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GEL-ADDITION PROCESS CHEMICAL STUDIES

— Quarterly Progress Report No. 3 —

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Compiled by

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Gel-Addition Project

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ABSTRACT

Development of the Gel-Addition Process for preparing plutonia-urania mixed oxide fuels has been extended from a study of the interaction of UO_2 gels and plutonium solutions (see previous quarterly reports^{1,2}) to include development of equipment for firing to oxides and methods for examining oxide microstructure. During this report period we have emphasized improving the uptake of plutonium on UO_2 gel spheres, decreasing the attrition and losses of gel spheres, and determining the distribution of plutonium in contacted gel and fired oxide spheres.

Notable success was achieved in each of these areas. Plutonium uptake ranging from 20 - 23% Pu/U + Pu was obtained in both gel and fired oxide spheres that had been double-contacted with Pu(IV) nitrate solutions. Attrition of UO_2 gel spheres contacted with nitric acid under inert atmosphere was reduced as low as 1%. Alpha autoradiographs of calcined gel-addition spheres showed uniform distribution of plutonium within each sphere, although a slight variation was noted between spheres.

Progress for the third quarter, ending March 31, 1967, is reported. The project is supported by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3714.

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1. INTRODUCTION

This is the third quarterly progress report covering a continuing program designed to apply the Gel-Addition Process for preparing nuclear fuels to the preparation of uranium-plutonium mixed oxides for fast reactor application.

The Gel-Addition Process has been derived from sol-gel technology developed at Oak Ridge National Laboratory and differs from it in that a single-component fertile sol is prepared, e.g., UO_2 , and converted to a single-component gel. (The sol-gel process involves a two-component sol and gel.) The gel particle shape is retained through the succeeding steps, hence any necessary particle-shape specifications can be applied at the gel stage.

Two principal advantages accrue: First, the fuel particles may be prepared and sized without commitment of fissionable material and thus without regard to criticality problems. Second, scrap recycle involves only a single-component system and therefore does not involve a chemical separation.

After the gel particles are prepared and screened, the fissionable material is injected by soaking the gel in an aqueous solution of the fissionable material. The reaction mechanism is still under study, but work to date has shown that UO_2 gels have a remarkable ability to pick up plutonium from nitrate solutions of all three of its common valence states, III, IV, and VI. Plutonium contents as high as 18% ($\text{Pu}/\text{U} + \text{Pu}$) were obtained easily in the early experiments.

The work this quarter has emphasized improving the uptake of plutonium, decreasing the deterioration and losses of the gel spheres, and determining the distribution of plutonium in contacted gel and oxide spheres.

2. CONCLUSIONS

2.1. UO_2 Sol Preparation

Stable urania sols can be prepared under reagent conditions different from those explored previously in this program. A stable sol resulted when the catalyst-to-uranium ratio was decreased two-fold, the urea-to-uranium ratio decreased two-fold (0.63 to 0.32), the nitrate-to-uranium ratio decreased slightly (4.6 to 4.05), and the formic acid-to-uranium ratio decreased two-fold (1.0 to 0.49) from previously used values.

2.2. UO_2 Gel Sphere Preparation

Large UO_2 gel spheres with less apparent deviation from the mean diameter can be prepared by spheroidizing urania sol in a recirculating column of organic. UO_2 gel spheres of about 800-micron diameter were easily prepared by injecting the sol as droplets into a recirculating bath of 2-ethyl-1-hexanol containing surfactants.

2.3. Controlled-Atmosphere Contacts

UO_2 gel attrition from chemical attack is generally decreased by performing acid contacts under an inert atmosphere. Although some tests are ambiguous, sphere destruction was below 10% in most cases and as low as 1% in several runs after inert atmosphere contacts with both HCl and HNO_3 .

2.4. Multiple-Contacting With Pu(IV) Nitrate Solutions

Plutonium uptake by UO_2 gel spheres can exceed 20% $\text{Pu/U} + \text{Pu}$ after a double-contact with Pu(IV) nitrate solution. Plutonium pickup of 20 - 23% $\text{Pu/U} + \text{Pu}$ was observed in both gel and fired oxide spheres after two 10-minute contactings with pH 0.3 Pu(IV) nitrate solution.

2.5. UO₂ Gel Oxidation

UO₂ gel spheres oxidize rapidly in air. For instance, the initial oxidation state of one batch of spheres increased from 2.17 to 2.27 after only a 30-second exposure to air.

2.6. Plutonium Distribution in Contacted Spheres

Uniform distribution of plutonium has been observed for single-contacted gel-addition spheres. Alpha autoradiographs of calcined, 800-micron UO₂ spheres showed uniform distribution of plutonium within each sphere.

2.7. Plutonium Analysis

The sulfate spectrophotometric method is not considered applicable to the analysis of plutonium in raw dissolver solutions. Results show that the plutonium analysis is often several-fold lower than it is when the coulometric titration method is used, because of Pu(IV) to Pu(VI) oxidation during the sphere dissolution step.

