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GEL-ADDITION PROCESS CHEMICAL STUDIES

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- E. C. Moncrief — technical consultation and technical management assistance.
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- R. M. Baber and V. D. Arthur — technical assistance in plutonium experimental chemistry.
- J. A. Hall — technical assistance in UO_2 sol and gel preparation.

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ABSTRACT

Development of the Gel-Addition Process for preparing plutonia-urania mixed oxide fuels has been extended from study of the interaction of UO_2 gels and plutonium solutions (see previous quarterly, BAW-3714-1¹) to include development of equipment for firing to oxides and methods for examination of oxide microstructure. Two improvements have been made in the preparation of UO_2 sols from uranyl nitrate: The reduction step ($\text{U}^{\text{VI}} \rightarrow \text{U}^{\text{IV}}$) is monitored to prevent nitrate co-reduction, and the uranous hydroxide filter cake is dispersed ultrasonically to a sol. The latter is a substantial improvement over digestion methods previously used.

Progress for the second quarter, ending January 1, 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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I. INTRODUCTION

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

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

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

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

During this report period the main emphasis has been on improvements in preparing UO_2 gels, on testing equipment for firing gels into oxides, and on developing methods for evaluating the mixed oxide products.

2. CONCLUSIONS

2.1. UO_2 Gel Preparation

The scale of UO_2 gel sphere preparation has been increased successfully from 15 gm to about 112 gm per batch.

The preparation of a stable UO_2 sol requires careful control of the reduction of uranium from the uranyl to the uranous state. Incomplete reduction, U(VI) residual, and over-reduction, nitrate attack, both give filter cakes that cannot be converted to sol. Ultrasonic agitation is a very convenient method for conversion of a filter cake to sol.

2.2. UO_2 Gel Contacting

Several test contactings of B&W-produced spheres from the first runs on the new gel-sphere apparatus have been completed. An organic contaminant in the gel interfered with separation of spheres from the aqueous phase, but permitted production of sufficient plutonium-containing gel for tests on firing apparatus and development of microstructural investigating methods. One 50 gm contacting was completed. The plutonium pickup in this run was 6.4% (Pu/U + Pu), and the uranium loss during contacting was approximately 25%.

2.3. Sphere Calcining

Test samples of both UO_2 gel and UO_2 gel containing plutonium have been calcined at 1200 C. The plutonium-containing materials showed some tendency to sinter together, and all batches produced a fired density lower than expected.

2.4. Oxide Characterization

Analysis of sieved samples after firing showed that there was no tendency for plutonium to concentrate in the fines, indicating that the 4-hour contact time used to date approaches a solid-liquid equilibrium

distribution of plutonium and that plutonium deposition in spheres is not a superficial phenomenon.

The low-density mixed oxides produced in the first calcinings dissolved readily in HF-HNO₃ solution.

Procedures have been developed for mounting and polishing fired spheres for examination of their microstructure.

2.5. Analytical Support

Analytical procedures for determination of uranium and plutonium in the same solution are under study. Promising spectrophotometric and coulometric procedures are available.

3. UO_2 GEL SPHERE MATERIAL (D. A. Nitti)

The previous quarterly report¹ contains a detailed description of the process and apparatus to be used for preparing 75 to 100 gm batches of UO_2 gel spheres by stirred vessel methods. This report summarizes the results from the first 10 experimental batches prepared. The general laboratory arrangement, the uranium reduction equipment, and sol and gel preparation equipment are shown in Figures 3-1 through 3-4.

With the specific exception of certain process variations that have been noted in the text, the procedures generally followed the process description already discussed.¹ Table 3-1 summarizes the essential process parameters for the first 10 batches, and Table 3-2 summarizes the analytical data.

3.1. Discussion of Batch Runs

The first batch contained 75 gm of uranium, the design size of the apparatus. Its processing was as expected (based on the preliminary experiments) in all respects except for the very light-green color of the precipitate and the difficulty in converting the precipitate to a sol. Stirring and heating a washed precipitate to form a sol is, at best, a delicate operation. If over-heated or if too much water is lost by evaporation, the uranium tends to precipitate instead of forming a sol. To avoid loss of the entire batch by precipitation, the sol-forming operation was stopped after water lost from the system by evaporation approached 10 ml. At this point, the system had not yet formed a good sol. It was expected that the suspension would be converted to a sol on aging; instead, a semi-rigid mass formed. This mass was fluidized by shaking and was successfully converted to a sol in an ultrasonic bath (80 kc) at 60 C. (Ultrasonic treatment was reported¹ to be a promising procedure in the previous progress report.) Within 3 hours, the suspension had

converted into a sol which was acceptable in every respect. It was stable; there were no nondispersibles or sediment; and its appearance was that of a dark mobile solution.

