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GEL-ADDITION PROCESS CHEMICAL STUDIES

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RELEASED FOR ANNOUNCEMENT
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ABSTRACT

The Babcock & Wilcox Company's Gel-Addition Process for preparing nuclear fuels was originated in their Nuclear Development Center; it is a modification of the general sol-gel process for producing high-density oxides. The sol-gel process has been studied at Oak Ridge National Laboratory and other sites for almost ten years. Gel-addition begins with the preparation of a single-component sol of fertile material which is then dehydrated to a gel. The resulting product is subsequently converted to a mixed gel by soaking it in an aqueous solution of fissionable material. The final product, oxide, is obtained by gel calcination. The process was originally used to prepare urania-thoria, and a study of its applicability to the urania-plutonia system is the subject of this project.

Urania gels have been contacted with plutonium in three valence states (III, IV, VI) in acid nitrate solution (pH approximately 0.5), and the uptake of plutonium has been measured for periods ranging from a few minutes to several hours. Plutonium(IV) seems to be the most promising, since it combines a high uptake (about 20% U/U + Pu) with ease of preparation. However, all Pu-HNO₃ solutions are corrosive to UO₂; therefore, gel attrition measurements have received considerable attention.

Progress during the first quarter, ending October 1, 1966, 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

1.1. Gel-Addition History

In 1962 Babcock & Wilcox¹ initiated a pilot plant study of U-233-O₂-ThO₂ recycle fuel preparation using the sol-gel flow sheet worked out by Oak Ridge National Laboratory (ORNL) during their Kilorod Project.² The process starts with the preparation of a thorium aquasol to which aqueous uranyl nitrate is added. Drying a sol of the proper composition yields a mixed oxide gel that can be fired at temperatures near 1150 C in a reducing atmosphere to produce a UO₂-ThO₂ solid solution of exceptionally high particle density and uniform composition.

During the pilot plant studies it was discovered that a mixed gel could be prepared by contacting a single component solid (ThO₂) gel with uranyl nitrate solution, as well as by drying a mixed sol. It was immediately recognized that urania-plutonia and even pure urania reactor fuels could probably be prepared by analogous methods. Early in 1966 B&W applied for a series of patents on the process, now known as the B&W Gel-Addition Process, and late in June 1966 the U. S. Atomic Energy Commission undertook support of a study of the process as applied to urania-plutonia fuels. This report summarizes the results for the first 3-month period of work, which ended October 1, 1966.

1.2. Gel-Addition Incentives

The Gel-Addition Process as applied to UO₂-PuO₂ preparation is now in the earliest stages of bench-scale experimental work; although it is too early to evaluate the total process, it is important to recognize the economic incentives involved. They can be summarized as follows:

1. Firing Temperatures Reduced It is anticipated that gel-addition products can be fired into oxide solid solutions at temperatures near 1150 C. This advantage, shared by sol-gel materials, represents significant savings in fuel and material costs relative to the conventional

temperature of about 1600 C used for firing of pellet materials prepared by oxide mixing and coprecipitation methods.^{3,4}

2. Scrap Recovery Costs Decreased Quality control of fuel involving the rejection of unwanted particle shapes and sizes becomes substantially less expensive if the particles constitute a one-component system. UO_2 and PuO_2 size control in gel-addition fuels would involve sizing UO_2 gel; the unwanted fractions could be recycled back to sol and re-gelled without requiring a Pu-U separation.

3. Particle Preparation Costs Reduced The processes involved in sol and gel preparation can be optimized by the usual methods of good chemical engineering practice, including automation and large batch sizes, if fissionable material is withheld until the particles are finished and sized. The savings arise from two main sources: elimination of the criticality hazard and decreased fissionable material inventory costs. It is hoped that gel particles can be made and stockpiled to await the last steps—plutonium addition and firing.

4. Spherical Powder Commercially Attractive The methods worked out at ORNL for preparation of spherical sol-gel materials showed very early that they could yield a good gel for gel-addition in the ThO_2 - UO_2 system;⁵ thus there was reason to expect that similarly prepared urania gel spheres would yield a suitable gel for plutonium-bearing fuels. The clear economic advantage in preparing a one-component gel containing little or no fissionable material makes the Oak Ridge process much more attractive commercially and opens up the possibility of using spherical oxide powders as feed material for vibratory compaction as well as dispersion fuels. The powder should be a nearly dust-free nuclear fuel.

1.3. Gel-Addition Chemistry

Thoria gels take up large quantities of uranium from aqueous uranyl nitrate; that is, hexavalent uranium in solution associates in some way with quadrivalent thorium in oxide gel form to give mixtures containing as much as 35% uranium.* At the same time other ions, for

*Although this high value was observed in one set of experiments in the B&W laboratories, there is no reason to conclude that it represents an upper limit.

example, Ra(II) and La(III), are apparently rejected or are at least not picked up in quantities even approaching the uranyl ion values. Moreover, little or no thorium appears in the aqueous solution.

1.3.1. Urania Stability

These facts suggest that the best possibility for a successful gel-addition process for UO_2 - PuO_2 fuels would involve contacting UO_2 gels with aqueous plutonyl nitrate. Urania sols and gels are more difficult to handle than their thorium analogs, however, because uranium is easily oxidized to hexavalent form in aqueous solution. Thorium exists only in quadrivalent form in solution.

Therefore, a major part of the laboratory investigation must deal with the question of urania gel stability in plutonium solutions. The question is complicated because hexavalent plutonium is a strong oxidant and readily converts dissolved* quadrivalent uranium to the hexavalent form.^{6,7} Moreover, nitric acid, a common solvent for UO_2 , also converts quadrivalent to hexavalent uranium. Since some free nitric acid is required to prevent hydrolytic precipitation or polymerization of plutonium solutions, UO_2 gels must resist the attack of both nitric acid and plutonium during the contacting steps of the process, at least until the plutonium reaches the desired level in the gel. Gel sphere attrition should not exceed some limiting but as yet unknown commercially acceptable value. The behavior of various gels under chemical attack is expected to vary widely with gel history, since the more highly hydrated materials should be oxidized most easily. The hexavalent uranium content of the finished gel is expected to be an equally important factor.

1.3.2. Plutonium Valence

Plutonium exists in three readily prepared valence states in aqueous solution—trivalent, quadrivalent, and hexavalent. Although earlier thoria work indicated the most promise for the hexavalent form, the lower valence states are not as chemically aggressive toward urania

* UO_2 gel is not a dissolved form of U(IV); hence the gel may survive an oxidative attack that would destroy a U(IV) solution.

and hence offer better possibilities for lowered gel attrition. The effects of changes in the plutonium valence state are therefore of major interest to the program, and much of the work reported in the following sections is directed toward methods of preparing plutonium solutions of known concentration in trivalent and hexavalent form. The starting solutions are in quadrivalent form and the others have been derived from it.

1.4. Experimental Approach

The laboratory work has naturally divided itself into four principal areas: preparation of urania gel, preparation of plutonium solutions, contacting experiments, and analytical support. Each of these areas is discussed in detail.

2. CONCLUSIONS

2.1. UO₂ Gel Preparation

Preparation of UO₂ spherical gels by the ORNL formate process in a stirred vessel yields a material of high U(IV) content which is relatively resistant to air oxidation and nitric acid attack. The process batch size is being extended from 10-15 grams to 100 grams or more. The product spheres range in size from about 20 to 150 microns (average, about 40 μ). A new procedure for converting uranous hydroxide filter cake to a UO₂ sol has been developed.

2.2. Plutonium Solution Preparation

Incoming Pu(IV) nitrate solutions can be converted virtually quantitatively in strong acid solutions to Pu(III) or Pu(VI) by methods which are reproducible and sufficiently rapid for laboratory work on gel-addition chemistry. Residual Pu(IV) can easily be separated from Pu(VI) preparations by ion-exchange methods.

2.3. Gel Contacting

An operating region has been found in which the solutions are sufficiently acid to suppress hydrolytic precipitation of some plutonium solutions, but not acid enough to dissolve UO₂ gel rapidly. In this region we have observed plutonium pickup as high as about 20% Pu/(U + Pu) from quadrivalent plutonium solution and 9% from trivalent plutonium. The pickup from hexavalent plutonium is in doubt because of severe sphere attrition.

Gels prepared by ORNL methods are clearly more resistant to Pu-HNO₃ attack than those made by NFS methods.

2.4. Analysis

Procedures are available for the analysis of plutonium solution using coulometric and complexometric titrations and spectrophotometry. Analytical development continues in the area of valence state measurements.

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

Because gel history is expected to have considerable influence on the extent of plutonium uptake by UO_2 gels, it is essential to use gels with a well-known history, at least for most measurements. Accordingly, apparatus has been assembled in the B&W laboratories for the production of UO_2 gel by the formate flow sheet worked out by the Oak Ridge Chemical Technology Division. Some tests were also run on UO_2 gels supplied by Nuclear Fuel Services at Erwin, Tennessee,* during the construction of large-scale gel preparation equipment in the B&W laboratories; they were intended to provide a basis for comparing the behavior of gels having grossly different histories.

