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ABSTRACT

Development of the Gel-Addition process for mixed plutonia-urania reactor fuels has continued. Various contacting techniques were tested for injecting plutonium into UO_2 gel spheres. Agitated-batch tests showed that 800-micron spheres are mechanically strong enough to withstand gentle agitation; contacting at 54 C does not materially increase the total pickup of hexavalent plutonium. Packed-column tests showed increased pickup of hexavalent plutonium with repeated contacting. A 20-gram bed of UO_2 gel was built up to 12% (Pu/U+Pu) by contact with three fresh samples of 0.92 M Pu(VI) at pH $\approx$ 4. The bed was dried between contacts. Oxidation was severe. Organic residues from the gelation process do not interfere strongly with plutonium pickup.

EDTA complexometric titration and coulometric titration gave good agreement on the plutonium assay of U-Pu mixed solutions. Organic interference in plutonium coulometry can be eliminated by boiling the platinum electrode in nitric acid.

A shakedown of the apparatus is complete for particle characterization by subsieve particle size determination, density determination by mercury and gas pycnometry, tap density measurement, particle crush strength determination, differential thermal analyses, and sorbed gas measurement. Ceramographic examination of unfired gel is used routinely to establish proper desiccant conditions for gel formation. Autoradiography on organic thin films has shown that Pu(VI) tends to remain on the sphere surface while Pu(III) permeates the entire sphere.

The capsule design and the safety analysis for reactor testing of mixed fuels are complete. Initial exposure will verify thermal and nuclear calculations. The irradiation program is under revision, and its scope will probably be increased.

A new task was added to the program. All sol and gel preparation work has been transferred to the new task, which is intended to establish

a pilot plant capability for industrial production of (U, Pu)O₂ particulate fuel. The ORNL mixed sol approach will be used.

This is the fifth progress report on the Gel-Addition Program; it covers the period from July 1 to October 31, 1967. The program is sponsored by the U. S. Atomic Energy Commission under Contract No. AT(30-1)-3714.

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1. INTRODUCTION

This is the fifth progress report on a continuing program designed to apply the Gel-Addition process for preparing nuclear fuels to the preparation of uranium-plutonium mixed oxide fast reactor fuel.

The Gel-Addition process was derived from sol-gel technology developed at Oak Ridge National Laboratory; it differs from it in that a single-component sol, such as UO_2 , is prepared and converted to a single-component gel. (The original sol-gel process involves a two-component sol.) The finished fuel is prepared by soaking the gel in an aqueous solution of the fissionable material and firing the mixed gel to the oxide. The economic incentive for the process lies in delaying the introduction of plutonium until the fuel particles have been prepared and screened. UO_2 gel can be made in production quantities with large-scale automated equipment and then stockpiled until it is needed. A mixed gel cannot be mass produced so easily because of the criticality and alpha hazard constraints imposed by the presence of plutonium.

The mechanism responsible for plutonium addition to UO_2 gel is not established, but UO_2 gels have been shown to pick up substantial quantities of plutonium in its trivalent, tetravalent, and hexavalent states from a variety of acid solutions. Work during this report period has emphasized the preparation of a large quantity of UO_2 gel spheres for a statistically controlled plutonium addition experiment, improvements in analytical and material characterization methods, and formulation of the irradiation testing program.

In the interim since the last report, a new task has been activated as part of the project. This task provides for the design and construction of a pilot line for the preparation of $(\text{U}, \text{Pu})\text{O}_2$ by the Oak Ridge mixed-sol approach. This flow sheet has received much more study than the Gel-Addition process and will make sol-gel materials available industrially on a nearer-term basis.

Since the establishment of the new task, responsibility for all sol and gel preparation work has been shifted into it from the Gel-Addition Chemistry task. This report, therefore, differs in format from the preceding ones in the series; sol and gel preparation studies are reported in section 7.

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 July 1 to October 31, 1967.

2. CONCLUSIONS

2.1. Gel-Addition Chemistry

The pickup of hexavalent plutonium by a packed bed of UO_2 gel increases with multiple passes, but oxidation damage to the gel is severe. Pu(VI) has also been shown to reside largely on the sphere surface.

The pickup of trivalent plutonium was substantially lower than that of hexavalent plutonium in a triple-column contact (6.6% Pu/U+Pu) versus (12% Pu/U+Pu), but Pu(III) is uniformly distributed through the spheres, at least after firing.

Gel spheres 800 microns in diameter, prepared by column methods, are more fragile than smaller-diameter spheres prepared in a stirred pot. In earlier tests the larger spheres fractured badly when contacted with plutonium solutions on the same agitator used for the smaller spheres. The mechanical attrition can be greatly reduced by using gentler agitation.

Contacting UO_2 gel in a column with many small liquid volume increments gives little or no increase in plutonium pickup, nor does increasing the contact temperature of a Pu(VI) solution. The presence of organic desiccants in UO_2 gel does not impede the pickup of plutonium substantially, since neither acid-washed gel nor gel shards prepared by tray-drying showed any improvement in plutonium pickup. Extensive water washing of UO_2 gel containing Pu(VI) reduces the measured pickup, either because the Pu(VI) is in leachable form or because it is abraded off the surface layer (see the first paragraph of this section).

2.2. Analytical

Complexometric titration and coulometry give good agreement on plutonium values in mixed U-Pu solutions. Interference by organics in mixed gels has been encountered during plutonium estimation by coulometry. The interference is apparently caused by deposition on a platinum

electrode surface and can be eliminated by boiling the electrodes in nitric acid.

The coulometric procedures now in use give linear titration curves for both plutonium and uranium. The plutonium plot is linear up to 10.5 mg and the uranium to 6.3 mg. These data were obtained in pure solutions of the metals and justify the use of coulometry at least for these simple cases. Coulometry gives reliable answers in solutions where uranium is the major constituent but not in solutions containing plutonium as the major ion. In the latter case, erroneously high answers are observed for uranium. Slightly high answers are also obtained for plutonium, but the error is smaller.

Analysis of stock Pu(IV) solutions showed the nitrite content to be immeasurably low, indicating that alpha radiolysis does not lead to accumulation of nitrites in plutonium nitrate solutions aged for several months.

2.3. Material Characterization

Ceramographic examination of gel spheres is a very useful method for adjusting the operating parameters of spheroidizing columns. The effects of changes in desiccant composition are easy to observe and to make a matter of record.

Alpha autoradiography by organic film methods is equally useful for determining the plutonium distribution in single oxide spheres. The method has provided proof for the distribution statements made in paragraph 2.1.

2.4. Irradiation Testing

Uncertainties in the nuclear calculations for plutonium-bearing materials require a short preliminary reactor experiment to verify the thermal and nuclear values used for capsule design in the irradiation program. Capsule design is complete and is presently undergoing safety review.

2.5. Mixed Sol Methods

UO₂ sols can be made routinely by precipitation-peptization methods developed at Oak Ridge. A definite improvement in the yield of stable sols during this report period shows that the procedure is sensitive

to the process variables and that considerable operator experience is essential.

Gel sphere quality is sensitive to the additive level in the organic desiccant. Severe cracking is observed if the water content is too low, presumably because rapid drying hardens the sphere surface too fast. Organic stripping by acetone wash after spheriodizing does not lead to cracking if air is excluded.

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

During this report period a number of different techniques for contacting UO_2 gel with aqueous plutonium solutions were tested. In this section data are reported on the following methods:

1. Repeated passage of Pu(VI) and Pu(III) solutions through packed columns of UO_2 gel spheres.
2. Batch contacting using extremely gentle agitation to reduce breakage of large spheres.
3. Column contact of UO_2 gel spheres using rapid throughput of small solution volume increments.
4. Effects of extensive washing on gel spheres containing Pu(IV).
5. Batch contact of gel spheres with Pu(VI) at elevated temperatures ($\approx 54^\circ\text{C}$).
6. Batch contact of tray-dried UO_2 gel shards.

3.1. Multiple-Contact Experiments

Previously reported experiments conducted with Pu(IV) have indicated that plutonium pickup can be increased by recontacting dried UO_2 gel spheres with fresh plutonium solution.³ Two experiments were performed to determine whether the same effect occurs with Pu(III) and Pu(VI).

In both experiments a blend of 800-micron spheres prepared from batch 11, 14, and 16 sol was contacted with fresh plutonium solution three times. These spheres were column-prepared and washed with acetone. In both tests packed bed columns were employed;⁴ the effluent was recycled twice through the column during each contact. The spheres were dried at 60°C and 15 inches mercury vacuum for periods varying from 90 minutes to 18 hours between contacts. After each run the spheres were dried in the column by pulling air through the bed for 5

minutes. Final drying took place in a vacuum oven (60 C, 15 in. Hg) overnight. The dried material was sieved (40 mesh, 420-micron opening) to separate whole spheres from fragments and from any residual precipitate.

