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PLUTONIUM (IV) OXALATE PRECIPITATION AND CALCINATION PROCESS FOR PLUTONIUM NITRATE TO OXIDE CONVERSION

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C O N T E N T S

PLUTONIUM(IV) OXALATE PRECIPITATION AND CALCINATION PROCESS FOR PLUTONIUM NITRATE TO OXIDE CONVERSION

ABSTRACT

The Plutonium(IV) Oxalate Precipitation and Calcination Process for converting plutonium nitrate to plutonium oxide is described for a 100-kg plutonium per day (Pu/day) throughput facility. Block flow diagrams, equipment flowsheets, and stream material balances are included. Advantages and disadvantages of the process, additional research and development necessary, and history of the process are also discussed. This report is one of a series describing various processes for converting plutonium nitrate to oxide. The information in this report should be used when comparing the various processes, and as a starting point for development of a prototype or plant-scale facility.

INTRODUCTION

Plutonium (Pu) recovered from spent nuclear fuel by the Purex solvent-extraction process is in the form of plutonium nitrate [$Pu(NO_3)x$] solution, whereas the starting material for fabrication of plutonium-containing fuel rods is solid plutonium oxide (PuO_2). It is, therefore, necessary to convert $Pu(NO_3)_4$ to PuO_2. If fuel fabrication plants are separated geographically from reprocessing plants, shipping regulations require plutonium to be in a solid form (1).[1] Therefore, PuO_2 is a logical product of a fuel reprocessing plant.

Many different processes for converting plutonium nitrate to oxide (PNO), exist; seven of which are considered in the Rocky Flats PNO project. This report describes precipitation of plutonium(IV) oxalate, with subsequent calcination of the precipitate to PuO_2. Other PNO processes, such as Fluidized Bed Direct Denitration, Mechanical Direct Denitration Using A Screw Calciner, Pu(III) Oxalate Precipitation, Batch Direct Denitration, Sol-Gel, and Peroxide Precipitation, are described in other reports of this series.

Each time an industrial or government organization considers building a plutonium nitrate-to-oxide facility, various candidate processes are compared before making a final selection. The process selected depends on the information the particular organization has concerning the process and the criteria developed by that organization. This report (and the others in this series) will provide a body of information which may be used as a basis for the comparisons.

For comparison, all the PNO processes are described for a fuel reprocessing plant having a maximum throughput of 100 kg Pu/day, based on a 1500-tonne per

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[1]Number in parenthesis refer to references at end of text.

year fuel recycle facility, feed containing 1% Pu, and an average operation of 300 days per year.

Feedstock to the PNO conversion unit is plutonium nitrate from the Purex process, and is expected to meet the ASTM C710-73 standard specification for plutonium nitrate solutions, as listed in Table I. This should result in a product that will meet the plutonium oxide impurity standards described in ASTM Standard C 757-74a. These and other plutonium oxide impurity standards are listed in Table II.

A waste treatment plant is assumed to be on site. Liquid wastes below discharge limits will be transferred to the waste treatment plant. Discharge limits are defined as 1×10^{-3} grams of Pu per litre of solution. Liquid waste streams that exceed this limit will be recycled to the PUREX plant.

Solid recycle and waste streams will be processed in one of two ways. Recycle plutonium oxide will be sent to the dissolution unit. (A special plutonium oxide dissolution module may be necessary if halogens are to be kept out of the main process stream.) Line generated solid wastes will be transferred to solid waste disposal.

Off-gas streams will be processed before release to the plant filter plenum. All required utilities are assumed to be provided. Resources which can be recovered (such as nitric acid) will be transferred by appropriate means to a utility system. Where needed for design calculations, standard plant values will be assumed for utilities (e.g., cooling water available at 27°C returned at 37°C).

Remote "hands off" operation and maintenance will be performed on those plutonium streams which require protection from radiation hazards. The plant facility should be designed so as to limit the whole body dose to 1 rem per year.

PERFORMANCE AND PHYSICAL PROPERTY REQUIREMENTS OF PuO_2 POWDER

Safety and Respirable Dust

Particles less than 4 μm in diameter are considered respirable dust and are undesirable from a safety standpoint. However, no standard specification requires that particles be larger than 4 μm.

Sinterability

PuO_2 powder from a conversion facility must pass a sinterability test before it can be accepted by a pellet fabricator. The sinterability test is described in ASTM Standard C 757-74a (1974) and Fast Flux Test Facility (FFTF) Standard RDT E 13-1T (1971). The pellets of pure PuO_2 are pressed and sintered under controlled conditions.

TABLE I. Specification for Plutonium Nitrate Solutions.

Element/Compound	Concentration
Uranium, ppm[a]	5,000
Thorium, ppm	30
Americium, wt. %	see spec, <0.28
Plutonium, g/l	50 to 250
Carbon	see spec, no visible TBP-hydrocarbon dilutents
HNO$_3$ Concentration, M	2 to 8
Chlorine + Fluorine, ppm	150
Sulfur, ppm	300
Zr + Nb, μCi/g	5
Gamma Emitting, μCi/g	40
Total of below, ppm Al, B, Be, Bi, Ca, Cd, Cr, Co, Cu, Fe, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ta, Ti, V, W, Zn	5,000
Total Equivalent Boron Content, ppm	10

From ASTM Standard C 710-73. "Standard Specification For Plutonium Nitrate Solutions". 1976 Annual Book of ASTM Standards Part 45 Nuclear Standards. Americium Society for Testing Materials. Philadelphia, Pennsylvania, 1976.