3.1. B&W-Produced Material

3.1.1. Process Description

The ORNL formate process described by McBride, with a few modifications, has been used for the current work.⁵ The basic flow sheet consists of the following steps:

1. Uranium Reduction A 0.5 M uranyl nitrate solution containing 1.3 M nitric acid and 0.26 M urea is reduced to U(IV) with free hydrogen at ambient temperature and pressure over a solid phase catalyst prepared by depositing metallic palladium on a thoria sol. (Catalyst preparation is described by McBride.⁶) Present batches start with a charge of 75 grams of contained uranium. All operations following the reduction are routinely carried out under a nitrogen blanket to prevent re-oxidation to hexavalent uranium.

*The material used was made available by special arrangement with the NFS staff. UO_2 gel is not one of their usual market products, but is prepared as an intermediate in the formation of UO_2 spherical fuels. Preparation methods are held proprietary by Nuclear Fuel Services.

2. Catalyst Separation The catalyst is readily separated from the mother liquor by a combination of decantation and filtration.

3. Hydrous Oxide Precipitation The hydrated oxide precipitates when the uranous solution is made 0.3 M in formic acid and is brought to pH 7.5 by slowly adding a mixture of 3.0 M aqueous ammonia and 0.5 M hydrazine hydrate.

4. Filtration and Washing The hydrated U(IV) oxide filters off readily on Whatman No. 42 filter paper in a Büchner funnel. Wash water volume is held to 30 ml per gram of uranium charge.

5. Sol Preparation The oxide filter cake is converted to a sol by heating it to 60 C and stirring vigorously. A charge of 75 grams U(VI) yields about 150 ml of sol at a concentration of 1.8 to 2.0 M.

6. Sphere Formation Dehydration of sol droplets by water extraction produces UO_2 gel spheres. The extractant is 2-ethyl-1-hexanol (2 EH) containing 1 volume percent of surfactant (0.5 vol % Amine-0 plus 0.5 vol % SPAN-80).^{*} For our purposes spheres are made by injecting sol into a stirred pot of fresh organic. The spheres are separated by decantation and filtration and are washed in pure 2 EH and in acetone. They are dried on a fritted disc filter funnel in inert gas at ambient conditions and are stored in sealed bottles under nitrogen.

3.1.2. Apparatus Description

Although the process is chemically straightforward, the dilute solutions used lead to large volumes. The resulting bulkiness and the need for an inert atmosphere impose some restrictions on equipment design and selection. The maximum uranium mass that can be handled easily in two small glove boxes is near 75 grams uranium; this set the batch size.

Catalytic reduction takes place in a 2-liter reaction vessel equipped with a four-neck cover accommodating the stirrer, the gas dispersion tube, the decanting dip tube and vent, and the filling port.

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^{*} These additives are proprietary products. Amine-0 is a complex tertiary amine produced by the Geigy Chemical Co. SPAN-80, produced by Atlas Chemical Industries, is sorbitan mono-oleate.

Since the reduction vessel is a sealed vessel purged with an inert gas before reduction is started, it is not housed in a glove box. The potential hazard of using hydrogen in a confined glove box is also eliminated.

After reduction the catalyst settles, and the reduced uranium solution is transferred into the inert-atmosphere glove box by suction. A fine fritted glass filter is included in the transfer line to remove any suspended catalyst.

The uranous nitrate solution is transferred to a 2-liter beaker for precipitation. Formic acid is added, and the beaker is jacked up to a fitted cover equipped with a separate inert gas purge, stirrer, pH electrode, and precipitant-addition line.

When the precipitation is complete, the slurry is poured through a table-type Büchner funnel. The filter cake is washed with deaerated water and partially dried by a stream of inert gas. The cake is converted to a sol in a 500-ml freeze-drying flask suspended in a 2-liter glass reactor vessel filled with water at 60 C. The two vessels are flanged to a cover equipped with a stirrer, purge gas line, and reflux condenser.

At this point the sol can be converted to gel in any required form by dehydrating. For sphere formation the sol is transferred to rubber-stoppered serum bottles (previously purged with inert gas) and transferred to a second nitrogen-filled glove box, which contains the sphere-forming equipment.

The two most common methods of converting sols into gel spheres are the column methods (spherical droplets are formed and permitted to settle through either a flowing or stagnant column of liquid) and the stirred-vessel method (spherical droplets are formed and suspended by the high shear imparted to the fluid by a stirrer).

Column methods usually produce larger and more uniform ($1000\ \mu$, $D_L/D_S \approx 2$) spherical particles, but they are generally slower and require more careful control; stirred vessels are generally limited to smaller spheres with a considerable range of particle sizes ($150\ \mu$, $D_L/D_S \approx 10$).

Stirred-vessel methods were chosen for production of the first gel spheres for the initial gel-addition experiments, partly because the equipment is simpler to install, but mostly because the

residence time in the solvent for all spheres in a batch is the same and is easy to control. Column-produced material will be used later in the program.

The present apparatus consists of a 4-liter beaker equipped with a three-blade turbine stirrer. About 50 ml of sol is injected into 3.5 liters of 2-ethyl-1-hexanol containing surfactants. After the spherical droplets gel, the stirring is stopped and the gelled spheres are allowed to settle. They are decanted, filtered, washed, dried, and stored for use.

3.1.3. Preliminary Experiments

Some preliminary experiments were improvised to gain some familiarity with the process while awaiting delivery of the planned apparatus.

The uranium reduction catalyst is palladium metal deposited on the surface of thoria sol particles and is prepared as follows: Thoria, prepared by calcining the oxalate at a temperature not exceeding 650 C, is converted to an aqueous sol containing 0.05 grams of palladium nitrate per gram of thoria (ThO_2 concentration: 100 to 200 gm/liter). The order of reagent addition seems immaterial; however, palladium nitrate solution should be mixed with thoria as soon as possible after it is dissolved in water. The resulting sol is opaque and light tan in color; it is somewhat unstable; the bulk of the thoria will settle. Refluxing for an hour or more converts it into a dark brown, translucent sol which is extremely stable and has only the slightest trace of sediment. The thoria particles in this sol are then coated with palladium by bubbling hydrogen gas through the sol at any temperature between 20 and 60 C. The resulting palladium-coated thoria catalyst is a flocculent black suspension which settles slowly and is easily resuspended for use.

The first attempt at preparing a U(IV) sol and U(IV) microspheres was only partially successful. Uranyl nitrate solution containing about 15 grams of uranium was successfully reduced to better than 99.3% U(IV); however, the U(IV) partly reoxidized during successive operations because of either residual oxygen or oxygen in-leakage in the glove box. The resulting oxide filter cake was too dry and too dense, and whipping it did not give a good sol: the material became sticky and lumpy. Water addition (20 to 30 ml) produced a black suspension.

Samples of this "sol" or suspension analyzed 62.3% U(IV). This suspension, injected into the organic drying agent, produced black spheres with a surface texture resembling coke or charcoal.

In the second experimental batch, re-oxidation in the nitrogen atmosphere of the glove box was suppressed by reducing air in-leakage and purging the box more thoroughly with nitrogen. Operations were accelerated and each reaction vessel was supplied with its own nitrogen purge. The U(VI)-U(IV) reduction required 6 hours and 21 mg of palladium; the yield was 22.5 grams of 99.8% U(IV). Both the precipitated U(IV) and the filter cake were gray-green. The cake was moist and much more voluminous than previously. This filter cake was successfully whipped into a fluid mass, but it was, at best, a difficult operation because the cake was somewhat thixotropic. The highly sheared portion of the material formed a fluid mass quite easily, but the portion more distant from the agitator had a tendency to set. The addition of a few ml of water greatly increased the fluidity of the system. After the material was a completely fluid, gray-green mass, it was heated to about 60 C: an opaque black sol formed. This final sol was stable but contained considerable black sediment. Analysis of a sample of the well-mixed sol indicated that it contained 77.3% U(IV) and was 35 wt % uranium (which corresponds to 2 to 2.5 M uranium). The stable portion of the sol, without the residue, was then injected into the 2 EH dehydrating mixture. The product yield was about 12 grams of gel spheres, which were considered acceptable on the basis of their shiny black surface and better oxidation control in the sol stage. Particle size range was about 15 to 150 microns.

The third experimental batch resulted in the successful production of about 9 grams of acceptable U(IV) gel microspheres. Twenty-five grams of uranium in nitrate solution was reduced, and the U(IV) was precipitated within 12 hours after the reduction was completed. The precipitation period was extended to almost 2 hours, which seemed to improve the general characteristics of the precipitate. The gray-green precipitate was filtered, washed with deaerated water, and dried in flowing nitrogen for 10 minutes. The final filter cake was much more moist and more voluminous than the previous ones and whipped into a fluid mass more easily. The material dried excessively during the

heating period which converts the fluid mass to a black sol. Water was added to fluidize the system again, but a large amount of non-dispersible residue resulted. The fluid portion of the product appeared to be a stable black sol, but it contained a large amount of black sediment. The stable portion of the sol, without the residue, was converted to gel spheres. The run yielded about 9 grams of gel spheres; they were shiny black under the microscope and had a particle size range of about 25 to 100 microns (average diameter about 40 microns).

