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GEL-ADDITION PROCESS CHEMICAL STUDIES
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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 mixed plutonia-urania oxide fuels has continued. In addition, the overall program has been extended to include the development of a pilot plant for the industrial production of $(U, Pu)O_2$ particulate fuel using the ORNL mixed sol approach. This new task also includes the sol and gel preparation studies.

During this report period, emphasis was placed on a statistically controlled plutonium addition experiment, improving analytical methods, irradiation testing of a calibration capsule (UO_2 -20 wt % PuO_2 fuel), and single and mixed sol studies. Notable success was achieved in each of these areas. Plutonium pickup mechanisms were hypothesized. Controlled-potential coulometric analysis of Pu(VI) in plutonium solutions was developed and adopted for regular laboratory use. The fabrication of capsules for use in inpile restructuring studies was started, since the results of a calibration capsule experiment confirmed the validity of the associated nuclear and thermal design parameters. Uranium dioxide sols and spheres can now be produced routinely using laboratory and pilot plant equipment.

Progress for the sixth quarter, which ended January 31, 1968, 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 sixth progress report on a continuing program designed to apply the Gel-Addition process to the preparation of uranium-plutonium mixed oxide fast reactor fuels. The Gel-Addition process was derived from sol-gel technology developed at the Oak Ridge National Laboratory; it differs from it in that a single-component fertile sol is prepared and converted to a single-component gel. The finished fuel, $(U,Pu)O_2$, is prepared by soaking the single-component UO_2 gel in an aqueous solution of plutonium and firing the mixed gel to the oxide. The mechanism responsible for the plutonium addition to the UO_2 gel is being studied.

During this report period emphasis was placed on (1) a statistically controlled plutonium addition experiment, (2) improving analytical methods, (3) irradiation testing of a calibration capsule (UO_2 -20 wt % PuO_2 fuel), and (4) single and mixed sol preparation studies. As mentioned in the previous quarterly report, a new task—Mixed Sol Preparation—was begun. The new task is responsible for all sol and gel preparation studies; this includes the design and construction of a pilot plant for the preparation of $(U,Pu)O_2$ by the Oak Ridge mixed-sol approach.

The Gel-Addition Program is supported by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3714. This report covers the period from November 1, 1967, to January 31, 1968.

2. CONCLUSIONS

2.1. Gel-Addition Chemistry

The mechanisms of plutonium—Pu(III), Pu(VI), and Pu(IV)—pickup by UO_2 gel were hypothesized. With solutions containing Pu(III) and Pu(IV), UO_2 gel behaves mainly like a porous, inert material into which plutonium solution is absorbed and from which it can be washed with water. With solutions containing Pu(VI), a chemical reaction apparently occurs between the aqueous plutonium and the UO_2 gel.

There is no improvement in Pu(III) pickup by acid-washed UO_2 gels. This indicates (1) that the gel pores are not blocked to any significant extent by organics, or (2) that a simple wash with dilute nitric acid is not capable of selective dissolution of the organics. The fact that there is no improvement in Pu(III) pickup by UO_2 gels produced from solvent extraction sols supports the hypothesis that UO_2 gels are inert to Pu(III).

2.2. Analytical Support

The analyses of Pu(IV) nitrate solutions performed by the Atlantic Richfield Company and by B&W can be expected to agree to within $\pm 1\%$. To obtain better agreement, the two companies would need to standardize their analytical methods.

Controlled-potential coulometry analysis of Pu(VI) in plutonium solutions, using a sulfuric acid electrolyte, proved satisfactory. This method was adopted for regular use in analyzing plutonium solutions.

2.3. Oxide Characterization

Sphere compaction studies have started. Following the developmental studies, UO_2 -20 wt % PuO_2 spheres (made by the mixed sol flow sheet) will be fabricated into irradiation test samples.

2.4. Irradiation Testing

The design of the 15 kW/ft capsules that will be used to determine the time required for inpile restructuring has been completed and safeguard approval for their short-time irradiation has been granted. Several of these capsules are being fabricated, since the results of the calibration capsule experiment indicated that the associated nuclear and thermal calculations are valid.

The preliminary design of the capsule and instrumentation for measuring the dynamic gas release behavior of particulate fuel is complete.

2.5. Mixed Sol Preparation

Uranium dioxide sols and spheres can be produced routinely using pilot plant equipment. Studies of mixed oxide sols, sphere-forming, and single and mixed oxide firing are under way.

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

3.1. Statistically Designed Experiment

3.1.1. Objectives

From earlier bench-scale studies,¹⁻⁵ it was concluded that plutonium pickup by UO_2 gels contacted with aqueous plutonium solutions was influenced by the following factors:

1. Contact time.
2. Contact temperature.
3. Plutonium oxidation state.
4. Plutonium concentration.
5. Solution acidity.
6. Gel sphere history.

Many experiments would be required if each of these variables was tested independently. Thus, a testing program was designed (in consultation with Mr. N. Soltys of B&W's Alliance Research Center) to obtain a maximum amount of information, at a high level of confidence, from a minimum number of tests. The information was to be analyzed using classical statistical methods. The objectives of the program were as follows:

1. To determine which factors have a significant effect on the plutonium pickup and to measure the magnitude of this effect.
2. To identify the significant interactions between two or three factors and to measure the magnitude of these interactions.
3. To determine the optimum combinations of the factors to maximize the amount of plutonium pickup.
4. To ascertain the reproducibility of the pickup process.

The experiment was not designed to provide definitive evidence of the applicability of gel addition as a process for preparing fuels for the

fast-breeder reactor programs, but to identify significant trends in the Gel-Addition process as well as the areas where additional experiments should be performed.

3.1.2. Selection of Contacting Conditions

The experiment was designed to yield the maximum amount of information about Pu(III) effects. Supplemental data concerning Pu(IV) and Pu(VI) effects were obtained for comparison. Previous results indicated that Pu(VI) does not distribute uniformly throughout a UO_2 -gel sphere;⁵ it concentrates in the outer layers. Because of hydrolysis, Pu(IV) is not in a desirable form for use at low acidities; however, sphere attrition dictates that the contacting work be done at low acidities. Because these difficulties had not been encountered in previous work with Pu(III), and since the pickup of Pu(III) seemed to be about equivalent to the pickup values encountered in Pu(IV) and Pu(VI) studies (e.g., sections 3.3.1 - 3.3.3 of reference 5), the major emphasis in the statistical program was placed on Pu(III) effects.

Due to the large number of previous contacting experiments,¹⁻⁵ it was relatively easy to select values for the variables of interest. The only restriction was that the effect of each factor had to be tested at three different levels with the intermediate value being midway between the extremes. Since trends can be extrapolated, no attempt was made to test at the limits of experimental capability. The following test conditions were selected because they encompassed most of the experimentally accessible regions and were readily attainable:

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

*Polymeric Pu(IV) will precipitate out of solution at the higher pH values.