[a] ppm refers to parts per million parts by weight of plutonium element.

TABLE II.   Plutonium Oxide Powder Specifications.

Properties	Amount Per Specification			
	ASTM[a]	FFTF[b]	ALKEM[c]	BARNWELL[d]
Uranium, ppm[e]	5,000	2,000	<2,600	5,000
Thorium, ppm	30	-	-	-
Americium, wt. %	See ASTM	See FFTF	0.25, 6 months	0.28
Plutonium, wt. %, dry	87.5	87.5	87.6	87.2
Oxygen: Pu ratio	1.95-2.0	1.95-2.0	2.0	-
Carbon	200	200	150	500
Nitrogen	200	200	50	200
Chlorine + Fluorine	125	75	75	125
Sulfur	300	300	-	300
Fe + Cr + N:	1,000	850	600	1,000
Zr + Nb, μCi/g Pu	5	-	-	5
Gamma Emitting, μCi/g Pu	40	-	<8	40
Moisture, wt. %	0.5	-	-	0.3
Total of below, ppm Al, Be, C, Ca, Cd, Cl, Co, Cr, Cu, F, Fe, Li, Mg, Mn, Mo, N, Ni, P, S, Si, Sn, Ta, Ti, W	5,000	5,000	2,500	5,000
Particle Size: max, avg, Micrometers	90, 10	90, <10	44, -	76, -
Surface Area, m^2/g	-	>2.5	>5.0 m^2/g	-
Bulk Density, g/cm^3	>1	-	2 ± 0.3	>1

TABLE II.   Plutonium Oxide Powder Specifications (Continued)

Properties	ASTM[a]	FFTF[b]	ALKEM[c]	BARNWELL[d]
Sinterability Test:				
Cold Pressure, kpsi	See ASTM	30-50	mechanically	-
Soak Temp & Time	$1550^\circ C$, 1 hr	$1550^\circ C$, 1 hr	blendable, UO_2	-
Sintered Density, %Theoretical	90	90	-	-

[a] ASTM Standard C 757-74a. "Nuclear-Grade Plutonium Dioxide Powder, Sinterable". 1976 Annual Book of ASTM Standards Part 45 Nuclear Standards Americium Society for Testing Materials. Philadelphia, Pennsylvania. 1976.

[b] RDT Standard E 13-1T. "Fast Flux Test Facility Ceramic Grade Plutonium Dioxide". Division of Reactor Development and Technology, United States Atomic Energy Commission. Washington, D. C. June, 1971.

[c] "Standard Specification of Plutonium Dioxide For Fabrication of Mixed Oxide Rods". Alkem Gmb H. Hanau, Degessa, West Germany. October, 1972.

[d] "Barnwell Nuclear Fuel Plant, License Application, PSAR". Docket - 50332 - 38. Allied-General Nuclear Services. Barnwell, South Carolina. July, 1974.

[e] ppm refers to parts per million parts by weight of plutonium element.

To pass the sinterability test, pellets should not flake or fracture easily. Flakes and fractures are caused, in part, by powders with inactive surfaces. That is, powders that have been over-calcined have closed internal pores which inhibit material flow during pressing and sintering. Therefore, the FFTF Standard specifies that the BET surface area, measured by gas absorption, be greater than 2.5 m^2/g. And, the Alkem powder specification requries a BET surface area greater than 5 m^2/g.

The sintered pellets of pure PuO_2 should have a minimum density of 90% theoretical density. The percent theoretical density increases as the size of the powder particles decrease, because smaller particles pack with less void volume. Percent theoretical density also depends on the shape of the particles.

Square prisms and round rosettes pack well. Powders containing rosettes must be prepressed and granulated before final pressing to smooth out the particle surface for dense packing. Therefore, all the powder specifications described in the tables require that PuO_2 particles be less than 90 μm. In addition, the ASTM and FFTF Standards require an average particle size of about 10 μm.

Canning Requirements

PuO_2 powders are stored and shipped in cans. To prevent build up in the cans due to radiolysis of contained water, the moisture content of the calcined PuO_2 is specified to be less than 2.5 wt. % (based on Pu) in the present FFTF specification. The moisture content allowed by Rockwell Hanford Operations will be reduced by 1980 to less than 0.5%, as specified in the ASTM Standard. Moisture content of PuO_2 depends on rate of temperature increase during calcining, the final temperature, and soak time at the final temperature.

Fuel Pellet Fabrication Requirements

A constant weight over a 6-day time period from the time of assay is important [2]. Powders with high surface areas tend to absorb moisture and environmental vapors. This absorption increases the PuO_2 weight and causes variable U-Pu oxide pellet densities. To prevent absorption, PuO_2 powders with high surface area are recalcined at 750°C to reduce the surface area to 1 to 5 m^2/g[2]. Alternately, PuO_2 with high surface area can be equilibrated with a high humidity environment and stored in a controlled atmosphere[3].

Near Stoichiometric PuO_2 is necessary for blending with UO_2 to form mixed-oxide fuels,[2] especially for 94 to 96% theoretical dense (TD) fuels. For lower density FFTF fuels of 90% TD, the stoichiometry can be adjusted to $PuO_{1.96}$ by sintering the U-Pu pellet in an argon - 8% H_2 atmosphere[4]. The FFTF Standard requires as calcined plutonium dioxide powder to have at least 85 wt. % Pu and requires at least 87.5 wt. % Pu after calcining at 950°C. Stoichiometric PuO_2 is 88 wt. % Pu.

