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**LIGHT WATER REACTOR FUEL RECYCLE PROGRAM
PLUTONIUM NITRATE-TO-OXIDE CONVERSION PROJECT
PROGRESS REPORT, JULY-SEPTEMBER 1976**

George D. Lehmkuhl

Chemistry Research and Development
PROCESS CHEMISTRY AND ENGINEERING GROUP

Work performed under 189 No. F-AL-10-001
for the
Savannah River Operations Office
U.S. Energy Research and Development Administration

Rockwell International

Atomics International Division
Rocky Flats Plant
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Golden, Colorado 80401

U.S. ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
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SUBJECT DESCRIPTORS

Plutonium Processing
Plutonium Nitrates
Plutonium Oxides

ROCKWELL INTERNATIONAL
ATOMICS INTERNATIONAL DIVISION
ROCKY FLATS PLANT
P.O. BOX 464
GOLDEN, COLORADO 80401

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for the
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Abstract. Fluid-bed direct-denitration was initially chosen as the primary process for converting plutonium nitrate to plutonium oxide. All direct denitration processes received higher ratings than those using precipitation-calcination. The selection was based on block flow diagrams and initial information on the processes under consideration. An updated selection of the primary process, based on more complete flow diagrams and information, will be made in March 1977.

This report summarizes information on the candidate conversion processes, and on the initial selection of the primary process.

INTRODUCTION

Work is being done at the Rocky Flats Plant, through the Savannah River Operations Office of the U.S. Energy Research and Development Administration (ERDA), to critically analyze and evaluate existing technology for converting plutonium nitrate to plutonium oxide, and to recommend improved flow sheets and equipment for this process.

Savannah River Laboratory (SRL) is coordinating Light Water Reactor (LWR) Fuel Recycle Program studies, such as this, at various ERDA and private industrial sites. These research and development activities are summarized quarterly by SRL.

Plutonium nitrate-to-oxide (PNO) conversion project studies this quarter involved: (1) selecting candidate processes, (2) developing flow diagrams, (3) collecting process information relevant to the primary process selection criteria, and (4) making an initial selection of a primary PNO conversion process.

The primary process selection will be updated in March 1977.

DISCUSSION

Candidate Processes:

Candidate PNO conversion processes were chosen in accordance with the gate criterion which allowed only those processes having at least pilot plant experience to be considered. The following candidate processes were chosen:

1. Plutonium(III) oxalate precipitation and subsequent calcination, used by the Savannah River Plant.
2. Plutonium(IV) oxalate precipitation and subsequent calcination, used at the Hanford site.
3. Plutonium peroxide precipitation and subsequent calcination, used by the Rocky Flats Plant.
4. Fluid bed direct denitration, developed by Argonne National Laboratories.
5. Mechanical direct denitration using screw calciners, developed at the Hanford site.
6. Batch direct denitration, used extensively in early denitration work.
7. The Sol-Gel process developed and used at Oak Ridge National Laboratory.

Figures 1 through 7, Pages 5 through 11, show flow diagrams for each of these processes.

TABLE I. Process Evaluation Results.

Criteria	Weighting Factor	Plutonium(III) Oxalate		Plutonium(IV) Oxalate		Peroxide Precipitation		Fluidized Bed Direct- Denitration		Mechanical Direct- Denitration		Batch Direct- Denitration		Sol-Gel	
		R ^a	P ^b	R	P	R	P	R	P	R	P	R	P	R	P
4.1.1	3	4	12	1	3	1	3	9	27	10	30	10	30	5	15
4.1.2	2.5	7	17.5	7	17.5	7	17.5	6	15	6	15	10	25	7	17.5
4.1.3	4	10	40	10	40	10	40	10	40	10	40	10	40	9	36
4.1.4	8	4	32	6	48	6	48	8	64	8	64	8	64	6	48
4.1.5	6	8	48	10	60	10	60	2	12	5	30	1	6	3	18
4.1.6	7	4	28	4	28	4	28	8	56	7	49	7	49	6	42
4.1.7	8	4	32	4	32	4	32	8	64	6	48	6	48	8	64
4.1.8	8	7	56	7	56	6	48	8	64	8	64	8	64	5	40
4.1.9	5	5	25	5	25	5	25	7	35	6	30	8	40	4	20
4.1.10	7	6	42	7	49	6	42	6	42	6	42	6	42	7	49
4.1.11	1	8	8	8	8	8	8	7	7	7	7	7	7	5	5
Totals			340.5		366.5		351.5		426		419		415		354.5

a= Rating

b= Product of weighting factor and rating

A process involving ammonium hydroxide precipitation, with fluidized-bed calcination of the slurry, is presently under pilot plant study at the G. E. Vallecitos Nuclear Center, Pleasanton, California. This process could be of future interest if tests prove satisfactory.

Primary Process Selection:

The initial selection of a primary PNO conversion process was made using the procedure and criteria set forth in previous Progress Report RFP-2573, Page 3, and was based on the flow diagrams shown in Figures 1 through 7, and on initial information on the processes under consideration. The weightings of these criteria were changed to reflect comments by several reviewers, as described in RFP-2573. An updated selection of the primary process will be made in March 1977, based on more complete flow diagrams and process information.

