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## HAZARDS AND EXPERIMENTAL PROCEDURE EVALUATION FOR: "STUDIES ON THE POLYMERIZATION AND HYDROLYSIS OF PLUTONIUM IN URANYL NITRATE AND NITRIC ACID SOLUTIONS AT ELEVATED TEMPERATURES"

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### ABSTRACT

It has been concluded that a number of the difficulties encountered at various points in the chemical treatment and processing of plutonium solutions is due to the formation of the polymeric form of  $\text{Pu}^{+4}$ . The polymerization process is irreversible since the polymer is not in true equilibrium with the monomeric ions. Even at high acidities the depolymerization is very slow and drastic conditions are required for the depolymerization.

The formation of polymeric plutonium in processing streams is very serious because it is not extractable and therefore passes into the waste portion of extraction or ion-exchange processes. In addition, the increased formation of the polymer at elevated solution temperatures, water dilution by leaks into piping or tanks carrying  $\text{Pu(IV)}$ , or contacting the solution with steam, can cause the plutonium to polymerize and then precipitate if the temperature exceeds the precipitation temperature. These conditions could result in serious criticality conditions, plugged lines, loss of plutonium to waste streams, and solutions which would require drastic treatment before becoming suitable for further processing.

This memo briefly reviews the present state of knowledge concerning the polymerization of plutonium and discusses in detail an experimental program that will provide some data on the polymerization of plutonium in the  $\text{UO}_2(\text{NO}_3)_2\text{-HNO}_3$  system, and data

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on some other aspects of the problem. The previous work, both here and elsewhere, is reviewed and a detailed description of the facilities set up for this investigation and their mode of operation is discussed. The overall program is evaluated from the point of view of hazard, health physics procedures, and personnel safety.

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## A: RELATED PROJECTS, HISTORY

As a result of the non-nuclear explosion in the Chemical Technology Fuel Reprocessing Plant and difficulties in obtaining plutonium material balances in the pilot plants, it was felt that the immediate implementation of the work to be described herein was very desirable. From the current knowledge of the chemistry of Pu(IV) and the operating experience, there are very strong indications that the difficulties that are being encountered at ORNL are due to the formation of Pu(IV) polymer at various points in the processing of fuel solutions, and in other chemical experimentation.<sup>(1)</sup> The recent very surprising discovery and recovery of some 100<sup>+</sup> grams of plutonium from a packed steam countercurrent scrubber points out further the need for the study of plutonium polymerization under various conditions.

The precipitation of colloidal plutonium resulting from its formation at unknown locations, or its accumulation at various processing points may result in the formation of critically unsafe masses and possible plugging of transfer lines. In addition, the Pu(IV) polymer is not extracted by the usual organic solvents used (it does appear to be extracted by DBP), and its presence in plant feed solutions results in a variable loss of plutonium to the aqueous waste, with the result that the analytical results do not give a true indication of plant operation. As far as is known, the extraction of the polymer by DBP has been observed, but has not been studied.

It is therefore imperative that such dissolving conditions as are used, and all further steps, be carried out in such a manner as to prevent the formation of the polymer. If, however, conditions for the formation of the polymer are "inadvertently" obtained, the possible presence of the polymer should be recognized and steps taken to depolymerize the plutonium (if at all possible under the conditions available), and further steps taken to assure proper sampling techniques.

## B: DISCUSSION OF EXPERIMENTAL PROGRAM

1. Other Recent Work

As a result of experiences similar to some of those mentioned above, some work<sup>(1,2)</sup> on this problem was done at the Hanford plant in 1957. The work done at Hanford was concerned solely with the polymerization and precipitation of plutonium(IV) in nitric acid solutions, and was determined as a function of acid and plutonium concentration at several temperatures up to 100°C. Their work in nitric acid covered the plutonium concentration range up to about 100 g Pu/l, and an acidity range from 0.01 to 0.6 M HNO<sub>3</sub>. They report that hydrolysis, polymerization, and precipitation take place in unstable solutions with a resulting increase in acidity, until an acid concentration sufficient for the formation of a stable true solution is reached. Except for colloidal sols formed from solutions of a few grams per liter (precisely the region of interest), the acidities become too high for the plutonium to remain as a stable polymer or colloid, and precipitation results.

