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by

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ABSTRACT

The study of the conversion of plutonium nitrate solution to solid plutonium oxide is an important phase of the light water reactor fuel recycle program. This report initiates a program at Los Alamos to recommend methods for safeguards and process control accounting for such conversions. We plan to use the LASL Dynamics Materials Control (DYMAC) concept to provide a suitable materials measurement and accounting system. This study will initially be concerned with the conversion via Pu(III) oxalate precipitation which has been proposed by the Savannah River Laboratory.

I. INTRODUCTION

Our study of the conversion of plutonium nitrate solution to solid plutonium oxide (PNO) includes a number of objectives. These are:

a. Reviewing the conceptual design of a baseline conversion plant prepared by the Rocky Flats Plant(RFP).

b. Developing automated measurement, control, and accounting of material flows for a PNO facility.

c. Proposing safeguards and process control accounting for other PNO designs as needed.

d. Developing and demonstrating nondestructive assay (NDA) instruments for these programs. Initial development will be conducted at the plutonium facility at LASL.

e. Demonstrating that a single large diversion or a series of small thefts of SNM will be detected by the proposed materials accounting system.

f. Estimating costs and impact of our program on the PNO facility.

h. Interacting as needed with the LWR Fuel Recycle studies.

The initial phase of this project is to examine the various proposals for converting plutonium nitrate solution to oxide powder. We need to define a conversion process in as much detail as possible in order to develop a meaningful materials measurement and accountability system. We will check each method for additional details as necessary and then construct an appropriate materials accounting system for the most promising process. At this stage we will tentatively divide the process into logical segments, which will be called unit process areas, in order to construct effective accounting and process control. Instruments and chemical analyses will be chosen to provide as timely material accounting as possible. The measurement capability and safeguards sensitivity will be estimated for the entire conversion process.

Process options and modifications that lead to better material controls will be suggested. Further modeling of material flow and continual refinement of the process will follow. If necessary, additional conversion processes may be analyzed in a similar fashion.

II. CONVERSION PROCESSES

Several methods for converting nitrate to oxide have been demonstrated and are certainly feasible for a PNO facility. These are direct denitration by evaporation and calcination; precipitation of plutonium peroxide followed by filtration and calcination; precipitation and subsequent filtration and calcination of either Pu(III) or Pu(IV) oxalate; and the formation of a plutonium polymer (sol-gel) followed by a drying operation. In Table I these methods, major operating steps, and laboratories in which the processes have been demonstrated, are given.

The direct denitration process was developed at ANL and at the Hanford site. It is the simplest and most direct conversion method. Fluid bed and mechanical direct denitration methods would require an evaporation step prior to calcination, while a batch process would require no feed preparation. The only waste streams would be the off gases and some nitric acid from the evaporation cycle. Equipment for continuous conversion has been operated at Hanford[1]. Since there are so few operations, the equipment will be relatively simple to operate and maintain remotely. However, corrosion caused by nitric acid fumes could be extensive. The direct denitration, unlike the other conversion processes, provides no decontamination from cationic impurities. Actual oxide production experience by this method is severely limited. It is not presently known if the PuO_2 product would routinely meet fuel specifications.

The method for precipitating plutonium peroxide was developed at Los Alamos[2] and has also been used at the Savannah River Plant (SRP)[3] and at Rocky Flats (RFP)[4]. The precipitate is formed by direct addition of hydrogen peroxide to the plutonium nitrate feed solution. Experience has included both batch and continuous operations. This method provides excellent decontamination from impurities. Excess peroxide in the filtrate is easily destroyed by heating. Remote operation and maintenance of the equipment is feasible. The potential decomposition of hydrogen peroxide in the system, which would cause a pressure surge and rapid release of gas, can be overcome by providing adequate venting. Precipitator units for peroxide precipitation at SRP, for example, were vented with 2-inch lines to contain gases generated during such a decomposition.[3] Relatively little is known about the physical characteristics of the PuO_2 powder produced by calcining the plutonium peroxide precipitate.