3. GEL-ADDITION CHEMISTRY (E. J. Kosiancic)

3.1. UO₂ Gel Sphere Preparation (C. A. Burkart)

Previous quarterly reports^{1, 2} completely describe the urania sol process and apparatus used for preparing 75 to 100 gram batches of UO₂ gel spheres by stirred vessel methods. This report discusses the preparation of one additional batch of gel spheres by a recirculating column apparatus.

3.1.1. Sol Preparation

UO₂ batch 11 was prepared by the general procedure described previously, but under different reagent conditions as follows:

1. A commercial 5% platinum-on-alumina catalyst* was substituted for the palladium-on-thoria catalyst used earlier.
2. The catalyst-to-uranium ratio was decreased about two-fold.
3. The uranium feed solution concentration was doubled (0.5 M to 0.98 M U).
4. The urea-to-uranium mole ratio was decreased two-fold (0.63 to 0.32).
5. The nitrate-to-uranium mole ratio was decreased slightly (from 4.6 to 4.05).
6. The formic acid-to-uranium mole ratio was decreased two-fold (from 1.0 to 0.49).

The preparation conditions for the batch are summarized in Table 3-1.

The use of commercial catalyst avoids the tedious procedure required to prepare McBride's catalyst.³ Other commercial catalysts will be tried in order to decrease the U(VI) to U(IV) reduction

*Obtained from Engelhard Industries, Inc., Newark, N. J.

time (the platinum-on-alumina catalyst worked satisfactorily, but did not decrease the reduction time in batch 11 as compared with the platinum-on-thoria catalyst).

Run 11 was the largest sol batch prepared to date (187 grams of uranium compared with the previous high of 113 grams). It was encouraging to find that a stable sol resulted, even when the reagent conditions were changed from previous values. This may indicate that stable sols can be prepared over a wider range of conditions than was previously anticipated.

3.1.2. Gel Sphere Preparation

UO₂ gel spheres prepared by the stirred vessel technique are too small (nominal average was 40 microns) for alpha autoradiography experiments (see section 4.4). Larger spheres (over 1000-microns in diameter) with less deviation from the mean diameter can be prepared by spheroidizing the sol in a recirculating column of organic.

A small column* (about 3 feet high and 5/8 inch at the neck) was assembled in an inert-atmosphere glove box in order to prepare larger, more uniform UO₂ gel spheres from sol batch 11. Figure 3-1 shows the column in operation. Sol is loaded into the syringe and injected (as droplets) into the recirculating bath of 2-ethyl-1-hexanol containing surfactants. As the spherical droplets gel, their density increases and they eventually pass through the neck restriction of the column where they are collected in batches. When operated continuously, the unit can produce about 70 grams of spheres in an 8-hour shift.

Approximately 126 grams of usable UO₂ gel spheres of about 800-micron diameter were prepared in the column run. Analytical results for the spheres are summarized in Table 3-2.

*The glass column was specially prepared by the Sentinel Glass Company, Hatboro, Pa. The design was taken from drawings furnished by the Chemical Technology Division, Oak Ridge National Laboratory.

Table 3-1. Preparation Conditions for U(IV) Gel Microsphere, Batch 11

<u>Reagent or process parameter</u>	<u>Value</u>
Uranium, gm	182.5
Uranium nitrate solution (0.98 <u>M</u> U and 3.97 <u>M</u> NO ₃), ml	780
Urea, gm	14.7
Pt on alumina catalyst, gm	1.2496
Total volume of solution, ml	944.7
Hydrogen flow rate, cc/min	300
Formic acid, (89.5%), ml	17
Precipitation time, hr	3.25
Volume of wash water, ml	1000
Approx drying time on filter, min	15
Approx volume of U(IV) sol, ml	500
Yield of gel spheres, gm	126 ^(a)

(a) A portion of the sol was not converted to spheres.

Table 3-2. Analytical Results for U(IV) Sol-Gel Preparation, Batch 11

<u>U(IV) sol</u>	
U(IV) content, U(IV)/U total, %	71.3
Uranium content, wt %	20.4
Nitrate-to-uranium mole ratio	0.041
<u>U(IV) gel microspheres</u>	
U(IV) content, %	70.7
Uranium content, wt %	71.0
Nitrate-to-uranium mole ratio	≈0

Figure 3-1. Organic Column for Dehydrating UO_2 Gel Spheres

3.2. UO_2 Contacting Experiments (E. J. Kosiancic, W. N. Bishop)

UO_2 gel samples were contacted with acid solutions (no plutonium present) to evaluate gel attack, and also with Pu(IV) solutions to measure uptake.

3.2.1. Controlled-Atmosphere Contacts Without Plutonium

The observation that UO_2 gels are rapidly air-oxidized (see section 4.1) suggests that freshly prepared spheres kept in an inert atmosphere and air-equilibrated spheres may react differently to acid attack.

To test this idea, 4-gram samples of spheres from batches 3, 4, 5, 6, and 10 were tested. The spheres were contacted with acid under inert atmosphere, both in the conditions of inert atmosphere storage and after a 24-hour air exposure, to note any difference in acid attack on the gel attributable to oxygen. Both HCl and HNO_3 were used to differentiate between oxidizing and non-oxidizing acids.

