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GEL-ADDITION PROCESS CHEMICAL STUDIES

— Quarterly Progress Report No. 8 —

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ABSTRACT

The development of the sol-gel process and related processes for preparing (U, Pu)O₂ fast reactor fuels has continued in Babcock & Wilcox's laboratories. Progress for the eighth quarter ending July 31, 1968, is reported. The program is sponsored by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3714.

During this report period development of the Oak Ridge mixed sol process was expanded. The last of the scheduled test work on the gel-addition process was completed with the demonstration that Pu(III) is picked up from aqueous solution and retained by UO₂ gels through at least two mechanisms. About half the Pu(III) picked up in a single contact was leached from the gel with either water or aqueous ammonia. The remainder was fixed. The total was fixed when the gel was dried before leaching. The total pickup from a 0.45 M Pu(III) nitrate solution was 4.7% (Pu/U + Pu) in one contact.

Procedures for polishing pellet specimens for ceramographic examination are nearly complete. HF-HNO₃ solutions give an excellent etch, but additional work is needed to find ways of stopping the etchant action at the required point.

Irradiation testing of sol-gel fuels was begun. One capsule containing (U, Pu)O₂ sol-gel spherical fuel was inserted in the BAWTR. Comparison pins of mixed oxide shards and pellets were included. The design heat rate is 15 kW/ft. Fuel preparation for irradiation specimen materials is continuing.

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1. INTRODUCTION

This is the eighth progress report on a continuing program of experimental work on sol-gel and related methods for preparing mixed uranium-plutonium oxide fuels for fast reactor application. The program is sponsored by the U.S. Atomic Energy Commission under Contract No. AT(30-1)-3714. This report covers the period May 1, 1968 to July 31, 1968.

In the previous report period emphasis was shifted from the gel-addition process to the mixed sol approach developed at Oak Ridge National Laboratory. Both of these processes are in the sol-gel family, but different procedures are used for making mixed (U,Pu)O₂ spheres. In the gel-addition technique, UO₂ gel spheres are prepared first and then converted to mixed gel by soaking the spheres in aqueous plutonium solutions. In the mixed-sol approach, separate sols of UO₂ and PuO₂ are prepared and mixed in the appropriate ratio to give a mixed sol which is co-gelled and then fired to mixed oxide.

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

2. RESULTS AND CONCLUSIONS

2.1. Gel-Addition Chemistry

Extensive washing of mixed gels prepared by soaking UO_2 gel in 0.45 M Pu(III) solution shows that under the contacting conditions used about half the Pu(III) picked up is in chemically bound form. The remainder is readily removed by either water or aqueous ammonia leaching unless the mixed gel is dried before being washed. If the gel is dried, the total picked up is fixed almost quantitatively.

Successive contactings have been shown previously to lead to high total plutonium content but also to severe gel degradation; thus, based on the present state of gel addition work, the process is judged to be of interest in thermal reactor fuel technology but is not yet ready for fast fuel application.

2.2. Analytical Support

Evaluated analytical procedures for measurement of the plutonium and uranium contents of mixed oxide fuels and for the isotopic analysis of plutonium are now available in the B&W laboratories.

2.3. Oxide Characterization

Standard procedures for the ceramographic examination of mixed oxide pellets are nearly complete. The polishing procedure is similar to that used for spherical oxide examination; HF-HNO₃ is used as an etchant. X-ray crystallographic procedures are still under study.

2.4. Irradiation Testing

The second capsule exposure under this contract was initiated in June 1968. The capsule instrumentation indicated a higher heat rate than that calculated. The exposure was terminated, and the calibration capsule was reinserted to determine whether the reactor was undergoing long-term changes. The results were the same as those obtained

previously, and the increase in heat rate was presumed to stem from the capsule design. A recalculation at the higher heat rate showed the capsule to be safely operable at full reactor power, and the irradiation is scheduled to resume in August 1968.

2.5. Mixed-Sol Preparation

A new thermal denitrator for PuO_2 sol preparation has been designed and built and is undergoing final checkout. A new spheroidizing unit is under construction. The new unit will replace the current bench-top glassware used for mixed gel sphere production and will provide better inert atmosphere control. Steam drying, improved sol injection apparatus and 2-EH recovery are also included. The unit should be completed in September 1968.