In view of the difficulty with the stirring and heating method of sol forming, it was decided to use ultrasonic treatment at 60 C for sol-forming operations in future experiments. This method consists of three steps:

1. Place the washed and dried filter cake into a freeze dry flask,
2. Partially evacuate the flask to avoid pressure buildup upon heating,
3. Place the flask into a holder and immerse it in the ultrasonic bath at 60 C.

The minimum time required in the ultrasonic bath has not been established, but overnight treatment has produced satisfactory results.

After observing the behavior of the apparatus during batch 1, it was apparent that the batch size could be conveniently increased to 150% of the design size; that is, from 75 to 112.5 gm of uranium.

There were no process difficulties with batch 2, but processing was interrupted by a site power failure. The ultrasonic sol-forming operation worked well for batch 2 and was easy to perform.

During the analysis of small samples from batches 1 and 2 it was noted that dissolved spheres produced cloudy solutions, indicating the presence of some contaminant, probably organic. The most likely sources were considered to be contaminated acetone, excessive lubricant in the sol-injection syringe, or an organic extracted from a length of Tygon tubing used to supply the acetone wash. All three sources were eliminated.

Batches 3 and 4 were processed without difficulty; a different batch of the catalyst was used. Solutions of the gel from these runs did not produce the cloudy solutions noted before, and it was concluded that the contaminant was no longer being introduced.

An attempt was made to measure the pH change as a sample of batch 3 filter cake converted to sol by aging. The pH decreased from 6.235 to 4.369 in 6 days, and a good sol still had not formed. Measurement of the pH of the good sol (batch 1) indicated an apparent pH of 2.50.

Operating difficulties began with batch 5. Although there were indications of an adequate hydrogen supply, the $U(VI) \rightarrow (IV)$ reductions were incomplete on the first two attempts, and the filter cakes refused to convert to sols. A search disclosed three cracked brass fittings in the hydrogen supply line. The site power failure referred to earlier had apparently caused a pressure surge which forced some uranyl nitrate into the hydrogen line. In the 6-week period between processing of batches 2 and 5, there was adequate opportunity for nitrate reduction to ammonia to take place. Ammonia is known to cause stress corrosion cracking of brass, which may account for the leak.

The batch 5 preparation was completed after the system was made operable, but it did not yield a satisfactory sol or high-quality spheres. The spheres appear to be excessively oxidized and probably will not be used for gel contacting studies.

Batch 6 was marked by a bearing failure in the power agitator used to keep the palladium-on-thoria catalyst suspended during the reduction step. The bearing was replaced and the reduction step was successful on the second attempt. The behavior of the filter cake and sol were normal in every way, and the spheres were deemed acceptable.

Batch 7 and those following were prepared using a new catalyst batch. Thoria for the catalyst was obtained from B&W stocks of steam-denitrated thorium nitrate.

Batches 7, 8, and 9 did not yield good sols. Filter cakes from all three runs gave suspensions similar to the material observed in batch 5. It was noted during batch 7 that the pH after reduction was almost as high as that observed during batch 5 operations (see Table 3-2). This was taken as evidence of over-reduction of uranyl nitrate. It is well known from the analytical chemistry literature that uranium cannot be estimated in nitrate from using Jones reductor methods, because the nitrate is partially reduced also, giving erroneously high results. Catalytic reduction of nitrate to ammonia would account for the high pH observed in batches 5 and 7. Batch 5 was sent through the reduction treatment several times, and could thus be over-reduced insofar as nitrate is concerned. Batch 7 was run on fresh catalyst which, if it were more active than the earlier preparations, could have produced over-reduction of batch 7.

Batch 8 results duplicated those of batch 7; neither batch could be converted to sol by extended ultrasonic treatment, by dilution, or nitrate adjustment.