The fourth experimental batch resulted in the successful production of about 45 grams of acceptable U(IV) gel microspheres. Uranyl nitrate solution containing 46.7 grams of uranium (after sampling) was reduced to more than 99.88% U(IV) in 4 hours using hydrogen gas at ambient conditions and about 45 mg of palladium on the catalyst. The U(IV) sol was precipitated within about 12 hours after the reduction was completed. The precipitation step was extended over a 2-hour period which, as in batch 3, seemed to improve the general characteristics of the precipitate. The gray-green precipitate, which appeared grayer than usual, was filtered, washed with deaerated water, and dried with N_2 for 10 minutes. The final filter cake was more moist and more voluminous than the previous filter cake, probably because of the increased thickness, which reduced the effectiveness of the N_2 drying period.

One of the principal objectives of this run was to determine whether the conversion of filter cake to sols could be improved or speeded up. About 20% of the filter cake was broken into large chunks and placed in a purged flask marked "sol 4A"; this material was converted to sol by allowing it to age. Another 20% of the filter cake was broken into large chunks and placed in a sealed flask (marked "sol 4B") to be converted to a sol using an ultrasonic bath at 60 C. The remaining 60% of the filter cake was easily whipped into a fluid mass using a variable speed stirrer. About one third of this fluid suspension was poured into a flask, marked "4C", and converted to sol by aging. The remaining suspension, about 40% of the filter cake, was placed in a double boiler to be converted by heating to 60 C with continuous stirring. This last sol showed signs of drying out in spite of a humidified N_2 purge and the addition of 15 ml of water. The heating and stirring were discontinued, and the black U(IV) sol was transferred to a purged flask marked "sol 4D".

Flask 4B, which still contained chunks of filter cake, was immersed in an ultrasonic bath at 60 ± 5 C for about 1-1/2 hours, after which it had the typical appearance of a U(IV) sol.

Within 24 hours after subdividing the filter cake, all four sols had the typical appearance of U(IV) sols. All had the same brownish-black color (in thin films), and all had some sediment. Sol 4D was slightly more viscous—probably because of water loss.

The stable portion of all four sols (without the residue) was converted to spheres. The product yield was about 45 grams of shiny black spheres with a particle size range of about 20 to 135 microns and an average diameter of about 40 microns.

3.1.4. Summary of Results From Preliminary Experiments

Table 3-1 summarizes the process conditions for the four experimental batch preparations of U(IV) gel microspheres using the ORNL formate process. Table 3-2 summarizes the reported analytical results for samples taken from the four experimental batches. In addition to the data summarized in the tables, the following points were clearly established by these preliminary experiments:

1. The palladium catalyst described in the McBride patent can be made without difficulty and gives almost quantitative yields of U(IV) by hydrogen reduction.⁸

2. The catalyst settles completely and can be separated from the uranous nitrate by decantation. Filtration of the decanted uranous nitrate serves as a backup precaution and is needed only toward the end of the decantation. Any appreciable quantity of catalyst readily plugs the filter.

3. Reduced uranium is very sensitive to re-oxidation. If it is re-oxidized to 20 to 25% U(VI) the batch will not form a suitable sol.

4. Precipitation of the hydrous oxide should be extended over about a 2-hour period. The resulting filter cake is easier to convert to a sol.

5. The filter cake must be kept wet at all times while it is being washed, or it will crack and not wash uniformly.

6. If excessive drying occurs during the sol-forming phase, the uranium seems to form an irreversible precipitate which results in a sol with a large amount of non-dispersible material.

7. Aging and ultrasonics seem to be the preferable methods of preparing sols from a filter cake. Water loss is negligible; hence the risk of forming an irreversible precipitate is minimized.

8. Microspheres in the 20- to 150-micron size range can be made consistently in a 4-liter beaker.

3.2. NFS-Produced Material

3.2.1. NFS Urania Gel Microspheres

NFS prepared urania gel microspheres from depleted uranium especially for this program. The spheres were formed in an organic liquid, washed with water, and vacuum-dried at 250 F. The manufacturer indicated that they contained about 1% zirconium as a sintering aid.

3.2.2. Characterization of NFS Material

To provide a basis for comparing gels prepared by ORNL methods and by other methods, NFS spheres were examined in some detail.

Microscopic examination showed that the NFS gel microspheres had good sphericity and a lustrous black surface texture characteristic of urania gel. The microsphere diameters ranged from 60 to 250 microns with an average of about 80 microns; B&W material diameters range from 20 to 135 microns with an average of about 40 microns.

Chemical analysis showed 72 wt % uranium, of which 70.2% was in the U(VI) form;* 7.7 wt % volatile matter (weight loss at 175 C); 1.7 wt % zirconium; and 0.37 wt % nitrate. After these weights are adjusted for the oxygen content of UO_3 , UO_2 , and ZrO_2 , there is

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*Theoretically, about 66.9% of the uranium in U_3O_8 is U(VI).

still about 5 wt % unidentified or unaccounted-for material. Chloride was sought but found to be at undetectable levels.

The spheres were compared with U_3O_8 by differential thermal analysis. The thermograms were quite similar if the spheres were first dried at 175 C to remove the volatile matter. A sample of spheres exposed to air was repeatedly weighed over a 2-month period to determine whether air oxidation affected the mass; no weight change was observed.

Chemical stability tests performed on the NFS microspheres generally indicate that

1. At concentrations above 2 N, the spheres are readily dissolved in both nitric and hydrochloric acids. At the lower concentrations the dissolution rate was much slower (on the order of 24 hours). At HNO_3 or HCl concentrations below 0.1 N, the spheres seemed to convert to sol readily but dissolve very slowly. The HNO_3 seemed to attack the spheres a little more quickly than the HCl . Ordinary UO_2 is insoluble in HCl , so the rapid attack of HCl on these spheres must stem from the high U(VI) content.

2. In demineralized water at about room temperature the microspheres clump together, but no clumping occurred at 0 and 100 C. Little or no visible reversion to sol, dissolution, or oxidation was caused by the water.

3. The spheres exhibited no apparent changes on exposure to acetone or ethanol. In early discussions the NFS staff expressed the opinion that their gel would decrepitate if contacted with acetone. This effect was not observed in the B&W laboratories; hence it is concluded that the age of the gel altered its usual behavior. A slow oxidation may account for the change.

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

Reagent or process parameter	Experimental batch No.			
	1	2	3	4
Uranium, gm	15	22.5	25	50
Uranium nitrate hydrate, gm	31.6	47.4	55.4	109.0
Concentrated nitric acid, ml	10.4	15.6	17.3	30.1
Urea, gm	2.0	3.0	3.2	6.3
Pd on ThO ₂ catalyst (3 mg Pd/ml ThO ₂), ml	3 + 2	7	7	15
Total volume of solution, ml	129	196	208	395
Hydrogen flow rate, cc/min	560	580	580	900
Hydrogen reduction time, hr	9	8	10	12
Formic acid, ml	1.6	2.4	2.5	5.1
Precipitant (NH ₄ OH + H ₄ N ₂ •H ₂ O), ml	100	115	126	248
Precipitation time, hr	1	1.5	2	2
Volume of wash water, ml	450	675	690	1410
Drying time on filter, min	15	10	10	10
Volume of filter cake, cc	17.5	50	55	150
Volume of U(IV) sol, ml	--	35	35	95
Yield of gel spheres, gm	0	12	8	45

Table 3-2. Summary of the Reported Analytical Results for the Experimental Batch Preparations of U(IV) Gel Microspheres

	Experimental batch No.			
	1	2	3	4
Uranyl nitrate dissolved in water				
U conc. mg/ml	--	67.0 ^(a)	260	326
Nitrate conc. mg/ml	--	39.55 ^(a)	155	183.5
Nitrate + U mole ratio	--	2.264 ^(a)	2.29	2.16
Uranyl nitrate dissolved in HNO ₃				
U conc. mg/ml	--	207	231	285
Nitrate conc. mg/ml	--	246.6	343	305.0
Nitrate + U mole ratio	--	4.57	5.70	4.11
Samples during U(VI) to U(IV) reduction				
U(VI) after 0 red. time, mg/ml	123	118.4	121.0	127.6
U as U(VI) after ≈4 hr red. time, wt %	1.4 ^(b)	0.2	1.5 ^(b)	0.12
U as U(VI) after ≈6 hr red. time, wt %	1.1 ^(b)	0.2/1.3 ^(b)	1.4 ^(b)	--
U as U(VI) after ≈12 hr red. time, wt %	--	--	--	0.18 ^(b)
Sample of reduced U(IV) solution after catalyst settled				
U as U(VI) 12 to 24 hr after reduction, wt %	0.7 ^(b)	2.7 ^(b)	1.8 ^(b)	1.2 ^(b)
Sample of bulk sol (with non-dispersibles)				
U as U(VI), wt %	37.7	22.7	20.96	16.21
U in sol, wt %	--	35	34.3/53.8	37.09
Nitrate + U mole ratio	--	--	--	0.236
Sample of decanted sol				
U as U(VI), wt %	--	24.5	22.62	21.47
U in sol, wt %	--	--	29.08	30.6
Nitrate + U mole ratio	--	--	--	0.0846
Sample of gel spheres				
U as U(VI), wt %	--	26.2	20.32	7.95 ^(c)
U in spheres, wt %	--	66.6 ^(c)	84.0 ^(c)	93.7 ^(c)
Samples of glove box atmosphere, vol %				
O ₂ - blank or control	--	--	4.7	--
O ₂ - after 350 ft ³ N ₂ purge	--	--	7.4	5.4
O ₂ - after 650 ft ³ N ₂ purge	--	--	5.9	--
O ₂ - after 850 ft ³ N ₂ purge	--	--	--	0.7

(a) Specially prepared sample of UNH solution.