3.1.1. Pu(VI) Triple Contact

The Pu(VI) stock solution was prepared by refluxing Pu(IV) (0.29 M Pu, 1.33 M HNO₃) for 6 hours and then reducing the volume by boiling until precipitation occurred; 1 M HNO₃ was added to redissolve most of the precipitate. The remaining insoluble olive-green residue—assumed to be polymeric Pu(IV)—was centrifuged off and discarded. Finally, the pH was adjusted to 4.0 by adding concentrated NH₄OH to yield a solution which was analyzed coulometrically to be 0.92 M in Pu(VI).

After the first pass of the plutonium solution in each of the three contactings, a light tan precipitate was observed in the effluent. Therefore, the final filtrates were centrifuged, and the solid and liquid phases were analyzed separately. Also after the first pass, a sample of spheres was withdrawn for analysis to determine whether recycling the effluent is necessary or desirable.

Visual and microscopic examination at the conclusion of the experiment showed that the surfaces of the spheres remaining in the +40 mesh split after both the first and second contacts were generally undamaged except for a few small cracks which were also observed on uncontacted spheres. However, all the solid material remaining after the third contact was yellow, probably UO₃. Under microscope these particles appeared to be spheres whose surfaces had been attacked severely. Since no large agglomerates were present, it was concluded that, rather than being a large quantity of residual precipitate, this material was UO₂ gel which had undergone a great deal of oxidation during the third contact. The procedure followed in this experiment is summarized on the flow sheet shown in Figure 3-1; Table 3-1 summarizes the results of the analyses.

Table 3-1. Summary of Data From Pu(VI)-UO₂ Contact Experiment

Contact No.	Wt of contacted UO ₂ gel, gm	Pu(VI) solution volume, ml	Pu(VI) concentration in liquid phase, M		Column contacting time, min	Solution pH		Effluent analysis No.	U in effluent, gm	Pu in effluent, gm	Pu + U in effluent, %	Gel sphere analysis No.	Sphere mesh splits	Wt of spheres, gm	Pu + U in gel spheres %
			Initial	Final		Initial	Final								
1	19.180	9.0	0.92		5.0	4.0	4.3					I-F-3	+40	2.859	1.7
												I-F-11	-40	0.222	1.7
	15.4			0.58	5.0	4.3	4.8	I-F-5(a)	0.22	1.24	84.9	I-F-4	+40	3.571	2.3
					5.0	4.0	4.6	I-F-6(b)	0.030	0.0565	65.3	I-F-12	-40	0.268	0.8
2	11.9	9.0	0.92	0.65	5.0	3.7	3.6	I-F-9(a)	0.39	1.40	78.2	I-F-7	+40	4.119	5.8
					5.0	3.6	3.7	I-F-10(b)	0.014	0.0414	74.9	I-F-13	-40	1.278	12.2
					5.0	3.7	3.7								
3	5.3	9.0	0.92	0.73	5.0	3.7	3.9	I-F-15(a)	0.45	1.58	77.8	I-F-8	+40	1.478	12.0
					5.0	3.9	4.2	I-F-16(b)	0.061	0.0340	34.9	I-F-14	-40	0.521	18.2
					5.0	4.2	4.1								

Total sphere dissolution = 8.7% (assuming 70% U in UO₂ gel).

Total sphere destruction = 16.6% (based on U content in +40 mesh contacted gel).

(a) Supernate.

(b) Precipitate.

Figure 3-1. Flow Sheet for Triple-Contacting Tests on UO₂ Gel Spheres

As can be seen from the data, the apparent plutonium content of the gel spheres more than doubled with each contact. Most simple mechanisms that can be proposed for the pickup process lead to the prediction that the plutonium content should increase by no more than a constant amount. One possible explanation for this apparent anomaly is that the plutonium exchanges with the uranium. Although the amount of uranium in solution increased with each contact, there is no obvious stoichiometric correlation between uranium increase and plutonium decrease. However, as mentioned previously, the spheres were severely damaged during these contacts; so possibly any such correlation is masked by the acid attack and/or the Pu(VI) oxidative attack on the UO_2 gel. Alternatively, it may be argued that a portion of the observed precipitate remains on the surfaces of the spheres even after the abrasion involved in screening. Since the analyses of these precipitates indicate that plutonium comprises 35 to 75% of the total metal, any residue would introduce a positive bias to the analysis. A third explanation is that the volume of solution (i. e., the amount of plutonium) per gram of spheres was increased with each contact. Thus, if the same percentage of plutonium is removed from the solution during each contact, the amount of pickup will increase. From the nearly identical plutonium content in sphere samples 1-F-3 and 1-F-4, it is apparent that very little advantage is gained by recycling the effluent. Actually, recycling may be disadvantageous since the first evidence of precipitation is seen in the effluent after the initial pass. That a portion of this plutonium-rich precipitate is retained in the sphere bed after subsequent passes was confirmed by a comparison of the plutonium content in the spheres from the coarse and the fine mesh splits. Mass balances for both plutonium and uranium were attempted, and the results are shown in Tables 3-2 and 3-3. The indicated errors represent one standard deviation based on the following estimated uncertainties:

1. 10% in assumed uranium content of UO_2 gel spheres.
2. 10% in assumed total metal content of contacted spheres.
3. 2% in analysis of Pu(VI) stock solution.
4. 5% in analysis of solutions containing both uranium and plutonium.

Table 3-2. Plutonium Mass Balance

Source	Analysis No.	Pu introduced, gm	Pu ^(a) recovered, gm	Percent recovery
Contact solution		1.976		
First sphere sample				
+40 mesh	1-F-3		0.036	
-40 mesh	1-F-11		0.003	
Second sphere sample				
+40 mesh	1-F-4		0.062	
-40 mesh	1-F-12		0.018	
Remaining spheres			0.280 ^(b)	
First effluent				
Supernate	1-F-5		1.24	
Precipitate	1-F-6		0.057	
Sub-Total for First Contact		1.976 ± 0.040	1.732 ± 0.070	87.9 ± 4.0
Contact solution		1.976		
Third sphere sample				
+40 mesh	1-F-7		0.108 ^(c)	
-40 mesh	1-F-13		0.034 ^(c)	
Remaining spheres			0.118 ^(b)	
Second effluent				
Supernate	1-F-9		1.40	
Precipitate	1-F-10		0.041	
Sub-Total for Second Contact		1.976 ± 0.040	1.701 ± 0.072	86.3 ± 4.0
Contact solution		1.976		
Fourth sphere sample				
+40 mesh	1-F-8		0.162 ^(c)	
-40 mesh	1-F-14		0.023 ^(c)	
Third effluent				
Supernate	1-F-15		1.58	
Precipitate	1-F-16		0.034	
Sub-Total for Third Contact		1.976 ± 0.040	1.799 ± 0.081	91.1 ± 4.5
Total for Experiment		5.928 ± 0.068	5.232 ± 0.129	88.2 ± 2.6

(a) Total metal content of contacted gel assumed to be 75%.³

(b) Pu content of the remaining coarses and fines assumed to be identical with analyzed sample.

(c) Analyzed value less the amount assumed to have been picked up in previous contacting(s).

Table 3-3. Uranium Mass Balance

<u>Source</u>	<u>Analysis No.</u>	<u>U^(a) introduced, gm</u>	<u>U^(b) recovered, gm</u>	<u>Percent recovery</u>
UO ₂ gel spheres		13.426		
First sphere sample				
+40 mesh	1-F-3		2.108	
-40 mesh	1-F-11		0.164	
Second sphere sample				
+40 mesh	1-F-4		2.616	
-40 mesh	1-F-12		0.183	
First effluent				
Supernate	1-F-5		0.22	
Precipitate	1-F-6		0.030	
Third sphere sample				
+40 mesh	1-F-7		2.910	
-40 mesh	1-F-13		0.842	
Second effluent				
Supernate	1-F-9		0.39	
Precipitate	1-F-10		0.014	
Fourth sphere sample				
+40 mesh	1-F-8		2.296	
-40 mesh	1-F-14		0.319	
Third effluent				
Supernate	1-F-15		0.45	
Precipitate	1-F-16		0.063	
Total for Experiment		13.43 ± 1.34	12.61 ± 0.57	93.9 ± 10.3

(a) U content of column-dried UO₂ gel assumed to be 70%.⁴

(b) Total metal content of contacted gel assumed to be 75%.³

Two additional errors are not reflected in the results in Tables 3-2 and 3-3:

1. It was not possible to remove all the spheres from the column, so additional losses of possibly 5% occurred.
2. There were small solution losses during the many necessary transfers.