Fuel preparation work for irradiation testing is in progress. UO_2 sol preparation includes three enrichment values: 0.7% ^{235}U (natural), 20% ^{235}U , and 93% ^{235}U . The first two will be used in BAWTR exposures and the last for EBR-II fuel. Preparation of the natural sol is nearing completion, and the 20% enriched sols are planned for next quarter. PuO_2 sol preparation for thermal exposures is nearly complete.

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

3.1. Pu(III) Fixation

It has been reported previously¹ that UO_2 gel spheres soaked in 0.5M Pu(III) solutions will pick up 4 to 8% plutonium [$(\text{Pu}/\text{U} + \text{Pu}) = 0.04$ to 0.08] in one contacting. In the process the gel behaves largely as a porous inert body.

To explore the Pu(III) behavior further, a 50 g mass of UO_2 gel spheres was contacted with Pu(III) solution and then subdivided into smaller samples, which were washed extensively with either pure water or aqueous ammonia. The results show that about half the plutonium can be leached out if the spheres are not dried after the contacting. Drying fixes most of the Pu(III) in place, and little, if any, can be removed by either ammonia solution or water washing. Details of the experiment follow.

3.2. Experimental Procedure

A 50.0 g sample of UO_2 gel was contacted with 250 ml of 0.45 M Pu(III) solution at pH 2.0 for 1.0 hour at ambient temperatures. After the solution was decanted, the spheres were divided into two groups. One group was dried overnight under an inert atmosphere (20 in. Hg, 100 C) and the other was left moist. Each was further divided into nine smaller samples which were treated as follows:

1. Not washed.
2. Washed 5 seconds with 5 ml demineralized H_2O .
3. Washed 5 seconds with 5 ml 1 M NH_4OH .
4. Washed 15 seconds with 5 ml demineralized H_2O .
5. Washed 15 seconds with 5 ml 1 M NH_4OH .
6. Washed 5 seconds with 15 ml demineralized H_2O .
7. Washed 5 seconds with 15 ml 1 M NH_4OH .

8. Washed 30 seconds with 15 ml demineralized H_2O ; repeated 10 times.
9. Washed 30 seconds with 15 ml 1 M NH_4OH ; repeated 10 times.

The washing was performed by adding the desired quantity of wash solution to the spheres, swirling for the appropriate length of time, and immediately decanting the solution. Following this treatment, each sample was dried under inert atmosphere (20 in. Hg, 100 C) overnight and dissolved for analysis. The wash water from the undried gel was blue, and the 1 M NH_4OH contained a green precipitate. During the repeated washings, these colors were observed in only the first two solutions. Thus it is apparent that at least a portion of the picked up Pu(III) can be removed readily by an aqueous wash. The effluent water from the dried gel was yellow, and the effluent 1 M NH_4OH contained a yellow-green precipitate. One possible explanation for this observation is that the UO_2 was partially oxidized during the drying and that both uranium and plutonium were partially removed by the washings.

The plutonium retention data from this experiment are summarized in Table 3-1.

Table 3-1. Plutonium Retained by Washed Gel

Wash solution	Wash time, sec	Undried gel ^(a)	Dried gel ^(a)
Not washed	--	4.7 ± 0.1	4.3 ± 0.7
5 ml H_2O	5	3.0 ± 0.2	3.5 ± 0.5
5 ml 1 M NH_4OH	5	3.5 ± 0.1	3.4 ± 0.5
5 ml H_2O	15	2.7 ± 0.2	4.8 ± 0.2
5 ml 1 M NH_4OH	15	2.5 ± 0.1	3.7 ± 0.1
15 ml H_2O	5	2.4 ± 0.4	4.4 ± 0.1
15 ml 1 M NH_4OH	5	2.5 ± 0.3	4.2 ± 0.2
15 ml H_2O (repeated 10 times)	30	2.1 ± 0.3	4.1 ± 0.4
15 ml 1 M NH_4OH (repeated 10 times)	30	2.3 ± 0.2	4.4 ± 0.1

(a) Errors are at the 95% confidence level on the mean of three determinations.