3.1.3. UO₂-Gel Sphere History

To avoid biases caused by differences in sphere history, a homogeneous stock blend containing 1.38 kilograms of UO₂-gel spheres was prepared (details are included in section 7.1). For each sphere contacting experiment, 5.0 grams of the blend were sealed in a 125-ml serum bottle which contained a nitrogen (N₂) atmosphere with less than 0.1% oxygen (O₂). Because each sphere sample came from the master blend, and because all samples were handled in an identical manner before contacting the plutonium solution, it was assumed that sphere history was a constant experimental factor.

3.1.4. Preparation of Plutonium Solutions

Criticality is controlled in B&W's laboratories by keeping the total mass of fissionable material below 220 grams in any one glove box. Thus it was not possible to prepare a single stock plutonium solution for each of the three oxidation states to be examined. The following procedures were carefully duplicated to prepare the required solutions.

3.1.4.1. Pu(III) Solutions

Pu(IV) nitrate stock solutions (188 to 246 gm Pu/l and 3.18 to 4.41 M H⁺) were concentrated to 1.2M in plutonium. While the solution was being stirred vigorously, sufficient 15.5M NH₄OH was added, by drops, to reduce the nitric acid concentration to 0.8M. After the mixture cooled, 1.50 moles of NH₂OH · HCl, as a saturated aqueous solution, were added for each 1.00 mole of Pu(IV) present. The resulting solutions were stirred for 30 to 60 minutes to allow for the reduction of Pu(IV) to Pu(III). The reaction was considered complete when Pu(IV) and Pu(VI) could not be detected spectrophotometrically.

3.1.4.2. Pu(IV) Solutions

Stock Pu(IV) nitrate solutions (246 gm Pu/l and 4.10M H⁺) were concentrated to 1.2M in plutonium. While the solution was stirred vigorously, the free acid content was reduced to 1.0M by adding drops of 15.5M NH₄OH. The Pu(III) and Pu(VI) levels in the final solution were below the spectrophotometric detection limits.

3. 1. 4. 3. Pu(VI) Solutions

The HNO_3 concentration in stock Pu(IV) nitrate solutions (230.9 gm Pu/l and 3.18M H^+) was decreased to 1.30M by adding 0.5M HNO_3 . The resulting solutions were refluxed for 8 to 16 hours to form Pu(VI), which was then concentrated to 1.0M in plutonium.¹ Spectrophotometric analysis indicated that only the hexavalent state was present.

3. 1. 5. Contacting Technique

For each contacting test, an aliquot containing 6.45 grams of plutonium was taken from the previously prepared plutonium solution (see section 3. 1. 4) of the appropriate oxidation state. The pH and the plutonium concentration of each aliquot were adjusted to the desired values by the addition of NH_4OH and demineralized water. The temperature of the solution was adjusted by an ice bath or a heated sand bath. The solution was then injected with a syringe into a serum bottle containing 5.0 grams of UO_2 -gel spheres (see section 3. 1. 3). As quickly as possible, the bottle was placed in either an ice bath or a heated sand bath on a thermovibrator (Precision Scientific Company, Chicago) and agitated gently for the desired test period. At the end of each run, the solution was decanted and the pH was measured; the spheres were then rinsed once with 5 ml of demineralized water. The water rise removed most of the contact solution adhering to the surface of the spheres; it was performed by rapidly adding the water, swirling the bottle twice, and immediately decanting. The spheres were dried (29 inches Hg vacuum and 60 C) and sieved on a 40-mesh screen (420-micron opening). Finally, both sieve fractions were weighed, and the entire +40 mesh split was submitted for uranium and plutonium analyses.

3. 1. 6. Test Results

The measured plutonium pickup values, expressed as $[\text{Pu}/(\text{Pu} + \text{U})] \times 100$ for each test condition, are listed in Tables 3-1, 3-2, and 3-3. Duplicate tests were made for several specific conditions to obtain a measure of the experimental reproducibility.

3.1.7. Analysis of Results (R. V. Carlson, NDC, and N. P. Bresky, ARC)

A cursory examination of the experimental data revealed several important trends. However, a complete statistical treatment of the data was performed to avoid overlooking any other significant trends. The technique of analysis of variance^{*} was used to identify the variables that have a significant effect on plutonium pickup. The effect of each variable was first tested using the assumption that the interactions between two or more of the variables were negligible. Then, by testing all the possible combinations of two variables, trend dependence on the interaction between two factors was identified.

3.1.7.1. Pu(III) Results

The results from ten duplicate contactings were used to obtain an estimate of the uncertainty in the plutonium pickup values. This uncertainty, expressed as the average relative error, is 14% of the pickup. In performing a statistical analysis, however, a more meaningful measure of the uncertainty or precision is the variance. The average variance^{**} was calculated to be 1.597; this corresponds to $\pm 2.9\%$ pickup. It should be pointed out that approximately 40% of the variance was introduced by the data (8.56% and 3.97% pickup; refer to Table 3-1) from a single duplicate contact. However, there is no statistical basis for rejecting this datum point.

Plutonium concentration had a significant linear effect on Pu(III) pickup. However, a better fit to the data is obtained if a second order term is added to the test equation. A significant linear trend with time was also identified. In addition, the interaction between Pu(III) concentration and temperature produced a significant trend, even though the temperature itself did not affect the pickup. The pertinent mean values of Pu(III) pickup are summarized in Table 3-4, and the average effects are plotted in Figure 3-1.

* At the 95% confidence level.

** Except for the average relative error, all measures of uncertainty are at the 95% confidence level.

3. 1. 7. 2. Pu(VI) Results

Since duplicate contactings were not performed with Pu(VI) solutions, an independent measure of the experimental error is not available. Therefore, all tests for significance used the same average error value as was used for the Pu(III) analysis. Plutonium concentration, contact time, and solution temperature had significant linear effects on Pu(VI) pickup. Because only one third of the entire testing array was run, the significance of trends dependent on the interaction between two factors is somewhat doubtful. Nevertheless, the pickup for Pu(VI) does appear to be influenced by the interaction between acidity and concentration, even though it is not affected by acidity itself. The pertinent mean values of Pu(VI) pickup are summarized in Table 3-5, and the average effects are plotted in Figure 3-2.

3. 1. 7. 3. Pu(IV) Results

In the contacting test performed at a temperature of 30 C, a 0.90M Pu concentration, a pH of 0.2, and a contact time of 240 minutes, the UO₂-gel sample dissolved completely. This also occurred during a second contact run under the same conditions. Thus, only 26 data points were available instead of the 27 required for the statistical treatment. In order to perform the data analysis properly, a value for this missing point was assumed. From the results of the other 26 tests, a pickup of 3.88% was determined to be a reasonable assumption.