(b) Analysis delayed about 24 hours.

(c) Questionable result, possibly due to instrument error.

4. PREPARATION OF PLUTONIUM SOLUTIONS (E. J. Kosiancic)

Input plutonium for the program was supplied by Isochem (Hanford, Washington) as quadrivalent nitrate solution at a stated concentration of 231 mg Pu/ml. A confirming analysis in the B&W laboratories showed 237 mg/ml. The free nitric acid level is about 3 M. All solutions were derived from this stock material.

4.1. Trivalent Plutonium

A number of reductants will reduce quadrivalent plutonium to the trivalent form,⁹ but all work to date on this project has been limited to hydroxylamine hydrochloride, $\text{NH}_2\text{OH} \cdot \text{HCl}$. The reduction is not difficult to follow since a pronounced color change takes place from the brown of the as-received Pu(IV) to the blue of Pu(III). The stoichiometry of the reaction in strong nitric acid solution has not been found in the literature; hence, in the earliest tests aqueous hydroxylamine was added stepwise until the blue color persisted. The reaction is accompanied by a strong effervescence and brown fumes from nitrogen redox products. Spectrophotometric examination of the resulting solutions revealed no Pu(IV). Pu(III) solutions are now routinely prepared for use by adding hydroxylamine hydrochloride directly to Pu(IV) stock solution and adjusting the free acid level to an indicated pH of 0.5 with aqueous ammonia.

Some qualitative information has been obtained on the stoichiometry of the reduction through the following experiments:

4.1.1. High-Temperature Reduction

Pu(IV) stock solution was held near 90 C and hydroxylamine hydrochloride solution was added in known small increments. The stock solution contained about 10 millimoles of Pu(IV); hence a 1:1 molecular stoichiometry would require about 10 mmol $\text{NH}_2\text{OH} \cdot \text{HCl}$ (~700 mg) for complete reduction. After three times this amount had

been added, Pu(III) was still undetectable in the solution. The addition produced an obvious reaction, so it must be concluded that under these conditions, the net reaction took place with nitrate (or nitric acid) instead of plutonium.

4.1.2. Room-Temperature Reduction

The above experiment was repeated at room temperature; after 1.2 grams $\text{NH}_2\text{OH} \cdot \text{HCl}$ had been added, the solution was stirred for an hour with no detectable reduction. Neutralization of some of the excess acid with aqueous ammonia brought immediate reaction and resulted in the blue color of Pu(III). When the free acid level was reduced to 1 to 2 M, about half the plutonium was trivalent. Another 0.8 gram of reductant was added and the pH was adjusted to 0.5. The reduction to Pu(III) was apparently quantitative.

In a third experiment 10 ml of Pu(IV) stock solution was treated with 0.8 gram NH_2OH at room temperature, and the pH was adjusted to an indicated 0.5. The plutonium was completely reduced.

These results indicate that there is a 1:1 stoichiometry between Pu(IV) and hydroxylamine in plutonium reduction in dilute nitric acid. High concentrations of nitric acid inhibit the reduction; in fact, the reaction becomes stoichiometric only in the region of pH 0.5. This conclusion is in accord with Allison's results, which show that hydroxylamine reduction of plutonium is faster in half molar than in one molar nitric acid ¹⁰

4.2. Hexavalent Plutonium

A number of oxidants will convert quadrivalent plutonium to the hexavalent form, but for this project only two have been studied to date—pentavalent bismuth (sodium bismuthate) and nitric acid. Use of the second oxidant has become standard practice, since it adds no foreign metal ions to the system (a particularly desirable characteristic for solutions to be used in gel-addition studies).

4.2.1. Bismuthate Oxidation*

In some preliminary tests large excesses of bismuthate oxidized the Pu(IV) stock solution to hexavalent form rapidly and quantitatively at 80 to 85 C. Bismuthate was selected from all the available metal ion methods because its solubility is comparatively low in the plutonium solutions used.

Tests of the bismuthate oxidation reaction yield were run at various Bi:Pu ratios. Samples of plutonium nitrate stock solution (5 ml, 261 gm/liter, 3.8 M free HNO₃) were mixed with 0.5 ml of 15 M HNO₃; varying substoichiometric amounts of bismuthate were added, and the solutions were stirred and heated at boiling for half an hour. The reaction was then stopped and the Pu(VI) yield was measured (see Figure 4-1). In all cases, the yield was less than that theoretically calculated for a 1:1 stoichiometry following the equation

At least two plausible explanations could account for the reduced yields: The reaction may be too slow for a quantitative yield in the allotted time, or, in addition to Pu(IV), reducing agents which react with the available bismuthate are present. The latter explanation is reasonable, because the intense alpha bombardment from concentrated plutonium solutions is known to produce an autoradiolytic reduction of Pu(VI). Radiolysis of nitrate solutions produces nitrites; hence, it may be expected that the Pu(IV) nitrate stock solution on hand contains considerable nitrite. It may be this nitrite "blank" which gives rise to the low Pu(VI) yield. In any event, the reaction shows almost a 1:1 stoichiometry at the equivalence point.

4.2.2. Ion-Exchange Separation of Pu(VI) and Bi(III)

Trivalent bismuth is a by-product of plutonium oxidation and, if left in the plutonium solutions, would give ambiguous results in

* This series of tests was run as part of B&W company-sponsored work before initiation of work under the Gel-Addition contract. The series is discussed here for completeness.

plutonium gel-addition tests. Accordingly, a series of ion-exchange experiments was run to determine whether a Pu(VI)-Bi(III) separation could be carried out conveniently by simple ion-exchange methods in nitrate solution. Pentavalent bismuth was not expected to be a problem, since it is reportedly unstable in nitric acid.¹¹

Trivalent bismuth in 5 M HNO₃ is weakly exchanged on cation resins ($K_D < 3$) and more strongly exchanged on anion resins ($K_D = 20$).^{12, 13} Data for plutonyl ion are not readily available, but the uranyl ion is moderately exchanged by both cation ($K_D = 6$) and anion ($K_D = 10$) exchangers.^{12, 13} Thus cation exchangers should retain the uranyl ion and pass Bi(III) in nitrate solution; by analogy, it was anticipated that similar results would follow for Pu-Bi solutions. That is, the plutonyl ion should be retained and Bi(III) should be eluted. These anticipated results were confirmed in the following experiment.

A column of Dowex-50-WX8, 50 to 100 mesh (about 0.5 cm² cross section by 20 cm long) was washed with water and with several column volumes of 5 M HNO₃. A Pu(VI)-Bi(III) mixed solution was loaded onto the column. The total charge was 1 ml of a solution 1 M in both ions. The load solution percolated through about half the resin bed during the loading and before the effluent drain was opened. The elution rate was 6 to 10 drops per minute and 5 M HNO₃ was used as eluent. Effluent fractions of 5 ml each (0.5 column volumes) were collected. Plutonium elution was followed by alpha-counting a small aliquot, and bismuth elution was followed by EDTA titration (see section 5.2). The separation was incomplete, but it does show that a longer column or smaller resin bed size would probably give a complete separation (see Figure 4-2).

4.2.3. Nitric Acid Oxidation

During a visit by B&W representatives to Hanford, Washington, R. S. Kingsley of the Isochem staff suggested that a nitric acid oxidation of plutonium to hexavalent form, followed by ion-exchange removal of residual Pu(IV), might be preferable to bismuthate oxidation. Nitrate oxidation has apparently not been described in the open literature and the suggestion was very welcome. In a series of scouting experiments the proper oxidizing conditions for the solutions on hand have been

determined, and nitric acid oxidation is now the preferred method for gel-addition work.

A number of 10-ml aliquots of Pu(IV) nitrate stock solution were diluted to 25 ml with dilute nitric acid and water to give a series of solutions with free nitric acid levels between 1.27 and 3.5 M. These were refluxed for periods up to several hours, interrupted periodically for sampling. The percentage of conversion to Pu(VI) was measured spectrophotometrically (section 6.3.3). The results (see Table 4-1), although not very reproducible (probably owing to small differences in reflux conditions), show that the more dilute acid solutions oxidize more rapidly, and that for the solutions of present interest quantitative conversion requires 2 to 3 hours in the concentration range 1.2 to 2.5 M.

4.3. Ion-Exchange Separation of Pu(IV) and Pu(VI)

Two experiments have been run to determine the effectiveness of the anion separation of Pu(IV) and Pu(VI) suggested by Kingsley (see paragraph 4.2.3).