These results show that about half of the total plutonium picked up from Pu(III) solutions was removed by leaching with either water or aqueous ammonia. There is thus an upper limit on the extent of chemical interaction between the gel structure and sorbed Pu(III) solution. The chemical interaction becomes virtually quantitative if the gel is dried, since almost no plutonium is washed from the dried gel. Fixing of Pu(III) by a drying step is probably due to plutonium oxidation to the extremely hydrolyzable quadrivalent state. Nitrate residues are a logical oxidant; moreover, UO_2 gels contain varying amounts of higher valence states of uranium, depending on the preparation and storage conditions, and these are also good oxidants.

3.3. Conclusions

Based on previously reported data, the mechanisms of plutonium pickup by UO_2 gel were hypothesized.² With solutions containing Pu(III) and Pu(IV), UO_2 gel behaves mainly like a porous, inert material into which plutonium solution can be absorbed and from which it can be washed with aqueous solutions. With solutions containing Pu(VI), a chemical reaction apparently occurs between the aqueous plutonium and the UO_2 gel.

Since the plutonium in UO_2 gel contacted with Pu(VI) solutions is not homogeneously dispersed³ and since sphere attrition during contact with Pu(VI) solutions is quite severe, plutonium in the +3 or +4 oxidation state is of the most interest to the gel-addition process. With this idea and the postulated pickup mechanisms in mind, four experimental approaches were proposed⁴ to increase the pickup of plutonium into the region of interest for fast breeder fuels:

1. Chemical fixation by hydrolytic or oxidation reactions.
2. Multiple contacting of dried gel with fresh plutonium solution.
3. Increased concentration of plutonium solution.
4. Preparation of UO_2 gel with a higher void volume.

The first approach has been tested using several techniques⁵ and has shown some promise; pickup values in the region of 5 to 10% were measured. With the second approach, pickup values somewhat in excess

of 10% have been observed. However sphere degradation becomes increasingly severe with each contacting. The third approach is limited by the solubility of plutonium to less than 2 M with normal aqueous plutonium solutions, but higher plutonium concentrations can be obtained with systems such as PuO_2 sols. Neither this nor the fourth approach has been tested.

The maximum pickup attained was near 10%, while values near 5% were typical. With plutonium contents in this region, the gel-addition process could be of interest to thermal fuel technology but not to the fast breeder reactor program. As a result, the emphasis for the fuel preparation work of this contact has been shifted to the ORNL mixed sol process.

4. ANALYTICAL SUPPORT (D. H. Schmitt)

4.1. Evaluation of Methods

During the present report period, no evaluation of methods was performed under this contract. However, several procedures used directly for or related to gel-addition work were studied in detail, and equipment was set up and partially checked out for additional analytical measurements under AEC sponsorship. The work was carried out as Phase I of the Los Alamos Scientific Laboratory (LASL) Program entitled "Examination of Fast Reactor Fuels," U.S. Atomic Energy Commission Contract No. AT(30-1)-3968. For the sake of completeness the results are partially reported here.

The program was established to determine the relative capabilities of several industrial laboratories in the characterization of FFTF* fuels. The project required the evaluation and standardization of several analytical methods which were then applied to sintered $\text{UO}_2\text{-PuO}_2$ pellets of the FFTF type. The pellet material was obtained from a single batch produced by the Pacific Northwest Laboratory (PNL) and divided among the different laboratories involved in this program. Even though the material was not a well-characterized standard, it provided a basis for comparing the capabilities of the laboratories to make the necessary measurements required for FFTF fuels.

Standardization of controlled-potential coulometric determinations of uranium and plutonium was completed, and formal standard operating procedures were written for these two determinations. The mass spectrometric determination of the isotopic composition of plutonium was

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* FFTF - Fast Fuel Test Facility - a test bed to be built at Pacific Northwest Laboratory for fast reactor fuels.

also evaluated and a method was written. The procedures were applied to the pellets, and the results have been sent to LASL for comparison with those from other laboratories.

Preliminary setup of equipment and evaluation of methods were also undertaken for the following measurements:

Oxygen to Metal (O/M) ratio.