Using the results from the nine duplicate runs with Pu(IV), the average relative error was calculated to be $\pm 7.43\%$ of the pickup. The average variance was calculated to be 0.2744; this corresponds to $\pm 1.2\%$ pickup. However, nearly 75% of the variance results from the use of the data in which 5.53% and 3.63% pickup values were measured (see Table 3-3). Again, there is no valid justification for rejecting either of these data points, so the average variance was used in the significance tests. Plutonium concentration, contact time, and solution temperature had significant linear effects on Pu(IV) pickup. Although some interactions between two factors seemed to be significant, it was not possible, due to the limited number of tests performed, to identify these factors with any reasonable degree of certainty. The

pertinent values for Pu(IV) pickup are summarized in Table 3-6, and the average effects are plotted in Figure 3-3.

3.1.7.4. Comparison of Oxidation States

Since the Pu(IV) tests were conducted at different levels of acidity, only the Pu(III) and Pu(VI) results are directly comparable. Considering the 27 tests run under identical conditions, the pickup of Pu(VI) was significantly higher than that of Pu(III). In only 7 of the 27 contactings was more Pu(III) picked up, and all but one of these contacts occurred at 3 C, where Pu(VI) pickup was at a minimum. The average pickup of Pu(VI) was 6.00%; for the comparable 27 tests with Pu(III), the average pickup was 4.16%.

3.1.8. Conclusions

Pickup mechanisms that are consistent with most of the data can be proposed. With solutions containing Pu(III), the UO_2 gel behaves mainly like a porous, inert material into which the plutonium solution is absorbed and from which it can be washed by water. Therefore, the linear increase in pickup with increasing plutonium concentration is as expected. The slow increase in pickup with increasing length of contact may indicate that a slow chemical reaction between the plutonium and the UO_2 gel is also taking place. However, since the pickup does not vary with temperature, perhaps a more reasonable explanation is that longer periods of time are necessary for the plutonium solutions to penetrate the smaller pores in the gel. Perhaps the increasing sphere attrition results in the closing of a number of pores, which prevents the plutonium from being washed out. Solubility product data indicate that Pu(III) should be soluble at the pH values used in these experiments.⁶ Hence, because of the washing technique and the possibility that the open sphere porosity depends on the contact conditions, it seems reasonable to assume that the washings were not conducted in a reproducible manner, and therefore, the experimental error can be attributed (in part) to the partial and irreproducible removal of plutonium by washing with water.

With Pu(VI) containing solutions, a chemical reaction apparently occurs between the plutonium solution and the UO_2 gel. The marked increase in pickup at higher contacting temperatures lends

strong support to this proposal. In addition, alpha autoradiographic evidence is consistent with a reaction pickup mechanism.⁵ This evidence shows that essentially all of the plutonium is concentrated in a shell around the outer surface of a UO_2 -gel sphere. If Pu(VI) is being picked up by exchanging with uranium or by chemi-adsorption at the surface, an increase in plutonium content should be expected with increasing plutonium concentration, contact time, and temperature.

With solutions containing Pu(IV) , the UO_2 gel again apparently behaves mainly like a porous, inert material. In this case—as opposed to Pu(III) —it should be nearly impossible to wash the plutonium from the sphere with water, because (1) Pu(OH)_4 is much less soluble in weak acid solutions than is Pu(OH)_3 , and (2) the pH rises sufficiently during contact to convert nearly all the Pu(IV) to the even more water-insoluble polymeric form.⁶ Hence, as has been shown, the experimental error should be much less for the Pu(IV) contact than for Pu(III) . For the Pu(IV) experiments, the bulk of the error could be caused by the difficulty in preparing Pu(IV) solutions at pH values from 0.2 to 0.8 in an identical manner. This problem arises from the non-reproducible hydrolysis of Pu(IV) if the rate and method of pH adjustment are not carefully controlled. The slow increase in Pu(IV) pickup at longer contacting times and higher temperatures is not necessarily inconsistent with the proposed mechanism. The pH of a Pu(IV) contact solution increases very rapidly, thus producing large polymeric particles. Most of these particles are undoubtedly too large to enter the pores in the UO_2 -gel spheres. However, over prolonged contact periods and at elevated temperatures, it is reasonable to expect a portion of the smaller particles to enter the spheres.

3.2. Contact With Acid-Washed Gel

It has been observed that considerable organic material is present in the acid solutions that remain after gel contact experiments. Indeed, one problem that has arisen is the interference of organics with the plutonium analyses. The apparent source of this material is the acid-dissolution of the uranium gel and its associated organics and/or the acid-dissolution of the organic matter present in the gel pores. Therefore,

it is possible that contact between the UO_2 structure and the plutonium solution is partially impeded by organics blocking the pores. If this is the case, then plutonium pickup should increase when the UO_2 gel is pre-treated with acid.

To test this idea, a sample of UO_2 -gel spheres from the statistical master blend was acid washed (10 seconds and 1.0M HNO_3) before contacting with a 0.6M Pu(III) solution at a pH of 0.5 at ambient temperatures. After allowing the contact to proceed for 10 minutes on the thermovibrator, the solution was decanted, and the spheres were dried overnight (at 60 C and 18 inches Hg vacuum). Pu(III) pickup measured 2.93%. The pertinent data from this run are summarized in Table 3-7.

The apparent carbon content was decreased 25% by the acid wash. About 3 to 4% of this value can be attributed to the relative increase in the weight of the sample due to oxidation of the uranium. Since it was noted that uranium was present in the wash solution, the remaining decrease in carbon content can be attributed to the release of organics sorbed on or near the surfaces of the spheres during the gelation step. However, even after an acid wash, the organic content is still quite large.

In the statistical experiment, under approximately the same experimental conditions, the pickup of Pu(III) was determined to be 4.94%. Therefore, it is apparent that there is no improvement in pickup by the acid-washed gel. This indicates that the gel pores are not significantly blocked by organics, or that a simple wash with dilute nitric acid is not capable of selective dissolution of the organics.

3.3. Contacts With ORNL Gel

A sample of gel prepared at the Oak Ridge National Laboratory (ORNL) was obtained for testing in the B&W program. This sample was prepared from sol made by the solvent extraction of nitrates.⁷ Since UO_2 gels prepared by different techniques were expected to differ in plutonium pickup capacity, a series of tests was run with the ORNL gel spheres. In addition, an attempt was made to obtain a better measure of the reproducibility in the pickup.

Five samples containing 5.0 grams each of UO_2 gel were prepared and contacted using the techniques of the statistically designed experiment

(section 3.1). A stock solution of 0.6M Pu(III) with a pH of 0.5 was prepared for use in all the tests. Each test was performed with 45.0 ml of the stock solution and was contacted for 10.0 minutes at 28 C. Extreme care was taken to treat each sample identically. The results are summarized in Table 3-8.