The Hanford work shows, in a beautifully clear manner, enough parameters of the system that was studied so that from a practical viewpoint one can know almost exactly under what conditions the polymer is likely to be formed. It is quite clear that it is practically impossible to dilute plutonium(IV) solutions with water or contact them with steam without the formation of colloid or polymer, because of the transient existence of regions of relatively high pH. Plutonium(IV) solutions should be diluted with acid, and never with water. Although the final acidity of such a dilution with water may be sufficient for stability, the rate of depolymerization is so small at even high acidities as to be negligible for almost all practical purposes; e.g. polymer formed at 80°C requires 15 days for 50%

depolymerization in 6 M  $\text{HNO}_3$ . Polymer or precipitates may be formed as a result of the dilution technique rather than as a result of a final acid deficiency.

The work at Hanford has shown that the rapid rate of polymer formation and the slow rate of depolymerization make possible the existence of the polymer in solutions subjected only to transient unstable conditions. The polymer may be formed by localized high temperatures in overheated pumps, by excessive heat of reactions, or may form in places where steam or water leaks might cause dilution. It may be precipitated at the place of formation or be carried by the solution as the colloid. The temperatures employed in concentration of a plutonium solution by evaporation must not exceed the precipitation temperature for that particular solution, because drastic treatment of the resulting solution of the polymer may be required before it will become suitable for further processing. In addition, these conditions could result in serious criticality conditions, and plugged transfer lines.

Polymer that is formed at higher temperatures is the most difficulty soluble and is most difficult to depolymerize. For polymer formed at 25°C the depolymerization (50%) in 2 M, 4 M, and 6 M nitric acid requires 20 days, 400 min., and 100 min. respectively. For the same depolymerization conditions, polymer formed at 80°C requires 1 year (2 M nitric acid), and 15 days (6 M nitric acid) for 50% depolymerization.

## 2. Previous Work at ORNL; Other Investigations

Relatively little work on the polymerization problem has been done in recent years. Much of the early work (1944-1945) was done by Kraus and co-workers<sup>(3)</sup> and has been summarized by himself<sup>(4)</sup> and others,<sup>(3b,c)</sup> and recently by Seaborg and Katz<sup>(5)</sup>. At the present time the basic knowledge concerning the polymerization of plutonium is quite meager. Seaborg and Katz<sup>(5)</sup> emphasize that the reasons for

why many things that occur are obscure, and that many observations deserve re-examination. In addition, early work was done at a time when plutonium was available in only rather small amounts. Within the last two years one of the present authors was engaged in a brief study<sup>(6)</sup> of some aspects of the polymerization of plutonium in sulfate systems. In addition to the results obtained with Pu(IV), some of the data indicate that a polymer of the +6 state ( $\text{PuO}_2^{++}$ ), can also form. Reasons were also suggested to explain the fact that the Pu(VI) polymer appears to be transformed back into the Pu(IV) state upon auto-depolymerization (which occurs only in strongly complexing systems). Kraus<sup>(4)</sup> has cited a small amount of data which also indicates that  $\text{PuO}_2^{++}$  can form relatively high molecular weight polymers.

In 1956 Ockenden and Welch<sup>(7)</sup> prepared some polymeric plutonium and made an interesting study of the polymerization and preparation of Pu(IV) colloidal solutions in nitric acid. They introduced the use of ion-exchange resins to remove ionic plutonium from polymer solutions produced by hydrolysis. They have prepared polymer with an estimated molecular weight range from a minimum of about 4000 to an estimated maximum of about  $10^{10}$ .

### 3. Scope of the Present Program

As has been indicated above, certain facts and/or trends are known concerning the polymerization of Pu(IV). Much of this was done in the very early days of the plutonium project, but very little work has been done since larger amounts of plutonium have become available. A very large amount of the work done to date has been of a qualitative or semi-quantitative nature, and very little of a fundamental nature.

Since many of the processes of great importance deal with solutions containing both uranium and plutonium, it has been decided that it is necessary to re-examine the hydrolysis and polymerization of plutonium in uranyl nitrate solution.

With the exception of a small amount of work (6) in some sulfate systems, practically all other work has been confined to the nitric acid system.

The present program for the uranium-plutonium system will begin with experimentation along the same lines as those used at Hanford (2) for the work in nitric acid solution. As was the case there, the spectrophotometric approach will be used. A fully equipped, automatic recording Cary Model 14 PM UV-Visible-Near-Infrared Spectrophotometric will be used for the measurements. The Hanford work will be essentially repeated for the uranium-plutonium system. This will cover the plutonium concentration range up to about 90-100 g Pu/l, and over an acidity range from 0.01 to 0.6-1.0 M. Temperature will be varied over a range from room temperature to 95°C; emphasis will be placed on the use of elevated temperature and of the use of plutonium concentrations of the order of a few grams per liter. The uranyl nitrate concentration will be maintained at 350 g. U/l, for most of the work.

