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GEL-ADDITION PROCESS CHEMICAL STUDIES

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ABSTRACT

Development of the Gel-Addition Process for mixed urania-plutonia fuels has continued. UO_2 sols have been prepared by the ORNL Formate Process. Gel spheres were made by drying sol droplets in a recirculating column containing a 2-ethyl hexanol bath. Carbon analyses at various steps show that at least half the carbon added (as urea and formate during sol preparation) remains in the sol. Gelation roughly triples the carbon level (C/U atoms ratio in gel = 1.5). A study of the gelation bath composition showed that nitrated organics do not appear in sufficient quantity to constitute a hazard.

Oxidation of Pu(IV) to Pu(VI) by nitrate has been confirmed to be first order in Pu(IV). Apparent half-times have been measured at 30 minutes and 10 minutes.

Plutonium pickup by UO_2 gel has been found to be extremely rapid. In contacting runs lasting between 10 and 20 seconds, Pu/U+Pu reached several percent from Pu(IV) solutions.

Ceramographic procedures have been developed for polishing and photographing unfired gel. Most gel samples examined show cracking.

Capsule design for in-pile testing of mixed oxide is complete.

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

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1. INTRODUCTION

This is the fourth quarterly 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 fuels.

The Gel-Addition Process was derived from sol-gel technology developed at Oak Ridge National Laboratory, and differs from it in that a single-component fertile sol, such as UO_2 , is prepared and converted to a single-component gel. (The original sol-gel process involves a two-component sol and gel.) The finished fuel is made by soaking the gel in an aqueous solution of fissionable material and firing the mixed gel to the oxide. The mechanism responsible for addition to the 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.

The project is supported by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3714; this report covers the period April 1 to June 30, 1967.

2. CONCLUSIONS

2.1. UO₂ Gel Preparation

The ORNL Formate Flow Sheet has been generally followed for UO₂ sol preparation. The process yields stable sols if the prescribed solution compositions and wash conditions are carefully followed. Sol instability results, particularly if acid depletion is too large during the U(VI) → U(IV) reduction step or if the "uranous hydroxide" precipitate is insufficiently washed.

The organic content of UO₂ gel is surprisingly high. Carbon/uranium atom ratios as high as 1.5 have been observed for raw gel. Acetone washing reduces the ratio to only about 1.0; vacuum heating at 225 C overnight reduces the ratio to about 0.6. About two-thirds of the organic content of the gel appears during the gelation step; the other third is already present in the washed filter cake used for sol preparation. The organic matter in the sol occurs both from formate added during the precipitation step and from urea added to the input uranyl nitrate before the U(VI) → U(IV) reduction. Gel spheres with diameters of about 800 microns are in routine preparation.

2.2. Pu(VI) Preparation

The preparation of Pu(VI) by nitrate oxidation is convenient and rapid. In its opening stages the reaction appears to be first order in Pu(VI), and the apparent half-time for the current series of experiments was about 30 minutes. Earlier measurements on solutions of different history gave an apparent half-time of about 10 minutes. The cause for the variation has not yet been established.

2.3. Gel Contacting

The pH of an acid solution contacted with UO₂ gel rapidly rises to about pH 3 and does not show any tendency toward saturation. As fresh acid is added, the pH rise continues to recur. This behavior is con-

sistent with a simple acid-base reaction between a strong acid and a hydrated metal oxide.

Large-diameter spheres ($\approx 800\mu$) have been used as a packed bed column for plutonium contacting. Pu(IV) pickup in a triple contacting using 10 gm of UO_2 gel and three fresh aliquots (15 ml each) of Pu(IV) gave about 2% (Pu/U+Pu) pickup in a total contact period of 60 seconds. Passing the same 20 ml aliquot three times through an 11-gram packed bed gave a pickup of about 2.4% (Pu/U+Pu) in 40 seconds total contact time.

2.4. Oxide Characterization

Abrasion tests involving self-abrasion of oxide spheres prepared by adding Pu(IV) to UO_2 gel show good agreement between the plutonium assay of fines and larger fragments. This is consistent with a negligible concentration gradient along the sphere radius. Autoradiographic studies indicate a uniform distribution of plutonium in both gel and oxide material prepared by contacting UO_2 gel with Pu(IV) solution.

2.5. Nitrogen Compounds in Contacted 2-EH

Some concern has been expressed over the possibility that gel prepared by injecting UO_2 sols into a column of 2-ethyl hexanol (2-EH) will give rise to unstable nitration byproducts through reaction of the nitrate in the sol with either 2-EH or the surfactants added to it. Since 2-EH can be recovered continuously by distillation methods, the accumulation of nitrogenous matter could be hazardous. Infrared and gas chromatographic analysis of used organics has demonstrated that if any nitrated compounds are generated, the quantity is well below hazardous levels for industrial operations.

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

3.1. UO₂ Gel Sphere Preparation

Previous reports in this series contain detailed descriptions of the processes and apparatus used for preparing UO₂ gel spheres.^{1,2,3} With a few minor exceptions, which have been noted, the ORNL flow sheet has been followed; the principal features are given in Figure 3-1.

The results of the first 10 experimental batches are given in BAW-3714-2;² similar data for batches 11 through 22 are reported in the following paragraphs.

3.1.1. UO₂ Sol Preparation (E. J. Kosiancic, C. A. Burkart)

Twelve batches of uranyl nitrate were reduced to the uranous form. Of these, seven were successfully converted to UO₂ sols. The remainder did not yield stable sols, and it is now suspected that an exceptionally large increase in pH during the U(VI) → U(IV) reduction may account for the difficulty in some runs.

The reaction of uranyl nitrate with hydrogen to give stoichiometric uranous nitrate can be written:

Since nitric acid is consumed, there is an accompanying pH increase, and to keep the pH from rising too far, free nitric acid is added to the mixture. Nitric acid and nitrate are also reducible by hydrogen; hence, over-reduction of the sample may increase the pH rise even further. It is therefore desirable to terminate the run as soon as the uranium reduction is complete. At the present time tests for the residual uranyl ion are carried out* as the reduction progresses. A negative result

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*An aliquot of the uranium solution is treated with oxalate to precipitate the large excess of quadrivalent uranium; ferrocyanide is added to the supernate, and if any uranyl ion remains, a brown precipitate forms.

Figure 3-1. UO_2 Sol Preparation

shows complete reduction, and the run is terminated. The measured pH of solutions that give good sols is about 0.3.

The loss of some runs was also reported by Whatley⁴ of Oak Ridge, who recommended changes in the basic flow sheet as follows:

1. Substitute formic acid for urea as the holding reductant in the first step.
2. Precipitate the hydroxide at a higher pH (9 instead of 7).
3. Wash all nitrate from the filter cake, and add free nitric acid to bring the nitrate level to the required value.

These changes were incorporated into the flow sheet, and runs 20 through 22 were made using the compositions shown in Table 3-1. The Oak Ridge values as given by McBride⁵ are also shown for comparison; the characteristics of the resulting sols are compared in Table 3-2.