The pickup by the ORNL gel was $3.57 \pm 0.58\%$. Under conditions identical to those described above, the pickup obtained with B&W spheres, prepared from precipitation-peptization sols, was $4.9 \pm 2.9\%$ (see Table 3-1). Therefore, on the basis of this experiment, there is little reason to expect a larger pickup of plutonium by UO_2 gels prepared by a different method. This result was unexpected but supports the hypothesis that UO_2 gel is inert to Pu(III). If ion exchange or surface reactions are involved, then the total pickup should vary with gel history.

The standard deviation of the mean in this experiment is approximately four-fold smaller than that observed in the statistically designed experiment. Part of this improvement can be attributed to the fact that in this case five, rather than two, samples were averaged. The remainder of the improvement is attributable to the use of only one Pu(III) stock solution, which minimizes composition changes, and to a greater emphasis on reproducibility in these tests as compared with the statistical experiment.

3.4. Redox Experiments

Solubility product data indicate that for the pH values approached in most of the experimental acid-gel mixtures, Pu(III) should be soluble, but Pu(IV) should be extensively polymerized.⁶ Partially based on this fact, it was hypothesized (see section 3.1.8) that UO_2 gels are inert to Pu(III). In Pu(IV) contact experiments, the pH of the solution rises rapidly; therefore, the plutonium is rapidly hydrolyzed. Most of the resulting polymeric particles are too large to enter the UO_2 -gel pores. The object of this experiment was to prepare Pu(IV) slowly at high pH values with the thought that the gel could provide nucleation sites for depositing plutonium on the gel surface.

In laboratory tests, it was observed that Pu(III) prepared by hydrazine reduction can be re-oxidized to Pu(IV) by heating for periods ranging up to a few hours. Therefore, in two tests, 10.0-gram samples

of UO_2 -gel spheres were contacted with 0.6M Pu(III) solutions (pH = 2.2) prepared by hydrazine reduction. In the first test the solution was heated (60 C) for 5 hours to a moist dryness. At this point large quantities of a green precipitate, presumably Pu(IV) polymer, were apparent. In the second test the solution was heated (67 C) for 90 minutes, at which time the spheres were covered with a green precipitate. The remaining Pu(III) solution was then decanted. Finally, in both tests, the spheres were thoroughly washed with demineralized water, dried overnight (at 60 C and 29 inches Hg vacuum), and sieved on a 40 mesh screen. Slides of the +40 mesh material were prepared, and a microscopic examination indicated that the surfaces of the spheres were free of any precipitate or other foreign matter. The results of these Redox experiments are summarized below:

	$\frac{\text{Pu}}{\text{Pu} + \text{U}}$ in coarse, %	$\frac{\text{Pu}}{\text{Pu} + \text{U}}$ in fines, %
Test 1	8.1	9.1
	8.1	8.9
Test 2	4.7	5.1

The results indicate that this technique may be promising. The relatively close agreement in the plutonium content in the coarse and fine samples, coupled with the results of the microscopic examination, indicates that the precipitate can be washed from the spheres and that plutonium can be firmly fixed in the spheres. The lower plutonium content in the second test is probably related to the amount of Pu(III) converted to Pu(IV).

Table 3-1. Data for Pu(III) Pickup^(a)

		Contact time, min								
		10			125			240		
		Temperature, C			Temperature, C			Temperature, C		
		3	30	57	3	30	57	3	30	57
0.9M Pu	Solution acidity, pH									
	0.5	5.34 5.04	5.34	2.20	3.74	4.78	4.81 3.90	6.02	3.48 1.84	5.56
	1.5	4.95 3.49	4.65	5.37	4.16	7.13	3.16	6.79	5.97	5.62
0.6M Pu	2.5	4.49	5.55	1.88	4.96	5.57	6.74	4.88	6.87	2.46
	0.5	6.05	4.94	3.44	6.23	3.28	3.42	5.64	4.59	5.41
	1.5	5.95	4.31	8.56 3.97	5.75	3.54 4.20	3.77	5.08 7.15	2.45	5.87
0.3M Pu	2.5	5.16	4.25	3.51	6.20	4.39	4.67	6.01	5.06	5.40
	0.5	2.25	1.49	2.12	2.01	1.31	3.04	2.01	3.18	4.46
	1.5	2.20	2.59	2.46	3.34	2.70	3.87	4.38	2.79	5.47
	2.5	2.02	2.29 2.55	3.09	3.13 2.72	3.26	3.53	4.68	3.57	6.20 5.79

(a) Values in the body of Tables 3-1, 3-2, and 3-3 are expressed as $[\text{Pu}/(\text{Pu} + \text{U})] \times 100$.

Table 3-2. Data for Pu(VI) Pickup^(a)

		Contact time, min								
		10			125			240		
		Temperature, C			Temperature, C			Temperature, C		
Solution acidity, pH		3	30	57	3	30	57	3	30	57
0.9M Pu	0.5	3.05	--	--	--	--	8.20	--	6.61	--
	1.5	--	7.03	--	4.93	--	--	--	--	13.6
	2.5	--	--	6.27	--	6.53	--	3.80	--	--
0.6M Pu	0.5	--	5.08	--	3.88	--	--	--	--	8.56
	1.5	--	--	5.73	--	6.44	--	4.32	--	--
	2.5	2.77	--	--	--	--	11.8	--	9.60	--
0.3M Pu	0.5	--	--	3.95	--	6.02	--	2.64	--	--
	1.5	2.22	--	--	--	--	5.53	--	7.41	--
	2.5	--	6.30	--	2.10	--	--	--	--	7.56

(a) Values in the body of Tables 3-1, 3-2, and 3-3 are expressed as $[\text{Pu}/(\text{Pu} + \text{U})] \times 100$.

Table 3-3. Data for Pu(IV) Pickup^(a)

	Solution acidity, pH	Contact time, min								
		10			125			240		
		Temperature, C			Temperature, C			Temperature, C		
		3	30	57	3	30	57	3	30	57
0.9 M Pu	0.2	3.67	--	--	--	--	4.30	--	(b)	--
	0.5	--	6.39	--	3.34	--	--	--	--	5.63
	0.8	--	--	2.58 3.05	--	5.53 3.63	--	3.74 4.42	--	--
0.6 M Pu	0.2	--	2.90 2.56	--	4.47 4.63	--	--	--	--	9.56 9.71
	0.5	--	--	3.04	--	2.51	--	2.81	--	--
	0.8	2.17	--	--	--	--	5.87	--	5.45	--
0.3 M Pu	0.2	--	--	1.87	--	3.00	--	3.52	--	--
	0.5	1.95 2.62	--	--	--	--	1.58 1.76	--	3.31 3.27	--
	0.8	--	2.12	--	2.12	--	--	--	--	5.39

(a) Values in the body of Tables 3-1, 3-2, and 3-3 are expressed as $[\text{Pu}/(\text{Pu}/\text{U})] \times 100$.