In the procedure, 4-gram sphere samples were weighed in an inert atmosphere box (nitrogen) and contacted with 10 ml of acid solution (HCl or HNO_3) made up at various pH values.* All solutions were purged with nitrogen before contacting. Just as in previous runs with plutonium-bearing solutions, the contacting time was held at 4 hours (ambient temperature). At the close of the run the spheres were decanted, washed twice with 10 ml of acetone, and allowed to dry overnight under nitrogen before weighing. Ten milliliters of concentrated H_3PO_4 were added before analysis to stabilize U(IV) . For analysis, the resulting solution (≈ 20 ml total volume) was diluted to 50 ml using dilute H_2SO_4 (1:1) and concentrated H_3PO_4 . Two aliquots were withdrawn: (1) one of 5 ml was diluted to 10 ml with concentrated HNO_3 and boiled to destroy organic matter and give a total uranium measurement, and (2) the other was titrated coulometrically to get the U(VI) content. The results are shown in Table 3-3.

* Anion content of both chloride and nitrate solutions was held at 3.8 M. Free acid was used, and the desired pH values were obtained by partial neutralization with concentrated aqueous ammonia.

Table 3-3. UO_2 Gel Acid Contacting Tests

Sphere batch of gel sample	3	4	5	6	10
U(VI) Content of Gel					
At prep time	15	24	NA	10	10
At contact time	40	47	27	44	24
24-hr air exp	48	51	57	44	35
Uranium Found in Aqueous Phase					
Condition 1					
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Note: Condition 1, 1st contact test (see stored sample);
Condition 2, 2nd contact test (spheres were air-exposed 24 hours between tests);
NA, analytical result not available

Several noteworthy items are observed for the samples analyzed to date:

1. Sphere destruction can be as low as 1% (batches 5 and 10) when contacting is performed under inert atmosphere.
2. Sphere destruction is about the same for HCl and HNO₃ under similar conditions.
3. The total uranium found in the acid phase seems to bear little relation to the U(IV)/U(VI) ratio measured in the gel when first prepared.

Several of the values for the pH 0.8 contacts in HNO₃ appear to be abnormally high. This may be a result of poor sphere separation in these tests (batch 4, condition 1 and 2; batch 6, condition 1) due to excessive foaming of the solutions from organics. Organic materials in substantial quantities were apparent in many of the acid solutions even though the finished spheres were acetone-washed and dried. Many solutions had a bronze color (completely different from the appearance of either quadrivalent or hexavalent uranium) and many solutions foamed severely. In many cases violent deflagrations occurred when the solutions were wet-washed with nitric acid.

The presence of organics is readily understandable if it is assumed that the surfactants used in the organic spheroidizing bath are easily picked up and retained by the UO₂ gel. Span-80 (sorbitan mono-oleate) is one used. This proprietary material is essentially an ester of a sugar and oleic acid and should be very sensitive to nitration. It should also exert a strong complexing action on quadrivalent uranium since complexing quadrivalent metals is a general property of polyhydroxy compounds.

The large quantities of organics found in the acid solutions used in these runs suggest that an acid wash step may be useful in the Gel-Addition Process as a way to reduce organic content of the gel before contacting with plutonium.

3.2.2. Other Contacting Tests Without Plutonium (W. N. Bishop)

Four-gram samples of batch 4 spheres were contacted with 10 ml samples of standard buffers at pH 1, 2, and 3. The pH

values were remeasured 30 seconds after contacting and again 1 to 2 hours later. In all cases the pH values rose sharply. Sphere recovery was almost 100% from the pH 3 solution and was near 70% from the two runs at higher acidity.

In other tests, gel spheres were given multiple contacts with HNO_3 to measure destruction and the final pH of the contacting solution. Three M nitric solution was neutralized to pH 1 using concentrated aqueous ammonia to give a solution resembling the acidity of our plutonium nitrate contacting solutions but without the side effects of plutonium redox reactions. Six 10-ml aliquots of this solution were contacted in succession with a 4-gram sample of UO_2 spheres. The spheres were washed with demineralized water between contactings, and the final pH of the contact solution was measured. Confirming similar past tests, no saturation effect was observed and all solutions approached pH 3.5. The gel recovery was about 50%.

This experiment was repeated, but the gel was vacuum dried for 1 hour at 60 C between contactings. Almost no difference in gel recovery was observed, and it appears that acid attack on the gel is not a sensitive function of gel hydration conditions.

3.2.3. Single-Contacting Tests With Plutonium

Two 14-gram samples of batch 11 spheres were contacted with Pu(IV) nitrate solution to provide samples for ceramographic and alpha autoradiography studies (see section 4.4). The contacting procedure was as follows:

1. Sixty milliliters of stock Pu(IV) nitrate solution (237 mg/ml and 3.18 M H^+) were adjusted to pH 0.5 by the addition of 25 ml concentrated NH_4OH . The adjusted solution was divided into two equal portions.
2. One portion of the adjusted plutonium solution was contacted for 1.5 hours with 14.69 grams of batch 11 UO_2 gel spheres (designated 1D82); the second portion was used to contact 14.27 grams of spheres under identical conditions (designated 1D84).
3. Each contact solution was decanted into a filter and collected. The dark green-black filtrate from portion one was labelled

1D81 (the pH was 0.8). The second filtrate (dark green) had a pH of 1 (it was labelled 1D83).