In selecting the primary process, using the weighting procedure referred to above, each of eleven criteria was assigned a weighting factor relative to its importance, and each process was given a rating for each criterion. The product of the rating and the weighting factor was then obtained. The total of these products for each process was used to determine the primary process.

Rating Criteria:

Discussed below, are the reasons for assigning the various ratings. The ratings and the weighting factors are tabulated in Table I.

Single Train Capacity – Criterion 4.1.1

These ratings were applied according to the number of process trains required for each process to produce the desired throughput. The high spread between

the direct denitration processes and the precipitation processes was deemed appropriate because the direct denitration processes could achieve the desired throughput using two process trains, whereas the precipitation processes used as many as 10. Two process trains would probably be required for any process used, in order to provide continuous operation during equipment repair periods.

Feed Preparation – Criterion 4.1.2

The spreads shown in the ratings for this criterion were not large because the processes will probably require little feed preparation. The rating of 10 was given to the batch direct denitration because it requires no feed preparation. The precipitation and Sol-Gel processes require only dilutions, whereas the fluid bed and mechanical direct denitration processes require an evaporation procedure.

Recycle Streams – Criterion 4.1.3

All of the processes except the Sol-Gel received ratings of 10 because there would probably be no significant recycle streams in any of them. Sol-Gel received a rating of 9 because it requires some, but not an excessive amount, of recycle.

Waste Streams – Criterion 4.1.4

The direct denitration processes received the higher ratings because the waste streams result mainly from the calcination step, whereas the precipitation processes contain other wastes in addition to those resulting from calcination. The Plutonium(III) oxalate process contains an additional waste stream of sodium nitrate, which could present a disposal problem. The Sol-Gel process generates organic waste streams which could prove difficult for waste-treatment.

Operating Experience – Criterion 4.1.5

The Plutonium(IV) oxalate and the peroxide precipitation processes received ratings of 10 because of the extensive operating experience

associated with each. The batch direct denitration process received a rating of 1 because of limited production experience with plutonium. Limited experience with plutonium in the fluid bed and Sol-Gel processes is also reflected in their ratings.

Remotability – Criterion 4.1.6

The PNO Project Team felt that the easiest processes to adapt to remote operation would be the direct denitration processes, with the fluid bed process being best suited. Again, an attempt was made to keep the spread between the high and low ratings at a minimum because all of the processes could possibly be operated by remote control if adequately designed. No evidence could be found to verify that any of the processes have been operated completely by remote control.

Maintenance – Criterion 4.1.7

The fluid bed and Sol-Gel processes showed evidence of being the most maintenance-free; therefore, they received the highest ratings. Again, the spread between the high and low ratings is not large because of the lack of experience with remote maintenance on any of the processes.

Environment and Safety – Criterion 4.1.8

Since this criterion could have political implications, the PNO Project Team felt that the spread in the ratings should not be great. The Sol-Gel process received the lowest rating because of fire and explosive hazards involved with the use of organic chemicals in the process. The direct denitration processes received the highest ratings because of their simplicity of operation and their lesser use of chemicals. All the processes are exposed in varying degrees to corrosive nitric acid. The peroxide precipitation process has the additional problem of rapid decomposition of the hydrogen peroxide if not handled properly.

Inventory Requirements – Criterion 4.1.9

The ratings given for this criterion are based on the amount of material in process at any given time, and also on the ease of conducting a periodic inventory. The batch direct denitration fit this criterion the best, while the Sol-Gel seemed to be the worst. Again, the spread is not large between the various processes.

**Compatibility of Product with
Subsequent Processing – Criterion 4.1.10**

On the basis of present information, the Plutonium(IV) oxalate and the Sol-Gel processes received slightly higher ratings because these two processes have been used to provide oxide for the fabrication of fuel rods. Since all of the other processes could provide a product that would meet present specifications, the spread was not large.

Relative Energy Consumption – Criterion 4.1.11

The PNO Project Team feels that little difference exists between the energy consumption of the various processes. The narrow spread of the ratings reflects this feeling. The precipitation processes seem to be the best of the processes in this respect, while Sol-Gel appears to require the most energy.

CONCLUSIONS

Table I shows that the fluidized bed process emerged as the primary one by a narrow margin over mechanical direct denitration. The mechanical direct denitration process was followed closely by batch direct denitration. The results indicate that, on the basis of present information, the direct denitration processes have a distinct advantage over the precipitation and Sol-Gel processes. As previously mentioned, future evaluations, based on more complete information, may change this conclusion.

ILLUSTRATIONS

Figures 1 through 7

Pu (III) OXALATE

FIGURE 1. Flow Diagram for the Plutonium(III) Oxalate Precipitation Process.

FIGURE 2. Flow Diagram for the Plutonium(IV) Oxalate Precipitation Process.

FIGURE 3. Flow Diagram for the Plutonium Peroxide Precipitation Process.

DIRECT DENITRATION (BATCH)

FIGURE 6. Flow Diagram for the Batch Direct-Denitration Process.

SOL-GEL

FIGURE 7. Flow Diagram for the Sol-Gel Process.

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