A Dowex 1X8 column, 0.5 cm² cross section by 10 cm long, 50 to 100 mesh, was washed with 2 M HNO₃, loaded with 1 ml of a 1 M plutonium solution—72% Pu(VI), and eluted with 2 M HNO₃. Virtually all the Pu(VI) eluted in 10 ml. The Pu(IV), evidenced by a green band, filled most of the column. No Pu(IV) was detected in the eluate.

A second column (5 cm² by 15 cm) of Dowex 1X8, 50 to 100 mesh, was washed with 2 M HNO₃, loaded with 10 ml of a 1 M plutonium solution—79% Pu(VI), and eluted with 2 M HNO₃. The brown Pu(VI) eluted as before, and a 90-ml fraction containing most of the Pu(VI) based on color was collected. This solution contained 20 mg Pu(VI) per ml; no Pu(IV) was detected. Some Pu(VI) was still being eluted but at lower concentration (based on color) than earlier. The Pu(IV) green band remained in the upper third of the column.

4.4. Autoradiolysis of Pu(VI)

Hexavalent plutonium solutions slowly reduce spontaneously to lower valence states. The intense alpha field in the solution is believed to be responsible.¹⁴ To check the effect on solutions used in this project, a sample of Pu(VI) prepared by bismuthate oxidation was allowed

to stand for an extended period and was sampled periodically to determine the Pu(VI) content. The data are reproduced as Figure 4-3; superficially, the reaction appears to be almost first order in Pu(VI) with an initial induction period. The apparent half-time is about 16 days; the induction period could be due to excess oxidant—Bi(V)—remaining in solution.

Table 4-1. Pu(IV) to Pu(VI) Percent Conversion

Free HNO ₃ conc	Experiment 1			Experiment 2			Experiment 3		
	1.27	1.5	1.75	1.3 ^(a)	1.5	2.0	1.5	2.5	3.5
Refluxing time, min									
5	43	42	41	--	--	--	--	--	--
10	55	49	47	--	--	--	--	--	--
15	72	63	62	63	75	69	--	--	--
30	89	83	79	72	88	80	--	--	--
60	97	96	95	--	98	89	--	--	--
90	--	--	--	--	--	--	99	90	57
120	97	100	100	--	--	--	--	--	--
150	--	--	--	--	--	--	100	98	65
180	100	100	100	--	--	--	--	--	--
222	--	--	--	--	--	--	100	100	82

(a) Heating mantle used instead of flask hot plate; less vigorous boiling observed.

Figure 4-1. Pu(IV)-Bismuthate Reaction Stoichiometry

Figure 4-2. Bi(III)-Pu(VI) Cation-Exchange Separation

Figure 4-3. Autoradiolytic Reduction of Pu(VI)

5. UO_2 GEL CONTACTING EXPERIMENTS (W. N. Bishop)

5.1. UO_2 Gel-Nitric Acid

Urania is known to dissolve in nitric acid. The resistance of UO_2 gels to acid attack is thus an important property, since plutonium solutions require free acid to prevent hydrolytic instability.

The dissolution of UO_2 in HNO_3 is not a simple acid-base reaction; oxidation is also involved because the uranium product is hexavalent and UO_2 contains quadrivalent uranium. The oxidants could include air, free nitric acid, or dissolved nitrate ion. Thus, even a solution partially neutralized with base could be aggressive toward UO_2 because of the residual acid and high nitrate level.

5.1.1. B&W-Produced Material

Small samples of spheres prepared by the ORNL process were contacted, in air at ambient temperatures, with nitric acid concentrations up to 2M. Dissolution was complete after 4 hours in 2M acid and after 6 hours in 1M acid. At 0.5 and 0.1M, dissolution was much slower, but was complete in less than 22 hours. At 60 C the rate increased, and complete dissolution occurred after 1 hour in 1M and 2.5 hours in 0.5M acid. Neither agitation, ammonium nitrate additions, nor the use of deaerated solutions had any observable effect. Thus, free nitrate and air are not important oxidants.

The spheres resisted HCl attack up to 12M for at least 23 hours.

5.1.2. NFS-Produced Material

The dissolution times for NFS gel spheres in various concentrations of nitric acid under ambient conditions are comparable to those for B&W spheres. The behavior in hydrochloric acid is quite different, however. B&W spheres did not dissolve within 23 hours in

any concentration of HCl up to 12 M. Within one minute after contact with NFS spheres, 12, 6, and 3 M HCl solutions showed a yellow coloration. Solutions 1.5, 0.75, and 0.38 M HCl became black (characteristic of UO_2 or U_3O_8 sols) shortly after contact with the spheres. Dissolution of the NFS spheres was complete within 10 minutes for 12 HCl, and required less than 23 hours for all concentrations including 0.38 M. This behavior is at least partially explained by the greater U(VI) content of the NFS gel.

5. 1. 3. pH Changes

The results of contact between plutonium solutions and urania gel spheres are discussed in detail in sections 5. 2 and 5. 3. In these experiments it was noted that the pH of the solution rose during the contact period. Because of limited sphere availability, only a few contacts could be made with B&W spheres; further investigation of the pH changes will be resumed when additional material is available. A similar but slightly greater pH rise was noted when NFS gel spheres were contacted with plutonium-dilute HNO_3 solutions. When 10 ml of a 1 M Pu (oxidation state III, IV, or VI), initial pH 0.5 to 1.0, is contacted with 4 grams of NFS spheres, the pH increases to 2.5 to 3 within a few minutes and remains stable at this value for several hours. There is no similar pH change in plutonium solutions not in contact with spheres, but it does occur when dilute HNO_3 solutions without plutonium are contacted with NFS gel spheres. The results of numerous contacts of dilute HNO_3 and NFS spheres indicate that both a black sol (UO_2 or U_3O_8) and a yellow solution are formed.

Since the pH becomes essentially constant after the initial rise, an acid pretreatment of the spheres was attempted in an effort to reduce or eliminate the pH rise during contact. Repeated contact of NFS gel spheres with fresh acid solutions gave no indication that the acid-uptake potential of the spheres could be saturated by pretreatment short of complete sphere degradation. The interaction of NFS spheres with HCl was very similar to the HNO_3 results.

5.2. UO₂ Gel-Plutonium

5.2.1. B&W-Prepared Material

The limited amount of UO₂ gel spheres prepared by ORNL methods available when the program began precluded a wide-scale investigation of plutonium-pickup behavior of this material. A few scouting experiments covering the three common oxidation states of plutonium and a range of pH values were performed.

Results of the acid resistance studies described in section 5.1.1 indicate that the maximum stable nitric acid concentration might be 1 M, or, more likely, 0.5 M. Preliminary studies showed that 1 M Pu(IV) precipitated at a pH between 1 and 2, and that 1 M Pu(III) and (VI) did not precipitate below a pH of 3. The pH values of the contacting solutions were chosen to lie between the limits of sphere destruction and plutonium precipitation.

The preparation of the Pu(III), (IV), and (VI) solutions is described in section 4. The solutions were all between 0.5 and 1 M Pu and contained about 6 to 7 M NO₃⁻. The stock solutions were adjusted to the desired acid values by the addition of concentrated NH₄OH. One contacting solution of Pu(IV) and one of Pu(III) were adjusted to 1 M HNO₃ by adding a calculated amount of NH₄OH. All other solutions were adjusted until the desired initial pH values were indicated on a pH-meter. In all contact experiments 4.0 grams of B&W spheres were shaken with about 10 ml of plutonium solution for 4 hours. In all of the contact experiments except 1B78, the solutions were separated from the spheres by decanting and six to eight washes with 5 ml of acetone. In several cases precipitates were evident when the contact was terminated. Separation of these precipitates from the spheres was very difficult, and we cannot estimate the amount of precipitate material retained by the spheres. The spheres in test 1B78 were separated from the contacting solution by filtration and three washes with 5 ml of H₂O.

The first experiments used Pu(IV) solutions, and the formation of precipitates indicated possible pH changes during the contact period. In subsequent experiments the pH was measured again at the termination of contact, and the pH had changed markedly in almost every case. After the solution and spheres were separated, the spheres

were dissolved and analyzed for plutonium and uranium content. The experimental conditions and results are shown in Table 5-1. The uranium recovery values represent losses from chemical attack, decantation, spillage, and a small sample for visual analysis. A separate analysis showed that 4 grams of spheres contained about 3 grams of uranium.

The ratio of $\text{Pu}/(\text{Pu}+\text{U})$ must be considered an upper limit in all cases where a precipitate formed; however, no experimental details cast doubt on the results of samples 1A7, 1A10, 1A11, 1A12, 1A13, 1A34, and 1B78. The extremely high $\text{Pu}/(\text{Pu}+\text{U})$ value for the Pu(VI) samples is questionable. Microscopic analysis showed numerous large, nonspherical brown particles among the spheres. The larger spheres were still black, but small spheres showed a brown coloration. The low sphere recovery for these samples and 1A9 were due in part to the extreme difficulty in separating large amounts of precipitate from the spheres. It is not possible to estimate the loss from chemical attack on the spheres.