Table 3-1. Sol Preparation Conditions, Runs 20 Through 22

	<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	3.94
Urea/uranium mole ratio, input uranyl nitrate	0.5	0.44
Formate/uranium mole ratio, at precipitation step	0.6	0.54
Wash solution volume, liters/gm uranium	0.3	0.02

Table 3-2. Comparison of Sol Properties

	<u>McBride</u>	<u>B&W</u>
pH	1.9 - 3.0 ^(a)	1.80 - 2.02
U(IV) content	84 - 98	76 - 79
Nitrate/uranium mole ratio	>0.1 ^(b)	<0.1

(a) One sol in the series gave a pH of 6.0; it was unstable and could be described better as a hydrous oxide suspension.

(b) Three samples of fourteen reported showed nitrate/uranium ratios of less than 0.1.

There are two main differences between the Oak Ridge and the B&W conditions outlined above. The first is the input uranium concentration (0.5M for ORNL, 1.0M for B&W), and the second is the water wash value (ORNL uses a 50% larger volume). Both these changes were made to raise the throughput without a corresponding increase in solution volumes, and it is still too early for a complete evaluation of their net effects.

3.1.2. Sphere Formation and Treatment

Some sphere-making and finishing steps in gel production have been reexamined during this reporting period. The tests to be described were initiated primarily to determine the variations in the carbon content of finished gels, since some process procedures are changed.

3.1.2.1. Carbon Sources

Carbonaceous matter is introduced at several points in the sol-gel process. In the first step of the procedure, uranyl nitrate is reduced to the uranous form in the presence of urea added to react with traces of nitrite present in the starting materials or which may form as a byproduct of uranium reduction. The reaction between urea and nitrite is rapid and quantitative and is commonly used by organic chemists to destroy nitrous acid residues. At the end of the reduction, formic acid is added and the uranium is precipitated with ammonia. The urea and formate distribute between the waste supernate and the precipitate. Some will remain with the UO_2 filter cake even after the washing steps. In fact, Hardy⁶ attributes the beneficial effects of formate to its complete coverage of the individual UO_2 crystallite surfaces during the conversion of the uranium filter cake to UO_2 sol.

Sphere formation involves the gelation of sol droplets suspended in an organic drying bath.* The freshly prepared gel is saturated with drying bath components and also contains some quantity of organics from the sol preparation steps. To remove most of the organics, gels are routinely washed in acetone. The final product

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* 2-ethyl-1-hexanol containing surfactant additives.

thus contains organics that were not removed in the acetone rinse, water that was not removed by the drying bath, and acetone.

Several finished gel samples were analyzed for carbon. The results showed that gels can easily measure 5 wt % carbon (1.5 atoms of carbon/atom of uranium), confirming the 2 to 4% reported by McBride⁵ for gels washed in methanol and dried.

A few tests were run on batch 19 (see Table 3-3) materials to indicate the major sources of organics. The C/U mole ratio from added urea in the original uranyl nitrate measured 0.34. Two aliquots were precipitated after the reduction; the first contained no added formic acid, and the second contained enough formic acid to give a formate/U mole ratio of 0.45. Both samples were precipitated with ammonia and converted to filter cakes. The washed cakes were sampled and assayed for carbon.

A C/U mole ratio of 0.16 was found for the precipitation carried out in the absence of formate, indicating that at least half of the urea in the system remained in the washed filter cake. The actual quantity could be much higher because an unknown portion of the input urea was probably converted to CO₂ during the uranium-reduction step.

The precipitation carried out in the presence of formate showed a C/U atom ratio of 0.40. Since there was an upper limit of 0.80 atom C/atom U (0.35 from urea, 0.45 from formate) in the uranous nitrate solution, at least half of the total carbon again remained in the washed filter cake. In the latter experiment there was no way to determine what fraction of the total observed carbon came from urea and from formate. A tracer experiment using C-14 tagged urea and formate would be very informative.

3.1.2.2. Vacuum Drying

Raw gel spheres are rigid and sufficiently dry to permit easy handling, but the organic and water contents probably vary from batch to batch, and in any event dehydration is incomplete.

To note the effects of more vigorous drying conditions, one gel sample (24 g, batch 14) was vacuum dried at 225 C. The drying oven used is an item of standard manufacture (National Appliance Company, Portland, Oregon) with an interior volume of about

Table 3-3. Summary of Batch Preparations of U(IV) Gel Microspheres Using ORNL Formate Process

	Batch											
	11	12	13	14	15	16	17	18	19 ^(d)	20 ^(h,i)	21	22
Uranium, gm	182.5	175.5	175.5	175.5	175.5	175.5	175.5	175.5	175.5	211.5	211.5	211.5
UO ₂ (NO ₃) ₂ , ml	780	750	750	750	750	750	750	750	750	750	750	750
Urea, gm	14.7	20.03	20.00	14.69	15.04	14.84	14.64	14.79	15.17	29.99	29.99	30.02
Pt on Al ₂ O ₃ catalyst, gm	1.25	1.75	1.75	1.73	1.78	2.69	2.28	2.35	2.60	2.60	2.60	2.58
Total volume of solution, ml	944.2	900	900	900	900	900	900	900	900	900	900	900
Hydrogen flow rate, std cc/min	300	300	300	300	300	375	375	375	375	375	375	375
Approx reduction time, hr	32.5 ^(j)	25	27	6	8	4	9	5	6	7.5	6	6
Formic acid (89.5%), ml	17	20	20	27	20	17	17	17	17	30	30	30
Precipitation time, hr	3.25	1.0	2.5	1.75	1.0	4	2.5	2	2.5	3	2	2
Volume of wash water, ml	1000	4000	4000	4000	3000	3400	4000	3000	4000	4000	4000	4000
Approx drying time on filter, min	15	10	10	10	10	12	12	10	10	10	10	10
Approx vol of U(IV) sol, ml	500	500	550	450	500	500	500	500	500	550	550	550
Yield of gel spheres, gm	126 ^(a)	None ^(b)	127	125	None ^(b)	219	None ^(b)	None ^(b)	None ^(c)	150	125	150
Uranous nitrate solution												
U(IV)/U total, %	NA		99.4	97.2	96.7	99.1	98.1	97.3	99.2	99	99.8	99.9
U, mg/ml	NA		196	197	200	208	206	203	201	258	230	250
Nitrate-to-uranium mole ratio	NA		4.33	4.93	2.7	4.45	4.2	4.7	4.5	6.05	2.4	3.3
pH of solution after transfer	0.34	NA	0.35	0.93	0.24	0.61	0.14 ^(g)	0.16	0.35	1.1	1.1	2 ^(e)
U(IV) sol												
U(IV) content, U(IV)/U total, %	71.3	85.4	71.4	81.5	78.8	81.2	53.3	62.3	73.9	76.4	78.4	77.8
Uranium content, wt %	20.4	21.9	25.8	19.3	26	21.7	25.7	21.7	26.3	29.9	21.0	25.5
Nitrate-to-uranium mole ratio	0.041	0.077	0.174	0.14	0.42	0.18	0.08	0.037	0.58	0.08	0.1	0.1
pH		NA								1.80	1.83	2.02
U(IV) gel microspheres												
U(IV) content, U(IV)/U total, %	70.7	NA	72.9	76.8 ^(f)	NA	83.6	NA	NA	NA	77.7	82.6	80.7
Uranium content, wt % U	71.0	NA	72.6	85.8	NA	64.3	NA	NA	NA	64.9	71.4	62.5
Nitrate-to-uranium mole ratio	0	NA	Undetected	0.05	NA	0.22	NA	NA	NA	0.45	0.6	0.4

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

(b) Sols were unstable.

