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GEL-ADDITION PROCESS CHEMICAL STUDIES

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ABSTRACT

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

During this report period emphasis was shifted to the Oak Ridge mixed sol approach, and development of the gel-addition technique continued at a reduced level. Oxide characterization work continued, and an irradiation program combining thermal and fast exposures was agreed upon.

Gel-addition experiments designed to increase the pickup of plutonium by UO_2 gels from aqueous solutions were begun; among the procedures tested, homogeneous hydrolytic precipitation of Pu(III) by urea during the pickup step showed the most promise. Pickup in one contact increased to about half the required value for fast reactor fuels.

Assay of both plutonium and uranium is now routinely carried out by weight aliquoting and controlled-potential coulometry. Shipper-receiver differences of about 2% in plutonium are still encountered. A method of measuring free acid levels in uranium and plutonium nitrates using ammonium oxalate as a complexing agent has been tested and is now in routine use.

Methods used to prepare specimens for ceramographic examination have been modified to eliminate polishing artifacts that interfere with microscopic examination. During examination of spherical UO_2 gels and oxides, small quantities of a second phase were observed and identified as silica from spectrographic and petrographic observations. Metallic inclusions observed in coprecipitated powders were removed by magnetic separation. The metallic particles are attributed to corrosive attack on a nickel alloy furnace liner. Irradiation specimens containing shards and pellets made from coprecipitated (U, Pu) O_2 powders

and spherical particles made from mixed sol-gel (U,Pu)O₂ were fabricated. The fuels for the irradiation specimens were characterized, and the specimens were fully inspected in preparation for irradiation during the next quarter.

Twenty-eight fuel capsule exposures are planned for the BAWTR to measure both the time required for restructuring of particulate fuels and their offgassing characteristics. Two 19-pin subassemblies will be exposed in EBR-II. Some pins will be removed after an exposure of 25,000 MWD/T and replaced with fresh material. A total of 76 fuel pins is planned for EBR-II.

The first laboratory run of mixed sol material is complete. UO₂ sol preparation was routine. Several PuO₂ sol preparations formed precipitates that did not resuspend after thermal denitration. Some conversion to Pu(VI) was noted.

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1. INTRODUCTION

This is the seventh 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 February 1, 1968, to April 30, 1968.

During this report period emphasis was shifted from the gel-addition process to the mixed sol approach developed at Oak Ridge National Laboratory. These two processes are both in the sol-gel family, but differ in the procedure 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.

In the following sections our conclusions are summarized and progress is reported in detail on clarification of gel-addition reactions, analytical support, characterization of the materials, the irradiation program, and the establishment of a mixed sol unit operations system.

2. CONCLUSIONS

2.1. Gel-Addition Chemistry

It was reported earlier¹ that there are marked differences in the gel-addition pickup mechanism for hexavalent plutonium and for the tri- or tetravalent forms. The latter two apparently see UO_2 gels largely as porous inert bodies in the pH ranges studied, but the former reacts strongly, depositing the plutonium in the outer layers of a gel sphere. Neither of these results is particularly desirable. In the first case, pickup is determined almost entirely by the gel void volume, the solution concentration, and the amount washed out afterward. In the second case, sphere attrition is severe, especially in repeated contacts.

During this report period gel-addition chemistry work has centered on techniques for improving pickup of tri- and quadrivalent plutonium by in situ changes of pH and plutonium valence. Adjustments of this kind can increase the pickup from the 4 to 5% region to about 7 to 10%, but this is still about half the required amount for fast reactor fuels.

2.2. Analytical Support

Differences amounting to several grams (in about 0.5 kg) of plutonium generally appear between the shipper's and B&W's assay of aqueous plutonium nitrate solution. The magnitude can be decreased by basing the analysis on plutonium assay in sealed ampoules prepared by the shipper and by eliminating all volumetric measurements; that is, basing measurements on weighed aliquots. These precautions have reduced the shipper-receiver differences to less than 2%.

Free nitric acid assay in mixed uranium-plutonium solutions can be carried out by base titration if the uranium and plutonium are complexed with ammonium oxalate. Changes in the relative humidity of the ambient air cause rapid and proportional changes in the water content of 2-ethyl hexanol.

The nitrate contents of gels and sols can be measured by ferrous ion titration if uranium and plutonium are removed by cation exchange. The precision is poor, however, in low nitrate samples.

2.3. Oxide Characterization

Methods reported earlier for examination of the microstructure of (U, Pu)O₂ require modification to eliminate features that were attributed to an unknown second phase but are now known to be due to relief polishing. The processes currently used at B&W have produced small but detectable quantities of a siliceous phase in at least one batch of sol-gel UO₂. The identification was made by both emission spectroscopy and petrographic examination. The presence of some boron indicates that the siliceous material results from Pyrex glass pickup.

Magnetic separation successfully removes metallic inclusions observed in some coprecipitated powders prepared in B&W's laboratories. The metallic particles have been traced to oxide spallation from a high-nickel-alloy furnace liner.

2.4. Irradiation Testing

Seventeen thermal reactor capsules (exposures varying from 1 to 81 days at heat rates from 6 to 20 kW/ft) will be used to determine the time required for restructuring of particulate fuels studied in this program.

Eleven thermal reactor capsules will be irradiated to determine the sorbed gas release behavior of particulate fuel. Irradiations will last about 30 days and will be run at heat rates from 6 to 20 kW/ft.

2.5. Mixed-Sol Preparation

The flow sheet for PuO₂ sol preparation requires thermal evaporation of an intermediate high nitrate sol and its conversion to a low nitrate sol by low temperature (≈ 250 C) pyrolysis. In a series of laboratory runs the final sol contained some sediment which was attributed to uneven heating during the pyrolysis. A new thermal denitrator is under design.

UO₂ sols can be made at will, but PuO₂ sols are considerably harder to make. In addition to the denitration problem already mentioned,

some sols have spontaneously oxidized partially to Pu(VI) with a proportionate reduction in sol yield. The causes are under study.

Blended sols can undergo segregation; strong agitation is required to minimize the problem during gelation. Additive levels of 0.4 vol % Span-80, 0.25 vol % Ethomeen-S/15, and 0.8 vol % water gave satisfactory gelation conditions. Drying in ethanol with an argon flush followed by 4 to 8 hours at 120 C in flowing nitrogen gave a satisfactory dry gel.

A firing cycle was selected after a series of test runs indicated that the carbon content could be held below 30 ppm and that particle densities near 95% TD could be achieved. O/M ratios of 1.99 are obtainable if a temperature ≥ 1200 C is held for 4 hours and there is good contact with the furnace atmosphere.

3. GEL-ADDITION CHEMISTRY (R. V. Carlson)

In previous reports^{1,2} it has been shown that when UO_2 gel microspheres are contacted with aqueous Pu(VI) solutions, the plutonium concentrates in a thin shell near the outer surface, whereas in gels contacted with aqueous Pu(III) or Pu(IV) solutions, the plutonium is uniformly distributed throughout. In addition sphere attrition during contact with Pu(VI) solutions is much more severe than with Pu(III) and Pu(IV) solutions.

In numerous experiments it has been observed that during contact of Pu(IV) solutions with UO_2 gel the pH increases very rapidly into the region in which nearly all the plutonium can readily convert to the insoluble Pu(IV) polymer. As a result, after the first few seconds of contact, the concentration of Pu(IV) available for pickup (i. e., Pu(IV) particles small enough to enter the gel pores) may be extremely low, and the pickup is apparently limited to a maximum of about 5%. An attempt³ to increase the pickup by inhibiting polymer formation through the addition of citric acid to complex the Pu(IV) was unsuccessful. Other experiments were performed⁴ in which polymer formation was minimized by adjusting the initial acidity of the Pu(IV) solution to more than 1 M. However, in these tests, sphere attrition was very great.