The conditions for contact of samples 1A7, 1A34, and 1B78 were the same—Pu(IV) at pH 0.5—but the contacts were made on different days, and the method of sphere-solution separation was different for 1B78. Plutonium pickup was very similar for all three. The Pu(IV) solutions, initially pH 0.5, became a deep blue after 15 to 30 minutes contact with B&W spheres. The other Pu(IV) solutions did not have this color, but contained a greenish flocculent precipitate. The solution, initially pH 1.4, became thixotropic after 4 hours.

It is interesting that the spheres contacted with Pu(IV) in 1M nitric acid dissolved, while most of those contacted with Pu(III) at the same acid concentration survived. Two factors probably contribute to this difference: The Pu(III) solution had an excess of hydroxylamine, which at least partially compensates for the oxidizing power of nitric acid; and Pu(IV) has a very strong buffering effect between pH 0 and 1.

5.2.2. NFS Material

5.2.2.1. Pu(IV)

The most promising results from plutonium contacting using B&W-produced material occurred with quadrivalent plutonium at an initial indicated pH of 0.5. The first contact experiments with NFS spheres attempted to duplicate these conditions. The results, shown in Table 5-2, were quite different. The final pH was higher, the plutonium precipitated, and the pickup was almost a decade smaller. The precipitation probably resulted from the higher final pH, and the lower pickup may be due, at least in part, to the precipitation of plutonium. The reproducible pickup is undoubtedly fortuitous, since it was very difficult to separate the spheres from precipitated plutonium.

The experiments reported in section 5.1.3 indicate that a pH rise during sphere contacting cannot be completely circumvented. The effect is most important with Pu(IV) because it precipitates at a comparatively low pH. The hydrolytic precipitation of Pu(IV) can be suppressed, however, by the addition of a complexing agent such as citric acid. Table 5-3 shows the results obtained from contacting Pu(IV)-citrate solutions with NFS spheres. The solution contained equimolar amounts of plutonium and citric acid. As the acid was mixed with concentrated NH_4OH , a brown precipitate appeared ($\text{pH} < 0$). The addition of NH_4OH was continued, and the precipitate redissolved at about pH 3 to give a wine-colored solution. The pH was raised to 9 (well on the alkaline side) without further precipitation.

The plutonium citrate solution, initially pH 0.5, contained a precipitate throughout the contact period. No precipitates were observed during contact in the solutions that were initially pH 3 and 8. The addition of acetone, after decantation of the contacting solution, led to precipitation of the residual plutonium solution. The presence of these precipitates makes interpretation of the pickup data uncertain.

These results suggested the need for an alternate sphere-solution separation technique. Another set of plutonium citrate solutions, initially pH 5 and 9, were prepared and contacted

with NFS spheres. The spheres were separated from the solution by filtration and different degrees of aqueous washing. The results indicate that there is very little, if any, plutonium pickup from a citrate medium, and that the filtration technique is satisfactory where there is no precipitate in the contacting solution.

Another possible way to suppress Pu(IV) precipitation is to start with a more acid contacting solution. A pH titration of Pu(IV) showed a strong buffering effect between pH 0 and 1. An initial pH of 0.3 was chosen, and two 10-ml aliquots of Pu(IV) stock solution (3.2 M HNO_3) were adjusted to pH 0.3 by the addition of concentrated NH_4OH . This solution was divided into three portions and contacted with NFS spheres for 5, 30, and 60 minutes. The sphere attrition and plutonium uptake results are shown in Table 5-4.

Twenty-five ml of Pu(IV) stock solution were adjusted to indicated pH 0.5 by the addition of concentrated NH_4OH .^{*} The solution was divided into three portions. Two portions were contacted with NFS gel spheres for 30 and 240 minutes. The results, shown in Table 5-4, are consistent with the contact experiments using solutions initially pH 0.3.

The remaining portion of the pH 0.5 Pu(IV) solution was contacted with B&W gel spheres for 4 hours. Table 5-5 shows the results of contacting identical solutions under the same conditions for the same time period with B&W and NFS spheres. It is possible that the high sphere attrition is connected with the lower plutonium uptake on the NFS spheres.

No Pu(IV) solutions contacted with NFS gel spheres exhibited the blue color shown by the solutions in contact with B&W spheres.

5.2.2.2. Pu(III)

Plutonium(III) polymerizes and precipitates less readily than Pu(IV). The pickup of Pu(III) by B&W spheres was

- - - - -
^{*} The measured pH was not the anticipated value, since the ammonia addition was calculated to give pH 0.3 based on the previous experiment. The time of base addition was decreased, however, so slow hydrolysis probably accounts for the pH change.

not as large as that of Pu(IV), but still was potentially useful. Plutonium(III) in the concentration range of these experiments will remain in solutions up to a pH of about 4.

The results of several experiments contacting Pu(III) solutions with NFS spheres are shown in Table 5-6. The variables investigated were initial pH, contact time, and plutonium concentration. The system of 10 ml of 0.5 M Pu(III) and 4 grams of NFS spheres seems to equilibrate to a pH of about 2.5, while the system with 100 ml of 0.05 M Pu(III) goes to a higher pH value. It is not surprising that the initial pH has little effect on the plutonium uptake, since the system rapidly buffers to a pH that is relatively independent of the initial value. The behavior of Pu(III) uptake as a function of time is similar to that shown by Pu(IV). Plutonium concentration has little influence on the pickup of Pu(III), particularly after long contact. This is very interesting and may indicate that the controlling factor is the availability of sorption sites or the rate of diffusion through the gel.

In two sets of experiments the plutonium solution was poured through the spheres in a fritted glass funnel of medium porosity. In the first set the solution passed through the spheres once; then the spheres were rinsed with pH 3 HNO₃. The time for the filtration was 2 to 3 minutes, and these results are consistent with the longer-contact experiments. In the second filtration experiment the solution was passed through the spheres several times, and the pH was readjusted to the initial value between each filtration. The solution, initially pH 2.5, did not change in acidity during the four filtrations, which required a total of 21 minutes. The solution, initially pH 1, was filtered twice completely and about 2 ml (of 10) was filtered on the third attempt. Apparently the degraded spheres clogged the frit, and 30 minutes were required for 2 ml to filter. Nine minutes were required for the first two passes. The pH after each contact with the spheres was 2.4, 2.1, and 1.9. The plutonium pickup for these two experiments is slightly higher than for the shaking contacts for a similar time, but this difference is not greater than the spread between values for the 4-hour contacts. Evaluation of the accuracy and precision of the analytical procedure and of the reproducibility of plutonium pickup are subjects for future study.

The agreement between the Pu(III) uptake by B&W and NFS spheres after 4 hours contact is excellent, although in view of the Pu(IV) results it could be argued that this agreement is coincidental. It is felt that this agreement is to be expected, and that the difference in acid resistance of the two types of spheres accounts for the variation in Pu(IV) uptake.

Plutonium(III) solutions are a beautiful deep blue, but immediately upon contact with UO₂ gel spheres the color changes to green. Solutions of Pu(III) adjusted to the pH of the green solution remain blue. A mixture of yellow U(VI) and blue Pu(III) would be green, but the speed of the color change and the large amount of U(VI) required cast doubt on this explanation.

5.2.2.3. Pu(VI)

Plutonium(VI) is a strong oxidant, and UO₂ is easily oxidized. Contact of Pu(VI) with NFS UO₂ gel spheres gave results quite different than those obtained with Pu(III) or Pu(IV). The most obvious difference was the appearance of the spheres after contact—a mixture of yellow and black material. Microscopic examination of a sample after 4 hours contact showed no intact black spheres and a large number of yellow globules. The contacting solution has a precipitate atypical of Pu(VI) after a short contact. Separation and analysis of this precipitate showed that it was yellow and that it contained both uranium and plutonium (perhaps a mixture of uranium and plutonium oxides). The use of a higher pH, lower Pu(VI) concentration, and short contact times did not prevent gross sphere degradation.

Table 5-1. Contact of B&W Gel Spheres With Plutonium Solutions

Date of contact	Contact solution			Spheres		
	Pu oxidation state	Initial pH	Final pH	Analytical number	U recovered, gm ^(a)	$\frac{\text{Pu}}{\text{Pu} + \text{U}}$
7/18/66	4	1 M HNO ₃	nm		(Spheres dissolved)	
	4	0.5	nm	1A7	1.59	0.183
	4	0.9	nm ^(b)	1A8	1.39 ^(b)	0.147 ^(b)
	4	1.4	nm ^(c)	1A9	0.30	0.057 ^(c)
7/25/66	4	0.5	1.8	1A34	1.67	0.207
9/8/66	4	0.5	1.9	1B78	1.28	0.182
7/19/66	3	1 M HNO ₃	0.0	1A10	1.48	0.015
	3	1.1	2.0	1A11	2.04	0.080
	3	2.0	1.9	1A12	2.28	0.090
	3	2.6	1.9	1A13	2.26	0.071
7/25/66	6	0.5	2.4 ^(d)	1A31	0.60	0.53 ^(d)
	6	1.0	2.6 ^(d)	1A32	0.34	0.50 ^(d)
	6	2.0	2.8 ^(d)	1A33	0.39	0.46 ^(d)

10 ml Pu solution + 4.0 gm B&W gel spheres; contact time 4.0 hr at ambient temperature; Pu = 1 M.