(c) Sols tended to gel before being added to sphere column.

(d) New catalyst used, obtained from Matheson Coleman & Bell (5% Pt on Alumina #PX 1267-2).

(e) pH electrode broken—hydronium paper used.

(f) Later analysis performed when determining C/U, % U = 75.1.

(g) pH electrode not functioning properly.

(h) Sol did not form spheres readily.

(i) New input uranium solution, 282 mg U/ml.

(j) Stirring rod broke during the reduction.

1.5 ft³. The furnace was purged with tank nitrogen for 20 minutes at 20 SCFH, and the nitrogen-purged sample was introduced as rapidly as possible while maintaining the nitrogen flow. After the door was closed, the oven was purged for an additional 5 minutes, and then the nitrogen flow was reduced ten-fold to 2 SCFH. The vacuum pump was turned on and a steady vacuum of 27 in Hg was maintained. The oven was held overnight at 225 C.

During the heating-drying operation the total weight loss was about 15%, and the carbon content decreased by almost half. The data are summarized in Table 3-4.

Samples of both vacuum-dried and acetone-washed gel are being prepared for microstructural studies.

Table 3-4. Vacuum Drying of UO₂ Gel

	<u>Weight, gm</u>	<u>Carbon content (C/U atom ratio)</u>
Acetone-washed gel	23.7	1.08
Vacuum-dried gel	20.2	0.58
Relative change	-15.6%	-46.2%

3.2. Preparation of Pu(VI) Solutions (E. J. Kosiancic, R. V. Carlson)

3.2.1. Pu(IV) Oxidation Kinetics

Additional information has been obtained on the kinetics of plutonium oxidation by nitrate in dilute nitric acid. Two new batches of hexavalent plutonium were prepared using the techniques described earlier.¹ The conditions were somewhat better controlled in the new runs, however, because the solution volumes were larger.

The two new input solutions were prepared by diluting Pu(IV) stock solution (240.8 mg Pu/ml) with 0.5M nitric acid to give solutions that were 0.27 and 0.29M in total plutonium, respectively. The nominal free acid levels were 1.26 and 1.33M, respectively (see below however), and the total batch volume was about 4000 ml in both cases. For both runs the solutions were equally distributed among

three refluxing assemblies heated independently. In the first run, samples were taken from each setup in succession by removing the apparatus from the heat and waiting 2 minutes for boiling to cease and for the reflux condenser to drain. The 1-ml sample was withdrawn and immediately diluted for analysis to 10 ml with 1M HNO_3 . The time was taken as the actual time that heat was applied. It is, of course, uncertain whether just the boiling (reflux) time or the total time at temperature is the appropriate independent variable in a kinetics plot; in any event the difference is small, and for data analysis the reflux time was chosen because earlier work seemed to indicate that the oxidation rate was accelerated by harder boiling.

Time ambiguities were largely eliminated in the second run. One of the reflux boilers was replaced by a two-necked flask, and all samples were withdrawn from it at intervals without interrupting the heating. Data from these two runs are presented in Table 3-5.

Table 3-5. Pu(IV) Oxidation Kinetics

Reflux time, min	Solution 1 (0.265 M Pu, 1.26 M HNO_3)		Solution 2 (0.29 M Pu, 1.33 M HNO_3)	
	Pu(VII)/Pu(IV) + Pu(VI)	[Pu(VI)]/[Pu(IV)] ₀	Pu(VII)/Pu(IV) + Pu(VI)	[Pu(VI)]/[Pu(IV)] ₀
0	0.0746	1.000	0.014	1.000
7	--	--	0.229	0.782
12	--	--	0.323	0.686
15	0.424	0.622	--	--
17	--	--	0.410	0.589
22	--	--	0.460	0.540
27	--	--	0.513	0.494
30	0.553	0.484	--	--
32	--	--	0.561	0.445
44	0.621	0.344	--	--
45	--	--	0.667	0.336
50	0.760	0.260	--	--
60	--	--	0.745	0.259
73	0.772	0.246	--	--
75	--	--	0.828	0.174
88	0.840	0.173	--	--
92	--	--	0.873	0.129
98	0.834	0.179	--	--
113	0.824	0.190	--	--
128	0.884	0.126	--	--
135	--	--	0.925	0.076
155	--	--	0.944	0.057
174	--	--	0.933	0.066
233	--	--	0.961	0.040
291	--	--	0.971	0.029
298	0.977	0.025	--	--
350	--	--	0.970	0.030
380	--	--	0.978	0.012

These data, plotted in Figure 3-2, show that, at least in the opening stages, the reaction is nearly first order in Pu(IV) with an apparent reaction half time of about 0.5 hour. The earlier work showed an apparent half time nearer 10 minutes.

3.2.2. Pu(VI) Solution Concentration

For gel-addition work, more concentrated solutions are needed than those resulting from the dilute nitric acid oxidations described in the preceding section. Therefore, it was decided to work out a concentrating procedure.

The first experiments were an attempt to precipitate a hydrated oxide by ammonia addition and to follow this with a centrifugation and nitric acid dissolution. The attempt was unsuccessful because the ammonia addition did not result in quantitative precipitation, but instead gave rise to a complex formation, presumably the same as that reported by McVey.⁷ In the second attempt the Pu(VI) solution obtained from the first test described in section 3.2.1 was adjusted to pH 3 by ammonia addition. The volume was reduced by boiling until precipitation occurred. Nitric acid (0.5M) was added to redissolve the precipitate. Although most of the precipitate dissolved, a fine insoluble residue remained. The solution was therefore centrifuged; from its olive-green color the precipitate was assumed to be polymeric Pu(IV), arising from unoxidized material. The remaining solution was again concentrated by heating until precipitation occurred; this second precipitate was easily dissolved by adding drops of 0.5M HNO₃. Finally, the pH was adjusted to 2.2 by adding concentrated aqueous ammonia. The final solution was analyzed spectrophotometrically and found to be 1M in Pu(VI).