Batch 9 was processed as a repeat of 7 and 8 except that provision was made for nitric acid addition to decrease the pH of the uranous nitrate if it should show the same high pH. The pH measured 0.865 and was reduced to 0.365 by adding the equivalent of 20 ml of concentrated acid. In spite of the acid addition, the filter cake yielded a suspension instead of a sol.

Batch 10 was planned to prove that over-reduction was the problem. Batch 10 was processed exactly like batches 7, 8, and 9 except that samples were taken after each hour of reduction. The tests indicated that reduction was essentially complete in 3 hours. The reduction was stopped after 4 hours, and the remainder of the process was completed in the normal manner. The result was that the pH of the uranous nitrate was 0.43, about the value for batches 1, 2, and 6, and the precipitate formed a good sol. Thus by avoiding over-reduction, possibly by following the reduction with oxidation-reduction indicator electrodes, processing difficulties during the reduction can probably be avoided. An intriguing question remains: What chemical conditions produced by over-reduction inhibit the formation of a good sol?

3.2. Summary of Results

1. Sol forming by aging may require well in excess of 6 days, which is contrary to the 24 hours indicated by preliminary experiments.

2. Sol forming in a closed vessel in an ultrasonic bath at 60 C seems to be better than the stirring and heating method.

3. The actual batch size of our apparatus is 112.5 gm of uranium with the present 0.5 M U flowsheet.

4. Care must be taken to avoid stress corrosion cracking of brass fittings, which results if nitrate should enter the hydrogen gas supply system.

5. The apparent pH decreases from about 6.3 to about 2.5 during the sol forming stage. (This is based on very preliminary data.)

6. If reduction is not complete, the precipitated hydrous oxide will not form a sol.

7. If reduction is carried too far, the precipitated hydrous oxide will not form a sol. To avoid over-reduction, specific attention must be given to reduction time and catalyst efficiency and, with other flow-sheets, to hydrogen concentration, uranium concentration, and speed of agitation. It would be most desirable to monitor the reduction process with oxidation-reduction indicator electrodes.

8. Uranous nitrate solutions with pH's greater than about 0.60 ± 0.05 seem to be over-reduced.

9. Organic contamination on the gel spheres may become a processing problem.

10. Crystallite size measurements (performed at B&W Research Center in Alliance, Ohio) have shown that the gel spheres from batch 1 have a crystallite size of about $100 \text{ \AA}$, and the spheres purchased from NFS are essentially amorphous (crystallite sizes below the resolution of the instrument, $\ll 25 \text{ \AA}$).

11. A large column capable of forming about 1 kg of spheres per day has been constructed as part of another B&W project; however, it has not yet been operated, tested, or calibrated. It will eventually be available to the gel addition project.

Table 3-1. Summary of Batch Preparations of U(IV) Gel Microspheres
Using the ORNL Formate Process

Reagent or process parameter	Batch No.									
	1	2	3	4	5	6	7	8	9	10
Uranium, gm	75	112.5	112.5	112.5	112.5	112.5	112.5	112.5	112.5	86.5
Uranium nitrate solution (0.5 M U + 2.3 M NO ₃), ml	520	780	780	780	780	780	780	780	780	600
Urea, gm	9.92	14.7	14.76	14.79	14.89	14.98	14.99	14.99	14.90	11.42
Pd on ThO ₂ catalyst, mg Pd	60	90	90	66	66	26.4	60	60	56	56
Total volume of solution, ml	640	960	960	960	960	960	960	960	958	743
Hydrogen flow rate, std cc/min	300	300	300	300	300	300	300	300	300	300
Approx hydrogen reduction time, hr	21.4	17	21	19	84 ^(a)	34 ^(b)	19	17.4	20	4.0
Formic acid, (89.5%), ml	12.7	19.1	19.1	19.1	19.1	19.1	19.1	19.1	19.1	14.7
Precipitation time, hr	2.2	1.8	2.2	--	--	2.1	--	1.5	--	1.5
Volume of wash water, ml	2250	3375	3375	3375	3375	3375	3375	3375	3375	3375
Approx drying time on filter, min	10	10	10	10	10	10	10	10	10	10
Approx volume of U(IV) sol, ml	160	250	250	250	--	250	--	--	--	--
Yield of gel spheres, gm	77.3	120.8	126.3	105.6	--	120.9	--	--	--	77.5

(a) Hydrogen cylinder was empty for some unknown portion of this period.

(b) Agitation was lost for at least half of this period.