- (a) Approximately 3 gm U in 4 gm spheres; non-recovered U due to chemical attack, handling losses, and samples for visual analysis.
 (b) A precipitate characteristic of Pu formed during contact.
 (c) The solution became thixotropic with a Pu precipitate during contact.
 (d) A precipitate, atypical of Pu, formed during contact.

nm: not measured.

Table 5-2. Contact of Pu(IV) Solutions With NFS Gel Spheres

Date of contact	Contact solution			Duration of contact	Analytical number	Spheres	
	Pu oxidation state	Initial pH	Final pH			U recovered, gm ^(a)	$\frac{\text{Pu}}{\text{Pu} + \text{U}}$
8/4/66	4	0.5	2.8 ^(b)	4 hr	1A82	1.20	0.026 ^(b)
8/10/66	4	0.5	2.7 ^(b)	4 hr	1A98	1.75	0.027 ^(c)
	4	0.5	2.6 ^(c)	30 min	1A96	1.27	0.028 ^(c)
	4	0.5	2.6 ^(c)	5 min	1A95	1.64	0.024 ^(c)

10 ml Pu solution + 4.0 gm NFS gel spheres at ambient temperature; spheres and solution separated by decantation and acetone rinses.

- (a) Approximately 3 gm U in 4 gm spheres; non-recovered U due to chemical attack, handling losses, and samples for visual analysis.
- (b) The solution became thixotropic with a Pu precipitate during contact.
- (c) A precipitate characteristic of Pu formed during contact.

Table 5-3. Contact of Pu(IV)-Citric Acid^(a) Solutions With NFS Gel Spheres

Date of contact	Contact solution			Sphere-solution separation	Spheres		
	Pu oxidation state ^(a)	Initial pH	Final pH		Analytical number	U recovered, gm	$\frac{\text{Pu}}{\text{Pu} + \text{U}}$
8/10/66	4	0.5(b)	3.3(b)	Decantation & acetone rinses	1A99	1.84	0.016(b, d)
	4	3.0	3.8		1B1	2.12	0.036(d)
	4	8.0	6.5		1B2	0.58	0.006(d)
8/11/66	4	5.0	nm	Filter only	1B4	1.94	0.0041
	4	5.0	nm	Filter & 1 water wash	1B5	2.44	0.0003
	4	9.0	nm		1B6	1.89	<0.0001
	4	9.0	nm	Filter & 4 water washes	1B7	1.65	<0.0001

Approximately 10 ml of 1M Pu solution + 4.0 gm NFS gel spheres at ambient temperature; contact for 3 hr on 8/10/66 and 4 hr on 8/11/66.

(a) Pu and citric acid in equimolar concentrations.

(b) A Pu precipitate was present before, during, and after contact.

(c) Approximately 3 gm U in 4 gm spheres; non-recovered U due to chemical attack, handling losses, and samples for visual analysis.

(d) A precipitate characteristic of Pu formed in the acetone washes.

nm: not measured.

Table 5-4. Contact of Pu(IV) Solutions With NFS Gel Spheres

Date of contact	Contact solution			Duration of contact	Analytical number	Spheres	
	Pu oxidation state	Initial pH	Final pH			U recovered, gm ^(a)	$\frac{\text{Pu}}{\text{Pu} + \text{U}}$
9/7/66	4	0.30	2.20	5 min	1B66	0.47	0.018
	4	0.30	2.15	30 min	1B68	0.54	0.050
9/8/66	4	0.50 ^(b)	2.20	30 min	1B74	0.49	0.043
9/7/66	4	0.30	2.15	60 min	1B70	0.47	0.060
9/2/66	4	0.30	1.85	3 hr	1B60	0.28	0.086
	4	0.30	2.10	3 hr	1B62	0.74	0.099
9/8/66	4	0.50 ^(b)	2.20	4 hr	1B76	0.33	0.093

Approximately 10 ml Pu solution + 4.0 gm NFS gel spheres at ambient temperature; Pu stock solution was neutralized with concentrated NH_4OH in the ratio 30 drops base to 5 ml stock solution.

(a) Approximately 3 gm U in 4 gm spheres; non-recovered U due to chemical attack, handling losses, and samples for visual analysis.

(b) pH adjusted to 0.5 by adding 150 drops concentrated NH_4OH to 25 ml Pu stock solution; this base/stock solution ratio should yield a pH of 0.3.

Table 5-5. Four-Hour Contact of Gel Spheres With Pu(IV)
Solutions — B&W and NFS Spheres Compared

Date of contact	Contact solution			Spheres			
	Pu oxidation state	Initial pH	Final pH	Mfd by	Analytical number	U recovered, gm ^(a)	$\frac{\text{Pu}}{\text{Pu} + \text{U}}$
9/8/66	4	0.5(b)	1.9	B&W	1B78	1.28	0.183
9/8/66	4	0.5(b)	2.0	NFS	1B76	0.33	0.093

10-ml aliquots Pu solution contacted with 4.0 gm
gel spheres at ambient temperature for 4 hr.

- (a) Approximately 3 gm U in 4 gm spheres; non-recovered U due to chemical attack, handling losses, and samples for visual analysis.
- (b) pH adjusted to 0.5 by adding 150 drops concentrated NH_4OH to 25 ml Pu stock solution; this base/stock solution ratio should yield a pH of 0.3.

Table 5-6. Contact of Pu(III) Solutions With NFS Gel Spheres

Date of contact	Contact solution			Duration of contact	Spheres		
	Pu(III) conc., M ^(a)	Initial pH	Final pH		Analytical number	U recovered, gm ^(b)	$\frac{\text{Pu}}{\text{Pu} + \text{U}}$
8/26/66	0.5	1.0	2.4	5 min	1B28	1.60	0.025
	0.5	2.5	2.6	5 min	1B32	1.74	0.028
	0.5	1.0	2.4	30 min	1B30	1.15	0.043
	0.5	2.5	2.5	30 min	1B34	1.64	0.044
8/30/66	0.5	1.0	2.5	4 hr	1B52	1.22	0.085
	0.5	2.5	2.4	4 hr	1B54	1.59	0.071
8/26/66	0.05	1.0	2.4	5 min	1B36	1.61	0.018
	0.05	2.5	2.8	5 min	1B38	1.83	0.009
	0.05	1.0	3.3	30 min	1B40	1.31	0.028
	0.05	2.5	3.8	30 min	1B42	1.69	0.032
8/30/66	0.05	1.0	3.3	4 hr	1B56	1.27	0.072
	0.05	2.5	3.8	4 hr	1B58	1.62	0.073
8/26/66	0.5	1.0	2.6	3 min ^(d)	1B44	1.57	0.016
	0.5	2.5	2.8	2 min ^(d)	1B46	1.57	0.012
8/30/66	0.5	1.0	2.4 - 1.9 ^(c)	9 - 39 min ^(c)	1B48	1.56	0.055
	0.5	2.5	2.5	21 min ^(e)	1B50	1.38	0.049

(a) Contact solution volume was 10 ml for 0.5 M Pu and 100 ml for 0.05 M Pu.

(b) Approximately 3 gm U in 4 gm spheres; non-recovered U due to chemical attack, handling losses, and samples for visual analysis.

(c) Contact achieved by pouring solution through spheres three times; pH re-adjusted to 1.0 before contact. Experiment terminated after only 2 ml (of 10) had filtered in 30 min on third contact.

(d) Contact achieved by pouring solution through spheres in a glass-fritted funnel under suction.

(e) Contact achieved by pouring solution through spheres four times.

6. ANALYTICAL SUPPORT

(C. J. Halva, R. H. Dodd, S. G. Khoury)

Complexometric, coulometric, and spectrophotometric analytical methods have all been used in support of gel-addition experiments. The general principles of the procedures are outlined in the following paragraphs.

6.1. Complexometric Titration

If a dissolved ion forms stable complexes, its concentration can usually be measured by adding a complexing agent to it in measured amounts. Some property of the system which undergoes a pronounced change when the complexing agent and unknown are present in exactly equivalent amounts is observed, and the appearance of the change denotes the "end point" of the titration.

EDTA,* among the strongest complexing agents known, is useful in complexometric titration because it reacts readily, not only with most metals, but also with many metal complexes. The latter are destroyed because they are less stable than the EDTA counterparts. Color is a convenient property to observe, and since almost all EDTA complexes are colorless, it is often convenient to convert the ion of interest into a colored complex and then destroy the complex with EDTA. The disappearance of color marks the end point. Procedures of this type have been used for both plutonium and bismuth determination.

6.1.1. Plutonium Determination

Plutonium and xlenol orange** form a red-violet complex which is destroyed by EDTA:

.

* Ethylene diamine tetra acetic acid.