Data is to be obtained on the rate and extent of polymerization of Pu(IV) under various conditions. The rate of depolymerization will be studied at various acid concentrations and at various temperatures. The importance of the temperature at which the polymer was formed will be studied with respect to the rate and extent of depolymerization. The presence of sulfate does not prevent polymerization of plutonium (cf. ref. 6), but does act as an agent to speed up the depolymerization (by complex ion formation). Thus, in the work on sulfate systems, the depolymerization was "auto-catalytic," i.e., the polymers formed at elevated temperatures, etc., reverted back to the ionic state (though somewhat irreversibly) slowly upon standing. With polymers formed in nitric acid (and probably other acids), this is not the case. Therefore, a study will be made of the effect of sulfate (and perhaps other ions that form strong complexes) on the depolymerization of the polymer in the nitric acid and uranyl nitrate-nitric

acid systems. As time permits, the effect of aging will also be investigated.

In addition, some experiments will be carried out similar to some that were made by Ockenden and Welch<sup>(7)</sup>, particularly with regard to the use of ion exchange methods for the preparation of pure solutions of the polymer. There are countless problems to be investigated with respect to the polymerization of Pu(IV), and practically nothing is known regarding the polymerization of  $\text{PuO}_2^{++}$ , except that high molecular weight polymers very probably exist for the +6 state. Certain selected problems will be looked into insofar as time, and the nature of the experimental apparatus and techniques available, permit. Unfortunately, the time available for carrying out these studies is limited at the present time.

Of particular importance is the equilibrium between the polymeric and monomeric hydrolyzed species. Unlike the case of the  $\text{Th}^{+4}$ , where the colloidal aggregates which form by hydrolysis appear to be in equilibrium with monomeric Th(IV) ions<sup>(4)</sup>, the polymerization of Pu(IV) appears to be irreversible, and no equilibrium is established between plutonium(IV) polymer and monomeric  $\text{Pu}(\text{OH})^{+3}$ . This problem has also been discussed by Kraus<sup>(4)</sup>, and by Seaborg and Katz<sup>(5)</sup> who have stated that the reasons for this difference, if indeed it does truly exist, are completely obscure. Kraus has reported<sup>(4)</sup> that U(IV) is similar in this respect, however U(IV) polymer has not been studied nearly as "extensively" as Pu(IV) polymer. If time permits, some effort will be made to study this equilibrium to some extent, by studying the effect of macro amounts of ionic plutonium on the depolymerization of Pu(IV) polymer in solutions of such a composition that the ionic plutonium added will not polymerize.

Some studies will also be made with the use of high-speed centrifugation studies (not ultracentrifugation). A Lourdes Model AX high-speed centrifuge (36,000 x G) has been installed within a completely sealed glove box. The centrifuge accommodates tubes from 1 to 50 ml. Therefore, sedimentation studies can be made to fractionate polymers of molecular weights that come within the speed range of the Lourdes AX, and the centrifuge can be used for other preparative and experimental work that is necessary.

## C: FACILITIES, EQUIPMENT, AND MODE OF OPERATION

To conserve the very limited space available, all equipment used within the glove boxes is miniaturized, or is the smallest equipment available which will suffice. All heating equipment within the glove boxes will be electrical.

1. Glove Box No. 1

This sealed glove box will be used for all chemical processes and manipulations, experimental studies of the polymerization and depolymerization processes, long term thermostating of plutonium solutions, centrifugations, etc., and the preparation of plutonium solutions for spectrophotometric examination. Solutions for spectrophotometric examination will be transferred in glass or polyethylene bottles, sealed in polyethylene tubing, into glove box No. 3, where the cell filling will be carried out.

"Glove Box No. 1" will probably consist of two separate new boxes (3' long) that are presently on order, which conform to all specifications now set up for high-level alpha work. One box will be used for the chemical processing as is discussed in section D, and the other one for the remainder of the work mentioned in the above paragraph.