Table 3-2. Summary of the Analytical Results for U(IV) Sol-Gel Preparations

	Batch No.									
	1	2	3	4	5	6	7	8	9	10
Uranous nitrate solution										
U(IV)/U(total), %	99.7	--	98.8	97.2	>99.8	99.7	99.8	99.3	99.7	98.8
pH	0.365	0.325	0.495	0.525	0.878	0.575	0.870	0.675	0.865	0.435
U(IV) sol										
U(IV) content, U(IV)/U total, %	74.9	81.8	81.9	83.2	65.0	--	--	50.0	--	79.3
Uranium content, wt %	25.6	26.8	23.3	20.9	23.4	22.7	--	21.7	--	22.0
Nitrate to uranium mole ratio	0.040	0.021	0.025	0.022	<0.025	0.041	--	0.042	--	0.053
pH	2.50	--	--	--	--	--	--	2.77	--	--
U(IV) gel microspheres										
U(IV) content, %	83.7	--	84.7	76.0	47.5	89.9	--	--	--	82.6
Uranium content, wt %	70.7	69.4	70.6	69.1	72.0	71.3	--	--	--	72.8
Nitrate to uranium mole ratio	<0.018	0	0	0.019	--	0.024	--	--	--	0.014
Crystallite size, Å	100	--	--	--	--	--	--	--	--	--

Figure 3-1. UO_2 Gel Preparation Facilities (WAS-67-2)

Figure 3-2. Uranyl Nitrate Reduction System (WAS-67-1)

Figure 3-3. UO_2 Sol Preparation Box — U(IV) Transfer in Progress (WAS-67-828)

Figure 3-4. UO_2 Gel Sphere Preparation (WAS-67-832)

4. UO_2 CONTACTING EXPERIMENTS (W. N. Bishop)

Two contactings of Pu(III) solutions with NFS spheres and four contactings of Pu(IV) with B&W spheres were completed. One large (50 gm) batch of spheres was contacted to provide material for the first sphere-firing tests. The experimental data on contactings have been extended to analysis of the contacting solutions. The plutonium chemistry facilities are shown in Figures 4-1 and 4-2. Figure 4-3 shows a small-scale contacting experiment in progress.

4. 1. Contact of Pu(III) With NFS-Produced Material

Approximately 30 ml of Pu(III) solution prepared by hydroxylamine reduction of $\text{Pu}(\text{NO}_3)_4$ as described in the first quarterly report¹ were adjusted to pH 2.5 by addition of aqueous ammonia. Two ml of the resulting solution were contacted for 4 hours with 4 gm of NFS spheres. The remainder (28 to 30 ml) was contacted for 4 hours with 12 gm of NFS spheres. Approximately 10 ml of Pu(III) solution were adjusted to pH 4.0 and contacted for 4 hours with 4 gm of NFS spheres.

The spheres were separated from the solutions by decantation and filtration, and washed with several 5-ml portions of water. The results of the analyses of the spheres, shown in Table 4-1, are consistent with those reported in the first report.¹ The contact solutions were analyzed and the results are discussed in section 4.3.

4. 2. Contact of Pu(IV) With B&W Spheres

The preparation of B&W spheres is described in section 3. Three contacts were made with batch 1 material to establish the behavior of the spheres with Pu(IV) solutions. The 10-ml portions of Pu(IV) stock solution were adjusted to pH values of 0.3, 0.5, and 0.7 by the addition of 3.4, 4.2, and 5.0 ml of concentrated NH_4OH . The solutions were

contacted for 4 hours with 4-gm batches of batch 1 spheres. The results of sphere analysis are shown in Table 4-2, and the solution analytical results are discussed in section 4.3.

The solutions foamed excessively during the shaking in contact with the spheres; in fact, there appeared to be almost no liquid in the flask. Some foam is always present when spheres are shaken with plutonium solutions, but none of the earlier contacts showed this degree of foaming. The Pu uptake was 1/3 to 1/2 of that previously obtained under similar conditions with other B&W spheres. The presence of foam is another indication of the presence of an organic contaminant as discussed in section 3.1.

A large amount of contacted spheres was required for firing and screening experiments. One-hundred ml of Pu(IV) stock solution were adjusted to pH 0.3 by the addition of 34 ml of concentrated NH_4OH . This solution was contacted with 50 gm of batch 1 B&W spheres for 4 hours.