3.1.2. Pu(III) Triple Contact

The Pu(III) was prepared by partially acidifying 1 part of 85% hydrazine hydrate with 3 parts of 1 M HNO₃ and then slowly adding 6 parts of stock Pu(IV) nitrate solution (240.8 mg Pu/ml and 3.36 M free acid) while stirring vigorously. Within 5 to 10 minutes after the final addition of Pu(IV), the solution was blue in color and had a pH less than zero. The pH was then adjusted to 0.3 by the addition of concentrated NH₄OH. The absorption spectrum from 600 to 1000 mμ was typical of Pu(III) with no indication of any Pu(IV) or Pu(VI). A coulometric titration of an aliquot indicated that the plutonium was present only in the +3 oxidation state and that the solution was 0.64 M in Pu(III).

A visual and microscopic examination of the contacted spheres at the conclusion of the experiment revealed that a number of them were broken. Beyond this, there was no change in appearance of the remaining spheres. Total gel attrition as measured by the uranium content of the -40 mesh fines was near 30%.

The results of this run are summarized in Table 3-4. The reason the pickup from the second contact is identical with the first is not clear. The relatively large number of spheres broken during this run is presumed to be related to the high acidity of the contacting solutions.

3.2. Batch Contact With Gentle Agitation

In a previous report² it was pointed out that most 800-micron spheres fracture when agitated by the technique used in early runs on spheres prepared by stirred-pot methods. Therefore, a series of tests was made at that time using packed-bed columns operated in a manner similar to that normally used with ion-exchange columns. However, column techniques have two drawbacks.

Table 3-4. Summary of Data From Pu(III)-UO₂ Triple Contact

Contact No.	Wt of contacted UO ₂ gel, gm	Pu(III) solution volume, ml	Initial Pu(III) concentration, M	Column contacting time, min	Initial pH	Final pH	Sphere analysis No.	Sphere mesh splits	Wt of spheres, gm	$\frac{\text{Pu}}{\text{Pu} + \text{U}}$ in spheres, %
1	20.31	36	0.64	15	0.3	2.3	1-F-29	+40	6.6525	3.1
				10	2.3	2.2	1-F-34	-40	0.3710	7.5
				5	2.2	2.4				
2	≈12	24	0.64	15	0.3	1.2	1-F-31	+40	2.9749	3.1
				10	1.2	1.3	1-F-35	-40	1.0055	1.2
				5	1.3	1.1				
3	≈6	12	0.64	15	0.1	1.3	1-F-33	+40	3.2297	6.6
				10	1.3	1.6	1-F-36	-40	1.0939	7.1
				5	1.6	1.5				

Total sphere destruction = 30% (i.e., uranium not in +40 mean split).

1. A very limited number of contacts can be performed simultaneously.
2. It is difficult to maintain precise temperature control.

Using a thermo-vibrator (Precision Scientific Company, Chicago), these two conditions pose no serious problem, and the agitation is far less vigorous than is the case with the Vortex Jr. shaker (Scientific Industries, Queens, N. Y.) used previously.

In order to determine whether this is a satisfactory technique, the following run was made. Ten grams of 800-micron UO_2 gel spheres from a blend of those prepared from batches 11, 14, and 16 sol and 25 ml of 0.6 M Pu(III) solution (pH = 0.5) prepared by hydrazine reduction of Pu(IV) were placed in a closed 60 ml bottle and agitated for 30 minutes. At the end of this period, the solution was decanted, and the spheres were rinsed with 15 ml demineralized H_2O into a fritted glass filter funnel. After the spheres were dried for 16 hours (60 C, 15 in. Hg vacuum), they were sieved on a 40 mesh screen. The Pu/(Pu+U) in the +40 mesh split was 0.022, a value nearly the same as reported in section 3.1.2 for a single Pu(III) contact. It was noted that the amount of sphere breakage during this run was quite small, and it was concluded that contacts performed by this technique yield results comparable with those obtained by the packed-column technique.

3.3. Column Contact With Small Liquid Volume

In a previous report,⁴ data were presented which indicated that the large pH rise observed in acidic solutions contacted with UO_2 gel is consistent with a simple acid-base reaction, the gel being considered a basic anhydride, i. e.,

Assuming this to be true, it is possible that as the pH rises, hydrolytic reactions complex the plutonium—especially Pu(IV)—before pickup can take place. This seems particularly likely for experiments in which packed-bed columns were employed because the entire plutonium solution was loaded onto the column at the beginning of each contact. With this in mind, three runs were made using packed-bed columns of 800-

micron UO_2 gel spheres and the same technique described in section 3.2, except for the fact that the plutonium stock solution was added a few drops at a time and then immediately pulled off by vacuum.

3.3.1. Pu(III) Test

A 0.73 M Pu(III) solution ($\text{pH} = 1.7$) was prepared from stock Pu(IV) by hydrazine reduction. A total of 25.0 ml of this solution was added, in drops, over a period of 5.0 minutes to a bed containing 10.52-gram spheres from batch 34 sol. A pH of 2.6 was measured for the effluent. The plutonium pickup by the spheres in the +40 mesh split was 4.9%, somewhat higher than that reported in section 3.2.2 for a single Pu(III) contacting.

3.3.2. Pu(IV) Test

Concentrated NH_4OH and demineralized H_2O were added to 30 ml of stock Pu(IV)* to bring the volume to 45 ml and to raise the pH to 0.2. This 0.65 M Pu(IV) solution was then added, a few drops at a time over a period of 30.0 minutes, to a bed containing 5.0 grams of spheres. The pH of the effluent was measured to be 0.55, and the plutonium pickup by the spheres in the +40 mesh split was determined to be only 1.3%.

3.3.3. Pu(VI) Test

The last two tests were conducted either for different contacting times or with solutions in which the acid and/or plutonium concentrations were somewhat different from those used before, thus making direct comparison of these data with previous data rather difficult. Therefore, in this test, three runs were made using different techniques but identical conditions. Two runs were made on the thermovibrator, one in a sealed bottle containing a nitrogen atmosphere, and the other in an open bottle. The third run was performed by adding the solution, by drops, to a packed sphere bed. The Pu(VI) stock solution was prepared by refluxing 150 ml of Pu(IV) (78 g/l, 1.12 M H^+) for 12 hours. A spectrophotometric analysis of the resulting solution indicated that more than 98% of the plutonium had been oxidized. After the

*231 gm Pu/l, 3.18 M H^+ .

pH was adjusted to 1.0 with concentrated NH_4OH , a coulometric analysis of the stock solution indicated that it was 0.30 M in Pu(IV). In all three runs, 50 ml of the stock solution were contacted for 35 minutes with approximately 11 grams of spheres from batch 21 sol. The data are summarized in Table 3-5.

Table 3-5. Summary of Pu(VI) Test

	<u>Contacted under nitrogen</u>	<u>Contacted in air</u>	<u>Contacted by modified column technique</u>
Weight of UO_2 gel spheres, gm	11.40	10.78	10.76
Pu/(Pu+U) in +40 mesh split	0.052	0.049	0.042

The results from these three tests indicate that with the packed-bed technique, the pickup is not enhanced by adding the solution by drops and keeping the residence time at a minimum. There are not sufficient data available to establish a convincing explanation of the observations; any one or more of the following may play a role:

1. The assumption that the pH rise is a simple acid-base reaction is incorrect.
2. The kinetics of the pH rise and the associated hydrolytic reactions are faster than the pickup kinetics.
3. The pickup mechanism does not depend on the pH rise.

3.4. Batch Contact With Pu(VI) at Elevated Temperature

So far, no data have been obtained on the variation of pickup with temperature. Since the rates of many chemical reactions increase markedly with increasing temperature, plutonium pickup by UO_2 gel spheres might also be temperature-dependent. For this run, Pu(VI) was prepared by refluxing a Pu(IV) solution (78 g/l, 1.12 M H^+) for 12 hours. After adjusting the pH to 1.0 with concentrated NH_4OH , a spectrophotometric analysis indicated that more than 98% of the plutonium

was hexavalent; a coulometric analysis indicated that the solution was 0.30 M in plutonium. Thirty milliliters of this solution (preheated) and 10.74 grams of 800-micron spheres from batch 21 sol were contacted for 60 minutes on the thermo-vibrator at $54(\pm 1)$ C. (A sand bath was used to maintain more precise temperature control.) Next, the solution was decanted and the spheres were washed with 2 ml of H_2O to remove most of the remaining solution and the precipitate that formed during contact. After the spheres were dried for 18 hours (60 C, 18 in. Hg vacuum), they were sieved on a 40 mesh screen.

It was estimated that the +40 mesh fraction contained over 70% of the total recovered sphere mass; the plutonium pickup measured 4.1%. An analysis of the post-contact solution indicated that it contained 1.76 grams plutonium and 0.26 grams uranium. Thus about 82% of the plutonium remained in solution, and only about 3.5% of the sphere mass dissolved.