PuO_2 powder must be blendable with UO_2 to give the following theoretical densities: Experimental Breeder Reactor (EBR) Fuel - 22-33% Pu, 94-96% TD; Fast Flux Test Facility (FFTF) Fuel - 22-30% Pu, 90.4% TD; Light Water Reactor (LWR) Fuel - 3-5% Pu, 94-95% TD. Pellet fabricators of mixed oxides can vary several parameters to achieve different TD's. The type of binder (if any), lubricant, sintering atmosphere and granulation size after prepressing affect the TD of the mixed oxide.

Uniformity of as-received PuO_2 is desirable so that pellet fabrication parameters don't have to be readjusted for each lot. Uniform PuO_2 particle size would allow pellet fabricators to mill for a constant time to obtain particles of a spec-

ified size. Variation in particle size from lot to lot requires frequent interruptions of the milling procedure for size analyses.

Dissolution of Unirradiated Fuel Pellets

UO_2 dissolves completely in boiling 12 $\underline{M}$ HNO_3, whereas PuO_2 requires fluoride ion (F^-) in the nitric acid[5]. Solid solutions of U-Pu which contain up to 30% Pu (the maximum tested) dissolve in boiling HNO_3 without F^- [3,5]. During irradiation of mixed oxides, the core of the pellet becomes hot enough to fuse the mixed oxide into a true solid solution of U and Pu oxides[5]. Irradiated cores of pellets are, therefore, more soluble than unirradiated mixed-oxide fuel. But the temperature at the outside perimeter of the pellet in the reactor may not exceed $600^\circ C$, which is not hot enough for the mixed-oxide to form a solid solution[2]. Therefore, F^- is necessary to completely dissolve the entire irradiated mixed oxide pellet.

Fluoride ion is extremely corrosive, and creates a hostile environment to the expensive fuel reprocessing equipment. Fluoride ion is also troublesome in the reprocessing procedure[5,6]. Therefore, fuel reprocessors don't want F^- in their plants. They have suggested the requirement that unirradiated fuel pellets be at least 99.5% dissolvable. Some reprocessors suggest 99.8% dissolubility[5].
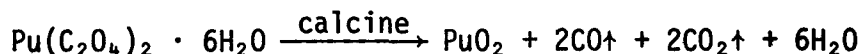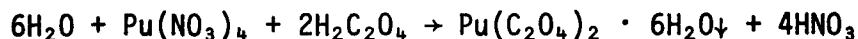
Unirradiated mixed oxides made by mechanically blending PuO_2 with UO_2 showed preferential dissolution of uranium in nitric acid without F^-. The residue was 8 to 10% of original Pu present in early studies[7]. But in most recent studies, as fuel pellet fabricators learned how to blend UO_2 and PuO_2 better, the residue was only 0.06% of the original Pu[5].

To achieve a homogenous blend of UO_2 and PuO_2, the two materials must have nearly the same surface area and particle size. High surface area PuO_2 particles of 40 m^2/g aggregate and do not blend well with intermediate surface area UO_2 of 3 m^2/g. By contrast, low surface area PuO_2 of 5 m^2/g blends well with UO_2 of 3 m^2/g[8]. The average particle size of the UO_2 currently used by Babcock and Wilcox is 0.75 μm. Therefore, Babcock and Wilcox mill the calcined PuO_2 until the particle size is 1 μm[2].

HISTORY

Precipitation and Calcination Reactions

Oxalic acid ($H_2C_2O_4$) is combined with an aqueous nitric acid solution of plutonium in the Pu(IV) state to give a precipitate of plutonium(IV) oxalate hexahydrate [$Pu(C_2O_4)_2 \cdot 6H_2O$]. The Pu(IV) oxalate is then calcined to plutonium dioxide. The reaction is:

$$6H_2O + Pu(NO_3)_4 + 2H_2C_2O_4 \rightarrow Pu(C_2O_4)_2 \cdot 6H_2O\downarrow + 4HNO_3$$

$$Pu(C_2O_4)_2 \cdot 6H_2O \xrightarrow{\text{calcine}} PuO_2 + 2CO\uparrow + 2CO_2\uparrow + 6H_2O$$

Oxalic acid ($H_2C_2O_4$) can be added to plutonium nitrate [$Pu(NO_3)_4$] (direct strike); plutonium nitrate can be added to nitric acid (HNO_3) (reverse strike); or oxalic acid and nitric acid can be added simultaneously as separate streams to a precipitation vessel (continuous process). Direct strike and reverse strike methods have been used in batch processes only.

Uses Of Pu(IV) Oxalate Process

The direct strike and continuous processes were originally developed as a final purification step prior to hydrofluorination and subsequent reduction of the fluoride to pure plutonium metal[9].

Pu(IV) oxalate-prepared PuO_2 has been blended with uranium dioxide (UO_2) and fabricated into nuclear fuel pellets in mixed-oxide fuel fabrication facilities[10]. Experimental Breeder Reactor (EBR) fuel and Fast Flux Test Facility (FFTF) fuel contain 22 to 30% PuO_2, while Light Water Reactor (LWR) fuel contains only 5% PuO_2.

The Pu(IV) oxalate direct strike batch process is used in Europe to reprocess spent nuclear fuel at Cadarach in France, Belgonucleaire in Belgium, and Alkem in Hanau, West Germany[10]. Alkem has fabricated more than 3,000 kg of thermal reactor recycled fuel[11].