Halogen content (chloride and fluoride).

Water evolution.

However, no results were obtained for the pellets because there was not enough time to evaluate the methods completely. This portion of the work is continuing. Complete details on the evaluation work and the results of the analyses may be found in Babcock & Wilcox report BAW-3968-1.⁶

4.2. Analytical Sample Load

During this quarter 113 samples were analyzed, representing a total of approximately 580 analyses. The analyses included total U, total Pu, U(IV)/total U, NO_3^- , O/M, free H^+ , and specific gravity.

5. OXIDE CHARACTERIZATION (J. M. Kerr)

5.1. Materials Characterization

Further modifications to the ceramographic specimen preparation method for pellet fuels were made in order to produce a specimen with a minimum of polishing artifacts. The resulting preparation method is slightly different from that used for sphere specimens.⁷ It consists of the following steps:

1. Mount in "Quick-Mount" room-temperature setting epoxy.
2. Grind in "Knuth Roto-Grinder" with 400-grit and 600-grit silicon carbide paper.
3. Apply a 1100 weight to the specimen and polish with 6-micron diamond paste on Nylon cloth for 1/2 hour using a "Syntron" vibratory bowl polisher on a control setting just sufficient to provide specimen rotation of 3 to 6 revolutions around the bowl per minute.
4. Polish finally for 1/2 hour with 1-micron diamond paste using a "Syntron" vibratory bowl polisher on a control setting just sufficient to provide specimen rotation of 3 to 6 revolutions around the bowl per minute.
5. Rinse the sample between the rough polishing step and the final polishing step and again after the final polishing step.

The specimens of (U, 20% Pu)O₂ pellets have been etched using the following solution at room temperature:

100 ml	70% HNO ₃
0.05 ml	48% HF
21 ml	H ₂ O

This solution gives an excellent etch in 40 to 60 minutes. Ordinary washing of the specimen is not sufficient to remove all of the etchant.

and more work is necessary to establish a suitable means of thoroughly removing or neutralizing the etchant to stop further action. A photomicrograph of a (U, 20% Pu)O₂ pellet prepared and etched using the foregoing method is shown in Figure 5-1.

Sample preparation methods for X-ray analyses samples are being developed. Briefly, the following steps are used:

1. For solid samples, mount in "Quick-Mount" room-temperature setting epoxy and grind to provide a flat surface.
2. For powder samples, mix a small amount of powder with a small amount of liquid mounting compound, allow to dry partially, and then mount this in an ordinary 1-1/4-inch diameter mount. The surface is then ground flat.
3. Spray the prepared surface with "Krylon" plastic spray to fix any contamination.

Detailed operating procedures for using the X-ray equipment with plutonium-bearing materials have been submitted for internal approval.

5.2. Fabrication Studies

Planning for the necessary "Sphere-Pac" development work was begun. Experimental work will begin in the next quarter. Efforts will be made to determine a suitable mixture of sphere sizes and vibration techniques to produce packed densities in the range of 85 ± 1 percent of theoretical in small-diameter, short-length specimens.

Figure 5-1. Microstructure of Polished and Etched
(U, 20% Pu)O₂ Pellet, 250X

6. IRRADIATION TESTING (C. J. Baroch)

6.1. Introduction

The Gel-Addition Irradiation Task, as described in the previous quarterly report,⁸ is divided into three subtasks:

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

The scope and progress on each of these subtasks are described below.

6.2. Time Required for In-Pile Restructuring

In this subtask, the effect of heat rate and time on the restructuring characteristics of sol-gel UO_2 - PuO_2 spheres and on angular particles and pellets prepared from coprecipitated UO_2 - PuO_2 will be evaluated. Seventeen capsules will be irradiated in the BAWTR. The time for restructuring at linear heat rates of 6, 10, 15, and 20 kW/ft will be determined. The program will include a comparison of the irradiation behavior of spherical particles prepared by ORNL and B&W.

In June 1968 the irradiation of capsule GA-2 was initiated. An irradiation at 15 kW/ft for 27 days was planned, but the capsule instrumentation indicated that one pin achieved a linear heat rate of 15 kW/ft when the reactor power was only 5 MW. Extrapolation of the data to the normal 6 MW operation of the BAWTR indicated that the capsule would operate at a power level higher than that indicated in the safety analysis. The capsule was removed after achieving an exposure of 3.2 EFPD.