The stainless steel boxes will be fire-proof, and will have safety glass viewing windows. The glove ports and end entry ports will have covers for fire and explosion protection, etc. The boxes will have a roughing filter inside, and will be connected to the re-designed off-gas system that is to be installed by July 1. The boxes will be maintained at 1/2 to 2" H<sub>2</sub>O vacuum at all times, with a minimum air flow of 5 cfm. The system will be automatic, with provision for rapid increase in air flow to 30 cfm, and will have a low limit (0.3" H<sub>2</sub>O) alarm system.

All entry and exit operations will be carried out by means of the completely sealed (double where necessary) polyethylene tube transfer technique. All heating

within the boxes will be electrical, and no inflammable solids, solvents, or gases will be permitted inside any boxes containing plutonium without first providing an inert atmosphere and a sensing element within the boxes. At present, it is thought that such operations will not be necessary.

a. Haake Model F Circulating Water Bath

This miniaturized, (12 x 6 x 8") German made, bath (2 liter cap.) will be used for temperature control (capable to  $\pm 0.001^{\circ}\text{C}$ ) of various pieces of equipment within the glove box. The advantage of this small bath is that it may be put inside the glove box, eliminating the need for circulation of water into and out of the "hot" glove box, as has been necessary in the past. This bath will provide a safe method for heating plutonium solutions or other apparatus for long periods of time.

b. Temperature Controlled Bath for Plutonium Samples

This small bath is essentially an insulated chamber of small capacity, heated by circulation of water from the Haake circulating bath through copper coils. This chamber is provided with a cover designed to hold vials or cells filled with plutonium solution for long term heating, so that polymerization or depolymerization studies can be made.

c. Lourdes Model AX High Speed Centrifuge

This relatively small centrifuge has a fixed tube position ( $54^{\circ}$ ) rotor with a capacity of (8) 50 ml tubes - permitting the centrifugation of  $\sim 350^+$  ml at one time. The centrifuge is capable of obtaining centrifugal forces up to 35,000 x gravity.

d. Thermostated Ion-Exchange Column

This unit will be used for final purification of the plutonium stock solution to be used. The ion-exchange column resin bed (60 mm. I.D. x 50 cm.

long) will be filled with about 1.5 liters of Permutit SK anion exchange resin. This column is surrounded by a thermostating water jacket. The thermostating water jacket is then surrounded by a vacuum insulating jacket. The thermostating water jacket contains a 10-15 turn spiral tube which passes into the resin column at the top of the resin bed, and is used for loading the plutonium solution onto the resin column. This permits the solution that is to be loaded onto the resin column to be brought up to column operating temperature ( $60^{\circ}\text{C}$ ) before being dripped onto the column. The plutonium solution will be pumped through the spiral by the pump described below. Down-flow loading and elution will be used. The column will have a capacity for about 60 g. of plutonium. Operation of the column and purification of the plutonium stock is described in section D.

e. Micro-Bellows Teflon Sealed Pump

This miniature pump is the Corson-Cervený, Micro-Bellows unit. The bellows, checks, and seals are made of Teflon. The pump is approximately 5 x 5 x 6" high, and has a continuously variable pumping rate from 300 to 6000 ml. per hour. The motor is 110v., 60 cycles a.c., heavy duty. This miniature pump will be used to pump the plutonium solution onto the ion-exchange column, and for all other pumping operations inside the glove box. This eliminates any communication with pumps (finger, etc.) outside the glove box.

f. Vacuum-Suction Pumps

The miniature (8" L x 3 5/8" W x 4 3/4" H) Dyna-Vac. pressure and suction pump will be used for vacuum supply (18" hg.), or pressure (18 PSI) needs within the glove box. This eliminates any communication of the glove box with external vacuum or pressure systems. The pump is rated at 600 cu. in. per minute, 1/5 h.p., 3100 RPM, and is provided with a stainless steel chamber and base.

### g. Miscellaneous Equipment

This box will contain other glassware and equipment as may be necessary for the optimum execution of the experimental program. Equipment, etc., removed from this box will be doubly sealed in thick polyethylene tubing, and will either be discarded (buried, etc), or if it is desirable to remove but re-use the equipment, it will be removed sealed in polyethylene, be doubly sealed with polyethylene, and then stored in a safe place. Leads for pH electrodes will be sealed and passed out of the glove box to the pH meter, which will remain outside and uncontaminated.