3.3. UO₂ Gel-Contacting Experiments (E. J. Kosiancic, R. V. Carlson)

Three sets of experiments are described in the following paragraphs: contacts of UO₂ gels with aqueous solutions containing no plutonium, contact with Pu(IV) stock solution, and contact with Pu(VI) prepared as described in section 3.2. Column-prepared gels (≈800μ diameter) were used.

Figure 3-2. Pu (IV) to Pu (VI) Oxidation Kinetics

3.3.1. Plutonium-Free Solutions

Early work¹ with UO_2 gel spheres prepared by Nuclear Fuel Services showed that acidic solutions undergo a large pH rise during contact with the gel. The same effect is seen with B&W-prepared material, and several experiments have been run to show the magnitude of the effect and to determine whether it can be suppressed. If satisfactory pH stabilizing methods could be found, for example, by pre-treating the gel or by buffering* the solution, the hydrolysis of plutonium would be less troublesome and Pu(IV) solutions would be more useful.

In the first experiments three 10-ml samples of commercial buffers (pH 1, 2, 3) made from KCl-HCl mixtures (0.5 M) were contacted in air with 4-gram samples of UO_2 gel (batch 4, see reference 1, p 3-11). The pH change was measured and the solution was decanted and analyzed for total uranium. The contacted spheres were also recovered and weighed. In all cases there was a rapid rise of about 2 pH units, and the contacted solution appeared gray or greenish, indicating quadrivalent uranium in solution. The first pH measurements were made within 30 seconds of the contacting and the last were made after 1 to 2 hours. Virtually all of the observed pH rise occurred before the first measurement. The data are summarized in Table 3-6.

Table 3-6. pH Changes of Acid Chloride Solutions^(a)
Contacting UO_2 Gel

Initial	Measured pH values	
	t = 30 sec	t = 2 hr
1.0	3.5	3.2
2.0	4.0	3.75
3.0	4.5	4.85
		(measured pH at 1 hr)

^(a) 10 ml of standard KCl-HCl buffer (Fisher Scientific Co.), 0.5M, 4 g UO_2 gel.

* A buffered solution contains dissolved compounds which react with both added acid and alkali and thus resist the natural tendency of the solution to change pH.

In a second set of tests, buffered nitric acid-ammonium nitrate solutions were contacted with UO_2 gel from the same batch and for the chloride tests. The solution was prepared by adding drops of aqueous ammonia to 3 M HNO_3 until pH 1 was obtained. The solution therefore contains about the same concentrations of "extraneous" ions as the plutonium solutions used for gel contacting studies.

Four grams of UO_2 gel were contacted in air with 10 ml of ammonium nitrate buffer for 5 minutes and the pH was monitored. The solution was pulled off and saved for uranium analysis. The spheres were washed with demineralized water and then recontacted with a fresh 10-ml sample of ammonium nitrate buffer, and the pH change was again monitored. This cycle was repeated until the spheres had been contacted with a total of five fresh 10-ml aliquots of buffer. The spheres were recovered and dried overnight at 60 C under 19 cm Hg vacuum. The dried spheres were then treated again with a fresh 10-ml aliquot of buffer. In every contacting a sharp pH rise of about the same magnitude (2 to 2.5 pH units) was observed. All of the solutions had final pH's ranging from 3.1 to 3.5. The uranium content of the first contact solution was large by comparison (≈ 2.4 millimole). The second solution showed much less (≈ 0.75 millimole), and the third, fourth, and fifth solutions even less (the last only 0.23 millimole). The sixth contact solution showed almost as much uranium as the first, which is not surprising since the gel was redried overnight and received considerable air exposure between the fifth and sixth contactings.

The third series of tests was a repeat of the second except that the spheres were dried at 60 C for 1 hour at 19 cm Hg vacuum between contactings. The result was similar to that observed in the second series except that the pH rise was somewhat smaller (about 0.2 pH units less). The amounts of uranium found in the aqueous phase varied widely. The data from the second and third series are given in Tables 3-7 and 3-8.

These tests demonstrate conclusively that UO_2 gel spheres do not become acid-saturated and that the rise in pH cannot be arrested by buffer additions of the types used in these tests.

Table 3-7. pH Changes of Acid Nitrate Solutions Contacted With UO_2 Gel (Successive Contacts With Fresh 10-ml Aqueous Nitrate Aliquots)

Contact	pH of contacting solution			Total uranium in contacted solution, gm	Color of contacted solution
	Start	30 sec	5 min		
	1	--	--	--	Colorless
1	1	3.0	3.4	0.571	Light green-yellow
2	1	3.4	3.5	0.176	Light gray
3	1	3.4	3.4	0.091	Light gray
4	1	3.3	3.3	0.066	Light gray
5	1	3.1	3.1	0.055	Light gray
6	1 ^(a)	3.1	3.55	0.427	Greenish

^(a) Spheres dried overnight in vacuum 60 C between steps 5 and 6.

Table 3-8. Successive Contacts With Fresh 10-ml Aliquots (Spheres Vacuum Dried Between Contacts)

Contact	pH of contacting solution			Total uranium in contacted solution, gm	Color of contacted solution
	Start	30 sec	5 min		
	1	--	--	--	Colorless
1	1	3.1	3.1	0.315	Light green
2	1	3.2	3.3	0.052	Light green-yellow
3	1	3.3	3.3	0.042	Light gray
4	1	2.7	3.0	0.155	--
5	1	3.2	3.2	0.050	Light green

The pH rises observed during the gel-contacting tests can be explained by at least three possible mechanisms:

1. The gel acts as an adsorbent, picking up acid by reactions that are surface-controlled. The pH rise is accounted for by the disappearance of acid from the aqueous phase.

2. The gel acts as an anion exchanger, exchanging hydroxide in the gel for the anions of the acid in the aqueous phase. The rise in pH follows from the appearance of hydroxide in the solution.

3. The gel and acid act as an acid-base system, and the rise in pH is simply the neutralization of dissolved hydrogen ion by the metal oxide (gel), which is considered to be a basic anhydride.

These three mechanisms are distinguishable experimentally. The first gives a reaction in which the equilibrium point is determined by the total effective surface area of the gel crystallites. The second involves the anions only, and a carefully controlled experiment would demonstrate whether a simple stoichiometric relation exists between the appearance of hydroxide (pH rise) and the disappearance of other anions. The third gives a reaction in which the rate of acid disappearance is dependent upon the crystallite size (the reaction is heterogeneous), but in which the eventual equilibrium point is dependent only upon the identity of the gel metal ions. Moreover, in this last case, soluble cations of the gel metal ion can be expected in the aqueous phase, and demonstration of a stoichiometric relation between the appearance of dissolved cations and the disappearance of the hydrogen ion would constitute a proof of mechanism 3. This same mechanism can also be proved by a different approach; both mechanisms 1 and 2 should show a saturation effect; that is, a second fresh aqueous phase contacted with the gel ought to show a smaller decrease in the hydrogen ion by either ion exchange or adsorption as the solid phase saturates. In mechanism 3 the pH rise will continue as long as there is any gel left.