The reason for the abnormally high linear heat rate produced by capsule GA-2 is unknown. The calibration capsule GA-1 was reirradiated to determine whether there were significant differences in thermal flux between December 1967, when GA-1 was first exposed, and June

1968. Both GA-1 and GA-2 were reirradiated under nearly identical conditions to determine whether there were significant differences between the capsules and between the previous irradiations. The operating conditions of capsules GA-2 and GA-1 during these irradiations are shown in Tables 6-1 and 6-2, respectively. The following results were obtained from this series of experiments:

1. The performance of the calibration capsule (GA-1) in July was essentially identical to that determined in December. Therefore, there are no significant long-term variations in the thermal flux within a given BAWTR test facility.

2. The characteristics of capsule GA-2 in July and June were nearly identical.

3. Most of the data obtained from the instrumentation indicated that capsule GA-2 produced about 10 to 15% more power than GA-1 did. Capsule GA-2 was designed to produce 10% more power than GA-1.

The maximum linear fission heat rate produced by GA-2 is 10% greater than the design heat rate. Safeguards approval for irradiating capsule GA-2 for approximately 27 EFPD was requested and received. Irradiation of the capsule is now scheduled to resume in August.

6.3. Sorbed Gas Behavior

In this subtask the pressure created by the sorbed gas released from particulate fuel during irradiation will be determined. If practical, each capsule will contain two pins in which the gas pressure is continuously monitored. One pin will contain spherical sol-gel particles and the other will contain angular coprecipitated particles. Gas release characteristics of spherical sol-gel particles prepared by ORNL and B&W will also be determined. By varying the linear heat rate, it should be possible to determine the extent of the gas release as a function of average fuel temperature. The fuel pins will be irradiated at linear heat rates of 6, 10, 15, and 20 kW/ft.

The detailed design of the capsules for the gas release experiments will not be completed until the pressure sensors are on hand; they are scheduled for August delivery.

6.4. EBR-II Irradiations

The irradiations in EBR-II will provide performance data on particulate fuels under the fast reactor conditions obtainable in EBR-II. In this task the effect of heat rate and burnup on the overall performance of pellets, spherical particles, and angular particles will be evaluated. The smeared density for all three materials will be about 85%.

Approval-in-principle has been received from Argonne National Laboratory to conduct encapsulated irradiations in row 7 of the EBR-II. Linear heat ratings of 8 to 10 kW/ft can be obtained in this position. A total of 38 fuel pins, of which 19 will be irradiated at any one time, will be required for the encapsulated irradiations.

The EBR-II facility was visited in late May to discuss the procedure and schedule for irradiating gel-addition materials in the EBR-II. The necessary drawings and design information were obtained so that the experimental description and hazards analysis could be started.

ANL has suggested that a 37-pin unencapsulated subassembly be shared with ORNL, who also propose irradiation of sol-gel fuels. This subassembly will be irradiated in the core region where linear heat ratings of 14 to 16 kW/ft can be obtained.

Investigation of various methods for sodium bonding of the encapsulated fuel pins was initiated. Trips to ANL and ORNL will be made in August to acquaint the B&W staff with sodium bonding equipment and inspection techniques in current use. During the trip to ORNL, the details of the 37-pin subassembly to be shared by ORNL and B&W will be formulated.

Table 6-1. Operating Conditions, Capsule GA-2

Item	Condition at 5.3 MW	Extrapolated condition at 6 MW
NaK temperature, F	980	1100
Max possible cladding temperature, F	1112	1250
Total max linear heat rates from T's, kW/ft	17.5	19.3
Total linear heat rate from lower T's, kW/ft	13.8	15.4
Max fission ^(a) linear heat rate from T's, kW/ft	15.3	16.7
Max total linear heat rate as determined by NaK temperature, kW/ft	15.6 - 17.0	17.9 - 19.3
Total fission heat rate as determined by NaK temperature, kW/ft	13.3 - 14.7	15.3 - 16.7

(a) Maximum gamma heat at 6 MW is 2.65 MW.