These results indicate that the spheres can withstand extended contacts at relatively high acidities and elevated temperatures and that the pickup of Pu(VI) is not highly dependent on temperature.

3.5. Column Contacts With UO_2 Gel Shards

The behavior of UO_2 gel shards toward Pu(IV) solution has been compared with that of 800-micron spheres in three column runs. Differences between shards and spheres can be anticipated for two reasons. First, spheres are prepared by drying suspended sol droplets in an organic dryer bath. Shards are made by direct tray drying of the sol. Both materials contain the organics used in sol preparation, but the shards do not contain the surfactants and 2-EH* solvent used for spheroidizing. Second, shards can be made in much larger sizes. In these experiments 800-micron (0.032 in.) spheres were compared with 1/8 in. (0.125 in.) and 1/4 in. (0.250 in.) shards.

A Pu(IV) solution with a molarity of 0.84 and a pH of 1.0 was prepared by adding concentrated NH_4OH to Pu(IV) stock. Three runs were made with packed-bed columns. The first contact was performed with

- - - - -
* 2-EH: 2 ethyl, 1 hexanol.

5.1 grams of 800-micron spheres from batch 34 sol, the second with 5.1 grams of shards from batch 12 sol, which were about 1/8 in. to a side, and the third with 5.2 grams of shards from batch 19 sol which were about 1/4 in. to a side. In all three runs, 10.0 ml of the stock solution was passed through the bed over a period of 6.0 minutes. After contacting, the gel samples were dried for 18 hours at 70 C and 13 in. Hg vacuum. Finally they were sieved on a 40 mesh screen. The weights and plutonium pickup values were measured in both size fractions, and the results are summarized in Table 3-6.

Table 3-6. Results of Pu(IV) Contacts

	<u>pH</u>		<u>Initial wt of UO₂ gel, gm</u>	<u>Mesh split</u>	<u>Wt of contacted UO₂ gel, gm</u>	<u>Pu Pu + U</u>
	<u>Initial</u>	<u>Final</u>				
Microspheres	1.0	1.7	5.1	+40	4.1	0.003
				-40	0.4	0.033
Large shards	1.0	1.5	5.1	+40	4.9	0.002
				-40	≈ 0	--
Small shards	1.0	1.6	5.2	+40	4.1	0.002
				-40	0.7	0.012

It is interesting to note the agreement in pH change, sphere attrition, and pickup for the spheres and for the shards. It is now believed that the very low pickup values observed in these experiments are related to the increase in size of the Pu(IV) polymer particles at higher pH values. The particle size obtained in these tests was probably so large that plutonium could not enter the gel. This indicates that the length of contact with Pu(IV) solutions is almost irrelevant unless some method is found for limiting the very rapid pH rise to values well below 1.0.

3.6. Effect of Water Washing After Contact

In most contact experiments the plutonium content of the -40 mesh fraction has been found to be substantially greater than that of the +40 mesh fraction. The unequal distribution has been attributed to the presence of a fine precipitate containing a large percentage of plutonium.⁴

and it has been tacitly assumed that none of this precipitate remains in the coarse fraction after sieving. If all traces of the contact solution and the associated precipitate are rinsed from the spheres before drying, there will be less ambiguity in the results. However, it is possible that a water rinse will also remove part or all of the picked up plutonium, especially if it is not chemically bound to the spheres. In the following experiment, an attempt was made to determine the effect of washing the contacted spheres.

The Pu(VI) contact solution was prepared by refluxing a Pu(IV) solution after its free acid concentration was reduced to 1.3 M. The pH was then adjusted to 3.8 by the addition of concentrated NH_4OH . A spectrophotometric analysis indicated that more than 98% of the plutonium in this solution was in the +6 oxidation state and that the plutonium concentration was 1.1 M. A total of 29 ml of this solution was passed through a packed bed containing 20.36 grams of 800-micron UO_2 gel spheres from a blend of those prepared from batches 11, 14, and 16 sol. The column effluent was recycled twice so that the total contact time was 15.0 minutes. Next, about 25% of the spheres were removed from the column before the first rinse and after each of the three rinses. The wash solutions were 10.0 ml, then 20.0 ml, and finally 30.0 ml of demineralized H_2O . The four sphere samples were dried for 18 hours at 60 C and 15 in. Hg vacuum, and they were sieved on a 40 mesh screen. The results are summarized in Table 3-7.

At first glance, it appears that a water wash removes plutonium from the contacted spheres. However, the very large plutonium content in each of the fine sphere fractions indicates an alternative explanation. As pointed out in section 5 of this report, Pu(VI) is present mainly as a surface layer on the spheres. Therefore, if the sphere surfaces were abraded in the sieving procedure, anomalously high values of the plutonium content in the fines would result. So a large percentage of the apparent decrease in the plutonium content of the coarse fractions could be due to this, rather than to the water washing. Work on the effects of prolonged washing will continue.

Table 3-7. Results of Water-Washing Experiment

Wt of UO ₂ gel, gm	Pu(VI) solution volume, ml	Pu concentration in liquid phase, M	Column contacting time, min	Contact solution pH		Total volume wash H ₂ O, ml	Effluent analysis No.	U in effluent, gm	Pu in effluent, gm	Gel sphere analysis No.	Sphere mesh spheres	Wt of spheres, gm	$\frac{\text{Pu}}{\text{Pu} + \text{U}}$ in spheres, %
				Initial	Final								
20.36	29	1.1	5.0	3.8	3.5	0.0	1-F-18 ^(a)	1.3	4.3	1-F-17	+40	2.77	3.1
			5.0	3.5	3.6					1-F-23	-40	0.26	19.4
			5.0	3.6	3.6								
~16.0						10.0				1-F-19	+40	4.10	2.0
										1-F-24	-40	1.13	13.5
~10.0						30.0				1-F-20	+40	3.18	0.7
										1-F-25	-40	0.70	14.2
~6.4						60.0	1-F-22 ^(b)	0.29	0.10	1-F-21	+40	4.32	1.2
										1-F-26	-40	1.18	14.4

(a) The final effluent from the column after contact.

(b) The combined wash solutions.

4. ANALYTICAL SUPPORT (D. H. Schmitt)

4.1. Plutonium Analysis

4.1.1. Complexometry

The complexometric titration of plutonium by ethylenedinitrilotetraacetic acid (EDTA), which has been reported previously,¹ has been further evaluated. One problem inherent in this procedure is that Pu(III), (IV), and (VI) have different titers with EDTA. To obtain a single oxidation state, the plutonium is reduced to Pu(III) and then is reoxidized quantitatively to Pu(IV). The reductants investigated include hydroiodic acid, sulfurous acid, potassium iodide, hydrazine, and 3% hydrogen peroxide. Hydrogen peroxide in 1 N nitric acid was found to be the best reductant because it was rapid (complete reduction in five minutes) and the excess could be destroyed by heating.

A comparison of results for plutonium analysis using EDTA titration and controlled potential coulometric titration on actual samples containing both plutonium and uranium are shown in Table 4-1.

Table 4-1. Comparison of Results for Plutonium Analysis by Complexometry (EDTA) and Controlled Potential Coulometry

Sample No.	Plutonium concentration, ^(a) mg/ml		Uranium concentration, ^(a) mg/ml (coulometry)
	EDTA	Coulometry	
I-F-5	11.87	12.42	2.23
I-F-9	14.72	14.01	3.94
I-F-15	15.77	15.80	4.53
I-F-28	15.72	15.76	5.80
I-D-25	54.08	53.95	41.21

(a) More work is needed on these samples to evaluate error limits.

The uranium was analyzed by controlled potential coulometry in both cases. It can be seen that the results of the EDTA method in most cases are in close agreement with the results obtained by coulometry. Evaluation work on EDTA methods will continue.

4.1.2. Controlled Potential Coulometry

A preliminary discussion of the ORNL method now in use was given in a previous report.^{3,6} During routine application of the method to UO_2 gels that had been treated with plutonium, erratic results were observed. It is well known that organics can interfere with reduction at a platinum surface. Since gels contain considerable organics, the erratic performance has been attributed to organic interference. Boiling the electrodes periodically with nitric acid has apparently solved the problem, and this treatment is now a standard part of the method.

It was also discovered that Pu(VI) cannot be reduced quantitatively in a perchloric acid electrolyte. Either a chemical reduction is required, or a sulfuric acid electrolyte can be used. Investigations are being conducted on these alternate measures.

In order to check the practical range of plutonium estimation by controlled potential coulometry, several samples of varying amounts of plutonium were titrated. The resulting readout voltages were then plotted against the number of milligrams of plutonium taken; the results are shown in Figure 4-1. From the linearity of the curve, it can be assumed that plutonium can be determined by this method over the range investigated.