The data in Tables 3-7 and 3-8 are clearly consistent with a simple acid-base reaction, but the stoichiometric relations are still in doubt and will be checked in further experiments.

3.3.2. Pu(IV) Solutions

In a previous report² it was mentioned that 800-micron spheres are badly broken up when shaken by the same techniques used

earlier on spheres prepared by stirred-pot methods. A series of contacting tests with Pu(IV) solutions has been made using packed bed columns operated in much the same way that ion exchange columns are used. The bed sizes were approximately 1/2 inch diameter by 5 inches long, and the solutions were pulled through by vacuum. A stopcock was included to provide for flow rate adjustments. Effluent could be recycled at will. Changing to a column provided two new experimental aspects: Exceptionally short contact times became feasible, and the gentler treatment gave less sphere fracture. In addition to these column tests, one additional shaker test was run to provide material for a grinding study.

Six column tests have been run, all on batch-13 gel spheres. The first three used acetone-washed spheres which were oven dried overnight at 225 C in vacuum; the other three used acetone-washed gel which had not been further dried. At the end of each contacting run the spheres were dried for 5 minutes by pulling air through the bed. The air-dried spheres were then vacuum dried (60 C) overnight. The dried material was sieved (40 mesh, 420 μ opening) to separate whole spheres from fragments and any plutonium precipitate found as a result of the pH rise. The same plutonium stock solution (237.3 gm Pu/liter; 3.18 M free HNO₃) was used throughout, but variations were made in acidity and total plutonium concentrations as noted.

Test 1 — Pu(IV) stock solution was adjusted to pH 0.4 by adding drops of concentrated aqueous ammonia. The final plutonium concentration was about 0.8 M. Three separate 15-ml aliquots of this adjusted stock were pulled through a packed bed containing 10.9 gm UO₂ gel. The contact time was 15 to 20 seconds per pass. The effluent samples were kept separate; pH's were measured and the solutions were analyzed for uranium content. The pH difference between the effluent and influent solutions was about 0.1 pH unit except for the first aliquot for which the pH rise was less than 0.1 unit. Each effluent sample contained between one-fourth and one-third of a gram of uranium (3.0 - 3.6% sphere attrition per pass). The recovered spheres showed 1.8% plutonium uptake (Pu/U + Pu) and the -40 mesh fines showed 2.1% plutonium uptake.

Test 2 — The same adjusted Pu(IV) stock was used as in test 1. One 20-ml aliquot was passed three times through an 11.4-gm

packed bed. After each pass the pH of the effluent was measured, and after the three passes the solution was analyzed for uranium content. The contact time was 10 to 20 seconds per pass and the total contact time was about 40 seconds. In the first pass the pH reached 0.5 (from initial 0.4) and did not change appreciably in the next two passes. About half a gram of uranium was found in the effluent after the third pass (4.6% sphere attrition). The intact spheres (+40 mesh) showed 2.4% plutonium uptake and the fines (-40 mesh) showed 7.9% plutonium uptake. The fines constituted about 15 wt % of the initial sample.

Test 3 — The same adjusted Pu(IV) stock was used as in test 1. One 20-ml aliquot was passed through three different fresh gel beds (9.8, 10.2, 11.8 gm, respectively). The pH of the effluent was measured after each pass, and the total uranium dissolved was measured at the end of the three passes. Owing to some sampling losses and non-quantitative transfers, the total solution volume decreased somewhat between passes, and the contact time also decreased (20, 15, and 10 seconds, respectively). The pH increased very little in the first pass and showed an overall rise of about 0.25 unit over all three passes. About 3% gel attrition was noted. The plutonium uptake measured in intact spheres was highest in the first pass, 1.6%, and decreased by about a factor of three in the third pass to 0.6%.

Test 4 — For this test unaltered Pu(IV) stock solution was used. A 20-ml aliquot was passed three times through a 9.3-gm bed of acetone-washed gel. The total contact time for all passes was about 45 seconds. In this extremely acid solution 25% gel attrition was observed. Plutonium pickup measured 3.6% in the intact spheres and 5.0% in the fines.

Test 5 — The same plutonium stock preparation was used for this test as for tests 1 - 3. One 20-ml aliquot was passed three times through an 8.7-gm bed of acetone-washed gel. The pH was noted after each pass, and the plutonium uptake was measured on the recovered spheres. The total contact time was about 45 seconds. This test was thus a repeat of test 2 except that the gel sample in test 2 was vacuum dried at 250 C. Two marked differences from test 2 were observed. First, the pH rise was much higher in test 5 (0.1 unit in test 2, 0.7 units

in test 5) while the uranium lost to the aqueous phase was two-fold lower (450 mg test 2, 210 mg test 5). The plutonium pickup measured in intact spheres was also lower (1.8% in test 5, 2.4% in test 2). The weight percent of broken spheres (-40 mesh material) was about the same in both cases.

Test 6 — This test was a repeat of test 5 except that the contact time was increased to 5 minutes per pass, giving a total of 15 minutes. The net change in pH was almost the same as that for test 5, but the gel attrition measured five-fold less (0.6%). The total plutonium pickup was 2.2% in the intact spheres, midway between the value observed for test 2 and test 5. The plutonium content of the fines was very high, however, ($\approx 20\%$) indicating substantial precipitation.

The data from these tests are reported in Table 3-9. Several tentative conclusions can be drawn:

1. The pH rise on contacting is less (or at least slower) for oven-dried gel than for material that is simply acetone washed.
2. The difference in plutonium pickup between gels finished by oven drying and acetone washing is small in column contactings.
3. The largest plutonium uptake by intact spheres was measured in the most acid solution where the predominating form was probably the Pu^{+4} ion.
4. Extending the contact time does not increase the pickup materially; in fact, more than anything else, it seems to increase plutonium precipitation (note the high pickup in the -40 fraction, test 6).

One additional point requires comment. During tests 1 and 3, gas evolution from the gel in the columns was noted. The gas has not been identified, but could have been air trapped in the gel pores and displaced when the gel rehydrated. This same effect has been observed previously during microscopic examination of spheres when they were moistened.

One shaker experiment was run during this report period. One-hundred milliliters of Pu(IV) nitrate stock (237.3 mg/ml, 3.18 M H^+) were adjusted to pH 0.3 by the addition of 24 ml of concentrated NH_4OH .