### 2. Glove Box No. 2

This glove box, similar to glove box No. 1, is also a completely sealed system. The box is approx. 40 x 40 x 36" with a gasket-sealed lucite top, and a lucite front containing 2 glove ports. Entry is through a 6" and a 12" dia. port on either end using the polyethylene tube, completely sealed technique. This box will be used solely for the emptying, cleaning, decontamination (when necessary), and drying of the spectrophotometer absorption cells, and other equipment as may be necessary. The box is equipped with a fireproof filtered off-gas system, air inlet filter and has (quadruple) 110v. a.c. electrical outlets, sealed on both sides. The glove box is also provided with a number of Swagelock 1/4" copper tubing pass through connectors that are sealed until used, and several quick-seal disconnects. The box is operated at 1/2 to 2" H<sub>2</sub>O vacuum.

### 3. Glove Box No. 3

This small glove box will be used exclusively for transferring plutonium solutions into spectrophotometric absorption cells. The solutions will be transferred into box 3 from box 1 using the polyethylene sealing technique. Clean cells (uncontaminated on the outside) will be transferred from box 2

into box 3. The cells will then be carefully filled in box 3, remaining uncontaminated on the outside, and will then be directly transferred into the sample compartment of the Cary Spectrophotometer using the polyethylene tube transfer technique. Alternately, one 6" port of glove box 3 will probably be connected directly to the 6" entry port of the spectrophotometer glove box (No. 4) so that the filled cells can be smeared on the outside (the smears will be transferred out sealed in polyethylene) and the cells then placed in the spectrophotometer compartment without the necessity of being sealed in polyethylene for external box-to-box transfer. If the box-to-box transfer is used there is more of a chance for spillage or leakage around the filling port, external cell contamination, and resulting possible contamination of the spectrophotometer compartments.

#### 4. Spectrophotometric System - Glove Box No. 4

The spectrophotometric system to be used is the Cary Automatic Recording Spectrophotometer, Model 14 PM, Serial No. 136 (U.V, Visible, Near-infrared), that has been in use at ORNL for the past two years. It has been moved into Alpha Laboratory No. 5, Bldg. 3508 for the work on the present project. This is a very expensive piece of apparatus and all precautions are being taken to insure that even though the level of activity is high, the main parts of the spectrometer and the laboratory will remain uncontaminated. All activity will be completely contained within the glove box systems.

It has been decided that the experimentated compartment end of the spectrophotometer and all service connections (21) associated with these compartments (water and gas purge lines, thermocouples, multiple power cables, etc.) must be completely contained and isolated in a separate glove box. It is

imperative that this be done because plutonium solutions will remain in beam position and be measured at intervals (and also automatically) for long periods of time. The solutions will be maintained at temperatures less than the boiling point ( $\leq 95^{\circ}\text{C}$ ). The reference cell system will contain no plutonium, but will be similarly heated.

The glove box system for the spectrophotometer will be used with the ports securely covered by neoprene gloves at all times. There are 3 pairs of glove ports for optimum manipulation of cells and apparatus. All entry to the system will be via a 12" and a 6" diameter, polyethylene tube entry port. The polyethylene sealed bag technique will be used.

The spectrophotometer is provided with all cells and the accessories that are necessary for carrying out the necessary experiments. An automatic programmer system is installed, which slaves the spectrometer, and runs spectra at pre-set intervals over multiples of a 24 hr. arranged program, unattended. For the many long term experiments necessary, the system will run 24 hrs a day, and can run overnight without personnel attention. During all runs the experimental system will be completely contained. The glove box enclosure system for the Cary Spectrophotometer is designed in such a manner that in the event of a spill in the box, or other accident, only the minimum parts of the machine will be contaminated. In the event of serious contamination these parts must therefore be replaced for non-alpha work subsequent to this experimental program. This replacement of some of the lesser expensive parts of the spectrometer would cost about \$3500-4000 for the compartments enclosed within the glove box.

#### 5. Glove Box No. 4

This glove box will be constructed of lucite (32" x 32" x 46") and will completely enclose the compartment end of the Cary spectrophotometer containing

the sample-reference compartment, the chopper compartment and the I.R. source-photomultiplier tube compartment. This box will be attached to the end of the spectrophotometer with a neoprene sealing gasket, and will be supported on a table.

The glove box features six, 8 inch glove ports, a 6 inch entry port and a 12 inch entry port. Two glove ports will be located at the level of the sample-reference compartment entries at the top of the box, and will be employed for the handling and manipulation of equipment and material in conjunction with a spectral measurement; the other four glove ports will be located at the base of the box and provide a means by which the ends of the spectrophotometer may be serviced.