Table 6-2. Operating Conditions, Capsule GA-1

Time of measurement	Reactor power, MW	NaK temp, F	Linear heat rate, kW/ft
December 1967	6.0	930 - 970	13.0 - 16.4
July 1968	5.5	870 - 960	12.5 - 15.2
July 1968 ^(a)	6.0	940 - 1030	13.6 - 16.7

(a) Extrapolated value from 5.5 MW reactor power.

7. MIXED SOL PREPARATION (R. N. Gurley)

7.1. Introduction

The laboratory unit operations system for the preparation of plutonia-urania sol-gel material by the precipitation-peptization flow sheet is being modified by (1) the introduction of an optimized thermal denitrator (in the thermal denitration step of the plutonia sol process), and (2) the introduction of optimized gelation equipment (i.e., sphere forming system).

The second major effort to prepare sol-gel material for irradiation testing has begun. Approximately 3 kg of uranium were converted to stable UO_2 sols, and approximately 0.9 kg of plutonium was converted to stable PuO_2 sols. In addition, sphere forming of natural UO_2 -20% PuO_2 fuel has begun.

7.2. Pilot Plant System (R. N. Gurley)

A thermal denitrator for use in the thermal denitration step of the plutonia sol process was constructed. Cold checkout of the unit is 90% complete, and the equipment is scheduled to be placed in service in the PuO_2 sol system during the month of August.

An optimized gelation system is being constructed. The features of the system are as follows:

1. Enclosed vessels (thus providing an inert atmosphere leading to a throughput efficiency increase).
2. Steam drying of spheres.
3. A simplified and versatile sol injection system.
4. A mixed sol feed system which will minimize segregation of the sols.
5. An increased throughput capacity.

6. Provisions for recirculating the 2 EH.
7. Tighter control of the entire unit operations technique.

The system is scheduled for completion during the month of September.

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

Preparation of approximately 4 kg of sol-gel material for irradiation testing has been initiated. All of the material will contain 20 wt % PuO₂ and 80 wt % UO₂. The ²³⁵U content will be 0.7% (natural U), 20% and 93%.

7.3.1. Preparation of Natural UO₂ Sol

A total of 2935 g of uranium was converted into stable UO₂ sols using the ORNL formate flow sheet.⁹ Each of the 10 batches contained from 222.9 g to 445.8 g of uranium. The only important effect caused by the increase in batch size was an increase in the time required for the initial reduction of uranyl nitrate [U(VI)] to uranous nitrate [U(IV)].

The results from the analyses of the stock uranyl nitrate acid solution are summarized in Table 7-1, and the run data from the sol preparations are summarized in Table 7-2. Fresh catalyst was used for each reduction except in batch 78.

Two of the 10 sol runs were lost. In batch 78 the catalyst had been previously used and had been in storage for several months; during the U(VI) → U(IV) reduction step a ferrocyanide test indicated incomplete reduction even after 80 hours running time. The run was abandoned, and the effects were attributed to poor catalyst condition. Remarkably, a strong odor of ammonia was noted when the reduction apparatus was dismantled. The ammonia could have originated from the nitrate or the urea originally in the system, so that in this run either the catalyst selectively reduced nitrate and/or urea, leaving the uranyl ion reduction incomplete, or the ferrocyanide test produced a misleading result. The observations are still unexplained. The other run loss occurred in batch 84. Through operator error the formic acid was not added before precipitation, and the run was abandoned when severe U(IV) oxidation occurred during the precipitation step. This observation shows the essential role played by formate in protecting the uranous

ion from reoxidation and raises some interesting questions on the exact mechanism involved.