The spheres were filtered, washed, and dried under 18 inches vacuum at 70 C overnight. The recovery was 40.8 gm. The analysis of these spheres is shown in Table 4-2. The material balance corresponds to about 25% loss of UO_2 . The details of firing and screening and the analysis of various sized fractions are reported in section 5.

4.3. Analysis of Contacting Solutions

The heavy analytical load during the first quarter of this project caused a large backlog of samples, principally the contacting solutions. These results are now available and are shown in Table 4-3 for Pu(III) solutions and Table 4-4 for Pu(IV) solutions contacted with NFS spheres. The analysis of Pu(IV) solutions contacted with B&W spheres is shown in Table 4-5.

In general, the results are consistent with the following statements:

1. Pu(IV) solutions are more corrosive than Pu(III) solution.
2. Sphere attack is greater for longer contact times, but the rate of attack decreases with contact time.
3. Higher initial acid strength is more corrosive.
4. B&W spheres show more resistance to attack than do NFS spheres.

In almost every case, the sphere attrition was greater than desirable. Enough has been learned to show that the Oak Ridge flowsheet gives a gel more chemically resistant than the NFS process does, and future sphere attrition studies will center on the material made by ORNL methods.

The extremely small amount of uranium in solution 1C 55 provides an indication that sphere attrition may be suppressed, but is puzzling when compared to 1C 53 and 1C 51. The contacting solutions were so similar that such divergent behavior is unexpected. One explanation of at least part of the difference probably lies in the method of obtaining the solution sample. For several reasons the sample for analysis was taken from a decanted portion of the solution. Some spheres, particularly when foam is present, are carried over in the decantation. After a time to allow for settling, an aliquot is pipetted and diluted to volume. It is possible that some spheres are pipetted into the analytical sample and dissolve while awaiting analysis. Sphere carry-over is certainly not reproducible and could be almost zero in some instances. If carry-over is important, it follows that samples 1C 53 and 1C 51 have erroneously high uranium contents.

Table 4-1. Contact of Pu(III) Solutions With NFS Gel Spheres

<u>Initial pH</u>	<u>Final pH</u>	<u>Pu solution volume, ml</u>	<u>Gel spheres, gm</u>	<u>Sphere analytical No.</u>	<u>Pu Pu + U</u>
2.5	2.5	30	12	1C 28	0.067
2.5	2.6	2	4	1C 34	0.040
4.0	2.7	10	4	1C 30	0.080

Table 4-2. Contact of Pu(IV) Solutions With B&W Gel Spheres

<u>Initial pH</u>	<u>Solution volume, ml</u>	<u>Weight of spheres, gm</u>	<u>Sphere analytical No.</u>	<u>Pu Pu + U</u>
0.3	13.4	4	1C 52	0.088
0.5	14.2	4	1C 54	0.068
0.7	15.0	4	1C 56	0.037
0.3	13.4	50	1C 58	0.064

Table 4-3. Analysis of Pu(III) Solutions Contacted With NFS Spheres

Sphere analytical No.	Solution analytical No.	Solution volume, ml	Pu concentration, <u>M</u>	Initial pH	Final pH	Duration of contact	Total U ^(b) in solution, gm
1B 28	1B 27	10	0.5	1.0	2.4	5 m	0.74
1B 32	1B 31	10	0.5	2.5	2.6	5 m	0.72
1B 30	1B 29	10	0.5	1.0	2.4	30 m	0.95
1B 34	1B 33	10	0.5	2.5	2.5	30 m	0.87
1B 52	1B 53	10	0.5	1.0	2.5	4 hr	0.87
1B 54	1B 55	10	0.5	2.5	2.4	4 hr	1.32
1B 36	1B 35	100	0.05	1.0	2.4	5 m	0.72
1B 38	1B 39	100	0.05	2.5	2.8	5 m	0.39
1B 40	1B 39	100	0.05	1.0	3.3	30 m	1.03
1B 42	1B 41	100	0.05	2.5	3.8	30 m	0.73
1B 56	1B 57	100	0.05	1.0	3.3	4 hr	1.19
1B 58	1B 59	100	0.05	2.5	3.8	4 hr	1.09
1C 28	1C 27	30 ^(a)	0.5	2.5	2.5	4 hr	2.25 ^(a)
1C 34	1C 33	2	0.5	2.5	2.6	4 hr	0.18
1C 30	1C 29	10	0.5	4.0	2.7	4 hr	0.95

(a) 12 gm of spheres was used for this contact experiment. All others were 4 gm.