4.2. Uranium Analysis

4.2.1. Complexometry

A method for the complexometric titration of U(VI) with ethylenedinitrilotetraacetic acid (EDTA) using PAN 1-(2-pyridylazo)-2-naphthol as the indicator with a spectrophotometric end point has been adopted from the literature.⁷ A range of 12 micrograms to 9 milligrams can be determined using this method with an accuracy of 5.0 to 0.1%, respectively. A titration assembly, as described in Fritz and Schenk is used to determine the endpoint at 555 nm.⁸

Figure 4-1. Working Range for the Analysis of Plutonium by Coulometry

4.2.2. Controlled Potential Coulometry

A tentative A. S. T. M. method has been adopted for the determination of uranium.⁹ It also can be used for determining uranium in solutions containing both uranium and plutonium, because plutonium is pre-reduced at +0.085 volt versus the standard calomel electrode (S. C. E.). The uranium is then measured using the reduction of U(VI) to U(IV) at -0.325 volt versus the S. C. E.

To determine a workable range for this method, several different amounts of uranium were analyzed, and the readout voltages (in millivolts) were plotted against the number of milligrams of uranium taken. The results are shown in Figure 4-2. From the linearity of the curve, it can be assumed that this method is applicable to the range investigated.

Coulometry can also be used to determine the U(VI) present in a U(IV) system stabilized with phosphoric acid. The average relative standard deviation of this method for 75 analyses of uranous nitrate solutions, sols, and gels for U(VI) was found to be 4.86%. The average relative standard deviations for total uranium content are shown in Table 4-2.

Table 4-2. Average Relative Standard Deviations for Uranium Analysis by Controlled Potential Coulometry

Sample description	No. of analyses	Average relative standard deviation, %
U(NO ₃) ₄	81	0.66
UO ₂ (NO ₃) ₂	9	0.26
Gel spheres	28	2.09
Sols	6	1.28
U standards ^(a)	21	1.07

(a) U₃O₈ dissolved in HNO₃; analyses were carried out in a glove box.

Figure 4-2. Working Range for the Analysis of Uranium by Coulometry

4.3. Uranium and Plutonium Analysis

4.3.1. Controlled Potential Coulometry

Using the previously described coulometric methods for plutonium and uranium, it is possible to determine both of them in the same sample without separation. In order to investigate the applicable ranges for the combined analyses, several mixed standards were prepared and analyzed. The results are shown in Table 4-3. From these results, it can be seen that these methods are applicable when plutonium is the minor component but not when it is the major one.

Table 4-3. Analysis of Plutonium and Uranium in Mixed Standards by Controlled Potential Coulometry

Sample No.	Plutonium concentration taken, mg/ml	Plutonium concentration found, mg/ml	Uranium concentration taken, mg/ml	Uranium concentration found, mg/ml
1	2.08	2.07 ± 0.05	10.32	10.14 ± 0.03
2	0.50	0.50 ± 0.03	12.29	12.10 ± 0.04
3	8.32	8.60 ± 0.10	2.58	3.08 ± 0.06
4	9.90	10.16 ± 0.05	0.62	3.05 ± 0.04

4.3.2. Calculations of Uranium and Plutonium Analytical Results

A computer program has been written to perform the calculations required by controlled potential coulometric determinations of plutonium and uranium. The program calculates the following quantities:

1. Absolute amount of uranium, mg.
2. Absolute amount of plutonium, mg.
3. Standard deviation of uranium analysis, mg.
4. Standard deviation of plutonium analysis, mg.
5. Relative standard deviation of uranium analysis, %.
6. Relative standard deviation of plutonium analysis, %.
7. Ratio of plutonium to total plutonium and uranium, %.

4.4. Carbon Analysis

A standard combustion-gravimetric method has been adapted for determining carbon in uranium sol and gel samples. A Fisher induction carbon apparatus (#10-465) is used, and the CO₂ generated is absorbed in a weighing-absorption tube containing Caroxite. In order to ensure complete combustion, it was necessary to mix the sample with an accelerator of pure iron powder and to have a minimum combustion time of 6 minutes. To obtain true sample weights for uranium sols, it was necessary to dry the samples to constant weight at 120 C (2 to 3 hours).

4.5. Nitrate Analysis

A volumetric oxidation-reduction method is used to determine nitrate in uranous nitrate and uranyl nitrate solutions. The method is an indirect one based on the following reaction:

The present method is an adaption of Leithe's procedure.¹⁰ Ferrous iron is added to a nitrate solution and the excess is titrated with potassium dichromate. The endpoint is determined potentiometrically. Since U(IV) will be oxidized under the same conditions, it is a principal interference. This interference has been eliminated in two different ways. In the first method U(IV) is oxidized with peroxide, and any excess peroxide is corrected for by titrating a blank. In the second method, the uranium is separated from the nitrate on a cation exchange column. The latter method is the preferred one, since the first method involves two indirect titrations and thus increases the probability of error in both precision and accuracy. In uranyl nitrate solutions the uranium is completely oxidized, and thus separation is not necessary.

Because the endpoint detection is potentiometric, this method has lent itself to the use of an automatic Fisher Titralyzer. A maximum of 16 samples can be automatically titrated in one cycle, and all titrations of this kind are now performed with this instrument. A statistical treatment of 72 analyses on uranous nitrate samples was carried out using this method; a relative standard deviation of 0.69% was found.

The use of a nitrate electrode was also investigated. From preliminary experiments, it appears that routine use of this electrode as an analysis method would require extensive development work.

4.6. Nitrite Analysis

A tentative nitrite method was used to determine the nitrite content of Pu(IV) solutions. Nitrite may be a contaminant stemming from radiolysis of the nitric acid.

The nitrite was determined by the spectrophotometric method of Bendschneider and Robinson.¹¹ However, since Pu(IV) absorbs in the same wavelength region, it was necessary to separate the plutonium from the nitrite. A cation exchange column was used for this purpose, and only immeasurable trace amounts of nitrite were found in the Pu(IV) solutions.

A semi-quantitative check on the method was performed by determining the plutonium using controlled potential coulometry with and without sulphamic acid present in the electrolyte. Nitrite is an interference in this method, and sulphamic acid is added to destroy any nitrite present. The two determinations were exactly the same, indicating that only very small amounts of nitrite—if any—were present in the Pu(IV) stock solutions.

4.7. Analytical Sample Load

During this quarter 330 samples were completed. This sample load represents approximately 1075 analyses. The analyses included total uranium total plutonium, U(VI)/U, NO_3^-/U , C/U, plutonium oxidation states, H_2O , O/M, O_2 in N_2 , and NO_2^- .

5. MATERIAL CHARACTERIZATION (J. M. Kerr)

During this report period the following ceramic fuel characterization methods have been made available for use:

1. Subsieve particle size determination.
2. Density measurement by mercury and gas pycnometry and particle tap density determination.
3. Particle crush strength.
4. Differential thermal analysis (DTA).
5. Sorbed gas content and release.

Ceramographic studies of gels and oxide samples have continued.

5.1. Subsieve Sizer

The subsieve sizer yields a measurement of average particle size from the permeability of a packed bed of the material to air flow. The data generated will be useful in evaluating the effectiveness of milling operations on various fuels and as an initial indication of the fuel sinterability.

5.2. Density Measurements

Techniques for density measurement have been developed in which gas and mercury pycnometry are utilized for sintered shapes and tap density measurements for fine powders. Knowledge of the density of particles is necessary in order to evaluate the packed density of fuel rods produced in Vipac fabrication. Pycnometric density measurements are used to determine the density of solid shapes and are applied to evaluation of the sintering behavior of powders. The apparatus for measuring tap density of powders is a graduated cylinder mounted on a device that provides a uniform and reproducible tapping motion. The data thus generated will be helpful in evaluating particle packing and particle-

density characteristics as well as the sintering characteristics of ceramic powders.

5.3. Particle Crush Strength

The particle crush-strength apparatus is diagrammed schematically in Figure 5-1. The apparatus was adapted from a similar unit built by R. Buxton at Oak Ridge National Laboratory. The unit contains a balance, two alumina crushing anvils, a sensitive microphone pickup connected to one anvil, a device for adding weight to one leg of the balance by water flow, and the associated electronic components to amplify the microphone signal of audible particle fracture. The data from this test will provide a qualitative means for evaluating the quality of the particles (internal cracks and voids should decrease particle strength) produced by different methods or from different batches.

5.4. Differential Thermal Analysis and Sorbed Gas Release

Differential thermal analysis (DTA) is a technique whereby the difference in temperature between a test sample and a standard (thermally inert) sample is measured as both samples are heated at a predetermined rate to a given temperature. Chemical and solid state reactions within the "unknown" sample, which are either exothermic or endothermic, can be detected by the change in the "unknown" sample temperature relative to the "standard" sample temperature.