4. Each batch of contacted spheres was washed four times with 5 ml portions of demineralized water. Sphere batch 1D84 was further washed with two 5 ml portions of acetone.

5. Each batch of spheres was dried overnight at 30 C under vacuum (18 in. Hg). Sphere sample 1D82 weighed 11.64 grams, and sample 1D84 weighed 12.45 grams.

6. Each batch of spheres (1D82 and 1D84) was divided approximately in half. One-half of each batch was sieved through a 40-mesh screen (1D82 yielded 2.63 grams of +40 mesh; 1D84 yielded 3.13 grams). The remaining spheres were mixed together (designated 1D85) and calcined as shown in Table 3-4. When these spheres were sieved through a 40-mesh screen, 4.96 grams were retained.

7. Uncontacted batch 11 UO_2 gel spheres were calcined under conditions identical to those used for spheres 1D85 (sample 1D86, Table 3-4). These spheres yielded 13.3 grams of +40 mesh.

The plutonium analyses of samples 1D82, 1D84, and 1D85 are given in Table 3-5.

The 22% weight loss for sample 1D86 agrees well with the uranium analysis of the gel (80.5% UO_2). A gel of empirical formula $\text{UO}_2 \cdot 4\text{H}_2\text{O}$ would give a weight loss of 21.0% on ignition, remarkably close to the observed value. More definitive studies on gel stoichiometry are planned.

In other tests, Pu(IV) uptake was studied from both HNO_3 and HCl solutions. Four gel samples (4 grams each from batches 3, 4, and 6, and one NFS sample) were contacted with pH 0.5 PuCl_4 .^{*} Four additional samples were contacted with Pu(IV) nitrate. The plutonium concentration was about 0.3 M in the chloride solutions and about twice as high in the nitrate solutions. Contact times were fixed at 4 hours. Analytical data are incomplete, but sphere attrition in all cases was

^{*}The PuCl_4 was prepared by precipitating the quadrivalent hydroxide with aqueous ammonia and dissolving the precipitate in HCl .

substantial, and plutonium uptake from the chloride solution was clearly smaller than from the nitrate.

Table 3-4. Sphere Calcining Conditions

Conditions	Contacted spheres (sample 1D85)	Uncontacted spheres (sample 1D86)
Calcining temperature, C	1150	1150
Time at max. temperature, min	180	180
Rate of temperature climb, C/min	5	5
Atmosphere used		
Heatup	Ar-6% H ₂	Ar-6% H ₂
Hold	Ar-6% H ₂	Ar-6% H ₂
Cooldown	Ar-6% H ₂	Ar-6% H ₂
Gas flow rate, SCFH	10	10
Weight of charge, gm	11.0328	17.2054
Weight of product, gm	9.6607	14.5172
Change in weight, gm	1.3721	2.6882
Change in weight, %	12.5	22

**Table 3-5. Plutonium Pickup on Sphere Samples
Prepared for Ceramographic Examination
(1.5-hour contact, 800-micron spheres)**

Sphere sample	Pu/Pu + U × 100
1D82	3.3
1D84	0.9
1D85	0.6

3.2.4. Multiple-Contacting Tests With Plutonium

The first double-contacting run has been completed. A 12-gram sample from batch 10 UO₂ spheres was contacted twice with fresh Pu(IV) nitrate solution (pH 0.3). Filtrate solutions from these

contactings were subsequently contacted with fresh batches of UO_2 spheres. The test resulted in plutonium pickups ranging from 20 to 23%. The procedure (see flowsheet Figure 3-2) was as follows:

1. Thirty milliliters of stock Pu(IV) nitrate solution (237.3 mg/ml and 3.18 M H^+) were adjusted to pH 0.3 with 9.4 ml of concentrated NH_4OH . This solution was contacted (contact A) for 10 minutes with 12 grams of batch 10 UO_2 gel spheres. After contacting, the solution was easily decanted into a fritted glass filter. The pH of the filtrate was 2.1. The filtrate (sample 1D16) was stored for further experimentation.

2. The contacted spheres were washed four times with 5-ml volumes of demineralized H_2O (each 5-ml wash solution and spheres were poured into a fritted glass filter). After vacuum filtering, the spheres were dried for 2 hours at 60 C (low vacuum). The weight of the dried spheres was 11.32 grams. A 0.9729-gram sample (1D17) was taken for plutonium analysis; the results are shown in Table 3-6.

3. A second 30-ml sample of stock Pu(IV) nitrate solution was adjusted to pH 0.3 as before. This solution was then contacted (contact B) for 10 minutes with the remaining 10.35 grams of previously contacted spheres (1D17). The solution was decanted, filtered through a fritted glass filter, and labelled 1D18. The pH of this filtrate was 0.5.

4. The twice-contacted spheres were washed into a fritted glass filter with four demineralized water washes, each of 5 ml volume. After vacuum filtering, the spheres were dried for 2 hours at 60 C as before. The dried product gave a total weight of 5.10 grams. A 1.0060-gram sample of spheres was labelled 1D19 and analyzed for plutonium (Table 3-6).