(b) 4 gm of gel spheres is equivalent to about 3 gm of uranium.

Table 4-4. Analysis of Pu(IV) Solutions Contacted With
NFS Spheres

Sphere analytical No.	Solution analytical No.	Initial pH	Final pH	Duration of contact	Total U ^(b) in solution, gm
1B 66	1B 67	0.3	2.20	5 m	1.63
1B 68	1B 69	0.3	2.15	30 m	1.95
1B 74	1B 73	0.5(a)	2.20	30 m	1.73
1B 70	1B 71	0.3	2.15	60 m	2.03
1B 60	1B 61	0.3	1.85	3 hr	1.37
1B 62	1B 63	0.3	2.10	3 hr	2.07
1B 76	1B 75	0.5(a)	2.20	4 hr	2.25

(a) The amount of base added to these solutions was equivalent to that which produced a pH of 0.3 for the other contact experiments.

(b) 4 gm of spheres was used for the contact experiments. This is equivalent to about 3 gm of uranium.

Table 4-5. Analysis of Pu(IV) Solutions Contacted With
B&W Spheres

Sphere analytical No.	Solution analytical No.	Initial pH	Duration of contact, hr	Total U ^(b) in solution, gm
1B 78	1B 77	0.5(a)	4	1.25
1C 52	1C 51	0.3	4	0.78
1C 54	1C 53	0.5	4	0.86
1C 56	1C 55	0.7	4	0.02

(a) The amount of base added to this solution was equivalent to that which produced a pH of 0.3 in other contact experiments.

(b) 4 gm of spheres was used for the contact experiments. This is equivalent to about 3 gm of uranium.

Figure 4-1. Plutonium Chemistry Line — North Face
(WAS-66-821)

Figure 4-2. Plutonium Chemistry Line — South Face
(WAS-66-816)

Figure 4-3. Gel Contacting Experiments (4-gm runs in progress) (WAS-67-845)

5. SPHERE CALCINING EXPERIMENTS (E. J. Kosiancic)

The first samples of Gel-Addition material were carried through a calcining step to provide material for development of microstructural study methods; hence, no real effort was made to obtain a high density product.

5.1. Description of the Calcining Furnace

A Lindberg/Hevi-Duty 51000 series high-temperature box furnace is located in a recess built into a 6 × 2 × 2 foot stainless steel glove box. The furnace has single-ended, spiral silicon carbide heating elements and a useful chamber 6 × 5 × 12 inches. It is built to maintain excellent temperature uniformity and is equipped with two thermocouples, one near the back and one near the front of the chamber. Maximum operating temperature is 1482 C.

The furnace is not gas-tight, however; the chamber is supplied at the back wall with an inert or reducing gas which flows through the chamber and exits at the small openings around the plug door located at the front of the chamber. With a relatively large gas flow, an inert or reducing atmosphere may be obtained.

This furnace is supplied with Lindberg/Hevi-Duty Model 59545 control console. The controller is capable of maintaining the temperature within ± 1 C; however, it is an off-on set point type and does not allow for a programmed heating cycle. A custom built (Hevi-Duty) controller with program capability has been attached to the Model 59545 to provide the heating and cooling cycle flexibility desired.

5.2. Calcining Tests

Two calcining runs were made with both plutonium-contacted and uncontacted gel spheres. The furnace conditions and oxide sample numbers are reported in Tables 5-1 and 5-2.

The calcined spheres appeared to be steel gray in color with a slightly rough surface rather than the expected shiny dark color. Only a very few spheres appeared to be damaged, and this percentage appeared to be the same for the contacted and uncontacted spheres.

Samples (1C 60, 1C 51, and 1C 62) showed a slight tendency to sinter together in the crucibles; in 1C 61 and 1C 62 the particles were easily separated and appear to be in excellent spherical form.

Sample 1C 60 had a much harder surface; in fact, the whole mass appeared in billet form. The surface layer could be separated into spheres easily, but the remainder of the billet could be separated only with difficulty. Weight losses were near 10%.

The size distribution of the fired product and the plutonium content density and physical appearance of each fraction were measured. These results are given in section 6.