Precipitation of Pu(III) oxalate is used routinely at Los Alamos in concentrating plutonium during recovery operations. The precipitate is easily handled and is filtered without difficulty. The sizes of individual particles and agglomerates of PuO_2 powder formed by calcining Pu(III) oxalate can be altered by changing procedures in the mixing of Pu(III) solutions with oxalic acid, by controlling the concentrations of the reactant, and by regulating temperature.[4] Decontamination from cationic impurities by a Pu(III) oxalate precipitation step are excellent. Losses of plutonium to the filtrate are quite low. SRP has considerable plant-scale operating experience with the Pu(III) oxalate process by batch and semicontinuous methods.[5]

Precipitation of Pu(IV) oxalate at Los Alamos usually has required rather stringent operating conditions such as control of rate of mixing, temperature adjustment, and a limited acid concentration range. The precipitate is quite fine and plutonium losses to the filtrate can be considerably higher than for the Pu(III) process. There has been extensive plant-scale operating experience with Pu(IV) oxalate at the Hanford site. The Pu(IV) oxalate method for the conversion process has been proposed by AGNS.[6] This process was chosen because it provides a good yield of very filterable precipitate which, in turn, is calcined to form a well-characterized PuO_2 powder.

The Pu(IV) process will require less reducing agent, but more oxalate, than the Pu(III) method. More gas would be evolved during calcination of the Pu(IV) oxalate because of the larger ratio of oxalate to plutonium. Both oxalate processes require valence and acidity adjustments prior to precipitation, produce sidestreams for recycle, and require considerable equipment that must be operated and maintained remotely.

Personnel at SRL believe that the Pu(III) oxalate process is probably a better choice because of simplicity of operation, easy filterability, tolerance to feed variations, low filtrate losses, and the data on the calcined product.[5] Obviously, personnel at AGNS believe that the Pu(IV) process is superior because the operations are proven and data show that the PuO_2 product can meet product specifications.[7] Since the filtrate would be recycled, relatively higher losses would not be serious. More study will be necessary and both methods may well be useful. Accountability, process safeguards, and additional data on calcined product may have to be examined before selecting either method.

In the sol-gel process developed by ORNL, plutonium nitrate feed is contacted with n-hexanol to form a sol-gel. After an evaporation step, the sol is dried at 300°C to form microspheres of PuO_2. The process, however, is quite complex and has not been demonstrated on an engineering scale.[8]

A comprehensive study of the advantages and drawbacks of each of these conversion processes is in progress at the Rocky Flats Plant.[9] A preliminary choice of the fluid bed denitration process has been indicated. However, an updated selection of the primary process will be made in March 1977.[10]

Additional study, first by a literature search and then by research and development, may be desirable to characterize the calcined PuO_2 powder formed by the various conversion processes. The effects of variations in conditions of precipitation on the product should be of great interest.

At present the Rocky Flats proposal is insufficiently detailed for LASL to develop an accounting and safeguards system for their recommended process. However, the proposals for the Pu(IV) oxalate conversion process by AGNS[6] and the Pu(III) oxalate conversion by SRL[11] do contain enough information for a preliminary analysis.

We plan to examine the SRL proposal in depth. We believe that many of the instruments, measurements, and procedures developed in this initial study should be applicable in providing safeguards and accounting for the other processes as well.

III. THE DYMAC CONCEPT FOR CONVERSION PROCESSES

The materials measurement and accounting system that we plan to apply to the PNO conversion process is an extension of the LASL Dynamic Materials Control (DYMAC) concept.[12] Recently developed technology for nondestructive assay (NDA), supportive computer operation, and data base management will be used for timely accounting. We will attempt to partition the PNO operation into a series of discrete accounting envelopes, call unit process accounting areas (UPs). Quantities much smaller than the total plant inventory can be controlled on a timely basis by drawing frequent material balances around these UPs.