For these reasons, the principal emphasis during this report period was on Pu(III) contacting experiments. It has been proposed⁵ that the pickup of Pu(III) takes place principally by an absorption mechanism, with the gel behaving as an inert, porous substrate. Based on the previous pickup data and the postulated mechanism, at least four experimental approaches appear to be capable of producing pickup values in the region of interest to the fast breeder reactor program:

1. Fix the plutonium in the UO_2 gel in such a way that it cannot be removed by a simple aqueous washing.
2. Contact dried gel several times with fresh plutonium solution. For this technique to be feasible, a method of decreasing sphere attrition must be found.
3. Increase the plutonium concentration into the region of about 3 M.
4. Increase the void volume in the UO_2 gel.

3.1. Pu(III) Fixation

Several new techniques have been used in an effort to increase the quantity of plutonium picked up by UO_2 gels. The concept behind each of these techniques involves the fixation of plutonium in the gel by precipitation of the hydroxide.

3.1.1. Quantities Normally Fixed

Ten grams of UO_2 gel spheres were contacted (with 40 ml of 0.6 M Pu(III) at pH 1.0) on the thermovibrator (Precision Scientific Company, Chicago) for 1 hour at ambient temperatures. After contact, the Pu(III) solution was decanted and its pH was measured and found to be 0.9. The spheres were then divided into two batches. Half were left unwashed, and the other half were washed 10 times with 10 ml aliquots of demineralized water. Finally, each sample was dried overnight in a vacuum oven (60 C, 29 in. Hg vacuum) and sieved on a 40-mesh screen (420-micron opening) to separate whole spheres from fragments. Since the quantity of fines was very small (≈ 0.1 g), only the coarse product was analyzed.

The pickup was measured as 10% in the unwashed sample and 1.8% in the washed sample. The latter is about two-fold lower than the pickup observed under similar conditions in the statistical experiment⁶ and is an upper limit for the amount of plutonium chemically bound in the gel. It is not clear from this experiment whether the plutonium remaining in the washed sample is indeed fixed in the gel or whether a more extensive wash over a longer period of time would have removed all the plutonium.

Some of the difference in the plutonium content of the two samples is attributable to residual contact solution on the unwashed sample.

But for all of the difference to be due to this effect, over 3 ml of the contact solution would have remained on the unwashed sample. This quantity is several times larger than the actual value, and it is clear that a large percentage of the plutonium picked up from a Pu(III) solution can be washed from UO₂ gel. Therefore, the results from this experiment are certainly consistent with the hypothesis⁵ that UO₂ gel behaves principally as an inert, porous material toward a Pu(III) solution.

3.1.2. Gaseous Ammonia Treatment of Gels

A 5.0-g sample of UO₂ gel was exposed for 20 minutes to an ammonia atmosphere before contacting with a Pu(III) solution. It was anticipated that the gel would absorb some ammonia and produce a sharper rise in the pH of the contacting solution, especially within the gel pores. Pickup was expected to increase by hydrolytic fixation.

The spheres were removed from the ammonia atmosphere and immediately placed in 50 ml of 0.5 M Pu(III) solution at pH 2.0. The contact was performed on the thermovibrator at ambient temperatures. After 1 hour the solution was decanted, and the spheres were washed four times with 10-ml aliquots of 0.1 M NH₄OH. Finally, the gel was dried (60 C, 29 in. Hg vacuum) for 18 hours and sieved on a 40-mesh screen.

The pickup was 5.1%; about 4% was observed in the statistical run⁶ under approximately the same conditions. Since the spheres in this test were washed much more thoroughly than those in the statistical experiment, it can be concluded that pretreatment of UO₂ gel with NH₃ gas leads to increased plutonium pickup. However, the pickup measured in this test is still three to four times below the desired level.

3.1.3. Aqueous Ammonia Treatment of Gels

In a second test to determine whether pickup could be improved by ammonia absorbed on the gel, a 5.0-g sample of UO₂ gel was soaked in 100 ml of 1.0 M NH₄OH on the thermovibrator for 1 hour at ambient temperatures. After decanting the NH₄OH, the gel was contacted (with 30 ml of 0.55 M Pu(III) at a pH of 1.5) on the thermovibrator for 2 hours at 50 C. The spheres were then washed thoroughly with 20 ml of 0.1 M NH₄OH, dried (60 C, 29 in. Hg vacuum), and sieved on a 40-mesh screen. The pH of the Pu(III) solution after contact was 1.8.

The pickup was 4.3% in the coarse sphere fraction and 4.8% in the fines. The difference between these two values is probably within the experimental error. This close agreement indicates that very little, if any, plutonium solution or precipitate was present after the spheres were washed. Although these results indicate some improvement in pickup when compared to the results from the statistical run,⁶ the value is still well below that desired.

3.1.4. Homogeneous Precipitation

In two tests, Pu(III) solution containing added urea was contacted with UO₂ gel spheres. Urea hydrolyzes rather rapidly near the boiling point of aqueous solutions,⁷ giving CO₂ and NH₃. This results in a homogeneous increase in the pH without local excesses of reagents. These tests were run with the hope that Pu(III) could be fixed in UO₂ gel by homogeneous hydrolytic precipitation.

In each test, 5.0-g UO₂ gel spheres were contacted with 75 ml of 0.13 M Pu(III) solution at an initial pH of 2.5. The samples were heated on the thermovibrator, and a sand bath was used for temperature control. In the first case, 1.0 g of urea was added to the plutonium solution; it was boiled for 5 minutes, cooled to 60 C, and measured for pH. The process was repeated until a total of 16 g of urea had been added. After the addition of 11 g, the pH remained constant at 4.8 until the final addition. In the second case, 16 g of urea were added initially. Then the solution was boiled for 5 minutes, and cooled to 60 C, and the pH was measured. This process was repeated until the solution had been boiled for a total of 1.5 hours. After 30 minutes of boiling the pH remained constant at 3.9 until the end of the run.

After drying (60 C, 29 in. Hg vacuum) and sieving on a 40-mesh screen, the plutonium pickup in the coarse sphere fraction was measured and found to be 4.9% in the first test and 9.9% in the second. The reason for the difference in pickup by the two samples is not clear. However, it should be noted that a pickup of 4.9% is nearly as large as any of the values observed with Pu(III) in the statistical experiment,⁶ but the solution in this test was only 0.13 M in Pu(III). Thus, these results are encouraging, and this technique will be tested further.

3.1.5. Oxidation During Contact

Previous results have indicated that the oxidation of Pu(III) to Pu(IV) during contact with UO_2 gel holds some promise for producing the desired levels of pickup. During the report period, this technique was used in two identical experiments which produced widely different results. In both tests, 5.0-g UO_2 gel microspheres were contacted on the thermovibrator with 40 ml of 0.6 M Pu(III) solution (pH 2.0) at 77 C. Each contact was terminated when the sample reached a moist dryness. The spheres were then washed thoroughly several times with 0.1 M NH_4OH , dried (60 C, 29 in. Hg vacuum), and sieved on a 40-mesh screen.

In the first case, the gel was reduced almost to powder, and the pickup of this material was 20.8%. In the second case, the gel retained its integrity, but the pickup was only 1.7%. The reason for the widely different results from these and previous tests is not clear at this time.

3.2. Pu(III) Triple Contact

Previously reported experiments^{8,9} have shown that plutonium pickup can be increased by recontacting dried UO_2 gel spheres with fresh plutonium solution. However, the results from the Pu(III) test¹⁰ seemed to be anomalous, since no increase in pickup was observed in the second contacting. In addition, the previous runs were performed with a column-contacting technique, and the spheres were not washed before drying. Therefore a triple contact of UO_2 gel with Pu(III) solutions was repeated. No special measures were taken to minimize the sphere degradation, since the principal purpose of this test was to determine whether the increase in pickup from a multiple contacting with Pu(III) was sufficient to warrant further study.