Pu(IV) oxalate-prepared PuO_2 has been used to make U-Pu carbide and nitride reactor fuels. Carbides and nitrides of U-Pu are expected to be second generation nuclear fuels because they have greater heat conductivity, greater dimensional stability in the reactor, and better containment of fission product gases[11]. To prepare U-Pu carbide or nitride, PuO_2 and UO_2 are mixed with graphite and heated. PuO_2 prepared by reverse strike and by Hanford's continuous Pu(IV) oxalate process has been used for this purpose[12,13].

$^{238}PuO_2$ heat sources have been used to power thermoelectric generators in space satellites and deep space probes. These heat source pellets contain 100% PuO_2 prepared from Pu(III) oxalate reverse strike procedures and from hydroxide precipitation. But recent experiments with Pu(IV) oxalate reverse strike prepared PuO_2 pellets show better dimensional stability and require fewer processing steps[14,15]. Possibly, heat source pellets will be made from Pu(IV) oxalate reverse strike-prepared PuO_2 in the future.

Chronology of Pu(IV) Oxalate Process

The Pu(III) oxalate process was developed at Los Alamos Scientific Laboratory (LASL), Los Alamos, New Mexico, in 1944 as a final purification step before plutonium was converted to the tetrafluoride, and subsequently reduced to Pu metal[16]. Hydroiodic acid was used to convert plutonium to the Pu(III) state. But the corrosiveness and cost of hydroiodic acid made its replacement or an alternate process desirable. As an alternate process, peroxide precipitation was developed at LASL in 1950 and tested at the Hanford Installation, Richland, Washington. But either an alcohol wash or a slow drying step was necessary in the Hanford procedure to prepare the peroxide precipitate for hydrofluorination [9]. After Brown and Reas[17] found that peroxide adjusted the valence of plutonium to the Pu(IV) state, regardless of whether the plutonium was in the Pu(III) or Pu(IV) state, attention at Hanford turned to the Pu(IV) oxalate process.

The direct strike batch process, described in Table III, was developed first and was used until a greater Pu throughput was needed. The batch process, with its 4-hour cycle time and relatively small capacity, necessitated costly maintenance of numerous process trains and equipment units. To avoid these shortcomings, the continuous process, using a rotary drum filter, was developed in 1956[18]. The Pu(NO$_3$)$_4$ and oxalic acid were added directly to the pan of the rotary drum filter. But the Pu(IV) oxalate particles were too small to filter and there was excessive Pu loss to the filtrate. However, the Pu(IV) oxalate particles increased in size after three throughputs. To increase particle size and to achieve more uniform filter cake properties, a precipitiation vessel was used in the plant by 1963[19]. Pu(NO$_3$)$_4$ and oxalic acid were added simultaneously, but as separate streams, to the bottom of the precipitation vessel, whose overflow then went to the pan of the rotary vacuum drum filter.

To prepare PuO$_2$ for fuel for the Experimental Breeder Reactor and the Fast Flux Test Facility (FFTF), Hanford used that part of their hydrofluorination equipment devoted to continuous precipitation and calcination of Pu(IV) oxalate. The calcination temperature was limited to 380°C because PuO$_2$ calcined above 480°C would not hydrofluorinate completely. But the PuO$_2$ calcined at 380°C was only 80 to 85 wt. % plutonium compared to 88 wt. % for pure stoichiometric PuO$_2$[19]. To meet the FFTF specification of 87 wt. % plutonium, Hanford added a second stage calciner which operated at 525°C. The continuous process used by Hanford until August 1976 is described in Table III. Throughput is 1 kg Pu per hour and a run is normally 100 kg Pu[20,21].

In 1970, Alkem, in West Germany, built a conversion facility based on their small scale process. Alkem selected the batch direct strike process because small quantities of plutonium could be processed separately as required by West German safeguard regulations. Their 5 kg Pu per batch, one batch per day facility was commissioned in 1972[22].

TABLE III. Pu(IV) Oxalate Process Parameters and Product PuO_2 Properties.

Property	Direct Strike Hanford 1951-1956	Direct Alkem 1972-1977	Direct SRL 1976	Reverse SRL 1976-1977	Continuous Hanford 1956-1976
Batch Size	NR[a]	5 kg	1 g	15 g	100 kg/run
Throughput	4 hr/batch	1 batch/day	lab scale	lab scale	1 kg/hr
[Pu] in Feed	10-100 g Pu/l	250 g Pu/l	5 g Pu/l	5 g Pu/l	250 g Pu/l
[HNO_3] in Slurry	2.5-3.5 $\underline{M}$	1.5-5 $\underline{M}$	1.1 $\underline{M}$	1.-2. $\underline{M}$	2.5-3.5 $\underline{M}$
Valence Adjust	50%H_2O_2, 50°C	room temp. 22 days	-	-	12%H_2O_2, 46°C
Strike Temp.	50°C	80°C max.	45°C	20-40°C	46°C
Oxalid Acid Concentration Addition Rate	1.0 $\underline{M}$ 45-90 min.	solid NR	1.0 $\underline{M}$ 10 min.	0.9 $\underline{M}$ not applicable	1.0 $\underline{M}$ continuous
Excess, Slurry	0.1 $\underline{M}$	NR	0.2 $\underline{M}$	0.2 $\underline{M}$	0.1 $\underline{M}$
Digestion Time	30 min.	1 hr.	30 min.	30 min.	30 min.
Digestion Temp.	50-60°C	80°C max.	45°C	25°C	46°C
Chill Slurry	<10°C	35°C	not chilled	not chilled	not chilled
Wash	0.05 $\underline{M}$ $H_2C_2O_4$ 2 $\underline{M}$ HNO_3	NR	NR	NR	0.06-0.4 $\underline{M}$ $H_2C_2O_4$ 2 $\underline{M}$ HNO_3
Filtrate, mg Pu/l	30-60	NR	40-60	40	NR
Calcination Atmosphere Temp. Increase Soak	air NR NR	N_2 several hours 575°C, 4 hrs.	air rapid 735°C, 2 hr.	air rapid 735°C 2 hr.	air 380°C, 1 hr. 525°C, 1 hr.