We are beginning by dividing the Pu(III) oxalate conversion process proposed by SRL into a series of such UPs. The flow sheet is given in Fig 1. Because the plutonium recycle in this process is operated somewhat independently of the main process stream and is bounded by tanks, it could well form a single UP. A second logical UP consists of the furnaces used for calcination. Therefore, the entire PNO process would be divided into three UPs such as: receipt tanks through precipitation and filtering; plutonium in the filtrate through the recycle hold tank; and calcining to product storage. Instruments will be selected to measure plutonium holdup, flow, tank level, weight, etc., so that the materials accounting can be as accurate as practicable. Our previous experience indicates that a materials accounting goal of 0.5% of daily throughput is probably feasible in this system.

Since the AGNS Pu(III) oxalate PNO system utilizes continuous flow, only two UPs would probably be used: the recycle stream and the main process stream from receipt tanks through precipitation, filtration, and calcination to product storage. Holdup in the calcination unit could be measured by cell-load balances. Many of the instruments would be the same as those used in the Pu(IV) process, and the 0.5% materials accounting goal would be maintained.

IV. NDA INSTRUMENTATION

There are a number of NDA methods that will be useful in the PNO facility. The line from the chemical separations facility to the receipt tanks will probably contain in-line flow meters and, if feasible, in-line instruments to determine isotopic ratios of the plutonium by γ-spectrometry as well as total plutonium by K-edge absorption densitometry. These measurements will probably be verified by chemical analyses in the analytical control laboratory.

The total plutonium in the receipt tanks and in the filtrate tanks will be determined by level, density and concentration analyses, or by weight. A rapid verification of plutonium concentration by an automatic, computer-connected method such as coulometry would be useful for each tank. The total plutonium product as PuO_2 powder will be measured by γ-spectrometry on samples and by load-cell weighings coupled to a computer for timely accounting. Neutron monitors will detect solids in-line and in the filtrate tanks, and γ-monitors can measure any plutonium holdup in the filters on the off-gas system. Plutonium in the solid wastes can be measured by neutron counters similar to those in use at the LASL plutonium facility.

The accuracy and precision needed to satisfy process control and safeguards requirements will be considered as this study proceeds. Instrumentation and analyses may be altered to meet such requirements, and alternative procedures may be examined.

V. TRIPS AND CONSULTATIONS

Trips taken during the quarter are summarized in Table II. At the end of this first work period, we have acquired some understanding of the various PNO processes. We have a clearer concept of the program. Finally, we are now in a position to study safeguards and process accountability requirements for a PNO facility.

VI. ACKNOWLEDGMENT

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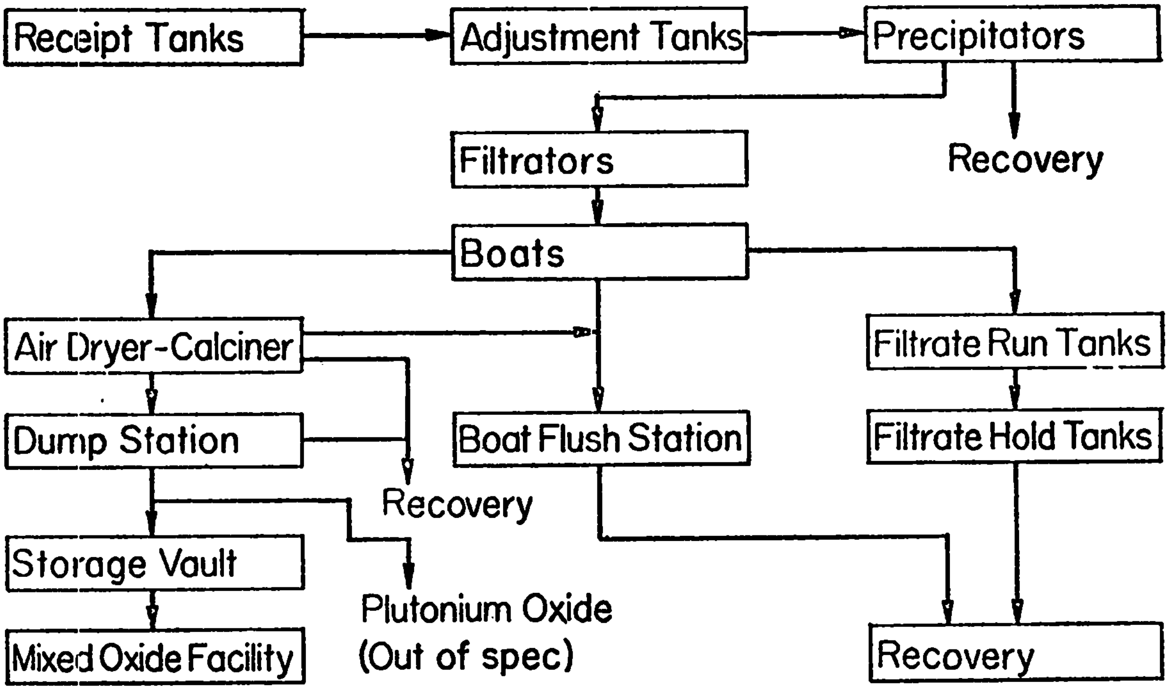