Table 3-9. Pu(IV) Contacting Tests

Contacting test	wt of UO ₂ gel sample, gm	UO ₂ gel history ^(a)	Pu(IV) solution volume, ml	Pu(IV) conc, mole/l	Column contact time, sec	pH of solution before contact	pH of contact solution after contact	U conc in the contact solution, mg U/ml	Total U dissolved, mg ^(d)	Sphere destruction ^(d)	Sphere mesh split	wt of spheres, gm	wt fraction, %	$\frac{Pu}{Pu+U}$, %	Total sphere contact time, sec
1	10.9	Oven dried ^(b)	15	0.8	15	0.4	0.3	22.2	333	3.6					
			15	0.8	30	0.4	0.5	18.3	274	3.0					
			15	0.8	30		0.6	22.2	333	3.6	+40 -40	5.39 2.07	72 28	1.8 2.1	75
2	11.4	Oven dried	20	0.8	20	0.4	0.5								
					10	0.5	0.5								
					10	0.5	0.5	22.5	450	4.6	+40 -40	9.24 1.63	85 15	2.4 7.9	40
3	9.8	Oven dried	20	0.8	20	0.4	0.6				+40 -40	6.89 2.00	78 22	1.6 2.7	20
	10.2	Oven dried			15	0.6	0.5				+40 -40	7.71 1.82	81 19	3.2 1.9	15
	11.8	Oven dried			10	0.5	0.65	41.4	828	3.0	+40 -40	9.31 1.39	87 13	0.6 2.8	10
4	9.3	Acetone washed ^(c)	20	1	15	0	0								
					15	0	0								
					15	0	0	83.3	1666	23.7	+40 -40	4.02 0.95	81 19	3.6 5.0	45
5	8.7	Acetone washed ^(c)	20	0.8	15	0.4	0.55								
					15	0.55	0.75								
					15	0.75	1.1	10.5	210	3.3	+40 -40	6.90 1.03	87 13	1.8 5.4	45
6	9.3	Acetone washed ^(c)	20	0.8	300	0.4	0.8								
					300	0.8	0.95								
					300	0.95	1.0	2.1	42	0.6	+40 -40	8.48 0.78	92 8	2.2 20.0	900

(a) All spheres obtained from batch 13 sol.

(b) Gel was vacuum dried at 225 C.

(c) Gel was acetone washed at room temperature to remove surface organics, no further treatment.

(d) Uranium content of acetone-washed spheres: U/total gel = 72.6 wt %.

Uranium content of oven-dried spheres: U/total gel = 85 wt % based on 15% wt loss on oven drying.

Fifty-four grams of UO_2 gel spheres from batch 3 were divided four ways, and each portion was contacted for 2 hours with a fourth of the volume of the adjusted plutonium solution. After contacting, the solutions were decanted from the spheres, and the filtrate was passed through a fritted glass filter. The pH of the filtrate was followed for almost 2 hours, and a final measurement was taken after 18 hours. Within the first 15 minutes the pH decreased from its initial value (2.1) to 2.0. At 18 hours the pH had decreased to 0.8. Both a slow hydrolytic process and an air oxidation could account for the increase in acidity; for example:

Further study is required to establish the correct mechanism.

The four contacted sphere samples were washed four times each with 5-ml volumes of demineralized water. The spheres were rinsed into a fritted glass filter funnel, and an additional 50-ml volume of wash water was added. Filtration was very slow and the filtrate appeared faintly green. The pH of the filtrate was 3.2 at the time, but decreased to 3.0 by the next day. The washed spheres were dried overnight at 60 C. The product yield was 32.64 gm. After a 1-gm sample was withdrawn for study, the remainder was sieved to determine the size distribution and the variations in plutonium content in the various size fractions. The sized spheres were remixed and calcined.

Sphere breakup was appreciable. The largest weight fraction was in the -200 + 325 mesh split. There was also a pronounced accumulation of plutonium in the smaller-sized fractions. Almost 15% of the total input plutonium used in the experiment was found in the gel-addition product.

The size and plutonium distribution data are reported in Table 3-10. The calcination procedure and conditions are shown in Table 3-11.

Table 3-10. Size and Plutonium Distribution in UO_2 Gel Contacted With Pu(IV) Solution

Mesh size — Tyler sieve	Weight, gm	Pu/Pu + U, mole %
+100	6.3023	8.5
-100 + 200	8.5480	9.4
-200 + 325	10.0297	12.6
-325	5.2397	13.4
(Total Pu in gel = 3.36 gm)		

Table 3-11. Calcination Procedure and Weight Changes in Pu(IV) -Contacted UO_2 Gel

Maximum temperature, C	1150
Time at temperature, min	180
Temperature rate of climb, °C/min	5
Atmosphere	
Heatup	Ar-6% H_2
Hold	Ar-6% H_2
Cooldown	Ar-6% H_2
Gas flow rate, SCFH	10
Weight of charge, gm	25.979
Weight of product, gm	23.060
Change in weight, gm	2.919
Change in weight, %	13

3.3.3. Pu(VI) Solutions

The Pu(VI) solutions prepared and concentrated as described in section 3.2 were contacted with UO_2 gel from batch 16 in a series of six experiments. In tests 1, 3, and 5 the gel was acetone washed only; in tests 2, 4, and 6 it was also oven dried overnight at 225 C and 30 inches Hg.

Six 10-ml aliquots of the 1M Pu(VI) stock were taken for the tests. Two were used as prepared; two were diluted with 0.5M nitric acid to 0.75M Pu(VI) ; and the remaining two were diluted with 0.5 M nitric acid to 0.50M Pu(VI) . Contactings were carried out using the

column method described in the preceding section. Solutions were run through the gel beds three times and held for 5 minutes in each pass to give a total contact time of 15 minutes for each test. After the third pass, all beds were dried by pulling air through them for an additional 5 minutes. The air-dried spheres were further dried for at least 16 hours at 60 C and 18 inches Hg.

In all six tests a light-tan material was noted in the dried spheres. When the spheres were screened, the tan material appeared with the -40 mesh fraction, and it is presumed to be plutonium solution residues from the drying processes.

Some foaming was observed, usually during the second and third passes. In some cases a precipitate formed during the second contacting step, and in all cases a precipitate formed in the effluent from the third pass.

Data from these six runs are summarized in Table 3-12. An effort was made to measure the uranium concentrations in the contacted solution. The results were not satisfactory, however, because the solutions all contained a precipitate which could be dissolved only by refluxing with 14M HNO_3 . Severe foaming accompanied the boiling, and losses of uranium by foaming voided the uranium results. Plutonium pickup was remarkably consistent. For these tests there is a linear relation between the plutonium uptake by the +40 mesh fraction and the initial plutonium concentration in the contacting solution for acetone-washed spheres. This relationship did not hold for oven-dried material, which showed about the same net pickup for all cases (3.0-3.5%). Sphere attrition was high as might be expected from a reaction between hexavalent plutonium and quadrivalent uranium. The pH changes for these runs were much smaller than have been observed for other contactings. In most cases the change was half a unit or less, and in the last test a pH decrease of 0.1 unit was seen.