TABLE III. Pu(IV) Oxalate Process Parameters and Product PuO$_2$ Properties
          (Continued)

Property	Direct Strike Hanford 1951-1956	Direct Alkem 1972-1977	Direct SRL 1976	Reverse SRL 1976-1977	Continuous Hanford 1956-1976
PuO$_2$					
Tap Density	NR	3.3 g/cm^3	NR	NR	2.4 g/cm^3
Surface Area	·NR	6-15 m^2/g	7 m^2/g	4.5 m^2/g	30-45 m^2/g
Particle Size	5-7 μm	12-26 μm	Bimodal 12 μm 40 μm	Unimodal 17.5 μm	95%<20 μm 90%<9-12 μm 50%<5 μm
Particle Shape	NR	NR	rosettes	square prisms	rosettes + square prisms + thin plates
Moisture, wt. %	NR	<0.4	NR	NR	2.5

^{a} NR means not reported.

The Alkem process is described in Table III([22,23]). No special measure is taken
to adjust the valence to the Pu(IV) state because the Pu(VI) formed during con-
centration by evaporation is reduced to an insignificant amount after 22 days
storage. Solid oxalic acid (H$_2$C$_2$O$_4$ · 2H$_2$O) rather than an aqueous 1 M solution
is used because the volume of liquid waste is reduced by 27% and the capacity
of the precipitation column is increased by 29%. The precipitation column has
an external recirculating loop equipped with heating and cooling coils. A sim-
ilar precipitation column is described later in this report, and in the equip-
ment flow diagram.

The Pu(IV) oxalate reverse strike method described in Table III([12,24,25]) is
still in the developmental stage. In 1976, Savannah River Laboratory, Aiken,
South Carolina, (SRL) began further development of the reverse strike batch
Pu(IV) oxalate process to make ^{238}PuO$_2$ spheres for heat sources for space sat-
ellites. The ^{238}PuO$_2$ was formerly made by plutonium hydroxide percipitation
at Mound. But hydroxide-prepared PuO$_2$ when hot pressed, gave pellets with re-
gions of low density which caused pellet fracture([24]). Both Pu(III) oxalate
direct strike and Pu(IV) oxalate direct strike PuO$_2$ particles were too large
and required extensive milling. Pu(III) oxalate reverse strike PuO$_2$, with its
smaller particles, is now used by both SRL and LASL to make ^{238}PuO$_2$. To con-
trol pellet shrinkage from post heat treatment, the calcined PuO$_2$ is milled,
presintered at 1100°C to 1300°C, prepressed, and granulated before hot pressing.

These pellets shrink 3% on subsequent heat treatment. However, Pu(IV) oxalate reverse strike PuO_2 particles can be hot pressed directly (without milling, presintering, prepressing, and granulation) to give pellets which shrink only 1.5% after heat treatment. Pu(IV) reverse strike PuO_2 of 15 to 20 μm has few if any particles less than 4 μm. This is a safety advantage because respirable dust is reduced. PuO_2 prepared by the continuous process was not tried as a heat source material.

Physical Requirements of PuO_2

The relationship between the physical properties (particle size, surface area, and moisture content) and the performance of PuO_2 during the sinterability test, storage in cans, pellet fabrication, and dissolution of mixed oxide fuel was discussed earlier.

For Pu(IV) oxalate PuO_2, particle size is primarily a function of precipitation parameters, as evidenced by very little change in particle size with calcination temperature[24,26].

For Pu(IV) oxalate PuO_2, surface area, tap density, and moisture content with its effect on powder fluidity are mostly functions of calcination parameters [8,22,23,27]. The surface area of PuO_2 powder is more than 10 times that calculated for solid particles. Most of the surface area is due to internal pores that are interconnected and open to the outside. Internal pores result from carbon product removal during decomposition. The particle retains the original skeleton of the oxalate particle[8,24].

Precipitation Parameters And Particle Morphology

1. Equilibrium Solubility of Pu

Pu(IV) oxalate was equilibrated at 25°C with various solutions of known nitric acid (HNO_3) and oxalic acid ($H_2C_2O_4$) concentrations, and the solubility in the solutions, mg Pu/l, was then determined. As HNO_3 concentration increased, the solubility decreased to a minimum at 2.5 $\underline{M}$ HNO_3, then increased again[9]. Solubility increased above the minimum due to Pu-nitrate complexes at higher nitric acid concentrations and, at lower nitric acid concentrations, due to Pu-oxygen polymers[28]. Almost parallel solubility curves were obtained for each of the 3 oxalic acid concentrations studied (0.05 $\underline{M}$, 0.1 $\underline{M}$, and 0.2 $\underline{M}$). Solubility increased as oxalic acid concentration increased due to Pu oxalate complex formation[9]. The minimum solubility was 10 to 20 mg Pu/l at 25°C.

Solubility increased with temperature from 5° to 80°C, but values were not reported.

2. Valance Adjustment

Hydrogen peroxide (H_2O_2) was found to be the most satisfactory reducing agent because it is non corrosive, inexpensive, acts rapidly at 50 to 55°C, introduces no foreign ions, and can be used with plutonium nitrate solutions of any acidity ([9]).