Direct transfer of the spectrophotometer absorption cells containing plutonium solution from box 3 will be made via a polyethylene tube connecting box 3 to box 4. The direct transfer should minimize the possibility of leakage or spillage as would be more likely to occur by transfer of the cell by the doubly sealed bag technique. All transfer of equipment through the 12 inch service port will be made by means of the doubly sealed polyethylene tube technique.

Twenty-six Swagelock interconnector fittings will be located on the back panel of the box and will provide a means by which gas ( $N_2$ , etc.), water, and thermocouple service lines will be connected to the glove box, and thence to the spectrophotometer compartments. The box will also be provided with a fire-proof off-gas filter, air inlet filter; and vacuum gauge and will be operated under  $1/2$  to  $2''$   $H_2O$  vacuum.

A miniaturized circulating water bath (Haake Model F; cf. Sect. C, 1, a) will be contained in the glove box and will provide a means by which the sample

absorption cell will be thermostated. The reference absorption cell will be thermostated by a bath which will not be contained in the glove box. Connection from the bath to the reference cell will be made by means of the Swage-lock fittings.

Complete containment will be maintained at all times to eliminate the possibility of contamination which could possibly occur in the absence of personnel for prolonged studies at elevated temperature.

#### 6. Polyethylene Tubing Sealer

This unit is a Vertrod Thermal Impulse Heat Sealer unit that will make a 3/4" wide seal through 2-6 thicknesses of seamless polyethylene tubing (50 mil. wall thickness). The maximum seal length is 20". The seal is such that the polyethylene tube itself will tear before the seal will. This unit and its power supply is mounted on a small mobile table, so that it may be positioned at all entry and exit ports of the glove box systems. The thermal impulse sealer is provided with continuously variable heating and dwelling (cooling) cycles of from about 5-30 sec., depending on the number of thicknesses to be sealed. Therefore, entry to and exit from the glove box units is relatively rapid.

#### 7. Sample and Reference Compartment Circulating Water Systems

##### a. Sample Compartment

Since the circulated water to the jacket of the sample cell would be contaminated with plutonium in the event of leakage or breakage of the cell, the circulating water bath system for the sample cell is completely contained within the spectrometer glove box. A Model F Haake miniature bath is used for this purpose. This bath was described under section C, (1), (a).

(b) Reference Compartment

The reference cell can be thermostated to a temperature equal to or different from the sample cell by a 5 gal. circulating bath that is outside the spectrometer glove box. Circulation from the bath to the cell is via a sealed entry line through the glove box wall to the cell, and a similar return to the bath.

8. Other Equipment

This includes all equipment outside of the glove box systems. Typical items are: the main body of the Cary Spectrophotometer and equipment associated with it; a 12 point automatic, strip chart, temperature recorder used for monitoring temperatures within the various glove boxes (if necessary) and within the sample and reference compartments of the spectrophotometer within the glove box; a Leeds and Northrup line operated pH meter, Cat. 7664; and a 5 gal. Precision Sci. Co. circulating water bath ( $\pm 0.001^{\circ}\text{C}$ ), used to thermostat the reference cell of the Cary Spectrophotometer.

**D: PURIFICATION AND PREPARATION OF PLUTONIUM STOCK SOLUTION**

This first phase of the program will be concerned with the preparation of a plutonium nitrate solution with a plutonium concentration between 200 to 400 g. Pu/l in 2.5 M  $\text{HNO}_3$ . This solution must be pure and must be free from other hydrolyzable ions, and have an accurately known isotopic composition, plutonium concentration, and acidity. The plutonium will be in the +4 valence state, to the exclusion of any significant amounts of the other valence states. Two plutonium stock solutions will be prepared: the major one in uranyl nitrate solution, 2.5 M excess  $\text{HNO}_3$ , 350 g. U/l, with a plutonium concentration between 200 to 400 g. Pu/l; the other solution will be the same except that no uranyl nitrate will be present.

This work will be carried out in glove box No. 1 which will be operated under completely sealed conditions; all transfer in and out will be via the doubly sealed polyethylene tubing technique. For the optimum design of experiments and apparatus, an amount of plutonium stock solution will be prepared initially that should suffice for the program. A rough stepwise schematic of the purification method is outlined below.