Table 3-12. Pu(VI) Uptake by UO_2 Gel

Test	Gel preparation ^(a)	Gel wt, gm	Pu(VI) contact solution pH				Spheres		
			Conc, M	Vol, ml	pH		Mesh size	Wt, gm	Pu U + Pu
					Initial	Final			
1	Acetone washed	9.97	1.0	10.0	2.1	2.6	-40 +40	0.12 10.15	0.068
2	Oven dried	12.74	1.0	10.0	2.2	2.6	-40 +40	1.26 9.76	0.080 0.030
3 ^(b)	Acetone washed	9.48	0.75	13.3	0.4	1.6	-40 +40	1.09 5.15	0.081 0.050
4	Oven dried	11.55	0.75	13.3	2.3	2.5	-40 +40	2.64 9.27	0.108 0.035
5	Acetone washed	9.26	0.50	20.0	2.1	2.4	-40 +40	-- --	0.153 0.034
6	Oven dried	12.78	0.50	20.0	2.6	2.5	-40 +40	3.04 9.45	0.090 0.035

(a) All spheres were taken from batch 16 sol.

(b) Contacted spheres were oven dried, then returned to the column for three more contact passes with the original effluent solution.

4. ANALYTICAL SUPPORT (W. N. Bishop)

4.1. Coulometric Analysis for Uranium and Plutonium

Most of the analyses for uranium and plutonium for this program have been carried out by controlled potential coulometric methods. In the early work of the program the titration times were excessively long (1/2 to 1 hour), and the precision was substantially worse than is normally obtained by coulometry. Dr. W. D. Shults of the Analytical Chemistry Division of Oak Ridge National Laboratory visited our laboratories during this quarter. His visit led to some modifications to our cell, principally to give greater stirring efficiency, and resulted in much shorter titration times (15 min for 5 mg of U) and improved precision. We gratefully acknowledge his contributions.

4.2. Analytical Sample Load

During this quarter 322 analyses were completed. The analyses included total U, total Pu, U(VI)/U, NO_3^-/U , C/U, and Pu oxidation state.

5. MATERIAL CHARACTERIZATION

(J. M. Kerr)

Several fired oxide samples have been examined. They were prepared by firing both pure urania gels and mixed plutonia-urania gels produced by gel-addition methods.

5.1. Dissolution Studies (E. J. Kosiancic)

Two 2-gm samples of fired oxide spheres were treated with 10 M nitric acid and 10 M nitric-2 M hydrofluoric acid mixtures. One sample contained about 7% Pu/U+Pu; the other was plutonium-free. The samples were dissolved at 100 C using a boiling water bath as a thermostat. Five-milliliter aliquots of preheated 10 M HNO₃ were added to each sphere sample and held at temperature for 5 minutes. The supernate was decanted and held for analysis. A fresh 5-ml acid aliquot was added, and the process was repeated until no further dissolution was observable (no coloration of the acid in 5 minutes). One drop of 2 M HF was added to each subsequent acid aliquot, and the acid treatment was continued until dissolution was complete.

The pure urania was much easier to dissolve than the mixed oxide. This same effect has been noted in (U,Pu)O₂ prepared by other methods. The UO₂ sample dissolved almost quantitatively in 10 M HNO₃. An addition of HF was required only for the last traces of residue. The mixed oxide required HF addition when the sample was only about half dissolved.

5.2. Abrasion Tests (E. J. Kosiancic)

When spheres made of mixed oxides are partially abraded, the same plutonium weight fraction should appear in each successive sample of abrasion fines if the oxide mixture is uniform. To provide some information on the plutonium distribution in oxides prepared by gel-addition methods, 23 gm of mixed oxide* spheres were placed in a ball mill and

* The oxide used in this test was prepared by contacting Pu(IV) solution with UO₂ gel at a measured initial pH of 0.3 (see section 3.3.2).

milled for 15 minutes. Since no other materials were added, self-abrasion was the only wear mechanism. The input material was all +400 mesh.

After the milling period, the recovered oxide was rescreened and showed a nearly even split between +400 mesh material and -400 mesh fines. The fines were dissolved and analyzed ($\text{Pu}/\text{U} + \text{Pu} = 19.1\%$).

The +400 mesh material was returned to the ball mill and remilled for another 15 minutes. A very small mass of -400 mesh fines was produced (0.2 gm) during the second milling operation, but both the fines and coarse material were dissolved and analyzed. The +400 mesh fraction showed $\text{Pu}/\text{U} + \text{Pu} = 19.7\%$, and the -400 mesh fraction showed $\text{Pu}/\text{U} + \text{Pu} = 18.5\%$. The agreement in these data provides some indication that the plutonium distribution is uniform.

5.3. Ceramography and Alpha Autoradiography (J. M. Kerr)

Ceramographic specimens were prepared from two sizes and kinds of spheres: minus 100 mesh, contacted UO_2 gels and plus 28 mesh uncontacted UO_2 gel spheres. The small spheres (-100 mesh) contained approximately 7% plutonium.

Previously, alpha autoradiography had not been successful on small spheres (-100 mesh) because of excessive scatter of the alpha particles. Techniques have now been established whereby we can resolve the plutonium distribution in these small spheres. Figure 5-1 shows the as-prepared ceramographic mount, and Figure 5-2 shows the alpha autoradiograph, both at 100X. The alpha autoradiograph was made by contacting the sample for 15 minutes using the aluminum filter discussed previously.³ The cellulose nitrate film was etched for 3 minutes with sodium hydroxide. The alpha autoradiograph seen in Figure 5-2 was rephotographed at 250X to determine the degree of "background" in the etched nitrate film, and to determine whether resolution of the areas where alpha track damage had occurred was possible. Good resolution of the areas where alpha tracks were present was possible, and although a fair degree of "background" (primarily small etch pits in the nitrate film) was present, it did not interfere with interpretation of the alpha autoradiograph. It was concluded that the technique was suitable for both small (-100 mesh) and large (+28 mesh) spheres, and that it should

Figure 5-1. Sample 1-C-58 — Dried Contacted
UO₂ Gel Spheres (as polished)

100X

Figure 5-2. Sample 1-C-58 — Dried Contacted
UO₂ Gel Spheres (alpha autorad-
iograph of same field as Fig. 5-1)

100X

be possible to go as high as 250X in magnifying the alpha autoradiographs. Examination of even smaller spheres should be possible using the technique developed. Examination of the alpha autoradiographs of these small spheres showed good uniformity of plutonium within spheres but some variations from sphere-to-sphere. This is similar to observations already reported.³

Ceramographic studies were made of two batches of large UO_2 gel spheres, one of which was acetone washed only and one of which had been additionally oven dried at 225 C under vacuum. Neither batch had been contacted or fired. The examinations were made to determine the microstructural differences, if any, between the two batches of spheres.