(b) This sample dissolved during contact; a value of 3.88 was used for this data point.

Table 3-4. Mean Values for Pu(III) Pickup

Experimental conditions	Pickup, % Pu ^(a)
0.30M Pu(III)	3.08 ± 0.45
0.60M Pu(III)	4.85 ± 0.43
0.90M Pu(III)	4.83 ± 0.57
Contact for 10 min	3.79 ± 0.57
Contact for 125 min	4.15 ± 0.55
Contact for 240 min	4.81 ± 0.55
0.30M Pu(III); 3 C	2.87 ± 0.79
0.30M Pu(III); 30 C	2.59 ± 0.58
0.30M Pu(III); 57 C	3.78 ± 0.99
0.60M Pu(III); 3 C	5.90 ± 0.26
0.60M Pu(III); 30 C	4.13 ± 0.63
0.60M Pu(III); 57 C	4.53 ± 0.75
0.90M Pu(III); 3 C	4.94 ± 0.73
0.90M Pu(III); 30 C	5.39 ± 0.99
0.90M Pu(III); 57 C	4.2 ± 1.3

(a) Errors listed are at 95% confidence limits for the corresponding mean value and do not reflect the uncertainty in each data point.

Table 3-5. Mean Values for Pu(VI) Pickup

Experimental conditions	Pickup, % Pu ^(a)
0.30M Pu(VI)	4.9 ± 1.6
0.60M Pu(VI)	6.5 ± 2.2
0.90M Pu(VI)	6.7 ± 2.3
Contact for 10 min	4.7 ± 1.3
Contact for 125 min	6.2 ± 2.1
Contact for 240 min	7.1 ± 2.5
Solution temp - 3 C	3.30 ± 0.74
Solution temp - 30 C	6.78 ± 0.94
Solution temp - 57 C	7.9 ± 2.3
0.3M Pu(VI); pH = 0.5	4.2 ± 1.9
0.3M Pu(VI); pH = 1.5	5.1 ± 3.0
0.3M Pu(VI); pH = 2.5	5.3 ± 3.2
0.6M Pu(VI); pH = 0.5	5.8 ± 2.7
0.6M Pu(VI); pH = 1.5	5.5 ± 1.2
0.6M Pu(VI); pH = 2.5	8.1 ± 5.3
0.9M Pu(VI); pH = 0.5	6.0 ± 3.0
0.9M Pu(VI); pH = 1.5	8.5 ± 5.1
0.9M Pu(VI); pH = 2.5	5.5 ± 1.7

(a) Errors listed are at 95% confidence limits for the corresponding mean value and do not reflect the uncertainty in each data point.

Table 3-6. Mean Values for Pu(IV) Pickup

Experimental conditions	Pickup, % Pu ^(a)
0.30M Pu(IV)	2.81 ± 0.88
0.60M Pu(IV)	4.3 ± 1.9
0.90M Pu(IV)	4.30 ± 0.84
Contact for 10 min	3.0 ± 1.0
Contact for 125 min	3.6 ± 1.0
Contact for 240 min	4.9 ± 1.6
Solution temp - 3 C	3.17 ± 0.64
Solution temp - 30 C	3.8 ± 1.1
Solution temp - 57 C	4.5 ± 1.9

(a) Errors listed are at 95% confidence limits for the corresponding mean value and do not reflect the uncertainty in each data point.

Table 3-7. Results From Pu(III) Contacts With Acid-Washed Gel

	Before acid wash	After acid wash	After contact
Total carbon, wt %	3.21	2.41	--
Total U(IV)/U, %	75.5	53.0	--
Pu/(Pu + U) in +40 mesh split, %	--	--	2.93
Pu/(Pu + U) in -40 mesh split, %	--	--	3.15
Spheres in +40 mesh split, gm	--	--	5.63
Spheres in -40 mesh split, gm	--	--	3.22

Table 3-8. Pu(III) Pickup on UO₂ Gel Prepared by Solvent Extraction Methods at ORNL

Sample No.	Final pH	Sphere attrition, %	Pu/(Pu + U), %
1	0.70	1.25	4.33
2	0.70	1.44	3.38
3	0.70	1.14	3.10
4	0.68	1.60	3.40
5	0.70	1.78	3.66
Mean values		1.44 ± 0.31 ^(a)	3.57 ± 0.58 ^(a)

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

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

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

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

4. ANALYTICAL SUPPORT*

(D. H. Schmitt)

4.1. Plutonium Analysis

4.1.1. Comparison of Analytical Results on Pu(IV) Nitrate Stock Solution Analyses

An experiment was performed to determine the relative accuracy of analyses performed by the plutonium shipper (Atlantic Richfield Hanford Company) and the receiver (B&W) on Pu(IV) nitrate stock solutions. The shipper, the receiver, and a referee (New Brunswick Laboratory) each analyzed samples from the same plutonium solution, and the results were compared. The shipper obtained five samples (6 ml each) from a Pu(IV) nitrate stock solution; these samples were sealed in glass ampoules. The shipper kept two of the ampoules, the receiver obtained two, and the fifth was sent to the referee. To avoid biases due to time-dependent changes in the solution, the samples were analyzed by the three laboratories on the same day.

The 26 analyses carried out in B&W's laboratory utilized three different dilutions prepared from the material in a single ampoule; the second ampoule was retained as a reference sample. Different-sized aliquots were taken from each dilution in order to minimize any possible errors associated with the pipetting and dilution steps. The aliquots were analyzed by controlled-potential coulometry. Two coulometric titrators were used, and each dilution was analyzed by three different analysts to minimize both the systematic errors inherent to the titrators and any random errors.

* In reference 5 it is pointed out that an improved nitrate analysis technique is now employed in the B&W laboratories. Because of the inherent inaccuracies of the earlier technique, all the NO_3/U mole ratios presented in Table 7-2 of reference 5 may be as much as 25% low.

The stock solution from which the original five samples were taken was also analyzed in a similar, but somewhat less rigorous, manner; a total of 23 analyses were performed. The results for both sets of analyses are listed in Table 4-1. The B&W results are compared below with those of the shipper and the referee:

<u>Sample sealed in glass ampoule - Pu content, mg/ml</u>		
<u>B&W (95% confidence limits)</u>	<u>New Brunswick Laboratory</u>	<u>Atlantic Richfield Hanford Company</u>
188.1 ± 0.6	186.4	188.2 188.15
<u>Stock solution - Pu content, mg/ml</u>		
186.8 ± 0.8	--	187.6

The agreement between the different laboratories was good; the difference was only about 0.5%. To obtain better agreement, the same method of analysis must be used by all the participants, and the analytical technique must be carried out on a weight basis. Volumetric measurements were used in the B&W work to conform to normal practice. The results indicate the relative accuracy that can be expected in the B&W laboratory.