**1. Plutonium source**

a. 80 g. Pu as  $\text{Pu}(\text{NO}_3)_4$  in  $\sim 2$  M  $\text{HNO}_3$  is available in approximately 4 liters of solution, located at present in the Isolation Laboratory; this solution is reasonably pure.

b. An additional 120 g. of plutonium will be obtained from the S. F. Accountability Department.

2. Acidity of Pu solution increased to 7.5 M  $\text{HNO}_3$ .

3. 1.5 l. of Permutit SK anion-exchange resin is to be slurried with 7.5 M  $\text{HNO}_3$  and then transferred to the ion-exchange column.

4. Vacuum jacketed ion-exchange column brought to 60°C operating temperature by Haake circulating water bath.

5. Resin washed with 7.5 M HNO<sub>3</sub>, for 5-10 column volumes. HNO<sub>3</sub> wash liquid is pumped by the Teflon micro bellows pump to the top of the column via the spiral tube in the water jacket, so that the wash liquid entering the resin bed is at equilibrium temperature.

6. ~ 60 g. of Plutonium as solution (2), is loaded (down loading) onto the resin column by pumping and preheating as in (5). The solution is loaded at 25-30 ml/min. With the column diameter that is used, the solution could be loaded at a rate of 100 ml/min.

7. After complete loading of the plutonium, the column is washed with 7.5 M HNO<sub>3</sub> containing 0.05 M HF (to remove any Th); column is at 60°C.

8. Resin column containing 60 g Pu is then washed with ~ 5-10 column volumes of 7.5 M HNO<sub>3</sub>, at 60°C.

9. The adsorbed plutonium is then eluted with 0.6 M HNO<sub>3</sub>, at a rate of ~ 20 ml./min.; column is at 60°C. 60 g. plutonium in 0.6 N HNO<sub>3</sub> is now purified and concentrated in ~ 3 liters (or less) of solution.

10. Solution analyzed at this point. (Pu, acid, isotopic purity, alpha spectrum, uranium, Th, etc.).

11. Solution is then analyzed for valence state purity and distribution at this point. Cary Spectrophotometer will be used.

12. If the analyses are satisfactory, solution (9) is evaporated to a plutonium concentration of between 200-400 g. Pu/l. This yields the Pu(NO<sub>3</sub>) stock solution in ~ 2.5 M HNO<sub>3</sub>.

13. For the preparation of a plutonium stock solution in  $\text{UO}_2(\text{NO}_3)_2$  solution (350 g. U/l.), a uranyl nitrate solution will be added to the solution from (9). The solution will have a uranium concentration and acidity, so that when the resulting solution is evaporated, the right plutonium and uranium concentrations, as well as the correct acidity, will be obtained.

14. If the solution prepared by ion-exchange is not pure enough, a peroxide (or oxalate, etc) precipitation of the plutonium will be made to rid it of undesirable impurities. Then, after dissolution of the precipitate, the plutonium will be carried through the ion-exchange procedure followed by subsequent concentration and acidity adjustments.

**E: ANALYTICAL SERVICES AVAILABLE**

The High Level Analytical Service Laboratory in the Isolation Laboratory will provide essentially complete analytical services for the project. They are equipped for high level alpha work with conventional chemical analytical techniques, as well as modern instrumental techniques such as coulometry, potentiometry, acidity measurements, chemical determination of plutonium concentrations, polarography, etc.

This laboratory also provides complete alpha, beta, and gamma counting services. In addition, a 256 channel alpha spectrometer is available for isotopic purity and other various analytical determinations.

The Analytical Service Laboratory will provide practically all of the analytical service required. One exception, is the determination of spectral characteristics, and valence state analyses which will be carried out with the Cary Spectrophotometer at the project site.

## F: HAZARDS AND HEALTH PHYSICS MONITORING

The experimental equipment and procedures have been described herein, with primary emphasis placed on the safety of personnel and to the containment of hazardous materials.

The equipment and clothing requirements for the personnel working in alpha lab 5 are:

1. Long sleeve contamination coveralls.
2. Rubber gloves taped to coverall sleeves.
3. Yellow shoes with shoe covers.
4. He shall have available on his person a dust respirator previously adjusted to fit properly.
5. Pocket meter.
6. Special film badge.

Upon removing arms from the glove boxes, the gloves and clothing are to be monitored for contamination. If it is contaminated, the clothing is replaced and the laboratory surveyed for the contamination source.

Upon leaving the laboratory the personnel will:

1. Remove rubber gloves.
2. Remove shoe covers.
3. Monitor clothing, hands, and shoes for contamination to prevent a spread of contamination to the hall of Bldg. 3508.

