepared from coprecipitated $\text{UO}_2\text{-PuO}_2$ will be evaluated. Seventeen capsules will be irradiated in the BAWTR. The time for restructuring at linear heat rates of 6, 10, 15, and 20 kW/ft will be determined. The program will include a comparison of the irradiation behavior of spherical particles prepared by ORNL and B&W.

In June 1968, the irradiation of capsule GA-2 was initiated, but the capsule instrumentation indicated that one pin achieved a linear heat rate of 15 kW/ft when the reactor power was only 5 MW. Extrapolation of the data to the normal 6 MW operation of the BAWTR indicated that the pins would operate at 15.3 to 16.7 kW/ft.¹¹ The higher heat rate, 16.7 kW/ft, is somewhat greater than that approved in the safety analysis, so that the capsule was removed after an exposure of 3.2 EFPD. The safety analysis was modified to include the higher heat rate and approval was received for the continued irradiation.

Irradiation of this capsule for 9.6 EFPD, the target exposure, was completed in October. The capsule is now stored in the hot cell pool until the post-irradiation examinations can begin.

Additional irradiations in this subtask will begin when suitable fuel has been prepared. These irradiations are scheduled to begin in February.

5.3. Sorbed Gas Behavior

In this subtask the pressure created by the sorbed gas released from particulate fuel during irradiation will be determined. If practical, each capsule will contain two pins in which the gas pressure is continuously monitored. One pin will contain spherical sol-gel particles and the other will contain angular particles prepared by crushing pellets. Gas release characteristics of spherical sol-gel particles prepared by ORNL and B&W will also be determined. By varying the linear heat rate, it should be possible to determine the extent of the gas release as a function of average fuel temperature. The fuel pins will be irradiated at linear heat rates of 6, 10, 15, and 20 kW/ft.

The five transducers ordered from Reuter-Stokes Canada, Ltd., were received toward the end of the quarter. Originally, it was planned to complete the design of the capsules for the gas release experiments when the transducers were received. However, the reduced funding in this program required postponing this work until later.

5.4. EBR-II Irradiations

The irradiations in EBR-II will provide performance data on particulate fuels under the fast reactor conditions obtainable in EBR-II. In this task the effect of heat rate and burnup on the overall performance of pellets, spherical particles, and angular particles will be evaluated. The smeared density for all three materials will be about 85%. The irradiations will involve the irradiation of one 19-pin encapsulated subassembly in row 7 of the EBR-II, and the irradiation of 18 unencapsulated pins in a subassembly to be shared with ORNL. The scope of these programs is shown in Tables 5-1 and 5-2.

During this quarter, ANL and ORNL were visited to acquaint the B&W staff with the various types of sodium bonding equipment and techniques for inspecting bond integrity. The system at ORNL was considered most suitable for our requirements. During the trip to ORNL, details of the 37-pin subassembly to be shared with ORNL were formulated. Shortly after this visit, the schedule for the Gel-Addition program was stretched out, and further work on the EBR-II Irradiations was postponed.

Table 5-1. Description of Fuel Pins Included
in Encapsulated Bundle

Burnup, GWd/T	Type of fuel ^(a)		
	Angular particles	Spherical particles	Pellets
25	3	3	3
50	4	3	3
75	3	4	3
100	3	3	3

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

Table 5-2. Description of B&W Fuel Pins to be
Included in Unencapsulated Bundle

Burnup, GWd/T	Type of fuel ^(a)		
	Angular particles	Spherical particles	Pellets
25	3	3	3
50	3	3	3
75	3	3	3
100	3	3	3

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

6. ANALYTICAL SUPPORT (D. H. Schmitt)

6.1. Moisture Analysis

6.1.1. Introduction

Determination of the moisture content is one of the measurements required in characterizing a nuclear reactor fuel. The method used must be capable of determining microgram amounts of water, since most specifications establish an upper limit in the range of 30 to 50 ppm. To obtain this sensitivity, a Consolidated Electrodyamics Corporation Solids Moisture Analyzer, type 23-321AMA was selected. Sensitivity of the instrument is $0.1 \mu\text{g H}_2\text{O}$, and it will operate from ambient temperatures to 1000°C .