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

Batch No.	Analysis No	No of analyses	Nitrate concentration, $M^{(a)}$	Uranium concentration, $M^{(a)}$	Nitrate/uranium, mole ratio ^(a)
77-89	4-D-29	3	5.18 ± 0.14	1.26 ± 0.05	4.11 ± 0.20
77-89	4-D-30	3	5.21 ± 0.03	1.24 ± 0.02	4.20 ± 0.06
77-89	4-D-31	3	5.22 ± 0.14	1.25 ± 0.13	4.18 ± 0.46
77-89	Mean	9	5.20 ± 0.04	1.25 ± 0.02	4.16 ± 0.06

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

Table 7-2. Data From Preparation of Natural UO_2 Sols

Batch No	Uranium reduced, g	Reduction time, hr	Apparent sol pH
77	445.8	16	NM ^(a)
78 ^(b)	445.8	>80	--
79	445.8	21	2.60
80	364.1	10.5	2.65
81	364.1	10.5	2.75
82	222.9	NM	2.37
83	364.1	8.5	2.62
84 ^(c)	364.1	9.0	--
85	364.1	NM	3.11
86	364.1	8.5	3.14

(a) NM - not measured

(b) Old catalyst was used, reduction did not proceed properly

(c) Formic acid inadvertently omitted

The eight stable sols were placed in four separate containers and cross-blended to provide a uniform feed for the preparation of the required natural UO_2 -20% PuO_2 microspheres. The results from the analyses of these sols are summarized in Table 7-3.

Table 7-3. Analyses of Blended UO_2 Sols

<u>Bottle No.</u>	<u>No. of analyses</u>	<u>U/g sol, mg^(a)</u>
I	8	213.8 ± 0.9
II	9	216.2 ± 1.2
III	9	213.0 ± 3.5
IV	9	210.9 ± 1.8

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

7.3.2. Preparation of PuO_2 Sol

About 890 g of plutonium were converted into stable PuO_2 sols using the ORNL precipitation-peptization flow sheet.¹⁰ Formation of Pu(VI) during the denitration step discussed previously¹¹ was suppressed by reducing the acid content of the Pu(IV) feed solution to 1 M and reducing the initial concentration of the precipitating solution to 4 M aqueous ammonia. (The Pu feed in earlier batches was 3.6 M , 4.4 M , or 6.3 M in H^+ , and the precipitant was 7.5 M or 15 M in NH_4OH .) Pu(VI) was not observed in previous batches until water was added to the denitrated powder in order to form the PuO_2 sol. However, several differences were noted in the behavior and the appearance of the material throughout the processing when lower acid and base concentrations were used:

1. The aqueous Pu(IV) oxide precipitate was a much darker green color.
2. The filter cake had nearly twice as large a volume ($\approx 0.9 \text{ l}$).

3. Fewer washes were required before the pH of the effluent was below 7.5.
4. The precipitate peptized much faster.

In addition, the PuO_2 sol could be made more concentrated. These observations have been made previously¹² and were important in identifying which step in the procedure induced Pu(VI) formation. Thus, it is apparent that high acid and/or ammonia concentrations during the initial precipitation result in the preparation of a form of hydrated Pu(IV) oxide which can be readily oxidized during the drying procedure and/or thermal denitration.

The run data from the 12 batches are summarized in Table 7-4. The decrease in baking time in the latter runs is probably due to an increase in the sand bath temperature. The baking temperature is not listed in Table 7-4 because there is no accurate way to measure it with the present equipment.

In batch 10 the precipitate was washed 13 times until the effluent pH reached 7.9 (as compared with the usual value of 7.5). In addition, some Pu(VI) was observed during the first attempt to suspend the denitrated powder, and the PuO_2 polymer was salted out. After decanting the supernate, the sol formed properly; no additional Pu(VI) was observed. One possible explanation for the large number of washings is the fact that some NH_3 was in the glove-box atmosphere. Thus, enough ammonia could have dissolved in the water during the washing procedure to raise the pH above 7.5 before filtering. Although the reason for Pu(VI) formation in this case is not clear, the same effect was observed on a previous occasion¹³ when washing, peptization, and denitration were carried out in the presence of ammonia. During the following 11 runs, ammonia was excluded from the box atmosphere, and neither an excessive amount of washing nor Pu(VI) formation was encountered.

In batches 14 and 15, the partially denitrated powder would not sol upon water addition. Normally, during the initial precipitation, Pu(IV) is added to the ammonia at a rate of 25 to 30 ml/min. However, owing to an equipment malfunction during each of these two runs, plutonium additions rates in excess of 100 ml/min were obtained for a short period of time. Three other differences from the normal operating conditions were also noted:

1. Fewer washings were required.
2. A larger quantity of HNO_3 and a longer period of time were required to peptize the filter cake.
3. During the evaporation to dryness, large amounts of dried sol turned from black to green before all of the sol was dry.