To insure the safety of personnel and to detect health hazard due to alpha activity the following will be employed.

1. The service of the Health Physics Division.
2. A continuous alpha air monitor to be located in alpha lab. 5.

3. A neutron detector to be located in alpha lab. 5 in the immediate vicinity of glove box 1 which will contain the bulk of the plutonium.

4. One or more portable alpha counters for surveying, smear counting, and monitoring; to be located in alpha lab. 5.

All alpha active material, and any contaminated material or equipment will be maintained in a complete state of isolation and will be doubly or triply contained in completely sealed glove boxes and/or polyethylene tubing.

It is felt that when the program is carried out in the manner described, the hazard to personnel, etc. will be essentially the minimum possible; and to obtain these minimum hazards, the experimental arrangements and containment are of such of a complexity that any further increase in complexity would seriously hinder or prevent carrying out the experimental work necessary. However, there are probably a number of places at which technique can be improved, and as these are discovered or pointed out, the appropriate changes will be made.

## G. CONCLUSIONS AND RECOMMENDATIONS

The project, as has been outlined, will certainly provide a considerable amount of data and information on the polymerization and depolymerization of plutonium(IV) in the nitric acid-uranyl nitrate system. The first part of the experimental work will be similar to the previously reported<sup>(2)</sup> work from Hanford on the plutonium-nitric acid system. Other aspects of the polymerization, as were previously mentioned, will be investigated as far as time permits. A certain amount of the work will be of an applied nature, since at the present time this information is badly needed. For the time being, this must suffice, since very little in the way of more fundamental research has been done on this problem. The work of Ockenden and Welch<sup>(7)</sup> at the Windscale works (U.K.A.E.A.), though excellent, has just barely scratched the surface of the problem. To our knowledge, no other work is being done or has been recently reported from a site equipped for work with plutonium.

One of the most interesting aspects of the problem is the degree of reversibility of the polymerization-depolymerization processes. It is hoped that some information (though somewhat indirect) can be obtained on this aspect of the problem. It should be emphasized that the spectrophotometric technique is by no means ideally suited for these types of studies. It is being used simply because this equipment is readily available and is operating, and because the proper equipment is not available at the present time, for work with high levels of alpha activity.

It is true that the presence of the polymer can be detected and measured by observing the visible absorption spectra and the absorption (and also light scattering) in the near ultraviolet spectral region. However, the results

themselves are qualitative to semi-quantitative with regard to the polymer concentration, but can be made essentially quantitative by a knowledge of the amount of ionic plutonium present, and the total plutonium concentration. It should be pointed out here that the polymer does not exhibit a constant molar absorptivity index, simply for the reason that there is no such thing as a given type of polymer. There are without doubt many types of polymer, the differences arising in molecular weights, methods of formation, etc. Each preparation will probably show varying spectral qualities. The amount of ionic plutonium present is obtained by spectral measurement either in the upper visible region or near-infrared region where interference from polymer is non-existent or minimal. In essence, the data, though obtainable, is rather indirect.

It has been apparent for some time that knowledge of the polymerization and depolymerization of plutonium(IV) (and probably plutonium(VI),  $\text{PuO}_2^{++}$ ) will remain very sketchy, inconclusive, and inadequate until the proper methods are used to study this and other actinide systems.

The proper methods are: ultracentrifugation techniques, light scattering methods, and other applicable methods standard in the polymer field. These methods have been the most fruitful methods of study for the hydrolysis and polymerization of inorganic systems for many elements other than the actinides, as evidenced by the work of Kraus and Johnson and their co-workers, especially in the field of ultracentrifugation. Kraus has discussed <sup>(4)</sup> some French work which shows that irreversible polymers of Th(IV) can also be formed at high temperatures, and says that the polymers (colloids) though at least partially "irreversible," may occupy an intermediate position between normal Th(IV) polymers and the "irreversible" plutonium(IV) polymers. The interesting thing about this French work is that it is the first concerted effort to characterize these polymers

(or colloids) of Th by methods standard in the polymer field.

In order to obtain very badly needed basic knowledge concerning the polymerization problem of the actinides it is strongly suggested that some work must be carried out using the proper or most suitable physical methods to observe some of the characteristics of these polymeric species. Although the spectrophotometric technique can indicate and give a meager amount of information concerning the polymer, it is severely limited in its application.

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