A total of 140 ml of Pu(III) solution (0.6 M, pH 1.5) was prepared by hydrazine reduction and divided into three equal aliquots. A 20-g sample of UO_2 gel spheres was contacted with the first aliquot on the thermovibrator for 2 hours at 50 C. After the solution was decanted, the spheres were washed thoroughly with about 25 ml of 0.1 M NH_4OH , dried overnight (60 C, 29 in. Hg vacuum) and sieved on a 40-mesh screen. Approximately a third of the spheres were then withdrawn for analysis. The remaining spheres were contacted with the second Pu(III) solution.

aliquot (50 C, 2 hrs) and recovered, washed, dried, and screened as before. About half of the spheres that had been contacted twice were withdrawn for analysis, and the remainder were contacted for a third time. The pH of the solution after contact was 1.8 in each case. The pickup values measured for the single-, double-, and triple-contacted spheres were 4.2, 6.9, and 10%, respectively. This indicates that the plutonium is fixed in the gel after drying in such a way that additional quantities can be picked up in subsequent contactings and cannot be readily removed by a simple wash. Therefore, this technique could provide a way to obtain pickup values in the region of interest. However, in this experiment, the sphere attrition was estimated to be about 25%. Thus, for the technique to be useful, means of suppressing the sphere degradation must be found.

3.3. Contact Under Vacuum

This test was performed to determine whether gases in the UO_2 gel pores inhibit the entry of plutonium-bearing solutions. A 5.0-g sample of UO_2 gel spheres was placed on the bottom of a side-arm filter flask. The top was closed with a one-hole stopper fitted to a glass buret. The flask was evacuated to a few millimeters Hg pressure, and the buret was opened to admit 20 ml of a Pu(III) solution (0.6 M, pH 2.0). The solution was decanted within 1 minute after entering the flask. The spheres were washed with about 15 ml of 0.1 M NH_4OH , dried overnight (60 C, 29 in. Hg vacuum), and sieved on a 40-mesh screen.

The pickup was 4.0%. Since this value is near those observed in other experiments with the same UO_2 gel (see sections 3.1, 3.2, and 3.3), it is obvious that the pickup takes place very rapidly. This certainly lends further support to the concept that the UO_2 gel behaves as an inert, porous substrate to Pu(III) solutions. In addition, these results indicate that the gel pores are not blocked by gases.

3.4. Surface Area Effects

To determine whether plutonium pickup is dependent upon the superficial surface area of the UO_2 gel, identical contactings were performed with spheres prepared by stirred pot methods (88-105 microns) and with four samples of tray-dried UO_2 gel shards. In each run, 5g of gel were contacted with 40 ml of 0.5 M Pu(III) solution (pH 2.0) on the

thermovibrator for 2 hours at ambient temperatures. After contact, the plutonium solution was decanted and the gel was washed several times with 10 ml of 0.1 M NH_4OH . Finally, the gel was dried (60 C, 29 in. Hg vacuum) overnight and screened to remove the particles which were finer than the corresponding starting material. In no case was the quantity of fines sufficient to submit for analysis. Three samples from the coarse fraction of spheres were submitted for analysis. The pickup values obtained are summarized in Table 3-1.

Table 3-1. Pickup by Small Spheres and Shards

<u>Particle</u>	<u>Particle size, microns</u>	<u>$\frac{\text{U}}{\text{Pu} + \text{U}} \times 100$</u>
Stirred-pot spheres	88 - 105	3.2
		2.7
		3.9
Tray-dried shards	>2830	2.3
Tray-dried shards	2380 - 2830	2.9
Tray-dried shards	1680 - 2380	3.3
Tray-dried shards	1410 - 1680	3.6

These results indicate that the pickup is not dependent upon the superficial surface area. Moreover, the observed pickup apparently is not sensitive to organics absorbed during the gelation process. Tray-dried shards are not organic-free because both urea and formic acid are used in preparing the sol; however, they do not contain residues from the 2-ethyl-1-hexanol used in sphere formation.

3.5. Pu(VI) Contacts

In three of the Pu(VI) contactings in the statistical experiment,⁶ the pickup was found to be more than 9%. These three tests were run again under nearly identical experimental conditions to confirm the high pickup values. The only change in the technique was to wash the contacted spheres with 0.1 M NH_4OH instead of demineralized water. The

contacting conditions for these tests are summarized in Table 3-2, and in Table 3-3 the results are compared with those from the statistical experiment.⁶

Table 3-2. Experimental Conditions for Pu(VI) Tests

	<u>Test 1</u>	<u>Test 2</u>	<u>Test 3</u>
Spheres contacted, g	5.0	5.0	5.0
Solution volume, ml	30	45	45
Pu(VI) concentration, <u>M</u>	0.90	0.60	0.60
Initial pH	1.5	2.5	2.5
Temperature, C	60	60	30
Contact time, min	240	125	240

Table 3-3. Results From Pu(VI) Tests

	<u>Test 1</u>	<u>Test 2</u>	<u>Test 3</u>
Pu/(Pu+U) in +40-mesh fraction, %	4.8	3.3	2.0
Pu/(Pu+U) in -40-mesh fraction, %	24.9	19.2	6.1
Pickup observed in statistical experiment ⁶ for +40-mesh fraction	13.6	11.8	9.6

The reason for the large difference in pickup under nearly identical conditions is not clear. However, during the second series of tests it was noted that the quantity of fines after screening was quite large. Therefore, since it has been shown that nearly all the plutonium in UO_2 gel contacted with Pu(VI) solutions is near the outer surface,¹ and since the plutonium content in the fines is quite high, it is assumed that the gel surfaces were more severely attacked in the second series of tests.

4. ANALYTICAL SUPPORT (D. H. Schmitt)

4. 1. Plutonium Analysis

4. 1. 1. Shipper-Receiver Differences

Some discrepancy regarding shipment 9 of plutonium nitrate stock solution was observed between the shipper (Atlantic Richfield Hanford Co.) and the receiver (Babcock & Wilcox). Therefore, to improve the possibility of agreement on shipment 10, the shipper sealed two samples in glass ampoules, one for analysis by the shipper and the other by the receiver. It was further agreed that the samples would be analyzed on the same day in order to equalize any chemical effects of alpha-autoradiolysis. The results for shipments 9 and 10 are compared in Table 4-1. It appears that shipment 9 underwent a concentration increase between the time of analysis by the shipper and that by the receiver. The results for shipment 10 are better, but it can be seen that more work is required to reduce the differences between the shipper and the receiver.

4. 1. 2. Weight Dilution and Aliquotting

The shipper-receiver differences in plutonium assay point up the need for better precision in many plutonium analyses. Accordingly, all analyses of this type are now routinely carried out on a weight basis instead of a volumetric basis. Table 4-2 (part A) shows the data spread obtained on triplicate analysis of three separate samples of a plutonium sol. Weighed aliquots were used, and the plutonium was measured by controlled potential coulometry. It is believed that the precision is near the best obtainable with present methods and equipment.

At the 95% confidence level of the mean value, the plutonium concentration was determined to be 152.5 ± 0.4 mg Pu/g sol, or

152.5 mg Pu/g sol $\pm 0.26\%$. The relative standard deviation of a single value is 0.37%.

4.2. Uranium Analysis

The precision of weight aliquotting and coulometric titration was investigated for the uranium case also. Table 4-2 (part B) shows the scatter observed in the uranium assay of a UO_2 sol. Three separate weight aliquots were analyzed coulometrically in triplicate. At the 95% confidence level of the mean value, the uranium concentration was determined to be 227.5 ± 0.6 mg U/mg sol, or 227.5 mg U/mg sol $\pm 0.26\%$. The relative standard deviation of a single value is 0.39%.

Further work is expected to improve the precision of uranium measurements.

Table 4-1. Assay of Plutonium Nitrate Stock Shipments 9 and 10

<u>Measurement</u>	<u>Shipper</u>	<u>B&W</u>
<u>Shipment 9</u>		
Plutonium content, g/l	233.59	$240.1 \pm 1.4^{(a)}$
Specific gravity	1.508	1.557
Free acid, mole/l	3.2	6.3
<u>Shipment 10 — bulk solution</u>		
Plutonium content, g Pu/g solu ^(b)	0.1553	$0.1531 \pm 0.0008^{(a)}$
Specific gravity	1.544	1.540
Free acid, mole/l	6.81	5.5
<u>Shipment 10 — sealed ampoule</u>		
Plutonium content, g Pu/g solu	0.1543	$0.1521 \pm 0.0004^{(a)}$
Specific gravity	nm	1.555
Free acid, mole/l	nm	nm

^(a) 95% confidence levels.