Fig. 1. Proposed PNO Flowsheet.

TABLE I

CONVERSION PROCESSES

Type	Steps	Experience
Direct denitration	Evaporation, calcination	ANL, HNL
Peroxide precipitation	Precipitation, calcination	RFP, LASL
Pu(III) oxalate precipitation	Valence adjustment, precipitaion, calcination	SRP, LASL
Pu(IV) oxalate precipitation	Valence adjustment, precipitation, calcination	HNL
Sol-gel process	Dilution, n-hexanol contact, calcination	ORNL

TABLE II

TRIPS AND CONSULTATIONS, October--December, 1976

Location	Dates	Contact	Purpose
RFP	Oct 5	G. D. Lehmkuhl	To establish contact and to determine status of RFP project in the Recycle Support Program
SRL-SRP	Nov 10-11	K. W. MacMurdo	To discuss our role in the PNO; to learn status of entire Recycle Support Program; and to tour SRP Separations Area.
AGNS	Dec 7-9	G. Molen	To tour and discuss BNFP and to discuss the PNO processes.

REFERENCES

1. R. E. Felt, "Equipment for the Direct Calcination of Plutonium Nitrate," Hanford Engineering Development Laboratory report RL-SEP-674 (December 1965).

2. J. A. Leary, A. N. Morgan, and W. J. Maraman, "Plutonium Peroxide Precipitation," Ind. Eng. Chem., 51, 27 (1959).

3. E. W. Mainland, D. A. Orth, E. L. Field, and J. H. Radke, "Production of Plutonium Metal," Ind. Eng. Chem., 53, 65 (1961).

4. Savannah River Laboratory Monthly Reports for the ^{238}Fuel Form Processes (1972-1976).

5. J. H. Radke, Savannah River Plant, private communication.

6. "Barnwell Nuclear Fuel Plant--Plutonium Product Facility Preliminary Safety Analysis Report," Allied General Nuclear Fuel Services, Barnwell, South Carolina, July, 1974.

7. G. Molen, Allied General Nuclear Fuel Services, private communication.

8. D. Bundquist, G. Bray, S. Donelson, J. Glang, T. Gozani, L. Harris, R. McNamera, D. Pence, and M. Bingham, "Material Control for a Reprocessing Plant," Science Applications, Inc., report SAI-76-747-LJ (August 1976).

9. "Composite Quarterly Report Light Water Reactor Fuel Recycle," DuPont report DPST-LWR-76-2-1 (March 1976).

10. G. D. Lehmkuhl, "Initial Selection of a Primary Process," Rocky Flats Plant report RFP-2590 (September 1976).

11. K. W. MacMurdo, Savannah River Laboratory, private communication, November 1976.

12. J. P. Shipley, D. D. Cobb, R. J. Dietz, M. I. Evans, E. P. Schelonka, D. B. Smith, and R. B. Walton, "Coordinated Safeguards for Materials Management in a Mixed-Oxide Fuel Facility," Los Alamos Scientific Laboratory report LA-6536 (February 1977).