These observations indicate that an undesirable form of the hydrous Pu(IV) oxide is prepared if the rate of precipitation is too rapid.

In each of the last 6 batches, the conditions during the initial precipitation step were rigidly controlled, and no problems were encountered. Thus it seems that successfully preparing stable PuO_2 sols by the precipitation-peptization flow sheet depends strongly on holding the proper conditions in the preparation of the hydrated Pu(IV) oxide.

7.3.3. Sphere Formation

Under the laboratory system presently being used in the preparation of urania-plutonia gel microspheres, both the sol and the gel are exposed to air during a portion of the operation and are thus partially oxidized. During previous mixed gel preparation runs,¹⁴ oxidation gave rise to two serious problems:

1. A large fraction of the spheres was cracked and thus rejected from the final product.
2. The surfactant levels in the 2-ethyl-1-hexanol had to be adjusted frequently to obtain a spherical product, probably because of the changing properties of the sol resulting from oxidation.

It has been found that the first problem can be minimized if the gel is soaked in concentrated NH_4OH for about 30 minutes immediately after its removal from the column. Samples of UO_2 gel subjected to this treatment have been washed with ethanol and air-dried with no observable cracking. Other samples of NH_4OH -soaked UO_2 gel that were dried under argon have subsequently been exposed to air for periods of up to 24 hours with no apparent damage.

The problem with oxidation of the sol can be minimized by not allowing the mixed sol to remain in a glove box with an air atmosphere for a great length of time. It has been found that under the previous operating procedure,¹⁴ a continuous argon purge is capable of

protecting the U(IV) sufficiently for at least two days, so that no re-adjustment of the surfactant levels is necessary.

A new batch of natural UO_2 -20% PuO_2 microspheres for irradiation testing in the BAWTR is being prepared. Except for the two changes mentioned above, the technique and the equipment are the same as those previously described.¹⁵ At the present time, about 100 g of gel have been produced from this run.

Table 7-4. Summary of Batch Preparation of Pu(IV) Sols

Batch No.	Stock solution		Pu input, g	4 M NH_4OH , l	No. washes	Vol H_2O per wash, l	NO_3^-/Pu mole ratio to peptize	Baking time, hr	Final NO_3^-/Pu mole ratio	Yield of denitrated powder, g	Pu recovered as sol, % ^(a)
	Pu, g/l	H^+ , M									
10	29.5	1.0	100.9	11.3	13	2.0	1.54	5.7 6.0	0.15 0.18	60 ^(b)	51
11	55.6	1.0	98.7	2.5	5	1.0	1.84	7.0	0.15	106	91
12	55.9	1.0	99.1	2.5	5	1.0	1.83	4.0	0.19	108	93
13	55.7	1.0	98.9	2.5	5	1.0	1.84	1.2	0.09	109	94
14	56.2	1.0	197.5	5.0	3	2.0	2.63	3.0 ^(c)	0.70 ^(c)	0 ^(c)	--
15	56.5	1.0	100.3	2.5	3	1.5	2.33	2.0 ^(c)	1.0 ^(c)	0 ^(c)	--
16	55.7	1.0	98.9	2.5	4	1.5	2.02	3.0	0.09	105	91
17	55.7	1.0	98.8	2.5	5	1.5	2.06	2.0	0.12	110	95
18	55.4	1.0	99.2	2.5	5	1.5	1.87	1.0	0.15	119	101
19	51.6	1.0	99.1	2.5	5	1.5	1.87	0.6	0.07	105	99
20	57.2	1.0	76.3	1.9	5	1.0	2.57	0.5	0.15	89	99
21	54.7	1.0	131	3.1	4	2.0	1.85	0.6	0.15	147	95

^(a) Assuming denitrated powder is 85 wt % Pu.

^(b) Yield decreased due to formation of Pu(VI).

^(c) Baking discontinued because powder would not resuspend.

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