5. The filtrate 1D16 (step 1) spontaneously increased in acidity and had a pH of 0.6 after approximately 24 hours. Twenty milliliters of this solution were contacted (contact C) for 10 minutes with 4 grams of batch 10 UO_2 gel spheres. After contacting, the solution was easily decanted into a fritted glass filter and the filtrate was labelled 1D20. The pH of this filtrate was 1.4. The separated spheres were washed and dried as before. 4.08 grams of dried spheres were recovered (sample 1D21, Table 3-6).

6. Twenty milliliters of filtrate 1D18 (pH 0.4, 24 hours after contacting) were contacted for 10 minutes with 4 grams of batch 10 UO₂ gel spheres. After the contacting, the solution was easily decanted into a fritted glass filter and the filtrate was labelled 1D22. The filtrate pH was 2.0. The contacted spheres were processed as described in step 2. The dried product weighed 4.2 grams (sample 1D23, Table 3-6).

7. UO₂ gel spheres 1D19, 1D21, and 1D23 (after removing the initial sample) were screened through a 325-mesh sieve and the +325 mesh fraction was sampled. The samples were labelled 1D19(2), 1D21(2), and 1D23(2). The remainder of the spheres were calcined to the oxide under the conditions shown in Table 3-7. The oxides were dissolved and analyzed for percentage plutonium.

The analysis (Table 3-6) shows good agreement between plutonium pickup on +325 mesh gel (1D19) and -325 mesh gel [1D19(2)]. This indicates that plutonium precipitates are not present in significant amounts. The fired oxide analysis (1D88) also confirms that total plutonium uptake was over 20% Pu/U + Pu. The low sphere recovery for sample 1D19 is attributed in part to losses during the decanting step (a clean decantation was difficult in this case).

Table 3-6. Plutonium Pickup and Sphere Recovery After Double-Contacting Experiment

Sphere sample No.	Pu/U + Pu × 100	Weight of spheres, gm		Sphere recovery, %(a)
		Before contacting	After contacting	
1D17 ^(b)	12.6	12.00	11.32	94
1D19 ^(b)	22.6	10.35	5.10	49
1D19(2) ^(c)	23.0			
1D88 ^{(c)(d)}	20.0			
1D21 ^(b)	12.7	4.00	4.08	102
1D21(2) ^(c)	10.4			
1D89 ^{(c)(e)}	10.0			
1D23 ^(b)	10.9	4.00	4.20	105
1D23(2) ^(c)	11.3			

(a) Ignores plutonium pickup.

(b) Unscreened sample.

(c) +325 mesh sample.

(d) Fired oxide sample of 1D19 (+325 mesh).

(e) Fired oxide sample of 1D21 (+325 mesh).

Table 3-7. Calcining Conditions for Double-Contacted Spheres

Condition	Sample		
	Gel 1D19(2) (oxide 1D88)	Gel 1D21(2) (oxide 1D89)	Gel 1D23(2) (oxide 1D90)
Calcining temperature, C	1150		
Time at max. temperature, min	180		
Rate of temperature climb, °C/min	5		
Atmosphere used			
Heatup	Ar		
Hold	Ar-6% H ₂		
Cooldown	Ar-6% H ₂		
Gas flow rate, SCFH	10		
Weight of charge, gm	1.3554	0.7048	0.1741
Weight of product, gm	1.0051	0.5278	0.1009
Change in weight, gm	0.3503	0.1770	0.0732
Change in weight, %	26	25	42

Figure 3-2. Flowsheet for Double-Contacting Tests on UO_2 Gel Spheres

4. OXIDE CHARACTERIZATION (J. M. Kerr)

Samples of gel and calcined materials have been carried through a series of characterization studies including gel oxidation, size distribution, plutonium distribution, and alpha autoradiography. The results are summarized below.

4.1. Gel Oxidation (L. T. Ramer)

It has been demonstrated that samples of UO_2 gel prepared by the ORNL methods are rapidly air-oxidized. Several grams of batch 6 UO_2 gel, which had been kept in the inert atmosphere in which they were produced, were deliberately air-exposed to determine the oxidation rate. The sample was dumped into an aluminum pan, and small samples were periodically withdrawn and immersed in phosphoric acid for coulometric analysis. (Since phosphoric acid is non-oxidizing, it presumably does not perturb the $\text{U(IV)}/\text{U(VI)}$ ratio in the sample at the time of dissolution.) A control sample of gel was analyzed without being air-exposed.

The data as reproduced in Figure 4-1 show rapid oxidation for several hours. Oxidation continued throughout the 30-day test period. To confirm the rapid oxidation during the first few minutes of air exposure, the experiment was repeated with spheres from batch 10 (the exposure time ranged from zero to 4 minutes). In this case, the initial oxygen-to-uranium ratio of the spheres was 2.17 instead of 2.10. As before, a plateau was reached at an oxygen-to-metal ratio of about 2.27, but this time after only 30 seconds (Figure 4-2).