^(b) See text for comments on change of units (paragraph 4.1.2).

Table 4-2. Precision of Weight Aliquotting and Controlled Potential Coulometry

A. Plutonium Assay in a PuO₂ Sol

<u>Sample</u>	<u>Pu content, mg Pu/mg sol</u>
1	153.1
	152.5
	153.2
2	152.2
	153.3
	152.7
3	152.0
	151.8
	152.0

B. Uranium Assay in a UO₂ Sol

<u>Sample</u>	<u>U content, mg U/mg sol</u>
1	226.6
	227.6
	228.9
2	226.3
	227.5
	228.8
	228.2
3	226.5
	227.0
	227.9

4.3. Free-Acid Analysis

In the past, the free acid content of plutonium, uranium, and mixed solutions has not been analyzed owing to the lack of a suitable method. However, the need for such measurements has been growing steadily.

A literature search showed that three basic techniques are in current use:

1. Ion exchange separation of hydrolyzable ions and subsequent acid-base titration.¹¹⁻¹³
2. Precipitation of hydrolyzable ions followed by a titration.¹⁴⁻¹⁶

3. Complexation of interfering ions allowing titration of the acid.¹⁷⁻¹⁹

The third method was chosen because of its simplicity, which is a significant advantage in glove box operations. Fluoride, citrate, tartrate, and oxalate anions were investigated since they are known to form some of the strongest uranium and plutonium complexes.

The complexing agents were added to Pu(IV) or U(VI) solutions of known acid concentration, and the free acid was titrated with a standardized solution of sodium hydroxide. The titration curve (pH versus volume of NaOH added) was plotted, and the end point was determined from this curve. The results were then compared to the known free acid values to determine accuracy and precision.

The reactions underlying the method can be briefly summarized by the equations.

where "M" is the hydrolyzable species and "L" is the complexing ligand. Reaction (3) is an interference whose extent is governed by (1). The suppression of (3) is the principle of the method. It is most readily accomplished by keeping $[M^{+n}]$ small by keeping $[L^{-m}]$ large and by selecting L so that the dissociation constants for $ML_x^{+(n-xm)}$ are as small as possible. Also, (4) competes with (1) to limit the availability of ligand; consequently, it is desirable for HL to have a large acid constant in order to drive (4) to the left.

The extent of (3), together with the acidic or basic impurities and the buffering capacity of the complexing agent (4), causes an over or undershooting of the end point in the titration curve, giving a bias in the free acid determination. Obviously the best complexing agent for the method is one that gives a minimum bias.

Investigation showed that the use of fluoride as a complexing agent is satisfactory in the uranium system, but presents formidable problems with plutonium. The complexes of PuF_x , $x < 4$ would not prevent precipitation at pHs above about 4. (The appearance of a precipitate was assumed to indicate hydrolysis.) PuF_4 is also a precipitate that causes H^+ trapping, yielding pH oscillations in the end point vicinity. Likewise, PuF_5^- and PuF_6^{2-} formed precipitates of NaPuF_5 and Na_2PuF_6 , respectively. These oscillations were also observed by Wooley, Money, and McGowan.²⁰

Tartrate forms strong complexes with both plutonium and uranium, but since the tartrate systems were observed to give a sizeable bias, it was decided to discontinue further study in favor of citrate and oxalate.

Before studies on the oxalate systems were begun, interest was focused primarily on anion chemistry. Sodium or potassium salts were generally used since they were most readily available. Initial studies on oxalate were begun arbitrarily with the ammonium salt. It was expected that the NH_4^+ ion would buffer the system somewhat and therefore flatten the titration curve, but initial interest was centered on whether or not the oxalate complexes were strong enough to prevent hydrolysis. Pflug and Miner¹⁷ reported the appearance of a precipitate and a sizeable bias for free acid determination in plutonium solutions when sodium oxalate was used as a complexing agent. They concluded that oxalate was unsuitable for preventing plutonium hydrolysis.

B&W's initial work with ammonium oxalate as a complexing agent showed no precipitate or bias in either plutonium or uranium systems. Subsequent work using sodium oxalate showed precipitation in both plutonium and uranium solutions at pHs as low as 4.5, confirming the Pflug and Miner observations on plutonium.

A possible explanation of this behavior lies in the buffering ability of the NH_4^+ ion on the system. Normally, as the titration of the free acid proceeds, the $[\text{H}^+]$ decreases as the $[\text{OH}^-]$ increases. Since precipitation occurs when sodium oxalate is used, it is obvious that the oxalate complexes are not as strong as one would hope in the face of high $[\text{OH}^-]$. Although the pH of the overall solution is not very high until after the end point is reached, the instantaneous pH at the solution interface, as base is added, is very high and the oxalate complex will probably not

prevent precipitation in the presence of this large $[\text{OH}^-]$. Using ammonium oxalate, the $[\text{NH}_4^+]$ is quite large, and the instantaneous pH at the solution's interface is decreased considerably by the reaction

Consequently, the oxalate complex is never faced with an extremely large $[\text{OH}^-]$ and precipitation is prevented.

Considerable support was given to this explanation of the role that the ammonium ion plays by conducting some pH titration tests of uranium and plutonium solutions containing sodium oxalate. Ammonium hydroxide was used as the titrant, and titrations of both metals were carried out with no sign of precipitation.

Having concluded that ammonium oxalate would prevent precipitation in both uranium and plutonium systems, experiments were conducted to compare it with sodium citrate to determine which was the more satisfactory. Blanks were run by titrating each of the salts dissolved in water with very dilute sodium hydroxide to determine the presence of any acid impurities in the reagents used. A very small blank was found with the sodium citrate, but it was not large enough to significantly affect the results in subsequent titrating. Ammonium oxalate gave no detectable blank.

All titrations were performed on solutions containing identical amounts of nitric acid and were titrated with the same known volume of sodium hydroxide solution. Titrations run on solutions containing only nitric acid and a complexing agent contained equimolar amounts of ligand. Actual free acid determinations of solutions containing hydrolyzable ions were carried out on equal molarities of either plutonium or uranium. In the last case, ligand was added in excess; that is, more than the stoichiometric amount needed to satisfy the highest coordination number for the hydrolyzable ion in question.

Figure 4-1 shows the effects of the two complexing agents on the titration curve of nitric acid. The weak acid formations of oxalate and citrate are evident in the high initial pHs and in the broadening effects on the curves. The buffering effect of NH_4^+ is apparent in the oxalate

system by the low pH at the end of the titration. (Also, note the slight bias in the citrate system.)

Figures 4-2 and 4-3 are plots of the two complexing agents in the uranium and plutonium systems, respectively. Again, note the persistent bias of citrate in both systems, about 1.7 divisions between its end point and that of the oxalate, which coincides with the true free acid end point. The increase in the sharpness of the oxalate curve in the plutonium system reflects a small excess as compared with the large excess used in the uranium system. Ideally, only enough ammonium oxalate should be added to the system to ensure the highest coordination number for the hydrolyzable ion. Any excess beyond this point serves only to broaden the titration curve. However, the addition of an obvious excess alleviates the problem of knowing the hydrolyzable ion concentration. Difficulty in determining the end point due to the broadening is overcome by taking derivative end points.

The appearance of a bias is almost inevitable in titrations in which the complexing agent is the salt of a weak acid. The weak acid formed upon dissolution of the salt limits the availability of the ligand for complexing according to the equations

The weaker the acid in (5), the smaller the concentration of ligand available for complexing and the greater the bias. The stronger the acid in (5), the greater the concentration of ligand. Thus, one would expect to see a larger bias for citrate than for oxalate. However, the lack of bias in the ammonium oxalate system is probably caused by the NH_4^+ buffering. The bias associated with the citrate system can be made quite small by adjusting the pH of the system to higher values, thus driving (5) to the right and enhancing (6), but this is a bothersome extra step.