Simultaneous determinations of these heat release or absorption characteristics, combined with the sorbed gas release as a function of temperature, are useful in determining how gases are retained within the samples. Additionally, DTA techniques help to elucidate sintering behavior.

The DTA and sorbed gas equipment is contained in one furnace arrangement. Simultaneous determinations can be run, although the sensitivity of the sorbed gas content measurement is limited to about 0.1 cc per gram of material. Steps are being taken to increase this sensitivity to 0.01 cc per gram by decreasing the chamber volume, but it is doubtful that the DTA mode and sorbed gas content mode of the device can be run simultaneously with the modification. The device operates to 1700 C in reducing, oxidizing, inert, and vacuum atmospheres.

5.5. Ceramographic Studies

In this report period ceramographic examinations were completed on 47 gel specimens and 9 oxide specimens. In addition, 8 alpha autoradiographic examinations were made.

Examinations of plutonium-contacted spheres were carried out to help evaluate the relative merits of using Pu(III) or Pu(VI) in the contacting solution. Two sets of spheres were contacted with plutonium solutions three times. Figure 5-2 shows the ceramographic section of fired oxide spheres after triple contacting with Pu(VI). Figures 5-3 and 5-4 are the alpha autoradiographs of the single- and triple-contacted samples using Pu(VI). Figures 5-5 and 5-6 show the ceramographic sections of fired oxide spheres that were single- and triple-contacted with Pu(III); Figures 5-7 and 5-8 are the alpha autoradiographs of these samples. The attack on the microspheres by the contacting solution increases with the number of contacts, and while it is not specifically shown in this series of figures, the attack is much more severe with Pu(VI) solutions than with Pu(III) solutions. The inhomogeneity of plutonium in the microspheres after contacts is illustrated markedly by the autoradiographs. These data are discussed in more detail in section 3.1 of this report.

Numerous ceramographic examinations were performed on gel sphere samples made to define optimum sphere column operation. Figures 5-9 through 5-14 show the effects on sphere appearance of sphere drying time, Ethomeen-S/15 content, and Span-80 content in the organic desiccant. Figure 5-9 shows a gel sphere made with a drying time of 20 minutes (Ethomeen-S/15 = 0.6%, Span-80 = 0.4%), whereas Figure 5-10 shows a gel sphere made with a drying time of 60 minutes (other conditions the same). Higher density and less internal cracking and porosity can be seen in the latter case. Figure 5-11 shows a gel sphere made with the Ethomeen-S/15 content below 0.4% (H_2O = 0.8%, Span-80 = 0.4%), and Figure 5-12 shows a sphere with the Ethomeen-S/15 content at 0.4% (other conditions the same). The last sample shows a marked decrease in internal porosity. Figure 5-13 shows a gel sphere made in the column with 0.4% Span-80 (H_2O = 0.8%, Ethomeen-S/15 = 0.6%), and Figure 5-14 shows a gel sphere made with a Span-80 content of 0.5% (other conditions the same). A marked decrease in internal porosity

and what appears as a soft rim is shown in the last case. These experiments are discussed in detail in section 7.

Ceramographic and alpha autoradiographic examinations are being performed routinely on both gels and oxides. Other characterization methods and apparatus are now available for tap density, subsieve analysis, density via fluid displacement, particle crush strength, and DTA-sorbed gas content.

Ceramography and alpha-autoradiography are useful evaluation tools that have been used to determine the effects of synthesis variables on gel sphere structures. To date, no correlation between microstructure and plutonium pickup has been found, but the plutonium oxidation state influences the homogeneity. Alpha autoradiography indicates that Pu(VI) is not distributed uniformly within oxide spheres, whereas Pu(III) is uniformly distributed.

Routine characterization of ceramic fuels will continue as the need arises during the next report period. The sorbed-gas-content apparatus will be modified to increase its sensitivity, and sorbed gas determinations will be performed on fuel samples.

Figure 5-1. Schematic Diagram of the Particle Crush Strength Test Apparatus

Figure 5-2. Ceramographic Section of Oxide Sphere After Three Contacts With Pu(VI)

150x

Figure 5-3. Alpha Autoradiograph of Oxide Sphere After a Single Contact With Pu(VI)

150x

Figure 5-4. Alpha Autoradiograph of Oxide Sphere After Three Contacts With Pu(VI)

150x

Figure 5-5. Ceramographic Section of Oxide Sphere After a Single Contact With Pu(III)

150x

Figure 5-6. Ceramographic Section of Oxide Sphere After Three Contacts With Pu(III)

Figure 5-7. Alpha Autoradiograph of Oxide Sphere
After a Single Contact With Pu(III)

Figure 5-8. Alpha Autoradiograph of Oxide Sphere
After Three Contacts With Pu(III)

150X

Figure 5-9. Ceramographic Section of Gel Sphere With Short Drying Time (20 minutes)

150X

Figure 5-10. Ceramographic Section of Gel Sphere With Near-Optimum Drying Time (60 minutes)

Figure 5-11. Ceramographic Section of Gel Sphere With Low Ethomeen-S/15 Content ($<0.4\%$)

Figure 5-12. Ceramographic Section of Gel Sphere With Near-Optimum Ethomeen-S/15 Content (0.4%)

150x

Figure 5-13. Ceramographic Section of Gel Sphere With Low Span-80 Content (0.4%)

150x

Figure 5-14. Ceramographic Section of Gel Sphere With Near-Optimum Span-80 Content (0.5%)

in this task will contain at least one pin having high density pellets and two pins with particulate fuel. Thus, particulate fuel can be compared directly with pellets of similar smeared densities.

6.1.2. Sorbed Gas Behavior

The rate of gas release from reactor-exposed particulate fuel will be determined. Capsules will be irradiated under static and cyclic power conditions at different heat rates. The pressures within the fuel pins will be monitored continuously to determine the extent of the gas release and the approximate average fuel temperature at which the release occurs. Some of the irradiations will be continued for about 30 days to determine whether the gases are reabsorbed by the fuel and/or cladding.

6.1.3. EBR-II Tests

The EBR-II irradiations are designed to obtain statistical data on fuel performance in a fast reactor. In this program the overall irradiation performance of gel-addition fuel will be evaluated at two different heat rates. Coprecipitated and/or sol-gel fuels will be compared with gel-addition fuel at only one heat rate. Prototypic bundle irradiations will be required to qualify particulate fuel fully. Part of the EBR-II irradiations could possibly be included in this bundle irradiation.

6.1.4. Thermal Conductivity of the Restructured Fuel

The thermal conductivity of restructured fuel will be determined. The scope of this subtask will be more clearly defined after a thorough review of the national program.

6.1.5. Sodium-Fuel Compatibility

This subtask is designed to determine the compatibility of particulate fuel with the sodium coolant. There are two potential types of fuel pin defects: those occurring during the initial startup when the sodium can infiltrate the as-fabricated powder, and those occurring after the fuel has been restructured.

The effect of sodium infiltration on sodium logging and sodium-fuel compatibility can be determined in static capsules. However, it will be difficult to assess fully, in a static capsule, sodium fuel

6. IRRADIATION TESTING (C. J. Baroch)

6.1. Program Description (C. J. Baroch, E. N. Harbinson)

During the past quarter the objectives of the irradiation task were broadened to include the evaluation of spherical and angular particles of $\text{PuO}_2\text{-UO}_2$. Fuels in the form of spherical particles (such as those produced by the Gel-Addition or Sol-Gel processes) and angular particles (such as those produced from crushed pellets) are included in the program. Data on thermal conductance, transient behavior, fuel swelling, gas release, and compatibility with the coolant will be required to qualify particulate fuels for use in an LMFBR.

A comprehensive program involving irradiations in thermal reactors, TREAT, and EBR-II is considered necessary to provide the data. The irradiation testing program is divided into six subtasks:

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

The objectives of each of these subtasks are identified below. Because some of the data required will be obtained from the national program, it was not possible to establish the scope of each subtask during the past quarter. The scope of each subtask will be established more adequately after the national program has been thoroughly reviewed.

6.1.1. Time Required for Inpile Restructuring

The effect of heat rate and time on the restructuring characteristics of gel-addition and sol-gel spheres and angular particles prepared from coprecipitated $\text{PuO}_2\text{-UO}_2$ will be determined. Each capsule

compatibility after restructuring occurs, because the coolant flow rate and the solubility of $\text{PuO}_2\text{-UO}_2$ in sodium could significantly affect the extent of the interaction. Hence, the current programs will only evaluate the effect of the infiltration. The effect of the fuel rod failure late in life is best evaluated in an inpile sodium loop, but outpile studies on defected exposed fuel will yield valuable data.