The observation that UO_2 gels are readily air-oxidized again raises the question of the mechanism of nitric acid attack on UO_2 . The reaction is not simply an acid-base reaction between an acid and metal oxide because the reaction product is U(VI) , not U(IV) . An oxidative attack is involved. By contrast, UO_2 is not soluble in HCl (a non-oxidizing

acid) according to the literature. The rapid air oxidation of UO_2 gel shows that all materials contacted to date with Pu-HNO_3 solutions contained a large fraction of oxidized material.

Since the beginning of the Gel-Addition Project it has been suspected that gel production history will strongly affect the interactions of gel and plutonium solutions. It is now certain that gel oxidation state measurements will have to be included among the routine tests.

4.2. Gel Size Distribution (E. J. Kosiancic)

A large-scale run (54 grams of gel) was undertaken to provide adequate material for microstructure work and for a series of tests to show whether $\text{Pu/U} + \text{Pu}$ ratios in fines vary as spheres are abraded by tumbling (see section 4.3). The abrasion tests are designed to provide additional evidence on the distribution of plutonium inside the spheres.

One-hundred milliliters of Pu(IV) stock were adjusted to pH 0.3 by adding 24 ml of concentrated aqueous ammonia (see flowsheet Figure 4-3). In a 2-hour contact comprising four small batches, a total of 54 grams of spheres (batch 3) was processed. The solution phase was decanted and retained for a series of pH measurements (see below). The spheres were filtered, washed with water, and dried overnight at 60 C. The recovered mass weighed 32.6 grams (attrition was approximately 40%), and it was noted that the wash water appeared gray, indicating a tendency for the spheres to revert to a sol under the conditions used. The recovered spheres were sieved into various size fractions after a sample was removed for chemical analysis; sieving results are as follows:

+100 mesh	6.30 grams
-100 + 200 mesh	8.55 grams
-200 + 325 mesh	10.03 grams
-325 mesh	5.24 grams

The supernate from the original contacting (sample 1D25) showed a slowly decreasing pH as follows:

<u>Measured pH</u>	<u>Time after sphere separation, hours</u>
2.1	0
2.0	0.25
2.0	0.5
2.0	0.45
2.0	1.0
2.0	1.25
2.0	1.5
2.0	1.45
0.8	18.0

4.3. Plutonium Distribution in Spheres After Contacting (E. J. Kosiancic/W. N. Bishop)

4.3.1. Gel Spheres

As reported previously,² two samples (one 50-gram and one 4-gram) of batch 1 spheres were contacted for 4 hours with Pu(IV) stock at ambient temperature. At the end of the contacting, both samples were dried.

The smaller sample was divided into two batches, one containing particles retained by a 200-mesh screen and one containing particles passed by a 200-mesh screen. The smaller particles would have the largest apparent plutonium content if the measured plutonium pickup were an artifact of hydrolytic precipitation. However, analysis proved that this was not the case. Remarkably, the larger spheres showed a larger plutonium fraction ($\text{Pu}/\text{U} + \text{Pu} = 0.104$) than did the smaller spheres ($\text{Pu}/\text{U} + \text{Pu} = 0.073$). The difference may be attributable to side effects caused by the large organic content in batch 1 spheres.

The larger (50 grams) sample was separated into two subsamples after contacting. One was screened into five size fractions: >100 mesh, 100 to 200 mesh, 200 to 325 mesh, 325 to 400 mesh, and less than 400 mesh, and the other was set aside for firing. The average plutonium pickup measured in the gel was 0.075 $\text{Pu}/\text{Pu} + \text{U}$. A somewhat higher plutonium content was found in the smallest sized fraction as shown in Table 4-1. There is a little evidence of a trend in pickup, and the observed scatter is due to analytical uncertainties, at least in part.

Table 4-1. Distribution of Plutonium on Contacted and Screened Gel-Addition Spheres

Mesh	$\text{Pu/U} + \text{Pu} \times 100$	Weight percent in in size range
+100	6.9	4.7
-100 + 200	5.1	32.9
-200 + 325	7.5	48.1
325 + 400	--	1.4
+400	10.5	12.9

Analysis of the contacting solution used in the 4-gram sample showed a uranium content of approximately 75 mg/ml. The total solution volume was about 10 ml; hence, the chemical loss of uranium was about 25% of the total used. Analyses of contact solutions used in earlier runs with Pu(III) and Pu(IV) solutions on NFS spheres showed as much as 75% dissolution in a 4-hour run.

4.3.2. Fired Spheres

Three samples of UO_2 gel were fired and screened for plutonium distribution:

1. A 22-gram sample of spheres from the large gel-contacting experiment discussed in section 4.2 above.
2. A 100-gram sample of NFS UO_2 gel.
3. A 5-gram sample of B&W UO_2 gel.

All were heated in argon (at 50 C/hr) to 1200 C, held at 1200 C for 2.5 hours in Ar-6% H_2 , and then cooled in argon; all had a weight loss of about 10%. The plutonium-containing spheres showed a tendency to sinter together and were difficult to break apart. The two plutonium-free samples were easily broken apart after firing. Size distribution data after firing are reported in Table 4-2. Plutonium analysis after firing showed what appears to be a random distribution among size fractions.