6.1.2. Principles of Operation

The CEC moisture analyzer operates on the principle of thermal evolution of sorbed or chemically combined water and electrolysis of the water at a constant potential. The electrolysis cell consists of two coaxial platinum spiral electrodes coated with a thin nonconducting film of phosphorous pentoxide, P_4O_{10} . Water evolved from the sample is swept into the electrolysis cell by a stream of dry inert gas and reacts with the P_4O_{10} to form a conducting film of phosphoric acids. Electrolysis of these acids releases hydrogen and oxygen gases which are swept from the cell by the inert gas stream. The current resulting from the electrolysis is used to charge an integrating capacitor to a predetermined potential, at which time the capacitor discharges. Discharge of the capacitor triggers a pulse counter and resets the capacitor for the next charging cycle. Each pulse corresponds to the electrolysis of $0.1 \mu\text{g}$ of water.

The maximum rate at which water can be electrolyzed is dependent upon the maximum counting rate of the pulse counter, which

is 40 counts per second or $4.0 \mu\text{g H}_2\text{O/sec}$. Since during the determination considerably more than $4 \mu\text{g}$ of water might be evolved per second, it is necessary to limit the amount of moisture that can reach the electrolysis cell in a given time. This is accomplished by an automatic metering valve which is operated by a servomotor. The motor positions the valve in response to the instantaneous counting rate in such a way that when the rate approaches 40 cps the valve closes to permit only 25% of full flow to the electrolysis cell. As the counting rate decreases, the valve opens again, so that the determination is completed in the minimum possible time. It is necessary to calibrate the counter circuit (a V to F converter) and verify correct operation of the servo actuated valve every few months. Also, it is necessary to adjust the background counting rate (because of the finite resistance of the P_4O_{10} film and the moisture contained in the sweep gas) to a definite value at the start of each day's work. The background counting rate is a part of the correction that must be applied to the raw data.

6.1.3. Description of Instrument

As presently operated, the instrument consists of two modules: one is principally the sample heating furnace, automated valve, and electrolysis cell, and the other contains the electronic circuitry and operating controls. For work with plutonium-bearing material the electronics module is mounted outside the glove box to facilitate maintenance, and is connected to the analyzer module by a multiwire cable. No changes to the electronic circuitry were necessary; the only modification to the module was a new cover to protect part of the instrument that was exposed when the analyzer was separated from the electronics. The analyzer parts are mounted on a specially fabricated base and are readily accessible for maintenance. A new design of furnace tube, much stronger than the original and therefore more suitable for glove box work, has been installed on the instrument. This tube is fabricated from Pyrex glass tubing and has much heavier walls than the quartz tube supplied with the instrument. It is opened through a 28/15 male spherical joint. Samples contained in nickel sample boats are inserted through this port. The furnace tube is capped with the female half of the spherical joint. This part is plugged with a close-fitting Teflon plug so that

there is no dead space within the cap. The plug was found to be essential in reducing "blank" results to an acceptable level, as will be mentioned later.

The sample is heated by a resistance heater wound around the outside of the furnace tube. The Pyrex furnace tube permits operation at temperatures up to 400 C. A Vitreosil fused quartz tube will be installed to permit operation at up to 1000 C. A thermocouple is mounted inside the furnace tube at the location of the sample boat. Its leads pass through the cool end of the furnace tube and are sealed with epoxy resin cement. This form of construction allows replacement of the quartz tube assembly at a cost of less than \$35, as opposed to over \$160 for an original replacement from the manufacturer. It is also much stronger and easier to operate than the original.

A hinged, perforated shield used to cover the furnace tube and electrolysis cell assembly has been removed from the instrument and discarded for convenience of operation. A microswitch operated by the closing of the cover controls power to the furnace winding. This will be replaced by a toggle switch on the electronics module.

6.1.4. Instrument Modifications and Method Evaluation

At the beginning of the report period a number of deficiencies were found in the instrument. Several different tubing materials were used for the passage of gases, and many of the joints leaked. Testing with detergent solution when the instrument outlet port was plugged revealed several leaks at tubing joints which were not apparent during non-pressurized operation. This point is significant when it is recalled that the automatic valve closes, thus increasing the system pressure, when the sample is evolving water that is to be determined.