6.1.6. Transient Tests

Data are required to define the effects of transients on the fuel movement in its as-fabricated and restructured conditions and to establish the allowable transients in each case. Transient testing of fuel during operation at temperature is also required to define further the operational limitations. The required testing will be established after the national program has been evaluated more thoroughly.

6.2. Capsule Design

The design of the capsules for the irradiations under subtask 1, Time for Restructuring, is complete. A hazards report covering the short-term irradiations is complete and has been submitted for review; approval should be received during the next report period.

Because of the uncertainties in the nuclear and thermal calculations, it was considered advisable to irradiate a calibration capsule. This capsule will be irradiated for short periods of time in various locations in the BAWTR. Hot cell examination of this calibration capsule is not planned, because it is only intended to verify nuclear and thermal calculations and to provide data for the design of subsequent capsules. The calibration capsule will be identical to those used to determine the time for restructuring. However, sintered pellets with a smeared density of 85 to 87% were used in place of vibratory-compacted powder. The calibration capsule is being fabricated and should be ready for irradiation in December.

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

Detailed descriptions of the processes and apparatus used for preparing UO_2 gel spheres have appeared in the earlier reports in this series.¹⁻⁴ The ORNL formate flow sheet, which has been followed closely, is summarized in Figure 7-1.

In the last report of this series several values were given for the flow sheet variables used in B&W work.⁴ Subsequent to the issuance of the report, some of the values were remeasured; the corrected quantities are given in Table 7-1 and have been entered in Figure 7-1. It was also stated incorrectly that changes suggested by Whatley⁵ were incorporated into the flow sheet; rather, Whatley's suggestions were listed to show the variations that may be introduced by different authors as the experimental progress is made on sol preparations.

Table 7-1. Sol Preparation Conditions,
Runs 20 Through 50

	<u>McBride</u>	<u>B&W</u>
Uranium concentration, input uranyl nitrate, moles/liter	0.5	1.118
Nitrate/uranium mole ratio, input uranyl nitrate	4.3	4.06
Urea/uranium mole ratio, input uranyl nitrate	0.5	0.42
Formate/uranium mole ratio at precipitation step	0.6	0.59
Wash solution volume, liters/gm uranium	0.3	0.02

Figure 7-1. UO_2 Sol Preparation

Fifty sol batches have been prepared. The results of the first 22 batches were given in two previous reports in this series.^{2,4} The results for batches 23 through 50 are given in Table 7-2 and are discussed below.

7.1. UO_2 Sol Preparation

(E. J. Kosiancic, R. V. Carlson, C. A. Burkart)

The reduction of 28 batches of uranyl nitrate was attempted; 27 batches were reduced to the tetravalent state. Fourteen good sols and one fair sol were produced; the other 12 were unstable and could not be used in the sphere-forming process.

Ten of the last 12 batches yielded stable sols. Since the same flow sheet was used for all runs, the reasons for the sudden improvement in stability must lie in the technique. Two possible explanations are available: First, the reduction times were generally longer, hence a more complete reduction may have occurred. According to Whatley,⁵ a longer reduction time may be necessary for complete reduction, since it has been observed that a new, unused catalyst is less active than one previously used and washed (see note e, Table 7-2). In any case, it would appear that the reduction step in the flow sheet may have a strong influence on the final product. Second, all 11 of the last precipitation cakes were well washed with 6 liters of demineralized water; most of the earlier batches were washed with considerably less water. This parameter does not appear to be the only one of importance, since 7 other batches were also washed with 6 liters of water; but only 3 of these yielded good sols. The results would indicate a need for a well-washed precipitation cake.

Sol batches 39 through 50 (with the exception of batches 40 and 43) were blended together to give a uniform feed for a large run in the sphere-making equipment.

7.2. UO_2 Gel Sphere Preparation (R. V. Carlson)

The UO_2 gel spheres prepared from sol batches 11 through 37 have been subjected to ceramographic and microscopic examinations. These indicated that there are wide variations in the amount and size of pores (>3 microns diameter) and the degree of surface and interior cracking, not only in spheres from different batches, but also in spheres from the

same batch. On the basis of an examination of ORNL spheres,* which were also synthesized from precipitation-peptization prepared sols, it was decided that the exterior of the desired product should be smooth and spherical and that the interior should be free from any cracking or porosity over 3 microns in diameter.** In an effort to optimize the synthesis variables, a number of 10 to 25-gram batches of spheres were prepared on both the bench scale and the pilot plant scale columns and were examined ceramographically and microscopically. The variables studied include the water, Span-80, and Ethomeen-S/15 content of the 2-EH; residence time in the organic; and drying conditions after removal from the column. In each set of runs, one parameter was varied over a reasonable operating range and the others were held constant near their apparent optimum value.

The spheroidizing test results indicated that the amount of cracking depends mainly on the water content of the organic desiccant, and that an acetone wash of the raw gel did not produce adverse effects if air was excluded. The amount of internal porosity apparently depends on the surfactant content in the organic, but this point requires further study.

Added details of the tests are given in the following paragraphs.

7.2.1. Water Content in 2-EH

The amount of sphere breakage and cracking varied inversely with the water content up to a value of 0.5 vol %. This is presumably because the exterior dries too rapidly and becomes too rigid to shrink properly as the interior dries. From 0.5 to 1.0 vol % water, the product appeared to be satisfactory.

7.2.2. Span-80 Content in 2-EH

The spheres appeared to be satisfactory with a Span-80 content from 0.5 to 0.7 vol %. Outside this range the product was deformed, and there was a marked increase in the amount of internal

*Provided by Dr. R. G. Wymer, Chemical Technology Division, Oak Ridge National Laboratory.

**Subsequent samples purchased from ORNL did not meet these criteria.

porosity. Even though the Span-80 content was varied from 0.1 to 1.0 vol %, very few spheres prepared in this set of runs were cracked (see Figures 5-13 and 5-14).

7.2.3. Ethomeen-S/15 Content in 2-EH

With an Ethomeen-S/15 content from 0.4 to 0.7 vol %, the amount of internal porosity was at a minimum, and from about 0.55 to about 0.75 vol %, the gel particles were nearly spherical. At less than 0.3 vol % Ethomeen-S/15, a large number of the spheres were cracked. However, from 0.3 to 0.9 vol %, very few cracked spheres were observed (see Figures 5-11 and 5-12).

7.2.4. Column Residence Time

From a series of runs with the water content at 0.8 vol %, it was observed that with a drying time of less than 40 minutes, the surface of the gel was badly pitted and generally badly cracked (see Figures 5-9 and 5-10). Of course, the proper column residence time is highly dependent on the water content in the 2-EH. Therefore, the results give only a qualitative indication of the effect of too short a drying time.

7.2.5. Acetone Washing and Oven Drying

The spheres prepared in each of three runs were split into four batches which were dried under one of the following sets of conditions:

1. By pulling N_2 through them for several hours.
2. By pulling N_2 through them and then heating in an N_2 atmosphere (125 C, 15 in. Hg) for about 18 hours.
3. By washing in acetone and then pulling N_2 through for several minutes.
4. By washing in acetone, pulling N_2 through for several minutes, and then heating in an N_2 atmosphere (125 C, 15 in. Hg) for about 18 hours.

As long as the gel was not exposed to oxygen until it was completely dry, no cracking or internal porosity was observed.

Table 7-2. Summary of Batch Preparation of U(IV) Gel Microspheres Using the ORNL Formate Process

Batch No. :	23	24	25	26	27	28	29
Uranium, gm	211	211	211	211	211	211	211
UO ₂ (NO ₃) ₂ , ml	750	750	750	750	750	750	750
Urea, gm	30.01	30.34	30.68	30.09	29.99	30.03	30.00
Pt on alumina, gm	2.60	2.70	2.62	2.69	2.82	2.82	2.57
Total volume of solution, ml	900	900	900	900	900	900	900
Standard hydrogen flow, cc/min	375	375	375	375	375	375	375
Reduction time, hr	7 ^(a)	6	4	5	4.5	4.5	4.5
89.5% formic acid, ml	30	30	30	30	30	30	30
Precipitation time, hr	2.0	2.0	1.25	1.5	1.25	1.5	2.5
Volume of wash water, l	4	4	4	4	4	4	4
Cake drying time, min ^(c)	10	10	10	10	15	10	10
Volume of U(IV) sol, ml	550	550	550	550	550	550	550
Sol condition	Fair	Poor	Poor	Poor	Poor	Good	Poor
Yield of spheres, gm	85 ^(b)	--	--	--	--	154	--
U(NO ₃) ₄ solution							
U(IV)/U (total), %	99.8	97.6	99.8	99.9	96.4	97.8	96.8
U, mg/ml	237	227	NA	247	254	251	285
NO ₃ /U mole ratio	3.8	2.2	2.3	3.7	3.22	3.52	2.91
pH after reduction							
U(IV) sol							
U(IV) content, %	74.4	72	52	49.5	66.6	NA	NA
U content, wt %	20.7	22.0	25.0	27.5	26.0	NA	NA
NO ₃ /U mole ratio ^(g)	0.1	2.5	0.1	0.035	0.064	NA	NA
U(IV) spheres							
U(IV) content, %	NA	--	--	--	--	75.7	--
U content, wt %	NA	--	--	--	--	79.3	--
NO ₃ /U mole ratio	NA	--	--	--	--	0.027	--

(a) Left under H₂ blanket for 48 hours.