Table 4-2. Plutonium Distribution in Sized UO_2/PuO_2 Spheres Fired at 1200 C

<u>Mesh size</u>	<u>Pu/Pu + U $\times$ 100</u>
-100 + 200	4.7
-200 + 325	7.6
-325 + 400	6.3
-400	4.6

The density of some of the fired particles was measured and found to be well below theoretical values, in some cases as low as 70% TD. This result was unexpected since most sol-gel materials sinter to approximately 100% TD. Changes in the firing cycle will probably increase the fired density to the expected value.

4.4. Alpha Autoradiography (L. D. Barnes)

Ceramographic specimens were prepared using UO_2 gel spheres. The material was examined as unfired gel (Figure 4-4) and calcined oxide (Figure 4-6), both after contacting with plutonium solutions. The normal ceramographic techniques used in mounting and polishing the spheres (the spheres are mounted in Quickmount) presented two problems:

1. It was difficult to obtain a smooth, scratch-free surface for examination without extensive undercutting of the soft, unfired gel spheres (Linde-A alumina powder was the polishing media used). This problem was solved by replacing the silk polishing cloth with a hard plastic base.

2. It was difficult to prevent disintegration of the spheres when water was used as the polishing fluid. This problem was solved by using ethylene glycol as the fluid.

Care was required to prevent sphere pull-outs caused by undercutting below the midplane of the spheres. When pull-out did occur, it generally caused extensive damage to the soft spheres, requiring complete repolishing.

Alpha autoradiographic techniques⁴ were used to confirm the distribution of plutonium in contacted gel spheres. The autoradiographs were made using a glass slide coated with a cellulose nitrate film. Aluminum foil (household variety, 0.6 to 0.7 mils thick) was used as a filter to screen out alpha particles with a large angle of incidence* to the slide (these particles cause a diffuse pattern on the film). The filter significantly improved the resolution of the alpha particle distribution in the spheres.

Initially, spheres of 30 to 40 microns diameter were used, but the resolution was poor because of the inherent scatter of the alpha particles. When 500 to 800 micron spheres were used the resolution was greatly improved. Figure 4-5 is an autoradiograph of a contacted unfired gel sphere (the same gel as shown in Figure 4-4). The radiograph shows a uniform distribution of the plutonium throughout the gel sphere.

Similar photomicrographs and autoradiographs were prepared for calcined gel-addition spheres (Figures 4-6 and 4-7). The radiograph shows a very uniform distribution of plutonium within each sphere, although some slight variability is evident from sphere to sphere.

- - - - -
* The angle that the alpha particle makes with a line perpendicular to the surface of the slide.

Figure 4-1. Batch 6 UO_2 Gel - $\text{U}:\text{O}_2$ Ratio Vs Air Oxidation Time

Figure 4-2. . Batch 10 UO_2 Gel - $\text{U}:\text{O}_2$ Ratio Vs Air
Oxidation Time

Figure 4-3. Flowsheet for Single-Contacting Test on UO_2 Gel Spheres

Figure 4-4. Photomicrograph of Contacted,
Unfired UO_2 Gel Sphere

Sample 1D84
(Batch 11 - Contacted 1.5 hr with pH 0.5 Pu(IV) feed solution.)

100X

Figure 4-5. Alpha Autoradiograph of Contacted,
Unfired UO_2 Gel Sphere

Sample 1D84
(0.6 to 0.7 mil Al foil used as filter.)

100X

Figure 4-6. Photomicrograph of Contacted and Fired UO_2 Gel Spheres

Sample 1D85
(Gels of Figure 4-3 calcined at 1150 C for 3 hr in Ar-6% H_2 .)

100X

Figure 4-7. Alpha Autoradiograph of Contacted and Fired UO_2 Gel Spheres

Sample 1D85
(Gels of Figure 4-4 calcined at 1150 C for 3 hr in Ar-6% H_2 ; 0.6 to 0.7 mil Al foil used as filter.)

100X

5. IRRADIATION TESTING (C. J. Baroch)

An irradiation program is being established to determine the performance of vibratory compacted gel-addition plutonia-urania under fast-reactor operating conditions. Capsule irradiations are planned in the BAWTR, and fuel pins will be exposed in the EBR-II.

A tentative BAWTR irradiation program has been designed. Parameters for the irradiations were established (Table 5-1) after consultation with B&W reactor core designers and after considering the requirements and limitations on pin irradiations in the EBR-II.

A number of fuel and operational variables were considered for evaluation in the irradiation program. The variables selected and the scope of the tests are summarized in Table 5-2. Other variables were considered for evaluation but were eliminated for various reasons. For example, stoichiometry was not included in the program because a large amount of data indicates that an oxygen-to-metal (O/M) ratio of 1.95 to 1.98 is about optimum for fuel performance. In addition, separate capsules were not considered necessary to evaluate surface heat flux, fuel movement, plutonium migration, or fuel-cladding compatibility. These parameters will be evaluated during the post-irradiation examination of other capsules.

It is thought that a total of 19 to 20 capsules will be required to determine the irradiation performance of gel-addition fuel and to compare it with coprecipitated powder fuel (where possible, each capsule will include a control pin containing $\text{PuO}_2\text{-UO}_2$ pellets prepared from coprecipitated powder). To qualify particulate gel-addition fuel for fast-reactor application will require an additional 15 to 20 capsules, which are not included in the current irradiation program.