H_2O_2 can both oxidize Pu(III) and reduce Pu(IV). The reaction of H_2O_2 with plutonium ions occurs stepwise. Brown and red peroxy complexes are formed successively, then blue Pu(III), and finally the desired Pu(IV)([29]). The reaction rate for reduction of Pu(VI) to Pu(IV) is slow at room temperature, but fast at 50 to 55°C. The reduction rate is increased by the presence of impurities, like iron salts, which catalyze decomposition of H_2O_2. Oxidation of Pu(III) to Pu(IV) is inhibited by sulfamic acid which stabilizes Pu(III) that has been formed by reduction with H_2O_2([9]). Other impurities which stabilize Pu(III) might also inhibit Pu(III) to Pu(IV) conversion.

3. Direct Strike Parameters

The average diameter of PuO_2 prepared by the Pu(IV) oxalate direct strike method is 12 to 26 μm. The parameters which need to be controlled and the effects of their variation on the size of Pu(IV) oxalate particles are:

(a) Adjust HNO_3 concentration in plutonium nitrate feed so the slurry will be 1.5 to 4.5 M HNO_3. Lower [H+] produces particles that are too small to filter and favors coprecipitation of impurities. Higher [H+] produces a gummy precipitate which is difficult to dry([9]).

(b) Adjust valence with 12 to 15 H_2O_2 wt. % (based on pure H_2O_2) at 50°C for 250 g Pu/l([20],[21]). Higher [H_2O_2], like 50% H_2O_2, causes excessive gas evolution and frothing at 250 g Pu/l, but is acceptable for 10-20 g Pu/l. Lower temperatures like 25 to 35°C produce incomplete conversion of Pu(VI) to Pu(IV) and Pu(III) to Pu(IV). Both Pu(III) and Pu(VI) oxalate are quite soluble at this adjusted nitric acid concentration. Incomplete conversion can cause appreciable Pu loss in the filtrate, considering that Hanford feed is 15 to 21% Pu(VI).

(c) Adjust oxalic acid concentration so that slurry will have 0.1 M excess. Less than 0.05 M excess and greater than 0.2 M excess increases Pu solubility and causes Pu loss in the filtrate. The 0.1 M excess is used to ensure enough excess to complex with contaminants like Fe and Al.

(d) Add oxalic acid over a 30 to 90 minute time period. Fast addition produces small particles and submicron fines which cannot be filtered and cause high Pu loss in the filtrate.

(e) Maintain strike temperature around 50°C. At 20°C, the particles are too small to filter. At 75°C the precipitate is gummy and its filter cake is difficult to dry. In the Alkem procedure, the maximum strike temperature is 80°C[23].

(f) Digest slurry at 50-60°C for 1 hour. Alkem digests for 1 hour at 80°C maximum. Digestion allows small particles with high surface energy to dissolve while larger particles with low surface energy grow in size.

(g) Chill the slurry to less than 10°C over a 20-minute time period to reduce Pu solubility and to prevent post precipitation during filtration, which blinds the filter media. Facer and Harmon found that slower cooling rates and lower temperatures had no effect[9]. Alkem chills the slurry to 35°C over a 1.5 hour time period[23].

(h) Control stirrer speed or agitation in the precipitation vessel. Too vigorous agitation can break up large particles and causes fines which can not be filtered.

(i) Wash the filtrate with a mixture of 2 $\underline{M}$ HNO_3 & 0.05 $\underline{M}$ $H_2C_2O_4$. Use 20 g of wash solution per gram of Pu in the cake[9]. Distilled water washes produce plutonium-oxygen polymers in the filtrate which can not be dissolved without adding F^-[21].

(j) Adjust plutonium feed concentration to prevent contaminants from forming suspended solids. Excessive amounts of aluminum can form solid $Al(NO_3)_3$ when HNO_3 is too high. Excessive amounts of sulfate can form plutonium sulfate $[Pu(SO_4)_2]$ if the feed is concentrated enough to exceed the solubility product of $Pu(SO_4)_2$. For pure $Pu(NO_3)_4$, which is free of contaminants, Pu concentration can be 1 to 550 g Pu/l[9].

(k) Adjust oxalic acid feed concentration to 1 $\underline{M}$ which is near saturation at 25°C. Higher concentrations require heating to keep the oxalic acid in solution. Solid oxalic acid can be used. But it must be added very slowly because the solid becomes occluded with Pu(IV) oxalate and further reaction is slow[9,23].

Savannah River Laboratory (SRL) prepared Pu(IV) oxalate-direct strike PuO_2 on the laboratory scale. SRL reported a bimodal particle size distribution of 11 and 40 μm, which was larger than Hanford's reported average particle size of 5 to 7 μm and Alkem's 12 to 26 μm particle size. Larger particles at SRL might have been due to less residence time in the ultrasonic particle dispersion bath before size measurement. The ultrasonic bath can break up loose agglomerates and fracture very thin plate shaped particles. For SRL particles, the mode at 11 μm corresponded to square prism- shaped particles, and that at 40 μm corresponded to rosettes which were aggregates of thin plate shaped particles.

4. Reverse Strike Parameters

For 1 gram of Pu per batch, the parameters which produce square 11-μm prisms and the effects of their variation are([25]):

(a) Adjust feed to 5 g Pu/l. Higher Pu concentration of 10 g Pu/l gives poorly formed square prisms plus fines. At 25 g Pu/l, the average particle size is 2 to 3 μm([12]).