The Pyrex tube presently in use was then designed and fabricated. The cap was made by closing the end of a Pyrex 28/15 spherical joint about 35 mm back from the ground surface. After the change was made, results reproducible to within the manufacturers' specifications were obtained, but blank results were about 80 to 100 μ g and seemed to vary with ambient humidity. Also, the results on samples of sodium citrate dihydrate and sodium tartarate dihydrate were about 12% low. These samples, 5 to 15 mg in size, were weighed to the

nearest 0.1 mg. The hydrate chemicals were felt to be reliable standards and thus were not suspected of causing the low results. The integrator (V to F converter) was next checked for calibration according to the procedure described in the Moisture Analyzer Instrument Manual. The procedure involves replacing the electrolysis cell with a resistor which can be adjusted to result in a 25.00 mA current in the integrator circuit, and then timing the collection of a certain number of counts. The integrator was found to be seriously out of calibration. The appropriate trimming potentiometer adjustment was made and the setting was secured with silicone rubber to prevent accidental shifting. It was noticed that the current varied by about 2% from "open circuit" to "titration" conditions. Nothing can be done about this short of complete rebuilding of the power supply. It is, fortunately, not a serious problem in actual analyses.

Following the recalibration, results with known amounts of sodium citrate or tartrate hydrates improved to the point of 97 to 100% recovery of the theoretical amount of water. Results with the standards were thus acceptable but still subject to improvement. Samples of the hydrate were placed in a saturated water vapor environment, then air dried (approximately 50% relative humidity) without improvement.

It was then noticed that the actual counting rate of the integrator was higher than 40 cps during the time of maximum evolution of water from the sample. The difficulty was traced to the automatic metering valve. The valve appeared to open and close correctly during a determination, until the outlet gas flow rate was checked with a flowmeter. It revealed that the valve actually remained fully open throughout the cycle. Adjustment of the valve according to the instrument manual corrected the difficulty. The design of this valve servo system includes two micro switches which serve to limit valve rotation. A single failure of one of these switches can result in the valve driving one turn farther open than it should be. The servo system will then regain control with the valve in the incorrect position. This condition can be reproduced at will by manually operating the micro switch. The valve was found to be operating three full turns beyond its correct position.

After correction of the valve condition, results with the citrate and tartrate standard materials improved to better than 99% of theoretical. Blank values remained high and variable.

In order to check the operation of the instrument with samples having approximately the same amount of water as can be expected in the fuel materials, a suitable secondary moisture standard was developed for routine checking of the instrument. Chromatographic grade alumina was found to have far too much water to be suitable, but chromatographic grade powdered silica proved to contain a convenient amount of water, approximately $0.6 \mu\text{g H}_2\text{O}/\text{mg silica}$. The sodium citrate and tartrate results were used to establish correct instrument operation before this value was determined. Then, by weighing various amounts of the powdered silica, the performance of the instrument was checked with various amounts of water.

It was noticed that the counting rate near the conclusion of a determination did not decrease in the exponential manner that would be expected for the instrument. Instead, the counting rate decreased almost linearly with time. It was thought that this might have been caused by adsorption of moisture on the walls of the furnace tube, then slow desorption by the sweep gas. At the same time, the role of the furnace tube opening procedure was examined, since it appeared reasonable that removal of the cap should cause the ingress of moisture to the furnace tube. Surprisingly, there was no appreciable difference in blank results whether the tube was open for 30 seconds or 5 minutes; thus no moisture was swept into the cell from the laboratory air.

When the end of the furnace tube was closed with a piece of Teflon tape (thus preventing access of the sweep gas to the hollow furnace tube cap), the blank values immediately dropped to 0 to 2 micrograms. Further experiments showed that a tight-fitting solid Teflon plug inserted in the glass tube cap, backed with epoxy resin to eliminate dead space, was nearly as effective in reducing blank values. The blank results proved to be $4.5 \mu\text{g}$ with a standard deviation of $0.7 \mu\text{g}$. This cap will be replaced with one machined from solid Teflon. Using the present furnace tube cap, the electrolysis proceeds rapidly to completion. Results with the silica secondary standards are presented in Table 6-1.

Table 6-1. Summary of Data, Water Sorbed in Silica

Silica taken, ^(a) mg	Net water found at 150 C, μg	Relative standard deviation, %	95% confidence limits for a single determination, μg
5	1.9	16	± 0.8
30	10.5	4.3	± 1.4
100	46.5	5.4	± 7.0

(a) The data presented were obtained by calculating the average weight of water obtained per milligram of silica sample for five samples having weights near those listed. Sample weights were measured to ± 0.01 mg; the amount of water found can be read to ± 0.1 μg.