Table 5-1. Parameters for Irradiation of Gel-Addition
Plutonia-Urania in the BAWTR

<u>Parameter</u>	<u>Conditions selected</u>
Fuel density, % theoretical	83 to 87
Fuel burnup (peak), MWD/T	100,000 to 125,000
Pin diameter, in.	0.250
Fuel type	UO ₂ -20% PuO ₂
Cladding type	304 stainless steel
Cladding temperature (surface), F	1200 to 1300

Table 5-2. Scope of Gel-Addition Capsule Irradiation Program

Variable to be investigated	Estimated number of capsules	Scope of test irradiation
Impurity level	3 to 4	Compare quality of $\text{PuO}_2\text{-UO}_2$ prepared by alternate processes. *
Absorbed gas release and fission gas release	4	Measure dynamic gas release rates; some capsules will be designed so that dynamic release rates can be measured.
Thermal conductivity	3	Compare post-irradiation microstructures of Gel-Addition fuel and control fuel; capsules will be operated at three different heat ratings (15, 20, and 25 kw/ft); curves of $\text{Kd}\theta$ will be estimated by assigning the temperatures associated with the various microstructures.
High burnup behavior	5	Provide data on fuel swelling and fission gas release rates at burnup to 125,000 MWD/T; only one set of conditions will be evaluated, but capsules will be examined at incremental burnups.
Cyclic operation	2	Measure thermal cycling effects on gas release rates.
Fuel-sodium compatability	2	Evaluate the effects of sodium logging and sodium-fuel interactions on fuel pin integrity; both previously de-fected fuel pins and pins intentionally infiltrated with sodium will be irradiated.

* Three to four capsules will be used to determine the irradiation behavior of various mixed oxide fuels made by the variations in the Gel-Addition process. The performance of these fuels will be compared with that of $\text{PuO}_2\text{-UO}_2$ powder prepared by coprecipitation. Sixteen additional capsules will be used to evaluate the one Gel-Addition feed material considered most suitable from these screening tests.

6. ANALYTICAL SUPPORT (W. N. Bishop)

6.1. Coulometric Plutonium Analysis (W. N. Bishop, R. H. Dodd)

In the coulometric titration procedure described previously,¹ plutonium in valence states greater than III is reduced to Pu(III) at -0.31 volt versus the standard calomel electrode (S. C. E.) and is oxidized to Pu(IV) at a potential of +0.07 volt versus the S. C. E. in a citric acid-aluminum nitrate medium. At these potentials, uranium is also reduced but is not reoxidized since its reaction is irreversible. Thus, the value obtained for the plutonium concentration need not be corrected for the amount of uranium present. However, the procedure does require excessive reduction time (1 hour is typical) when the solution U/Pu ratio is much above two.

A procedure being investigated by Shults⁵ may decrease the time required to titrate mixed uranium-plutonium solutions. In this procedure, uranium is neither reduced nor oxidized. Plutonium is reduced at +0.56 volt versus the S. C. E. and oxidized at +0.88 volt versus the S. C. E. in a 1 M perchloric acid-0.02 M sulfamic acid electrolyte using a platinum gauze electrode. The sulfamic acid is added to destroy any nitrite that may be present. Nitric and hydrochloric acids do not interfere. However, the sulfuric acid concentration in the supporting electrolyte solution should be maintained below 0.007 M since the sulfate ion strongly complexes Pu(IV) and lowers the value of the Pu(IV)/Pu(III) couple⁶ (Table 6-1).

6.2. Plutonium Oxidation State After Sphere Dissolution

A colorimetric procedure for simultaneously determining uranium and plutonium in the same samples has been described previously.² The procedure is based on spectrophotometry of sulfate solutions in contrast to the nitrate spectra used previously in this project.

Table 6-1. Redox Potentials of the Pu(IV)-to-Pu(III) Couple in Different Media

Media	Redox potential, E_0 (volt versus S. C. E.)
1 <u>M</u> HClO_4	0.705
1 <u>M</u> HNO_3	0.700
1 <u>M</u> HCl	0.707
1 <u>M</u> H_2SO_4	0.500

Feed solutions for the procedure were routinely prepared by refluxing contacted gel-addition spheres (gel or fired oxide) in 60 to 90% HNO_3 until total dissolution was obtained (typically 0.5 to 2 hours for fired oxide; less for gel).

Recent results show that the plutonium analyses by the sulfate spectrophotometric procedure are often several-fold lower than those determined by coulometric titration. The discrepancy is attributed to oxidation of Pu(IV) to Pu(VI) during refluxing (the sulfate method is specific for Pu(IV)). As proof, an aliquot of Pu(IV) stock solution, a sample of uncontacted UO_2 gel spheres, and 10 ml of fuming HNO_3 were refluxed for 10 minutes. After dilution to 1 M HNO_3 , an aliquot analysis showed over 75% Pu(VI) by the nitrate spectrophotometric procedure.¹ Based on these results, the sulfate spectrophotometric methods are not considered applicable to the analysis of plutonium in raw dissolver solutions without prior adjustment of Pu(VI) to Pu(IV).

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