Figure 4-1. Comparison of Complexing Agents for HNO_3 Titration

Figure 4-2. Comparison of Citrate and Oxalate in $\text{UO}_2(\text{NO}_3)_2$ System

Figure 4-3. Comparison of Citrate and Oxalate in $\text{Pu}(\text{NO}_3)_3$ System

Consequently, ammonium oxalate was chosen, since this method requires only the addition of excess reagent to the solution in question and then a standard acid-base titration. The lack of any detectable bias using ammonium oxalate also affords the method the usual good precision and accuracy associated with standard acid-base titrations.

4.4. Water Content of 2-Ethylhexanol

Since the water content of 2-ethylhexanol is an important parameter in the sol-gel process, it was decided to determine the water uptake of the 2-ethylhexanol as a function of time. A sample of 2-ethylhexanol was taken on November 10, 1967, and split into two fractions. One was kept in a closed container and the other was left open to the atmosphere. These two samples were then periodically analyzed for water content for 140 days. It can be seen that the results for the sample in the closed container (Figure 4-4) are fairly constant within the experimental error. However, the results for the open container are quite erratic. For the last three measurements, the temperature and the relative humidity in the laboratory were recorded on the day of analysis (Table 4-3). The table shows that the water content varies with the climatic conditions. Additional evidence was obtained by putting two samples of 2-ethylhexanol into two desiccators, one containing a desiccant and the other a layer of water on the bottom of the desiccator. The desiccators were sealed and the samples were allowed to come to equilibrium for three days. However, the sample in the wet atmosphere was cloudy, indicating that it was not at true equilibrium. Since the purpose of the experiment was to show that the relative humidity was a great factor in the water content of the 2-ethylhexanol, both samples were analyzed without waiting for true equilibrium to be reached. From the results (Table 4-4) it can be seen that the water content is indeed proportional to the relative humidity. In conclusion, it can be stated that the water content of 2-ethylhexanol will remain relatively constant in a tightly sealed container and will vary with climatic conditions in an open or loosely sealed container. (NOTE: All water analyses were performed using the standard Karl Fischer method.)

Table 4-3. Water Content in 2-Ethylhexanol as a Function of Temperature and Relative Humidity

<u>No. days from initial determination</u>	<u>Temperature, F</u>	<u>Relative humidity, %</u>	<u>Water content, vol %</u>	
			<u>Sample in open container</u>	<u>Sample in closed container</u>
136	80	27	0.166	0.0449
142	79	40	0.345	0.0675
149	76	36	0.259	0.0529

Table 4-4. Water Content in 2-Ethylhexanol as a Function of Relative Humidity

<u>Sample identification</u>	<u>Water content, vol %</u>	<u>Temperature, F</u>
Initial (Rel humidity: 27.5%)	0.208	78
Dry atmosphere	0.0439	76
Wet atmosphere	1.979	76

Figure 4-4. Water Uptake of 2-Ethylhexanol Vs Time

4.5. Nitrate Analysis

The nitrate method discussed previously²¹ has been extended to include nitrate analysis on uranium sols and uranium gels. UO_2 sols and gels can be dissolved in hot concentrated hydrochloric acid. A few drops of 1:1 hydrofluoric acid added at the end of the dissolution period seem to ensure complete dissolution and to stabilize the solution. The uranium can be separated from the nitrate using a cation exchange column (Dowex 50-X8). Since the nitrate concentration is quite small, a known standard amount of nitrate is added to the sample after the ion exchange separation. The sample is then analyzed for nitrate according to the previously described procedure.²¹ In order to obtain the actual amount of nitrate present, the nitrate added is subtracted from the nitrate found.

A short statistical examination of the nitrate method for uranium sols and gel spheres was performed. All the nitrate analyses were performed in triplicate. To determine the relative precision of the whole method, including dissolution, separation, and analysis, several samples of sols and gel spheres were split into duplicate or triplicate samples. The results are shown in Table 4-5. It can be seen that the reproducibility is not very good and is much worse than that found for uranous nitrate samples (1.71% at 95% confidence limits). However, it is not too surprising, since much smaller amounts of nitrate are being determined. The present precision is adequate for our needs if sample 3 is disregarded. It is felt that better precision can be obtained with this method if future determinations require it.

4.6. Analytical Sample Load

During this quarter 200 samples submitted for analysis were completed. This sample load represented approximately 880 analyses, including total U, total Pu, $\text{U(IV)}/\text{total U}$, NO_3^- , H_2O , C, pH, O/M, free $[\text{H}^+]$, specific gravity, and qualitative ion spot tests.

Table 4-5. Statistical Examination of Nitrate Method for UO_2
Sols and Gel Spheres

Sample	Sample description	Nitrate found, mg	Relative precision at 95% C. L. on nitrate analysis only, %	Average nitrate found, mg	Relative precision at 95% C. L. on complete determination, %	Relative standard deviation on complete determination, %
1-A	Gel spheres	0.43	2.29	0.42	47.9	5.33
1-B	Gel spheres	0.40	3.28			
2-A	Gel spheres	1.50	5.59	1.50	16.6	6.67
2-B	Gel spheres	1.40	10.1			
2-C	Gel spheres	1.60	6.91			
3-A	Gel spheres	1.40	10.4	1.21	205	22.8
3-B	Gel spheres	1.01	6.63			
4	Sol	4.00	0.00	--	--	
5	Sol	5.70	12.6	--	--	
6	Sol	2.00	6.33	--	--	
7-A	Sol	1.40	1.47	1.40	35.6	14.3
7-B	Sol	1.20	1.32			
7-C	Sol	1.60	2.81			
8-A	Sol	0.98	0.30	1.15	33.0	13.3
8-B	Sol	1.18	2.33			
8-C	Sol	1.28	0.75			
Average: 67.6						12.5
(Discard Set No. 3) Average: 33.3						9.90

5. OXIDE CHARACTERIZATION (J. M. Kerr)

5.1. Materials Characterization

Ceramographic examinations of both spheres and pellets are included routinely as part of the information needed to characterize (U, Pu)O₂ fuel produced in this program. Previous specimen preparation techniques have been modified because of extreme tearing or pull-out of the sample.²² The modified technique developed to produce suitable pellet and sphere specimens is as follows:

1. Mount the specimen in "Quick-Mount" room-temperature setting epoxy.
2. Using "Knuth Roto-Grinder," grind the specimen first with 400-grit and then 600-grit silicon carbide paper.
3. Using "Syntron" vibratory bowl polisher on as low a control setting as possible, polish the specimen with 6-micron diamond paste on nylon cloth for 1 to 2 hours.
4. Using 1-micron diamond paste in a Syntron vibratory bowl polisher, final-polish the specimen for 15 to 20 minutes.

Figure 5-1 shows the sphere specimen prepared by the modified method for comparison with a sphere specimen prepared by the previous method as shown in Figure 5-2. The specimen appeared much smoother and pore-free when using the new technique. Figure 5-3 shows a pellet specimen prepared by the modified method for comparison with a pellet specimen prepared by the previous method as shown in Figure 5-4.

During a detailed examination of a batch of UO₂ spheres, very minor amounts of what appeared to be a second-phase material were observed. This phase was tentatively identified by petrography as a silica-rich phase. A spectrographic analysis showed high silicon and boron contents, confirming the identification. The source of silicon is unknown,

but could have been present as an impurity in uranyl nitrate stock used in gel preparation, or could have been added by pickup from glassware used in gel preparation. Abrasion from the Pyrex stirrers used in the $U(II) \rightarrow U(IV)$ reduction step in UO_2 sol preparation is another possibility, so these stirrers are being replaced with stainless steel stirrers. This small quantity of second-phase material is not expected to significantly affect the irradiation performance of the fuel.