Table 5-1. Summary of Calcining Run 1

<u>Gel sample</u>	<u>Mass, gm</u>	<u>Oxide sample No.</u>	<u>Notes</u>
Pu(III) contacted with NFS UO ₂ gel (1C 36)	4	1C 37	Material used in dissolution spot tests.
Uncontacted NFS UO ₂ gel	4	1C 38	Material used in dissolution spot tests.

Furnace conditions

Heatup rate = 50 C/hr
 Time at max. temp = 2.5 hr
 Cooldown rate ≈ 80 C/hr to about 600 C, then slower
 Max. temp = 1200 C
 Heatup atm = Ar-3.75% H₂
 Cooldown atm = Ar

Table 5-2. Summary of Calcining Run 2

<u>Gel sample</u>	<u>Mass, gm</u>	<u>Pu U + Pu</u>	<u>Oxide sample No.</u>	<u>% wt loss on calcining</u>	<u>Notes</u>
Pu(IV) contacted with B&W batch 1 (1C 58)	21.89	0.064	1C 60	9.8	Material used in Pu distribution studies.
Uncontacted B&W gel spheres batch 1	4.999	0	1C 61	10.0	
Uncontacted NFS gel spheres	96.573	0	1C 62	10.4	

Furnace Conditions: Same as Run 1

6. OXIDE CHARACTERIZATION (E. J. Kosiancic, L. D. Barnes)

Samples of calcined materials have been carried through a series of characterization studies including size distribution, plutonium distribution, density, dissolution characteristics, and microstructures. The results of these first experiments are summarized below.

6.1. Plutonium Distribution (E. J. Kosiancic)

Samples of oxide materials 1C 60, 1C 61, 1C 62, and the unfired gels 1C 58 and 1C 52, were screened into various sized fractions (see sections 4 and 5 for sample history). Selected fractions were analyzed for the plutonium-to-total-metal ($\text{Pu/U} \div \text{Pu}$) ratio to determine whether there is any indication of plutonium segregation into the fines. Table 6-1 summarizes the available data.

6.2. Density Measurements (E. J. Kosiancic)

Two samples of fired material were checked for final particle density. The measurements were made in a 25-ml water pycnometer weighed on a four-place balance. One sample was remeasured using a gas displacement pycnometer. Both air and helium were used as gases. The observed densities for most materials were well below the expected values, indicating the need for a more sophisticated firing procedure. Data are summarized in Table 6-2.

6.3. Dissolution Tests (E. J. Kosiancic)

Two samples of oxide were treated with HF-HNO_3 to obtain some information on their dissolution rates. Both were derived from NFS-produced gel. One had been through the Gel-Addition Process and contained about 6% plutonium, the other was plutonium-free. Both samples appeared to dissolve instantly and both left a white residue — either zirconia used by NFS as an additive in their process or silica leached from the glassware by HF. These studies will be continued.

6.4. Microstructure (L. D. Barnes)

A series of ceramographic specimens was prepared for microstructural examination from NFS gel spheres. Material was examined as unfired gel, fired oxide, and fired oxide containing plutonium by Gel-Addition. Spheres were imbedded in Quickmount^{*} and polished. Polished specimens of as-received gel spheres were uniformly round and dense in appearance immediately after polishing, but showed evidence of nonuniform degradation after several days' exposure to water. The appearance of the water-etched specimens showed three effects: a uniform rough surface; an etching out of apparent grain boundaries; and no attack on different individual spheres in the same specimen mount. Polished specimens of fired UO_2 varied from a very dense structure to a highly porous low-density structure. Calcined polished spheres containing plutonium were also nonuniform in appearance, and several specimens showed a ring structure. In this initial work the distribution of the plutonium was not determined. During the next quarter, alpha autoradiographic work will be initiated in an attempt to establish the plutonium distribution, and photomicrographs of polished specimens will be made to examine the microstructure in more detail.

* Quickmount is a proprietary product available from Fulton Metallurgical Products, Pittsburgh, Pa.