(b) Adjust nitric acid (HNO_3) concentration in the plutonium feed to 1.1 $\underline{M}$ HNO_3. This gives 11-μm particles and 40 to 45 mg Pu/l in the filtrate. At 2.0 $\underline{M}$ HNO_3, the mode of the particle distribution is slightly larger (11.5 μm) and Pu loss in filtrate is less (20 mg Pu/l). No data are reported for [HNO_3] more dilute than 1.1 $\underline{M}$.

(c) Adjust strike temperature to 25°C. At 35°C, the particle distribution can be bimodal. The mode corresponding to larger particles is due to presence of rosettes which are clusters of square and round plates. At 50°C, the particles are large square plates (18 μm) which are too thin for good compaction during pellet fabrication. Thin plates can agglomerate easily to form large rosettes. Large rosettes are undesirable because they require extensive milling before pressing.

(d) Adjust oxalic acid ($H_2C_2O_4$) concentration (before plutonium nitrate is added) to 0.9 $\underline{M}$ $H_2C_2O_4$. At 0.5 $\underline{M}$ plus 3 $\underline{M}$ HNO_3 in the oxalic acid, the particles are bimodal with one mode corresponding to poorly formed prisms and the other corresponding to fines.

(e) Increase batch size from 1 g Pu/batch to 15 g Pu/batch. The particle size distribution mode increases from 11 to 17.5 μm, with very slight increase in standard deviation from 4.9 to 5.8 μm.

5. Continuous Process Parameters

Continuous process Pu(IV) oxalate prepared PuO_2 has some 60 μm rosettes. But the average particle size is 5 μm. The distribution for several runs was([30]): 95% of particles <20 μm, 90% of particles <9 to 12 μm, and 50% of particles <5 μm. The shape of the particles less than 12 μm were mostly rosettes with some square prisms.

The parameters for the continuous process are listed in Table III. Effects of parameter variation have not been investigated. Contents of the valence-adjust vessels, the precipitation column, and the rotary drum vacuum filter pan are at 46°C because they are all in the same glovebox with the calciners.

The continuous process with 2 separate feed streams is like a combination of the direct strike and reverse strike methods. The parameters like [HNO_3], strike temperature, [$H_2C_2O_4$] in the feed, and digestion time, are optimal for direct strike, but not for reverse strike. Conditions present in the continuous process which would produce fines if the process were performed by direct strike are high [Pu] in the feed (greater than 5 g Pu/l) and low [$H_2C_2O_4$] in the slurry (less than 0.9 $\underline{M}$). A condition in the continuous process which would produce large aggregates if the process were performed by reverse strike is the high temperature (greater than 25°C).

One can conjecture that if the continuous process parameters were set for optimal reverse strike conditions (decrease Pu feed concentration of 5 g Pu/l, raise [$H_2C_2O_4$] in the slurry to 0.9 $\underline{M}$, and decrease the strike temperature to 25°C), the direct strike conditions would be far from ideal. Pu loss in the filtrate would be very high due to Pu complexes and many of the Pu(IV) oxalate particles would be too small to filter due to the 25°C strike temperature.

Calcination And Decomposition Of Pu(IV) Oxalate

1. Calcination Parameters

The decisive calcination parameters are the rate of temperature increasing during oxalate decomposition, final temperature, and holding time. These parameters affect bulk and tap density, surface area, water content, powder fluidity, and percent loss on ignition.

As the <u>final calcination temperature</u> was increased to 1000°C, the PuO_2 bulk and tap density increased, and the BET surface area decreased[8,27]. For constant 30-minute dwell times in the calciner, the BET surface area dropped from 43 m²/g at 350°C to 4 m²/g at 760°C[8].

As <u>rate of temperature increase</u> was decreased by longer holding times of several hours at selected temperatures along the heating curve, water content of PuO_2 decreased from 1 wt. % to less than 0.4 wt. %. Powder fluidity improved as water content decreased[22].

The Alkem calcination procedure, described in Table III, produces PuO_2 with BET surface area of only 6 to 15 m²/g, tap density of 3.3 g/cm³, and less than 0.4 wt. % moisture. N_2 is used in the calciner furnace. The rate of temperature increase is controlled. The temperature is kept constant for several hours at different points on the temperature curve. The holding time at the final temperature of 575°C is 4 hours. Oxalate depth in calcination crucibles is kept less than 3 cm. Otherwise, CO, which is formed during decomposition of the oxalate, will burn on the powder surface and cause deterioration of the ceramic properties and excessive carbon content of the powder.

The Hanford calcination procedure for their continuous process is described in Table III. The Hanford procedure produces PuO_2 with BET surface area of 35 to 45 m^2/g, tap density of 2.4 g/cm^3, and 2.5% loss in weight (after calcining at 950°C) which is mostly water. This 2.5 wt. % moisture content is too high to meet the ASTM specification of 0.5 wt. %. Air is used in the calciners. Temperature increase is not controlled. Pu(IV) oxalate enters the first stage calciner maintained at 380°C. The first stage calciner is a rotary screw type. The second stage calciner is maintained at 525°C. It is a vibrating transfer type.

The Savannah River Laboratory (SRL) calcination procedure produces PuO_2 with a BET surface area of 7 m^2/g for direct strike and 4.5 m^2/g for reverse strike. Tap density and percent moisture are not reported. The oxalate is calcined at 735°C for 2 hours. Temperature increase can not be controlled because $^{238}Pu(IV)$ oxalate self heats to 350°C due to alpha radiation. The specific alpha activity of ^{238}Pu is 250 times that of ^{239}Pu.