During routine ceramographic examination of the pellets to be used in the irradiation specimens, excessive amounts of a metallic-appearing phase were noted in the matrix of $(U, Pu)O_2$. Figure 5-3 shows a typical microstructure. By microscopic examination at various stages of processing, it was found that the metallic inclusions were being introduced by flaking of the metallic retort liner in the powder calcining furnace. This was verified by dissolving some of the inclusions in picric acid and analyzing the solution for metallic ions. Iron, chromium, and nickel, which are major constituents of the retort liner, were found. The particles were found to be magnetic, so a small hand magnet was used to separate some of the particles from the powder material. The powder was pelletized and examined ceramographically (Figure 5-5). A comparison of Figures 5-3 and 5-5 shows that the magnetic separation was partially effective (note the differences in magnification between the figures). A magnetic separator was set up, and the remaining powder material was passed through it several times. Pellets and shards produced from this material had microstructures similar to that shown in Figure 5-6. Irradiation specimens were made from the magnetically separated powder.

5.2. Fabrication Studies

Pellets and shards were produced and irradiation specimens were fabricated before it was found that the material contained metallic impurities. This material was scrapped, and the "reclaimed" feed material was used to produce enough pellets and shards for one specimen each. Two specimens made by the sphere-pac method were made, but one was rejected because of low density. The pellet and shard specimens were fabricated to match the density of the remaining sphere-pac specimen. The smeared density of these specimens [all $(U, 20\% Pu)O_2$] is 81 to 82%

of the theoretical density. Techniques used for packing the spheres were similar to those developed at ORNL insofar as the particle size split and the mode of vibration were concerned. The shaker system used is shown in Figure 5-7. The sphere-pac apparatus consists of a Syntron model F-TO-A vibrator mounted on a 45-degree plane to introduce both horizontal and vertical modes of vibration. The acceleration in the horizontal mode has been measured at the shaker head and reported to be seven times that of gravity, while acceleration in the vertical mode is two times that of gravity. It is felt that this is adequate to produce sphere fuel rods of 81 to 85% smeared density using either binary or blended bed loading techniques.

Figure 5-1. Ceramographic Section of Fired (U,Pu)O₂ Spheres, Unetched (Modified Specimen Preparation Method)

Figure 5-2. Ceramographic Section of Fired (U,Pu)O₂ Spheres, Unetched (Previous Specimen Preparation Method)

Figure 5-3. Ceramographic Section of (U,Pu)O₂ Pellet, Unetched — Note Metallic Phase (Modified Preparation Method)

Figure 5-4. Ceramographic Section of (U,Pu)O₂ Pellet, Unetched (Previous Preparation Method)

Figure 5-5. Ceramographic Section of (U, Pu)O₂ Pellet After Cleanup by Hand Magnet (Unetched)

Figure 5-6. Ceramographic Section of (U, Pu)O₂ Pellet After Cleanup by Magnetic Separator

Figure 5-7. Syntron Magnetic Vibrator Used to Produce Sphere-Pac Specimens

6. IRRADIATION TESTING (C. J. Baroch)

This task of the Gel-Addition Program is divided into three subtasks:

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

During this report period, the scope of each of these subtasks was approved by the USAEC. The scope and progress for each subtask are described below.

6.1. Time Required for In-Pile Restructuring (E. N. Harbinson)

This subtask will evaluate the effects of heat rate and time on the restructuring characteristics of sol-gel $\text{UO}_2\text{-PuO}_2$ spheres and angular particles prepared from coprecipitated $\text{UO}_2\text{-PuO}_2$. Seventeen capsules will be irradiated in the BAWTR. The operational characteristics for each capsule are listed in Table 6-1. The linear heat rates listed in the table represent minimum, average, peak, and overpower peak conditions for oxide fuels operating in an LMFBR of current design. The irradiation behavior of spherical particles prepared by ORNL will be compared with that of particles prepared by B&W.

Each capsule will include at least one pin of high density pellets and two pins of particulate fuel. The smeared densities in both pellet and particulate fuel pins will be about 82%. The density is limited to that achievable when packing two size fractions of spherical particles. Thus, the restructuring characteristics of particulate fuels will be compared directly with those of pellets after operation under nearly identical conditions.

The design of the capsules to achieve linear fission heat rates of 6, 10, 15, and 20 kW/ft has been completed. The design of the capsule

that will operate at 15 kW/ft (fission heat only) while maintaining the surface temperature of the cladding at 1200 F was described in the last progress report.²³ The design of the 6, 10, and 20 kW/ft capsules is similar to that of the 15 kW/ft capsules except that the cross sections must be modified to maintain the surface temperature of the cladding at 1200 F regardless of the heat generation rate. Cross sections of the 6, 10, and 20 kW/ft capsule designs are shown in Figure 6-1.

Fabrication of some capsule parts has been initiated, and the remaining materials have been ordered. Irradiation of the first capsule at 15 kW/ft for 27 days is scheduled to begin during the next quarter. Subsequent capsules will be irradiated as soon as the spherical fuel particles can be prepared.

6.2. Sorbed Gas Behavior (E. N. Harbinson, A. V. Munim)

This subtask will determine the pressure created by the sorbed gas released from the particulate fuel during irradiation. The 11 capsules included in the subtask are described in Table 6-2. 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 coprecipitated particles. By varying the heat rate it should be possible to determine the extent of the gas release as a function of average fuel temperature. Some of the capsules will be operated under cyclic power conditions to determine whether the extent of gas release is influenced by temperature cycling. Each capsule will be irradiated for about 30 days to evaluate interaction between sorbed gases and the fuel or cladding. The gas release characteristics of spherical sol-gel particles prepared by ORNL and B&W will be compared.

Although the detailed design of the capsules to be used in determining the sorbed gas release behavior of $\text{UO}_2\text{-PuO}_2$ has not been completed, the pressure sensor design has been selected. A sketch of the sensor, which was designed by Reuter-Stokes Canada Limited, is shown in Figure 6-2. The first group of these sensors has been ordered for delivery during the next report period.

Table 6-1. Time for Restructuring

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

(a) Capsule planned.

(b) No capsule planned.

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

Table 6-2. Sorbed Gas Release Experiments

Heat rate, kW/ft	Mode of operation		
	Static		Cyclic
	B&W fuel	ORNL fuel	B&W fuel
20	x ^(a)	x	x
15	x	x	x
10	x	-- ^(b)	x
6	x	--	x
15 then 20 ^(c)	x	--	--

(a) Capsule planned.

(b) No capsule planned.

(c) This capsule will be irradiated at 15 kW/ft until equilibrium pressure is achieved; the heat rate will then be increased to about 20 kW/ft to determine whether additional gas will be released.

Figure 6-1. Cross Sections of Capsule Designs

Figure 6-2. In-Pile Pressure Sensor

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

Irradiations in EBR-II will provide performance data on particulate fuels under fast reactor conditions. The irradiation tests to be run in EBR-II are described in Table 6-3. The effects 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 smeared density in the pellet pins will be achieved by using 94% dense pellets and a large diametral gap.

The EBR-II irradiations will require two 19-pin subassemblies and a total of 76 fuel pins. Nine of the 19 pins in each subassembly will be removed after 25,000 MWD/T burnup. These nine pins will be replaced with pins that will be irradiated to a burnup of 100,000 MWD/T. When the remaining 10 rods from the initial loading have achieved a burnup of 50,000 MWD/T, they will be removed and replaced with pins that will be irradiated to a burnup of 75,000 MWD/T.

Preliminary work involving the EBR-II irradiations was initiated. A letter report describing the proposed irradiations was sent to ANL. Arrangements were made to visit the EBR-II facility and to become familiar with the requirements for fueled irradiations in EBR-II.

Table 6-3. EBR-II Irradiations

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

7. MIXED-SOL PREPARATION (C. A. Burkart)

7.1. Introduction

Uranium sols, plutonium sols, uranium dioxide spheres, plutonium dioxide spheres, and mixed urania-plutonia dioxide spheres can be produced routinely using laboratory equipment. The equipment can produce about 1 kg per week of the mixed oxide fuel. Optimization of the unit operations equipment is underway. Also, a study is underway to determine the important areas for future engineering efforts.

A major effort at Babcock & Wilcox to provide sol-gel material for irradiation testing has been completed. The Oak Ridge mixed sol process (precipitation-peptization flow sheets) was followed in the preparation of (U, 20% Pu)O₂ microspheres.