4.1.2. Controlled-Potential Coulometry of Pu(VI) Solutions

It was mentioned in a previous report that Pu(VI) cannot be reduced quantitatively in a perchloric acid electrolyte.⁵ Pu(VI) can be quantitatively reduced, however, in a sulfuric acid electrolyte that contains no iron. Iron must be absent because it is reduced and oxidized at the same potentials as the plutonium and is thus interpreted as plutonium. The method for analyzing Pu(VI) via a sulfuric acid electrolyte, as described by W. D. Shults,⁶ proved to be satisfactory and has been adopted for use.

4.2. Uranium and Plutonium Analyses

4.2.1. Relative Precision in Controlled-Potential Coulometric Analyses of Pu(VI)-U

In the statistical experiment (see section 3), 38 samples of uranium gel spheres contacted with Pu(VI) were submitted for analysis. Each sample was analyzed in triplicate for uranium and for plutonium by controlled-potential coulometry. The ratio of plutonium to plutonium-and-uranium was then calculated. The relative standard deviations for both the uranium and plutonium were calculated for each sample. The average relative standard deviations were found to be 0.763% for uranium and 1.33% for plutonium. The average relative standard deviation for the ratio of plutonium to plutonium-and-uranium was found to be 1.51% by the method described by Laitinen.⁹ The average relative 95% confidence limit for the ratio of plutonium to plutonium-and-uranium, where the analyses of plutonium and of uranium are done in triplicate, is 3.75% (for the calculation technique, see reference 9).

4.2.2. Precision of the Pu/(Pu + U) Results Using Duplicate Sample Analyses

During the statistical experiment, several samples were split into duplicate samples after dissolution. These duplicates were assigned different sample numbers and were then submitted to the analytical group for a check on the reproducibility of the controlled-potential coulometric methods for determining Pu/(Pu + U) ratios. Duplicates were submitted for each different plutonium oxidation state contact experiment. In one case, during a Pu(III) contact experiment, a sample was split into five identical samples and submitted as five different samples. The results of these tests of analytical reproducibility are summarized in Table 4-2.

4.3. Chloride and Fluoride Trace Analysis

We have investigated the use of solid-state specific ion electrodes in the quantitative determinations of chloride and fluoride impurities in nuclear fuel materials. The impurities are separated from the fuel materials by pyrohydrolysis and then analyzed. Preliminary curves of the concentrations of chloride or fluoride in an acetate buffer solution versus electrode potential were obtained. The curves were linear, and

the calculated slopes, over the concentration range of 2 to 100 ppm, approached the theoretical values. Further investigations are being conducted to determine which buffer should be used routinely and to determine which techniques are suitable for the application of the electrodes to actual analyses.

4.4. Analytical Sample Load

During this quarter 210 samples were analyzed, giving a total of approximately 1100 analyses. The analyses included total U, total Pu, U(IV)/total U, NO_3^- , H_2O , C, pH, and O/M.

Table 4-1. Results of Pu(IV) Nitrate Stock Solution Analyses

Sample sealed in glass ampoule

<u>Sample dilution</u>	<u>Titration No.</u>	<u>No. of titrations</u>	<u>Pu content, (a) mg/ml</u>	<u>Rel std deviation, (b) %</u>
A	1	6	184.9 ± 1.5	0.74
A	2	4	184.6 ± 0.8	0.27
B	1	5	188.8 ± 0.7	0.29
B	2	4	189.3 ± 2.5	0.86
C	1	3	190.2 ± 3.7	0.81
C	2	4	190.9 ± 4.5	1.49
Average		26	188.1 ± 0.6	0.82

Stock solution

A' B' C'	1	13	186.4 ± 0.4	0.91
B' C'	2	10	187.1 ± 0.6	1.18
Average		23	186.8 ± 0.8	1.04

(a) 95% confidence limits.

(b) Rel std deviation = $S/\bar{X} \times 100$

where S = standard deviation
 $\bar{X}$ = sample mean

Table 4-2. Results of Duplicate Sample Analyses

No. of duplicate sets	Sample No.	[Pu/(Pu + U)], %	Absolute difference, %	Average of duplicate samples, %	Relative difference, (a) %
Pu(III) Contact Experiments					
1	1-G-61	2.67	0.05	2.70	1.85
	1-G-67	2.72			
2	1-G-65	2.30	0.02	2.29	0.87
	1-G-68	2.28			
3	1-G-75	7.19	0.11	7.14	1.54
	1-G-79	7.08			
4	1-G-76	5.58	0.31	5.57	5.57
	1-G-80	5.39			
	1-G-81	5.70			
	1-G-82	5.68			
	1-G-83	5.52			
5	1-G-90	3.15	0.23	3.04	7.57
	1-G-93	2.92			
6	1-G-94	3.39	0.06	3.42	1.75
	1-H-5	3.45			
7	1-G-99	3.96	0.01	3.97	0.25
	1-H-6	3.97			
8	1-H-4	5.66	0.53	5.40	9.81
	1-H-7	5.13			
9	1-H-12	5.68	0.12	5.62	2.14
	1-H-22	5.56			
10	1-H-16	6.79	0.10	6.74	1.48
	1-H-23	6.69			
11	1-H-19	6.41	0.09	4.38	2.05
	1-H-24	4.32			
12	1-H-28	3.70	0.43	3.49	12.32
	1-H-22	3.27			
13	1-H-34	2.25	0.01	2.26	4.42
	1-H-42	2.26			
14	1-H-51	6.24	0.09	6.20	1.45
	1-H-55	6.15			
15	1-H-68	3.41	0.15	3.49	4.30
	1-H-73	3.56			
Average					3.82

$$(a) \text{ Relative difference} = \frac{\text{absolute difference (\%)}}{\text{average of duplicate samples (\%)}} \times 100 = \%$$

Table 4-2 (Cont'd)

No. of duplicate sets	Sample No.	[Pu/(Pu + U)], %	Absolute difference, %	Average of duplicate samples, %	Relative difference, (a) %
Pu(IV) Contact Experiments					
1	1-G-27	2.98	0.05	3.01	1.66
	1-G-28	3.03			
2	1-G-30	5.47	0.04	5.45	0.73
	1-G-31	5.43			
3	1-G-42	5.83	0.09	5.88	1.53
	1-G-48	5.92			
4	1-G-47	1.87	0.00	1.87	0.00
	1-G-49	1.87			
5	1-G-52	2.58	0.01	2.59	0.39
	1-G-58	2.59			
6	1-H-81	3.55	0.05	3.53	1.42
	1-H-86	3.50			
7	1-H-88	2.09	0.16	2.33	6.87
	1-H-92	2.25			
Average					1.80
Pu(VI) Contact Experiments					
1	1-I-15	13.81	0.42	13.60	3.09
	1-I-27	13.39			
2	1-I-19	11.26	0.51	11.52	4.43
	1-I-28	11.77			
3	1-I-23	4.64	0.69	4.30	16.05
	1-I-29	3.95			
4	1-I-7	9.60	0.35	9.78	3.58
	1-I-24	9.95			
5	1-I-11	6.02	0.15	5.95	2.52
	1-I-25	5.87			
6	1-I-12	7.03	0.25	6.91	3.62
	1-I-26	6.78			
Average					5.55
Average (discard set 3)					3.45