(b) Large portion of the sol was spilled.

(c) Dried under a stream of N₂ at room temperature.

(d) New UO₂(NO₃)₂ stock solution.

(e) New catalyst used for each run instead of washing between runs.

(f) Sol batches mixed for use in statistical experiments.

(g) The method used for this analysis has been shown to be inadequate.

(h) Sol batches mixed for use in statistical experiment.

(i) Did not reduce in 24 hours.

NA: Not available.

Table 7-2. (Cont'd)

Batch No.:	30	31	32	33	34	35 ^(d)	36
Uranium, gm	211	211	211	211	211	211	211
UO ₂ (NO ₃) ₂ , ml	750	750	750	750	750	750	750
Urea, gm	30.13	30.09	29.97	30.10	30.01	29.99	29.99
Pt of alumina, gm	2.32	2.69	2.91	2.60	2.58	2.61	2.58
Total volume of solution, ml	900	900	900	900	900	900	900
Standard hydrogen flow, cc/min	375	375	375	375	375	375	375
Reduction time, hr	2.5	2.5	2.5	3.5	3.0	2.5	3
89.5% formic acid, ml	30	30	30	30	30	30	30
Precipitation time, hr	1.25	1.5	2.0	1.5	1.5	1.5	NA
Volume of wash water, l	4	6	6	6	6	6	6
Cake drying time, min ^(c)	10	10	10	15	15	10	10
Volume of U(IV) sol, ml	550	550	550	550	550	550	550
Sol condition	Poor	Poor	Poor	Good	Good	Good	Poor
Yield of spheres, gm	--	--	--	150	177	233	--
U(NO ₃) ₄ solution							
U(IV)/U (total), %	97.5	96.7	98.0	97.9	97.2	98.8	98.6
U, mg/ml	263	275	230	219	281	240	254
NO ₃ /U mole ratio	3.31	3.77	3.48	3.17	2.31	2.74	3.46
pH after reduction							
U(IV) sol							
U(IV) content, %	NA	NA	69.3	75.2	75.9	78.7	74.4
U content, wt %	NA	NA	24.6	23.4	20.6	24.0	21.7
NO ₃ /U mole ratio ^(g)	NA	NA	0.077	0.051	0.116	NA	NA
U(IV) spheres							
U(IV) content, %	--	--	--	NA	NA	NA	--
U content, wt %	--	--	--	NA	NA	NA	--
NO ₃ /U mole ratio	--	--	--	NA	NA	NA	--

(a) Left under H₂ blanket for 48 hours.

(b) Large portion of the sol was spilled.

(c) Dried under a stream of N₂ at room temperature.(d) New UO₂(NO₃)₂ stock solution.

(e) New catalyst used for each run instead of washing between runs.

(f) Sol batches mixed for use in statistical experiments.

(g) The method used for this analysis has been shown to be inadequate.

(h) Sol batches mixed for use in statistical experiment.

(i) Did not reduce in 24 hours.

NA: Not available.

Table 7-2. (Cont'd)

Batch No.:	37	38	39	40	41 ^(e)	42 ^(c)	43 ^(e)
Uranium, gm	211	211	211	211	211	211	211
UO ₂ (NO ₃) ₂ , ml	750	750	750	750	750	750	750
Urea, gm	29.98	30.00	29.36	30.00	30.00	30.00	30.00
Pt on alumina, gm	2.66	2.60	2.68	2.59	2.60	2.60	2.59
Total volume of solution, ml	900	900	900	900	900	900	900
Standard hydrogen flow, cc/min	375	375	375	375	375	375	375
Reduction time, hr	2.5	13.5	16	(i)	8	8.5	8.25
89.5% formic acid, ml	30	30	30	--	30	30	30
Precipitation time, hr	1.5	1.5	1.0	--	1.25	1.0	1.0
Volume of wash water, l	6	4	6	--	6	6	6
Cake drying time, min ^(c)	10	10	10	--	30	60	60
Volume of U(IV) sol, ml	550	550	550	--	550	550	550
Sol condition	Poor	Poor	Good	--	Good	Good	Poor
Yield of spheres, gm	--	--	(f)	--	(f)	(f)	--
U(NO ₃) ₄ solution							
U(IV)/U (total), %	98.7	99.3	92.5	--	NA	99.3	99.4
U, mg/ml	236	270	221	--	NA	231	250
NO ₃ /U mole ratio	3.98	2.77	4.32	--	NA	4.48	4.02
pH after reduction							
U(IV) sol							
U(IV) content, %	77.4	77.6	NA	--	NA	NA	NA
U content, wt %	22.3	23.5	NA	--	NA	NA	NA
NO ₃ /U mole ratio ^(g)	NA	NA	NA	--	NA	NA	NA
U(IV) spheres							
U(IV) content, %	--	--	(h)	--	(h)	(h)	--
U content, wt %	--	--	--	--	--	--	--
NO ₃ /U mole ratio	--	--	--	--	--	--	--

(a) Left under H₂ blanket for 48 hours.

(b) Large portion of the sol was spilled.

(c) Dried under a stream of N₂ at room temperature.(d) New UO₂(NO₃)₂ stock solution.

(e) New catalyst used for each run instead of washing between runs.

(f) Sol batches mixed for use in statistical experiments.

(g) The method used for this analysis has been shown to be inadequate.

(h) Sol batches mixed for use in statistical experiment.

(i) Did not reduce in 24 hours.

NA: Not available.

Table 7-2. (Cont'd)

Batch No. :	44 ^(e)	45 ^(e)	46 ^(e)	47 ^(e)	48 ^(e)	49 ^(e)	50 ^(e)
Uranium, gm	211	211	211	211	211	211	211
UO ₂ (NO ₃) ₂ , ml	750	750	750	750	750	750	750
Urea, gm	30.00	30.00	30.00	30.00	30.00	30.00	30.00
Pt on alumina, gm	2.60	2.60	2.60	2.61	2.60	2.60	2.60
Total volume of solution, ml	900	900	900	900	900	900	900
Standard hydrogen flow, cc/min	375	375	375	375	375	375	375
Reduction time, hr	8.5	9.0	8.5	8.5	8.5	8.5	8.5
89.5% formic acid, ml	30	30	30	30	30	30	30
Precipitation time, hr	1.25	1.25	1.25	1.25	1.0	1.0	1.0
Volume of wash water, l	6	6	6	6	6	6	6
Cake drying time, min ^(c)	20	20	15	15	15	15	15
Volume of U(IV) sol, ml	550	550	550	550	550	550	550
Sol condition	Good	Good	Good	Good	Good	Good	Good
Yield of spheres, gm	(f)	(f)	(f)	(f)	(f)	(f)	(f)
U(NO ₃) ₄ solution							
U(IV)/U (total), %	99.6	99.5	99.2	99.1	99.4	98.6	98.6
U, mg/ml	240	234	230	226	230	221	228
NO ₃ /U mole ratio	3.68	3.84	4.3	4.47	4.18	4.18	4.25
pH after reduction							
U(IV) sol							
U(IV) content, %	NA	NA	NA	NA	NA	NA	NA
U content, wt %	NA	NA	NA	NA	NA	NA	NA
NO ₃ /U mole ratio ^(g)	NA	NA	NA	NA	NA	NA	NA
U(IV) spheres							
U(IV) content, %	(h)	(h)	(h)	(h)	(h)	(h)	(h)
U content, wt %	--	--	--	--	--	--	--
NO ₃ /U mole ratio	--	--	--	--	--	--	--

(a) Left under H₂ blanket for 48 hours.

(b) Large portion of the sol was spilled.

(c) Dried under a stream of N₂ at room temperature.(d) New UO₂(NO₃)₂ stock solution.

(e) New catalyst used for each run instead of washing between runs.

(f) Sol batches mixed for use in statistical experiments.

(g) The method used for this analysis has been shown to be inadequate.

(h) Sol batches mixed for use in statistical experiment.

(i) Did not reduce in 24 hours.

NA: Not available.

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