7.2. Pilot Plant System (R. N. Gurley, C. A. Burkart)

The design, procurement, and assembly of a laboratory unit operations system for the preparation of plutonia-urania sol-gel materials by the Oak Ridge mixed sol flow sheet (precipitation-peptization) has been completed. The system is operational and is now being used to prepare mixed plutonia-urania sol-gel materials for irradiation testing. The total throughput is approximately 1 kg of oxide per week. The system is being optimized by applying technology advances as obtained from the Oak Ridge National Laboratory and from studies at B&W. Currently, the optimization effort is concentrated in two areas:

1. The upgrading of the thermal denitration step in the plutonia sol process by the introduction of an optimized thermal denitrator.
2. The introduction of optimized gelation equipment (i.e., the sphere forming system).

A study is underway to determine the technical and economic feasibility of converting the system (including the use of solvent extraction

techniques) into a unit operations system capable of producing kilogram quantities of fuel to specifications.

7.3. Preparation of (U, 20% Pu)O₂ Microspheres (R. V. Carlson)

The first major effort to prepare sol-gel material for irradiation testing has been completed. Although the initial results have been summarized previously,²⁴ all of the results will be discussed here.

7.3.1. Preparation of UO₂ Sol

The UO₂ sols were prepared in batches using the ORNL formate flow sheet.²⁵ Twenty-six batches (numbers 51 - 76), each containing 211.5 g of uranium were prepared, and 23 yielded stable sols. Batch 52 was lost when a large excess of NH₄OH was added during the precipitation step, and batches 57 and 66 were lost when over-reduction occurred.

No analyses were performed on either the uranous nitrate solutions or the sols. However, the stock uranyl nitrate acid solutions were analyzed, and the results are summarized in Table 7-1.

Table 7-1. Composition of Stock Uranyl Nitrate Acid Solutions

<u>Batch No.</u>	<u>No. of analyses</u>	<u>Nitrate concentration, M(a)</u>	<u>Uranium concentration, M(a)</u>	<u>Nitrate/uranium mole ratio(a)</u>
51 - 55	6	5.34 ± 0.08	1.25 ± 0.10	4.27 ± 0.35
56 - 65	3	5.49 ± 0.08	1.29 ± 0.02	4.25 ± 0.10
66 - 76	3	5.36 ± 0.18	1.28 ± 0.02	4.19 ± 0.17

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

7.4. Preparation of PuO₂ Sol

The PuO₂ sol was prepared in batches using the ORNL precipitation-peptization flow sheet.²⁶ This process consists of six general steps:

1. Pu(IV) is precipitated as the hydrous oxide from a nitric acid solution using a 100% excess of NH₄OH.

2. The precipitate is washed with water and filtered until the pH of the effluent is less than 7.0.
3. The precipitate is resuspended in water and digested for 2 hours at 90 to 100 °C.
4. Peptization is accomplished by adding dilute HNO_3 until the NO_3^-/Pu mole ratio is in the range of 1.5 to 2.5; i. e., $\text{NO}_3^-/\text{Pu} = 1.5/1 \rightarrow 2.5/1$.
5. After evaporation of this high-nitrate sol, the NO_3^-/Pu mole ratio is reduced to 0.1 to 0.2; i. e., $\text{NO}_3^-/\text{Pu} = 0.1/1 \rightarrow 0.2/1$ by thermal denitration at about 250 °C.
6. The denitrated powder is resuspended in water to form the PuO_2 sol and is then concentrated to about 1 M.

In these runs, the quantity of base needed to precipitate the hydrous Pu(IV) oxide was determined by titrating an aliquot of Pu(IV) nitrate stock with 0.1 M NaOH. From the titration curve, the quantity of NH_4OH required for a 100% excess was calculated. Then Pu(IV) was added to vigorously stirred NH_4OH at a rate of 25 to 30 ml/min. Next, the precipitate was washed several times with 2 to 3 liters of demineralized water by stirring for 10 to 30 minutes. After peptization, the high-nitrate sol was dried at ± 140 °C in a stainless steel beaker and thermally denitrated (a sand bath was used for temperature control). Periodically during denitration, about 0.5 g of powder was removed from the beaker, suspended in water, and titrated with 0.1 M NaOH. From this titration curve, the NO_3^-/Pu mole ratio was calculated by assuming that the powder contained 80 wt % plutonium and that the moles of NO_3^- were equal to the moles of H^+ .

The conditions for the seven runs made are summarized in Table 7-2. As indicated in the table, each batch of sol was divided into smaller sub-batches during the thermal denitration step (if the NO_3^-/Pu mole ratio is reduced to less than 0.1, then the denitrated powder cannot be resuspended). Thus, even if one sub-batch were excessively baked, a reasonable sol yield would still be possible from a run.

The first two batches were relatively successful, but the yield in batch 1 was quite low because of small losses during each of the many transfers and filtrations and because of the large number of samples taken for NO_3^-/Pu determination during the baking. The length of baking and the number of washes were rather excessive in run 1 because of a lack of experience with the process. However, as can be seen from Table 7-2, these problems were minimized in run 2.

Table 7-2. Summary of Batch Preparation of Pu(IV) Sols

Batch No.	Stock solution		Pu input, g	Conc NH_4OH , f	No. washes	NO_3^-/Pu mole ratio to peptize	Baking time, hr ^(a)	Final NO_3^-/Pu mole ratio ^(a)	Denitrated powder yield, g
	Pu, g/l	H^+ , M							
1	186.8	4.41	100	1.54	13	1.90	11.5	0.15	28.1
							16.5	0.15	
							15.5	0.15	
2	186.8	4.41	102	1.35	4	2.22	6	0.25	121.9
							3.5	0.20	
3	249.9	4.41	110	1.02	9	1.99	2.75 ^(b)	NM	0 ^(c)
							2.75 ^(b)	NM	
4	240.1	6.3	109	1.33	8	2.27	4	0.25	25.5 ^(d)
							3.5	0.25	
							3.5	0.25	
5	240.1	6.3	101	1.23	8	1.88	3	0.14	70 ^(d)
							4	0.11	
							2	0.17	
6	120 ^(e)	3.6 ^(e)	101	1.28 ^(f)	7	1.99	6	0.18	71 ^(d)
7	120 ^(e)	3.6 ^(e)	101	1.28 ^(f)	12	2.50	8	0.11	76.3 ^(d)
							8	0.16	

(a) Each batch was divided into smaller sub-batches during thermal denitration.

(b) Between 2.5 and 2.75 hr color of powder changed from shiny black to dull green.

(c) Upon resuspending dull green powder, Pu(VI) observed and batch discarded.

(d) Yield reduced because of formation of Pu(VI).

(e) 420 ml of original stock was diluted with 420 ml of 1.0 M HNO_3 .

(f) This concentration of NH_4OH was diluted with an equal volume of water before precipitation.

In the remaining five batches, a serious problem arose—the denitrated powder would not resuspend. The difficulty was traced to the presence of Pu(VI) which salted out the PuO₂ polymer. In order to remove the Pu(VI), it was necessary to slurry the powder a number of times with H₂O, allow it to settle, and decant the supernate containing Pu(VI). Obviously this decreased the sol yield considerably. In runs 6 and 7, both the initial feed and the NH₄OH were diluted, but this did not result in any noticeable reduction in Pu(VI) formation. Studies are now in progress to determine how to avoid the formation of Pu(VI) during PuO₂ sol preparation.

7.5. Sol Blending

The procedure followed in blending several PuO₂ or UO₂ sol batches involved pouring each batch into a container which was then closed tightly and vigorously agitated manually for 3 to 5 minutes. Next, each sol blend was analyzed for wt % of metal. Based on these analyses, the quantity of each sol necessary to prepare a (U, 20% Pu)O₂ sol was calculated. Then, under an N₂ atmosphere, the appropriate quantity of UO₂ sol was weighed out and placed in a three-necked, 4-liter glass jug. After this jug was transferred to the sphere-preparation box (air atmosphere), a preweighed amount of PuO₂ sol was added quantitatively, and the container was manually agitated for 10 to 15 minutes. Then a withdrawal tube, which extended to the bottom of the jug, was fitted into one of the necks, a 2-inch magnetic stirring bar was placed in the jug to provide continuous agitation, and during the first run a 1/2-inch layer of kerosene was carefully poured on top of the mixed sol to protect the UO₂ from air oxidation.