(a) Relative difference = $\frac{\text{absolute difference (\%)}}{\text{average of duplicate samples (\%)}} \times 100 = \%$

5. OXIDE CHARACTERIZATION (J. M. Kerr)

During this report period 18 ceramographic samples, 18 tap density measurements, 29 mercury pycnometer measurements, 18 subsieve analyses, and one sorbed gas content determination were run. Uranium dioxide-20 wt% PuO_2 pellets for a calibration capsule (see section 6) were fabricated from coprecipitated material and characterized. An additional 170 pellets of UO_2 -20 wt% PuO_2 were fabricated for capsule irradiation during subsequent periods. Characterization of these pellets is not complete. Uranium dioxide-20 wt% PuO_2 shards, which will be vibratory compacted, have been obtained via the cold press, fire, and crush route. This material and the spherical fuel material will be compacted for use as irradiation samples. Preliminary investigation of sphere compaction techniques has begun.

5.1. Materials Characterization

Ceramographic examinations were performed during this report period as part of an experimental program to determine a suitable firing cycle for UO_2 -20 wt% PuO_2 spheres. Uranium dioxide spheres are being used in the preliminary investigation. Figure 5-1 is a photomicrograph of a ceramographic section of the best sample of fired UO_2 spheres prepared so far. This material has a particle density of approximately 10.4 gm/cm^3 (94% TD) as determined by mercury pycnometry. Additional modifications to the firing cycle will be made to maximize the density of fired UO_2 (and UO_2 -20 wt% PuO_2) spheres.

The sensitivity of the sorbed gas apparatus has been increased to 0.01 cc of gas per gram of solid material. This instrument was used to measure the sorbed gas content of the pellets that were used in the calibration capsule (see section 6).

An apparatus to measure the crush strengths of individual particles is now operational. This instrument will be calibrated with the one at

ORNL. Thoria spheres of various sizes (obtained from ORNL) will be used as the calibration standard. This calibration will be completed during the next report period.

5.2. Fabrication Studies

Pellets were fabricated for a calibration capsule (see section 6). Table 5-1 summarizes the pertinent properties of the fuel (coprecipitated material) and the loaded fuel pins. Figure 5-2 is a photomicrograph of a ceramographic section of a typical $(U, Pu)O_2$ calibration capsule pellet showing the microstructure of the pellet material.* Figure 5-3 is an alpha autoradiograph of a typical fuel pellet showing the plutonium distribution in the pellet. The pellets were fabricated by screening the coprecipitated feed material through a 200 mesh sieve, prepressing at 40,000 psig, granulating through a 20 mesh sieve, and pressing at 30,000 psi. The pellets were then fired at 1650 C for one hour in a He-6% H_2 atmosphere. A binder was not used, nor were the pellets ground.

Sintering runs were performed, using a technique similar to the one described above, to produce 170 UO_2 -20 wt% PuO_2 pellets which will be used in future irradiation test capsules. The properties of the feed material and of the final pellets are similar to those listed in Table 5-1. Additional sinterings were conducted to produce pellets having densities of $\geq 95\%$ TD. Crushing and sizing operations produced Vipac feed material from these pellets; the Vipac material will be compacted for use as irradiation samples. Characterization of the 170 pellets and the Vipac material will be completed during the next quarter.

One kilogram of coarse (-35 to +40 mesh) and fine (-325 mesh) ThO_2 spheres has been procured from ORNL; it will be used in the development of a sphere compacting technique. A "Syntron" vibratory tubular feeder will be the source of vibration. Following the development of the compaction technique, UO_2 -20 wt% PuO_2 spheres—made by the mixed-sol flowsheet—will be fabricated into irradiation test samples.

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*Subsequent to the initial preparation of this report, the apparent structure in the photomicrographs was shown to be an artifact of specimen preparation. This anomaly will be discussed in the next quarterly report, BAW-3714-7.

Table 5-1. Properties of (U, Pu)O₂ Material in Calibration Capsule

Powders

Tap density, gm/cc	2.244
Subsieve size, microns	0.40

Loaded pins

Smear density of fuel, % TD	86 ± 1
Pu/(Pu + U), %	20 ± 0.5
O/M ratio	1.97 average
Cl content, ppm	<120
F content, ppm	<72
Sorbed gas content, cc/gm fuel	0.017 - 0.014

Figure 5-1. Ceramographic Section of Fired UO₂ Spheres (Unetched), Photomicrograph

Figure 5-2. Ceramographic Section of a (U, Pu) O₂ Calibration Capsule Pellet (H₂O₂-H₂SO₄ Etch), Photomicrograph*

Each Division = 1 mil 500X

*See note on page 32.

Figure 5-3. Ceramographic Section of a Calibration Capsule Pellet, Autoradiograph

Each Division = 1 mil 250X

6. IRRADIATION TESTING (C. J. Baroch)

The Gel-Addition Irradiation Program, as described in the previous quarterly report,⁵ is divided into the following subtasks:

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

During the past quarter, an effort was made to establish the scope of each subtask. Discussions were held with personnel at Oak Ridge National Laboratory and Battelle Northwest Laboratory to determine the extent of their irradiation programs. Following these discussions, the revised Gel-Addition Irradiation Program was prepared for submittal to the AEC.

Although the scope of each subtask has not been completely established, authorization to begin work on subtasks 1, 2, and 3 was received from the AEC.

6.1. Time Required for Inpile Restructuring (E. N. Harbinson)

Safeguard approval was received for the short-term irradiation of capsules designed during the previous quarter (see section 6.2, reference 5). The first capsule was designed to operate at 17.91 kw/ft (15 kw/ft from fission heat in the fuel and 2.91 kw/ft from gamma heat in the capsule components). When the capsule is operating at 17.91 kw/ft, the surface temperature of the cladding should be approximately 1200 F. Using the THERMOS code, it was determined that natural UO_2 -20 wt % PuO_2 fuel would achieve the desired linear heat rate.

Because of the uncertainties in the nuclear and thermal calculations, it was considered advisable to irradiate a calibration capsule. Subsequently, a capsule was fabricated and irradiated in the BAWTR; Figure 6-1 is a diagram of this capsule. The results of the irradiation are summarized in Table 6-1; these results indicate that the capsule design parameters are satisfactory. The design of capsules for operation at 6, 10, and 20 kw/ft was initiated after the nuclear and heat transfer calculations were confirmed. A description of these capsules will be included in the next quarterly report.