In the as-polished condition, little or no difference could be observed between the particles dried under the two different conditions. Two different etchants were then used, one at two different concentrations. The standard UO_2 etch, 10% H_2SO_4 -90% H_2O_2 , and the same etch diluted 50% by water provided two conditions. Glacial acetic acid diluted 50% by water was the second etchant used. Figure 5-3 shows the acetone-washed sample etched with the concentrated H_2SO_4 - H_2O_2 etchant. Figure 5-4 shows the oven-dried sample etched with the same etchant. It should be pointed out that while the areas bounded by the cracks appear to be grains, such is not the case, since these dried gels have an extremely fine grain size on the order of 80 Å or less. A striking difference is observed between the two samples. The structure in the column-dried sample is quite similar to that seen in tray-dried ThO_2 - UO_2 gels, but on a micro-scale. The structure is full of microcracks which extend to the surface of the spheres, producing a very "open" structure. The oven-dried material is much more dense; the cracks are finer and the structure is not as heavily attacked by the etchant. There also appears to be a hard case or shell on the surface which is not penetrated by the internal crack structure. In both figures there appears to be a fine structure within the areas bounded by the cracks. This could not be resolved optically, and electron microscopy will be attempted. The dilute etchant, used on the same spheres for the same time (20 seconds), did not attack either sample appreciably.

Figure 5-3. Sample 4A-41 — Column-dried Un-
contacted UO_2 Gel Sphere

Figure 5-4. Sample 4A-34 — Oven-dried Un-
contacted UO_2 Gel Sphere

Figure 5-5 is a photomicrograph of an acetone-washed sample treated with acetic acid etchant. Since the micrograph was taken at 100X rather than the 250X of Figures 5-3 and 5-4, the cracks are much larger than those observed in Figures 5-3 and 5-4. Part of this cracking probably resulted from the handling, mounting, and polishing of the spheres. Generally, the acetic acid etchant is less aggressive than the concentrated $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$ etchant. Oven-dried material is apparently unaffected by the acetic acid mixture. As previously noted, a fine structure appears within the areas bounded by cracks in the sample etched with acetic acid. This fine structure is shown at 500X in Figure 5-6. The field shown in Figure 5-6 is in the center of Figure 5-5, and the tip of one of the family of fine cracks seen in Figure 5-5 is seen in the upper right of Figure 5-6. Some porosity, as well as the remnants of several polishing marks and cracks, can be seen, but no real resolution of fine structure composition is obtained. It is possible that the remnants of very fine polishing marks give the appearance of a substructure, since it is very difficult to obtain scratch-free samples of unfired gel for examination at high magnification.

Satisfactory ceramographic techniques are now established for both dried gels and fired oxides. Microstructural differences between acetone-washed gel spheres and oven-dried gel have been observed. Oven-dried spheres show a much tighter, more dense structure which is less susceptible to attack by etchants. Furthermore, the oven-dried spheres exhibit less tendency to break up with handling; that is, they are mechanically stronger than the acetone-washed raw gel.

Ceramographic study will continue as a characterizing technique. In particular, a correlation between microstructure and plutonium pick-up will be sought.

Figure 5-5. Sample 4A-41 — Column-dried Un-
contacted UO_2 Gel Sphere

Glacial Acetic- H_2O etch

100X

Figure 5-6. Sample 4A-41 — Column-dried Un-
contacted UO_2 Gel Sphere

Glacial Acetic- H_2O etch

500X

6. IRRADIATION TESTING

(C. J. Baroch, E. N. Harbinson)

The program to determine the irradiation performance of gel-addition $\text{PuO}_2\text{-UO}_2$ consists of 19 to 20 capsules to be irradiated in the BAWTR, and 10 to 15 pins to be irradiated in the EBR-II. Three to four of the 19 to 20 capsules will be irradiated to determine the behavior of fuels prepared by variations in the Gel-Addition Process. The remaining capsules and pins for the EBR-II will be used to evaluate in detail the one gel-addition fuel that is considered most suitable during the screening tests. A detailed description of the program is presented in BAW-3714-3.³

Before the capsule design work was initiated, discussions were held with persons from GE-NED and PNWL concerning capsule designs. The preliminary capsule design for the screening irradiations has been completed. A schematic diagram of the capsule is shown in Figure 6-1, and the design parameters are listed in Table 6-1.

Each of the screening capsules will contain three fuel pins: two will be filled with $\text{PuO}_2\text{-UO}_2$ powders, and one with pellets prepared from coprecipitated $\text{PuO}_2\text{-UO}_2$. All of the fuel pins will have smeared densities of 83 to 87%. The capsules are designed to operate at a linear heat rate of about 15 kw/ft and a cladding surface temperature of 1200 F using 20% PuO_2 in natural UO_2 . Analysis of the available data indicates that a linear heat rate of 15 kw/ft will produce significant microstructural changes in the powder fuel, but central melting will not occur.

The hazards report for the capsule design shown in Figure 6-1 was initiated and should be completed by the end of the next quarter.

Table 6-1. Parameters for Screening Irradiation of Gel-Addition Fuels

Parameter	Condition
Number of pins	
Powder	2
Pellet	1
Pin diameter	
OD, inch	0.250
ID, inch	0.220
Cladding	Type-304 SS
Cladding surface temperature, F	1200
Smeared density of fuel, %	85 ± 2
Linear heat rate, kw/ft	≈ 15
Surface heat flux, Btu/hr-ft ²	$\approx 750,000$
Duration of test, days	≈ 30
Fuel burnup, MWD/T	≈ 6500

Figure 6-1. Diagram of Irradiation Capsule

7. ORGANIC DRYER STUDIES*

(F. D. Timmons,
B&W Research Center, Alliance, Ohio)

7.1. Purpose

Economical use of the gel-addition process for producing nuclear fuels requires recycling of the solvent, 2-ethyl-1-hexanol (2-EH). This investigation was initiated to determine whether an explosion hazard may arise from the formation and accumulation of nitration products of 2-EH and the surfactants used in the process.

7.2. Summary of Work

Samples of recycled 2-EH were obtained from Oak Ridge National Laboratory (ORNL) after 1430 and 1530 hours of use. These samples were analyzed by gas-liquid chromatography (GLC) and infrared (IR) spectrophotometry to identify the principal reaction products of 2-EH. Reactions between 2-EH and HNO_3 were carried out at elevated temperatures to obtain enough of these reaction products for detailed analyses. The overall rate of the 2-EH- HNO_3 reaction was studied by ultraviolet spectrophotometry.

7.3. Results

The only products of the 2-EH- HNO_3 reaction under the Gel-Addition Process conditions were aldehydes. The overall reaction was found to obey a first order rate law at $53 \pm 1^\circ\text{C}$; $k = 10.45 \times 10^{-8} \text{ sec}^{-1}$.

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* This chapter summarizes a task set up specifically to investigate the possibility that unstable nitrated organics may form during recycle of the organic dryer used in UO_2 sphere production. The work was carried out at B&W's Alliance Research Center and has been reported in detail by informal memorandum. This chapter is a condensation of the results.

7.4. Conclusions

No explosion hazard is inherent in the Gel-Addition Process (using 2-ethyl-1-hexanol as a dehydrating agent for converting urania sols into gels) as a result of nitration of any organic species in the system. No further work on this subject is planned.

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