Table 6-1. Sphere Screening and Plutonium Distribution Tests

Sample	Mesh size	Wt	Wt % in fraction	$\frac{\text{Pu}}{\text{U} + \text{Pu}}$ %
1C 60 (oxide)	+100	0.6938	3.6	
	-100 + 200	4.2800	22.4	4.7
	-200 + 325	8.5991	44.9	7.6
	-325 + 400	1.5590	8.1	6.3
	-400	4.0102	20.9	4.6
		19.1421	99.9	avg 7.5
1C 61 (oxide)	+100	0.0949	2.3	
	-100 + 200	1.5087	35.9	
	-200 + 325	2.0358	48.4	NA
	-325 + 400	0.3552	8.4	
	-400	0.2114	4.2	
		4.2060	99.2	
1C 62	+100	45.0776	53.8	
	-100 + 200	38.7750	46.2	NA
		83.8526	100.0	
1C 58 (gel)	+100	0.6411	4.7	6.9(a)
	-100 + 200	4.5246	32.9	5.1(a)
	-200 + 325	6.6173	48.1	7.5(a)
	-325 + 400	0.1962	1.4	--
	-400	1.7703	12.9	10.5(a)
		13.7495	100.0	avg 7.5
1C 52 (gel)	+200	NA	NA	10.4
	-200			7.3
				avg 8.8

(a) Spectrophotometric measurement - all others are coulometric titrations.

Table 6-2. Densities of Fired Gel Samples

<u>Sample</u>	<u>Size fraction</u>	<u>Sample wt, gm</u>	<u>Sample density, gm/cc</u>	
			<u>Water pycnometer</u>	<u>Gas pycnometer</u>
1C 60	-200 + 325	2.0023	11.06	
		1.9518	8.0	
		2.0196	7.66	
		1.6665	7.16	
		0.6767	8.46	
			avg 8.47	
1C 62	+100	3.2916	7.50	6.92 (air)
		4.3204	7.47	
		3.7787	7.05	7.26 (He)
		38.9460	7.1	
		5.6312	8.26	
		19.4728	7.16	
		4.7413	7.76	
		3.3171	7.76	
			avg 7.51	

7. ANALYTICAL SUPPORT (R. H. Dodd)

Methods used for analysis of samples generated in the Gel-Addition studies have included those discussed in the first quarterly report.¹ Two new techniques have come under study during this report period.

7.1. Coulometric Uranium Analysis

Plutonium can interfere with uranium analysis by coulometric titration since both are reduced at the low electrode potentials used to date. Corrections for the plutonium contribution can be applied and, if the correction is small, no serious error results. However, if the plutonium content is appreciable, the plutonium correction produces some uncertainty, particularly if its valence state distribution is not well known.

An improved procedure for uranium determination is being investigated. It has been derived from suggestions made by W. D. Schults,² Analytical Chemistry Division, Oak Ridge National Laboratory. The method begins with a prereduction of Pu(IV) and Pu(VI) at +0.075 V versus the standard calomel electrode (S. C. E.). At this high value U(VI) is not coreduced. The uranium is then measured by reduction at -0.31 V versus S. C. E. This procedure circumvents the plutonium interference.

7.2. Spectrophotometry U-Pu Mixtures

A colorimetric procedure for simultaneous determination of uranium and plutonium in the same samples is extremely desirable in Gel-Addition work. Puechl's method³ involving the spectra of sulfate solutions is under study. The procedure is based on spectrophotometry of sulfate solutions in contrast to the nitrate spectra used previously in this project. At 417.5 m μ both plutonium and uranium sulfates show absorption peaks, whereas at 665 m μ only plutonium absorbs significantly. Both spectra are shown in Figure 7-1.

Standard curves for uranium and plutonium have been prepared for concentrations up to 25 mg U/ml and 10 mg Pu/ml. Figure 7-2 shows the Beer's Law plots.

Application of the method to uranium-plutonium mixtures involves measurement of the total absorbance at 665 m μ to get the plutonium concentration. The uranium concentration is derived by measurement of the total absorbance at 415.5 m μ , converting this to an "apparent" uranium concentration and deducting from this 60% of the plutonium concentration already measured. The result gives the uranium concentration with sufficient accuracy for the Gel-Addition scouting experiments currently in progress.

Development of methods for codetermination of mixtures will continue.

Figure 7-1. Spectra for Pu(IV) and U(VI) Sulfate in 4 M H_2SO_4

Figure 7-2. Beer's Law Plots for Plutonium and Uranium in Sulfate Solution

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- ² Schults, W. D., Oak Ridge National Laboratory, Private Communication, September 29, 1966.
- ³ Puechl, K. H., NUMEC-P-70 Project Report, April - June 1961.

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