Since the calibration capsule experiment was successful, the fabrication of the first two 15-kw/ft capsules, which will be used to determine the time required for inpile restructuring, was initiated. The capsules should be ready for irradiation during the next quarter.

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

We have completed the preliminary design of the capsule and instrumentation for measuring the dynamic gas release behavior of particulate fuel. It is anticipated that the final system will be similar to that used in the Plutonium Recycle Test Reactor experiments.¹⁰ The vendors of the pressure transducers and other special components required for the system have been contacted. A description of the capsule and the related system should be available for the next quarterly report.

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

Preliminary discussions were held with personnel at Argonne National Laboratory (Idaho Falls, Idaho) concerning the requirements for irradiations in the EBR-II. Additional discussions will be held with the EBR-II staff when the scope of the EBR-II irradiation program has been approved by the AEC.

Table 6-1. Results of Irradiating the Calibration Capsule(a)

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

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

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

Figure 6-1. Gel-Addition Irradiation Capsule

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

The design of the pilot plant system for the production of plutonia-urania sol-gel material is underway, and the flow sheets for the preparation of plutonia and urania sols were selected. The effort was then concentrated on the design of the urania sol production line.

During this quarter the major part of the mixed sol development work was devoted to the production of urania sols using the ORNL flow sheet and to the operation of the pilot plant gelation equipment. Work was also started on the preparation of one kilogram of UO_2 -20 wt % PuO_2 microspheres which will be subjected to irradiation testing.

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

The design of the urania sol preparation system for the plutonia-urania sol-gel pilot plant is essentially complete. Specific equipment design and the procurement of materials are in progress. The design capacity of the equipment is 0.75 kilogram of uranium sol per batch, with a throughput rate of at least two batches per week. The process conditions are essentially identical to the conditions that have been successfully demonstrated with the existing bench-scale equipment.

7.2. Pilot Plant Gelation Equipment (R. V. Carlson)

The initial test runs with the pilot plant gelation equipment were devoted to determining the optimum operating conditions.⁵ The throughput rate for each of these test runs was about 10 to 25 grams of UO_2 per batch. Following the test runs, a near-capacity, two-day run was undertaken to provide enough UO_2 spheres for the statistical contacting studies (see section 3). A secondary purpose was to increase the in-house pilot plant experience in U(IV) sol and sphere production techniques. A uniform feed for the gelation column was prepared by thoroughly blending sol batches 39 through 50, excluding batches 40 and 43 (see Table 7-2

in reference 5). An analysis of the sol feed and the pertinent column operating parameters for this two-day run are summarized in Table 7-1.

After the spheres were removed from the gelation column they were washed thoroughly with acetone (to remove any 2-EH that remained on the surfaces) and dried by pulling nitrogen through the bed for 15 to 30 minutes. An acetone wash was used, since it has been shown that acetone does not react with gel surfaces.^{11,12} The spheres were then put through a riffle six times to obtain a homogeneous stock. The blended stock was heated in a nitrogen atmosphere (using a vacuum oven, 120 C, 15 inches Hg) for about 18 hours to ensure complete dryness. The spheres were then sieved (+40 mesh screen, 420-micron openings) to remove the fragments and the fines. Figures 7-1 and 7-2 are photomicrographs of ceramographic sections from the UO_2 stock blend. The sphere in Figure 7-1 is typical of the material that was produced. However, porosity or voids are present in a few of the spheres (see Figure 7-2).

The total mass of acetone-washed product from this large run was approximately 1.8 kilograms, and the mass of the oven-dried material was about 1.6 kilograms; the total yield of usable spheres was 1.38 kilograms. Table 7-2 is a summary of the analytical results from this run.

7.3. Mixed Oxide Preparation (R. V. Carlson)

Approximately one kilogram of mixed UO_2 -20 wt % PuO_2 sol is being prepared by the sol-gel process; this material will subsequently be irradiated in the BAWTR.

The UO_2 sols are being prepared by the ORNL formate flow sheet. Of the 15 batches (numbers 51 - 65) attempted, each containing 211.5 grams of uranium, 13 have been successful. Batch number 52 was lost when a large excess of NH_4OH was added during the precipitation step. In batch number 57, over-reduction occurred.

The preparation of PuO_2 sols is also in progress. Two batches, each containing 100 grams of plutonium, were attempted via the ORNL flow sheet, and both runs were successful.

Gel firing studies have started. The initial firings, utilizing the CO_2 firing cycle suggested by ORNL,¹³ are being performed with B&W UO_2 gel. After the firing technique is mastered, mixed oxide gel microspheres will be fired.

Table 7-1. Conditions During Large Run on Pilot Plant Gelation Equipment

	Run A	Run B
Sol volume, l	1.5	3.5
U content of sol, <u>M</u>	1.32 ± 0.05	1.32 ± 0.05
U content of sol, wt %	24.3 ± 0.3	24.3 ± 0.3
U(IV)/U(total) in sol, wt %	80 ± 4	80 ± 4
C in dried sol, wt %	1.1	1.2
Sol feed rate, cm ³ /min	2.25	2.25
2-EH volume, gal ^(a)	55	110
2-EH flow rates, gal/min		
Tangential	2.0	2.1
Axial	0.70	0.70
Two-fluid nozzle	0.046	0.046
Dry drum to wet drum	0.047	0.047
Water content in 2-EH, vol %	0.8	0.8
Surfactant content in 2-EH, vol % ^(b)		
Span-80	0.4	0.4
Ethomeen-S/15	0.5	0.5
Sphere residence time, min	≈ 75	≈ 75

(a) 2-EH: 2-ethyl-1-hexanol.

(b) These additives are proprietary products. Span-80, produced by Atlas Chemical Industries, is sorbitan mono-oleate. Ethomeen-S/15 is a complex tertiary amine produced by the Armour Industrial Chemical Company.

Table 7-2. Results From Large Run on Pilot Plant Gelation Equipment

	Total U in gel, wt %	U(IV)/U, wt %	Carbon, wt % ^(a)
Acetone-washed gel from late 1st day	77 ± 2	86 ± 4	3.9
Acetone-washed gel from early 2nd day	66 ± 2 ^(b)	87 ± 4	3.3
Acetone-washed gel from late 2nd day	80 ± 2	84 ± 4	3.0
Blended gel before oven drying	77 ± 2	85 ± 4	3.5
Blended gel after oven drying	84 ± 2	77 ± 4	2.6
Blended gel after oven drying and screening	83 ± 2	78 ± 4	2.9

(a) The precision of these carbon measurements was not determined.

(b) All of the acetone may not have been dried from this sample before it was analyzed.

Figure 7-1. Ceramographic Section of a Typical UO_2 -Gel Sphere (Un-etched), Photomicrograph

Figure 7-2. Ceramographic Section of a UO_2 -Gel Sphere Showing Porosity or Voids (Unetched), Photomicrograph

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