** {3, 3'-bis[N, N-di(carboxymethyl)-aminomethyl]-O-cresolsulfonthalein}, available from Fisher Scientific Company.

The displaced dye is a golden yellow; hence the end point of the titration is noted as the point of disappearance of red-violet. This procedure was apparently first applied to plutonium by Brown, Rogers, Mershad, and Amos, and has been used for assaying incoming Pu(IV) nitrate solution.¹⁵ The formula of the complex was reported by Milyukova and Nemodruk.¹⁶

6.1.2. Bismuth Determination

Bismuth(III) and thiourea form a weak yellow complex which is easily bleached by EDTA; hence the end point is noted when the solution becomes colorless. The method described in Fisher Chelometric Indicators for Metal Titrations has been successfully applied to the assay of bismuth in solutions containing a six-fold higher plutonium concentration.¹⁷

A preliminary experiment demonstrated the applicability of the method. The experiment involved titration of a series of solutions, all of which contained 26 mg of Pu(IV) and from 0.5 to 20 mg of Bi(III). The results are shown in Figure 6-1. For a very accurate procedure, a plot of titrant volume against known Bi(III) mass should be independent of Pu(IV) mass, linear, and should pass through the origin. The observed curve is very nearly linear and passes through the origin; hence the method is deemed acceptable for present purposes. It probably justifies added study. One difference was noted between titration of pure Bi(III) solutions and titration of Bi(III)-Pu(IV) mixtures: the end point changed from colorless to pale blue, probably because of Pu(IV)-XO complex formation. These results are consistent with the extreme stability of the Bi-EDTA complex. Its formation constant is anomalously high and has been estimated near 10^{26} .¹⁸ The Pu(IV)-EDTA formation constant is probably smaller by several orders of magnitude.

6.2. Coulometric Titration

Materials that can be rapidly converted electrolytically from one valence state to another can be determined if the total number of coulombs required to make a quantitative conversion is measured, and if

no other simultaneous reactions take place. Uranium analysis is commonly carried out coulometrically.

Coulometric titrators of the type used in this program impress a fixed, controlled voltage across an aqueous cell containing the unknown quantity of material.* Electrodes are platinum and mercury. The cell draws current until the sample has been consumed and current flow ceases. Part of the current is routed to a condenser which accumulates a charge proportional to the total current passed and acts as the integrator. At the end of the reaction the condenser charge is measured with a potentiometer to obtain the total number of coulombs required. In practice, the capacitor voltage is used directly to obtain total sample mass from an empirical calibration curve.

6.2.1. Plutonium Determination

Plutonium is determined by controlled potential coulometry in a citric acid, aluminum sulfate electrolyte. Plutonium in valence states greater than III is initially reduced to Pu(III) at -0.31 volt versus the standard calomel electrode (S. C. E.) using a mercury electrode. The readout voltage for this reduction step is disregarded. Pu(III) is then oxidized to Pu(IV) at a potential of $+0.07$ volt versus S. C. E. The cycle is repeated if desired. The current (coulombs) required to oxidize Pu(III) to Pu(IV) and to reduce Pu(IV) to Pu(III) is equivalent and directly proportional to the total amount of plutonium. The quantity of plutonium present is obtained from a series of runs with a known plutonium content. The method is applicable to 50 mg of plutonium in a sample aliquot.

Uranium, which is present with plutonium in most of the samples analyzed, does not interfere with the plutonium determination. Uranium is reduced at -0.31 volt, but since the reaction is irreversible, uranium is not reoxidized as is plutonium.

* There are three instruments in current use: two built by Indiana Instrument and Chemical Corporation, Bloomington, Indiana, and one built by NUMEC, Apollo, Pa. All are controlled potential devices.

The method used here was adapted from the Rodden compendium.¹⁹ The assistance of Dr. Joseph DiSalvo of Indiana Instruments and Chemical Corporation is acknowledged.

6.2.2. Uranium Determination

Uranium is determined by controlled potential coulometry in a 1N sulfuric acid electrolyte. U(VI) is reduced to U(IV) at a potential of -0.31 volt versus S. C. E. using a mercury electrode. The current (coulombs) required to reduce the hexavalent uranium to quadrivalent uranium is directly proportional to the amount of uranium present. The method is applicable for the determination of up to 30 mg of uranium in a sample aliquot; it was also adapted from procedures similar to those quoted by Rodden.²⁰

In samples where Pu(IV) and Pu(VI) concentrations are relatively high, reduction of Pu(IV) and Pu(VI) causes some interference in the uranium determination. When the Pu(III) content is large relative to Pu(IV) and Pu(VI), this interference is minimized. Estimates have been made of the Pu(IV) and Pu(VI) interference, and these corrections are applied to results of sample analyses where Pu(IV) and Pu(VI) concentrations are high.

Another method presently under investigation reportedly circumvents the Pu(IV)/Pu(VI) interference. The method involves pre-reduction of Pu(IV) and Pu(VI) to Pu(III), followed by reduction of U(VI) to U(IV) at another potential. U(VI) is not reduced in the pre-reduction step.

6.3. Plutonium Spectrophotometry

6.3.1. General

Spectrophotometric measurements are extremely useful for determining the concentrations and identities of dissolved colored ions. The shapes of the absorption spectra identify the ions involved, and the light transmission at selected wave lengths determines the masses (or concentrations).

All measurements have been made with a Beckman Model B spectrophotometer because it is small enough to enclose in a glove box and simple to maintain. The instrument covers the range from 320 to 1000 mμ, but requires a change of phototube to take full advantage of

the available range. One tube type covers the 320- to 600-m μ region and the other covers the 600- to 1000-m μ region. The inconvenience of changing tubes in a glove box makes it extremely desirable to work out procedures that are limited to one end of the spectrum.

The three common valence states of plutonium can be conveniently distinguished spectrophotometrically if the absorption spectra of the individual pure states are available.²¹ Means of obtaining these spectra are discussed in the following paragraphs.

6.3.2. Plutonium Spectra

The Pu(III) spectrum has been obtained by dissolving plutonium metal in hydrochloric acid and diluting to 5.2 mg Pu/ml. Pu(IV) nitrate stock was diluted to 5.2 mg/ml with 1.5 M HNO₃; Pu(VI) was obtained by the methods given in section 4.2 and was prepared at the same concentration in 1.5 M HNO₃. All three absorption spectra are shown in Figure 6-2.

6.3.3. Valence State Determinations

Quantitative spectrophotometry is based on the amount of light transmitted by a reproducible thickness of solution at a fixed wave length. The logarithm of the ratio of light intensity transmitted by the unknown to that transmitted by the pure solvent is defined as the "absorbance" of the solution, and if the absorbance is linear with concentration, the solution is said to obey Beer's Law.

Pu(IV) solutions exhibit a broad absorption peak at 650 m μ . The absorbance of a series of solutions of known Pu(IV) content was measured. Figure 6-3 demonstrates the linear variation with concentration and provides a calibration curve for Pu(IV) determination. Pu(VI) interference in the 650-m μ region is small. The peak at 610 m μ is narrow and low and is spaced far enough from the Pu(IV) peak at 650 m μ to avoid much interference.

Pu(VI) spectra were prepared by the nitrate oxidation method described in section 4.2.3, and residual Pu(IV) was removed by the ion exchange method discussed in 4.3. Solutions were prepared 1.5 M in HNO₃ using coulometric procedures for standardization. Beer's Law plots show the 940-m μ absorbance to be linear with concentration (Figure 6-3). The strong peak at 820 m μ is extremely useful for

qualitative identification of Pu(VI) but apparently does not follow Beer's Law. Therefore, it has not been used for quantitative Pu(VI) determination.

Pu(III) spectra were prepared by hydroxylamine reduction of Pu(IV). The peaks at 560, 595, 660, and 890 m μ all followed Beer's Law. The 890-m μ peak has less interference than the others and has been used for quantitative work. Its plot is included in Figure 6-3.

6.3.4. Valence State Mixtures

Mixtures of Pu(III) and Pu(IV) interfere in the 890-m μ region, since Pu(IV) gives a broad background superimposed on the Pu(III) peak. The interference becomes less important as the Pu(III) content increases. Pu(III) provides negligible interference with a Pu(IV) measurement at 650 m μ because the 660-m μ Pu(III) peak is too narrow; however, in solutions of high Pu(III), the Pu(IV) level is difficult to determine accurately because its 650-m μ peak is difficult to resolve. For solutions of this kind, the sharp peak at 470 m μ is used and a short-wave-length phototube must be used.

Mixtures of Pu(IV) and Pu(VI) yield good values for the Pu(IV) level because Pu(VI) interference is negligible at 650 m μ . Pu(VI) levels based on a 940-m μ measurement are high, however, unless a correction for Pu(IV) interference is applied. Analysis of known Pu(VI)-Pu(IV) mixtures has shown that the correct Pu(VI) value is obtained if the apparent Pu(VI) concentration is reduced by 20% of the Pu(IV) level.

Development work continues on analytical procedures for determining mixed plutonium valences.

Figure 6-1. EDTA Titration of Bi(III) in Excess Pu(IV)

Figure 6-2. Plutonium Spectrophotometry

Figure 6-3. Beer's Law Plots for Plutonium in Nitrate Solution

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