6.2. Oxygen-to-Metal Analysis

6.2.1. Introduction

The Fisher Scientific Company's Thermogravimetric Analysis System, Model 10-560-100, has been adapted for use in determining oxygen-to-metal (O/M) ratios in uranium oxide, plutonium oxide, and mixed uranium and plutonium oxides. The method is based on oxidation and/or reduction of the oxides and measurement of the weight changes accompanying these reactions. The procedure is adapted from a method developed by W. L. Lyon.¹² For a mixed oxide the sample is dried in an argon atmosphere at 110 C, oxidized in air at 900 C, and reduced in a 94% nitrogen—6% hydrogen atmosphere.

6.2.2. Method Evaluation

The method is now in use for the analysis of uranium oxide samples. In this analysis the sample material is first ground to a finely-divided form using a mortar and pestle. The use of an electrically powered grinder has been eliminated since it was found that heat generated by the grinder was sufficient to partially oxidize the uranium oxide. Following sample preparation the sample material is transferred to the sample pan of the thermogravimetric analysis (TGA) apparatus. The furnace tube is closed and the dry weight of the sample is taken after the sample is exposed to an argon atmosphere for 1 hour at 110 C.

The atmosphere is then changed to air, and the sample is oxidized to U_3O_8 at 750 C. The oxidation begins at approximately 125 C and is generally complete by the time that the temperature reaches 400 C. The temperature is next increased to 750 C to ensure quantitative oxidation. The temperature is then lowered to 110 C, and the oxidized weight is taken at 110 C in an argon atmosphere. The data presented in Table 6-2 were obtained from analyses of uranium dioxide pellets.

Table 6-2. Oxygen-to-Metal Ratios as Determined in Uranium Oxide Pellets

Pellet No.	Oxygen-to-metal ratio	Average O/M	Deviation from average	Rel std deviation, %
1	2.050	2.043	0.007	0.31
	2.039		0.004	
	2.039		0.004	
2	2.223	2.239	0.016	0.69
	2.254		0.015	
	2.239		0.000	
3	2.223	2.223	0.000	0.00
	2.223			
	2.223			

Although no work has been done using the TGA apparatus for analysis of oxygen-to-metal ratios in mixed uranium and plutonium oxides, some preliminary work has been done with plutonium oxide. In the analysis of a mixed oxide the dry weight is first determined in the same manner as with uranium oxide samples. The sample is next oxidized in air at 900 C to convert uranium oxide to U_3O_8 and plutonium oxide to PuO_2 . It is then exposed to a reducing atmosphere in which the U_3O_8 is reduced to UO_2 . For valid results the PuO_2 must not be reduced during this step. Since PuO_2 is rather easily reduced to a substoichiometric oxide,¹³ an experiment was performed to determine whether this could be expected to occur during the reduction of U_3O_8 to UO_2 . The sample of plutonium oxide was first air oxidized to PuO_2 at 900 C for 1 hour, then exposed to a 94% nitrogen—6% hydrogen atmosphere at the

same temperature for one additional hour. No reduction in sample weight was observed. It was therefore concluded that reduction of PuO_2 would not be expected to occur under these experimental conditions.

In the analysis of a mixed oxide sample, it is important that the U_3O_8 produced during the air-oxidation step be reduced to UO_2 . The National Bureau of Standards uranium oxide chemical standard No. 950a was used to evaluate the completeness of reduction of the uranium oxide. A sample of the standard uranium oxide was air-oxidized at 900 C to ensure the stoichiometry of the U_3O_8 . The U_3O_8 was then reduced in an atmosphere of 94% nitrogen—6% hydrogen at several temperatures in the range of 775 C to 900 C. The reducing gas flow rate was maintained constant at 200 cm^3/min throughout the series of experiments. The data obtained are presented in Table 6-3.

Table 6-3. Oxygen-to-Metal Ratios as Determined in
NBS U_3O_8 Reduction Experiments

<u>Temperature, C</u>	<u>O/M on reduced sample</u>
775	2.013 ^(a)
840	2.026
900	2.010

(a) Average of six determinations.

The results indicate that a temperature of 900 C is required to obtain an oxide of composition $\text{UO}_{2.010}$. Others^{14,15} have also found difficulty in reducing uranium oxide to $\text{UO}_{2.000}$ and have obtained $\text{UO}_{2.010}$ at a temperature of 800 C with a gas flow of 500 cm^3/min . Several experiments are now planned to determine the extent of this problem.

6.3. Analytical Sample Load

During this quarter 119 samples were analyzed, representing a total of approximately 564 analyses. The analyses included total U, total Pu, NO_3 , H_2O , and isotopic composition of uranium.

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Esleeck, SH	Travis, CC/TRG
Grant, SP	Webb, RA
Gurley, RN	Whitaker, BW