During the first sphere-forming run, it was discovered from the quality control analyses that the PuO₂ sol slowly became concentrated near the bottom of the jug. This indicated that the PuO₂ sol contained particles that were large enough to tend to settle and that a magnetic stirrer cannot provide adequate axial mixing if there is any tendency for sol segregation to occur. Therefore, in the second sphere-forming run, the stock sol blend was manually agitated for 3 to 5 minutes just before each withdrawal, and the sol container was continuously purged with argon to minimize oxidation of U(IV). Samples were withdrawn from every

third or fourth sphere batch for analysis. The results from this quality control are summarized in Table 7-3. It should be noted that the range in $\text{Pu}/(\text{Pu} + \text{U})$ values (18.3 - 21.4%) and the average deviation from the mean ($\pm 0.75\%$) are well within the accuracy of these measurements because only a single determination was made for each sample. Therefore, it is apparent that no sol segregation occurred during the second sphere-forming run.

Table 7-3. Quality Control Results From Second Run

<u>Sample No.</u>	<u>Sample type</u>	<u>$\frac{\text{Pu}}{\text{Pu} + \text{U}} \times 100^{(a)}$</u>
5-C-79	Column spheres	21.4
5-C-80	Column spheres	19.6
5-C-81	Column spheres	18.7
5-C-82	Column spheres	19.0
5-C-83	Stirred-pot spheres	20.0
5-C-84	Column spheres	20.9
5-C-85	Mixed sol	19.6
5-C-86	Column spheres	18.4
5-C-86	Column spheres	21.2
5-C-87	Column spheres	19.1
5-C-88	Column spheres	20.4
5-C-89	Column spheres	20.1
5-C-90	Column spheres	19.8
5-C-91	Column spheres	18.9
5-C-92	Column spheres	18.3
5-C-93	Mixed sol	20.8
5-C-94	Column spheres	18.9
Mean value		$19.71\%^{(b)}$

(a) Only one determination was made for each of these datum points.

(b) Average deviation from the mean is 0.75%.

7.6. Sphere Forming

All of the microspheres were prepared in batches with 50 ml of mixed sol as the nominal charge per batch. The large spheres ($\approx 450\mu$ diameter) were formed by drying sol droplets in a 4-ft glass column with a counter-current flow of 2-EH. The injection system consisted of a two-fluid nozzle and a 50-ml syringe equipped with a constant-speed drive mechanism. The nominal drying time was 1 hour. The small spheres ($<44\mu$ diameter) were formed by injecting 50 ml of sol into a pot containing 4 liters of 2-EH, which was vigorously stirred mechanically. After drying for about 30 minutes, the spheres were allowed to settle for about 30 minutes and were then separated from the organic by filtration.

After formation, each batch of spheres was washed on a filter several times with ethanol. Argon was used to force the ethanol through the filter and to predry the washed spheres. Then, the spheres were transferred to an oven and dried (120°C , 15 in. Hg) for 4 to 8 hours. During this step, N_2 was continuously flushed through the oven.

Before preparing these spheres, a systematic series of scouting experiments was performed to determine the necessary surfactant levels in the 2-EH. From these tests, it was decided that 0.40 vol % Span-80, 0.25 vol % Ethomeen-S/15, and 0.8 vol % H_2O were adequate. During the runs, the surfactants were thoroughly mixed in the 2-EH outside the box by manual agitation. The initial 6-liter charge of organic to the in-box reservoir was also mixed with the appropriate amount of water. During each sol injection, 4 liters of dry 2-EH containing surfactants were bled into the reservoir in order to maintain an approximately constant water content in the organic. Then, after each batch of spheres was dried, 4 liters of organic were pumped out of the box into a liquid waste drum.

The spheres formed properly until near the end of the runs when it became necessary to increase the Span-80 to Ethomeen-S/15 ratio to prevent coalescence of the sol droplets. The need to readjust the surfactant levels was apparently related to the oxidation of U(IV) over a period of several days.

7.7. Sintering

Before attempting to fire the mixed gel, several tests were run with UO_2 gel. In each test, several small gel samples (15 to 25 g) from different batches were fired in order to determine the effects of sphere history on the final product. It has been reported²⁵ that a final product with lower carbon content can be prepared by air exposing the gel before firing. Therefore, a number of the gel samples were treated in this manner.

The firing cycle is necessarily complicated because of the need to oxidize the carbon in the gel without oxidizing the gel to such a degree that the spheres crack. In addition, the carbon must be removed before a great deal of sintering occurs, or else a low density product will result. Then, after carbon removal, the uranium must be reduced to obtain an O/M ratio of about 2.00. The firing cycles used were based on those suggested by ORNL studies.²⁵⁻²⁷

From the results of seven test firings, the following firing cycle was selected for sintering the mixed gel:

Under CO_2 Flow

1. Heat to 450 C at 50 C/hr.
2. Heat to 600 C at 25 C/hr.
3. Hold at 600 C for 1 hr.
4. Heat to 900 C at 50 C/hr.

Under N_2 - 6% H_2 Flow

1. Heat to 1250 C at 150 C/hr.
2. Hold at 1250 C for 4 hr.
3. Cool down.

This cycle is based on the conclusions derived from the test firings:

1. The carbon content in the product does not seem to be dependent upon the gel-sphere history.
2. Rapid heating (more than ≈ 50 °C/hr) at temperatures below about 600 °C results in a porous product which appears to contain a relatively high carbon content (> 100 ppm).
3. Gross cracking in the gel does not "heal" during the firing.
4. Air exposure of the gel for several hours before firing does not appear to result in a lower carbon content in

the product and does appear to result in a lower particle density. In addition, the air exposure causes a large number of gel spheres to crack.

5. Particle densities in the region of 95% TD are possible with the firing cycle selected.
6. Values of the O/M ratio in the range of 1.98 to 2.00 can be readily attained with the firing cycle selected if good exposure of the entire sample to the furnace atmosphere is permitted and a temperature $\geq 1200^{\circ}\text{C}$ is held for at least 4 hours.
7. The carbon content can be reduced to less than 30 ppm with the selected firing cycle.

7.8. Final Handling

After firing the mixed-gel microspheres, the oxide was screened in order to separate the desired sizes from the remainder of the product. The coarse sphere fraction was then passed over a roundometer (Wald Industries, Inc., Huntington, Penn.) to separate the rounds from the non-rounds. A total of 34.7 g of spheres below 44μ and 239.9 g of spheres from 350 to 500μ was obtained.

Samples were submitted for full characterization. The ceramographic examination (see section 5) indicated the presence of only one phase in the mixed oxide. The only other results available are the confirmation of the plutonium content (see Table 7-4) and the measurement of the O/M ratio for the blended spheres (1.99).

It is felt that the mixed-oxide microspheres contain a minimum of 20 wt % plutonium for three reasons:

1. The metal content of the input sols was known within about $\pm 1\%$.
2. The quality control samples averaged about 20 wt % plutonium (see Table 7-3).
3. The coarse and fine spheres were prepared at the same time from the same sol. Therefore, the difference in plutonium content for the two size fractions is not likely to be real. Moreover, the routine accuracy in determining the plutonium content in a mixed-oxide sample on a volume-dilution basis is approximately $\pm 5\%$.⁶

Table 7-4. Confirmation of Plutonium Content in Mixed Oxide Spheres

Sample No.	Sample type	$\frac{\text{Pu}}{\text{Pu} + \text{U}} \cdot \%^{(a)}$
4-D-1	Coarse spheres	18.22 ± 0.87
4-D-2	Coarse spheres	18.64 ± 0.50
4-D-3	Fine spheres	19.86 ± 0.35
4-D-4	Fine spheres	19.63 ± 0.87

(a) Errors on the mean for a triplicate determination are at the 95% confidence level.

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