2. Mechanism of Decomposition and Stability of Pu(IV) Oxalate

Thermogravimetric studies at NUMEC[31] indicated that a gradual decomposition of the oxalate occurred during storage at room temperature. The thermogravimetric curves for <u>fresh</u> Pu(IV) oxalate showed three distinct stages of decomposition in both nitrogen and air atmospheres. The first stage was attributed to loss of water and occurred between 50 and 130°C for both air and nitrogen atmospheres. The second stage occurred between 150 and 250°C for both air and nitrogen. The third stage occurred between 250 and 350°C in air and between 250 and 450°C in nitrogen atmosphere. The thermogravimetric curves for <u>18 day old</u> Pu(IV) oxalate did not show the second stage of decomposition, but the first and third were present in both air and nitrogen atmospheres. The weight after drying was compared with the final PuO_2 weight for identical samples determined on different days. The data indicated that fresh oxalate was 3% decomposed while 18 day old oxalate was 17% decomposed. Further evidence that decomposition at room teperature had occurred was obtained from x-ray examination. Faint but definite PuO_2 lines were observed in the diffraction pattern of the aged sample.

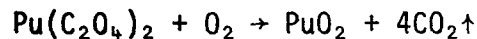This room temperature decomposition was attributed to a α radiolysis or localized α decay heat[31].

NUMEC suggested that the mechanism of decomposition involved formation of plutonium carbonate as an intermediate. The suggested reactions (after loss of water) were: $Pu(C_2O_4)_2 \rightarrow Pu(CO_3)_2 + 2CO\uparrow$ and $Pu(CO_3)_2 \rightarrow PuO_2 + 2CO_2\uparrow$. Analysis of off gases during decomposition would be necessary to confirm the suggested mechanism of decomposition.

3. Products of Decomposition

Calcination in a nitrogen atmosphere would give the following reaction:

$$Pu(C_2O_4)_2 \xrightarrow{N_2} PuO_2 + 2CO\uparrow + 2CO_2\uparrow$$

But, calcination in air could provide enough oxygen to convert the carbon monoxide to carbon dioxide:

$$Pu(C_2O_4)_2 + O_2 \rightarrow PuO_2 + 4CO_2\uparrow$$

Calcination in an ample supply of air would make the heat of reaction more negative because heat is released when CO and O_2 react to form CO_2. This released heat may be the reason why the 3rd stage of calcination in an air atmosphere occurs at a lower temperature than in a N_2 atmosphere.

Filtrate Treatment

Pu(IV) oxalate fines and excess oxalic acid in the filtrate are decomposed by oxidation with HNO_3 during filtrate evaporation to 10 $\underline{M}$ HNO_3. A gummy residue results if no $KMnO_4$ is added[9]. Hanford adds just enough $KMnO_4$ to maintain a permanent purple color in the filtrate before it is evaporated[21]. The concentrated filtrate is recycled back to the separations facility for Purex solvent extraction.

Selection of the Pu(IV) Oxalate Process

The particle sizes from the different processes are: direct strike, 12-26 μm; reverse strike, 17 μm at 5 g Pu/l and 2-3 μm at 25 g Pu/l; and continuous process, 90% <9 to 12 μm and 50% <5 μm. None of the processes require milling in the conversion facility. But PuO_2 from all the processes requires milling in the pellet fabrication facility to 1 μm for adequate blending with 0.75-μm UO_2. Adequate blending is necessary for subsequent dissolution of unirradiated and irradiated fuels in a fuel reprocessing facility.

Continuous process PuO_2 has too many particles less than 4 μm and can present a respirable dust problem. Reverse strike conditions for particle sizes greater than 4 μm require dilute Pu solutions of 5 g Pu/l. This means that $Pu(NO_3)_4$ from the Purex process would have to be diluted from 30 to 50 g Pu/l to 5 g Pu/l, which would increase the process and waste volume 6 to 10 times.

Therefore, the direct strike method was selected for the Pu(IV) oxalate process description and for comparison with other Pu nitrate-to-oxide conversion processes.

PU(IV) OXALATE PROCESS DESCRIPTION

Feed Storage

Plutonium nitrate feed solution is taken from the Separations Plant and stored in slab tanks having capacity of approximately 10,000 litres, adequate for about 4 weeks accumulation of feed stock. The feed solution is assumed to have a Pu concentration of 250 g/l, and a HNO_3 concentration of 3 molar. The Pu concentration is reduced to 150 g/l by the addition of very dilute HNO_3. The feed storage tanks are manifolded slab tanks of 4-inch thickness. The other vessel dimensions and number of vessels have been left to engineering design. The vessels will require cooling because of a decay heat of 60 BTU/hr/kg of Pu. The means of cooling, whether ventilation, cooling coils, etc., has also been left to engineering design. These factors will be the same for any of the processes studied and, therefore, need not be considered in detail for the purpose of process evaluation and selection.

Precipitation

The plutonium nitrate solution is transferred by metering pump to the precipitator trains as called for by the operator. Precipitation of plutonium nitrate to plutonium oxalate is performed in 10 precipitators operating in parallel. The precipitation is a batch process with a total process time of one hour. A metered quantity of feed stock is fed to a free reactor, the batch size being three litres. The adjusted solution is heated to $50^{\circ}C$, then seven ml of 50% hydrogen peroxide is added for valence adjustment of the Pu to the IV state. 7.2 litres of one-molar oxalic acid is then added to the reactor over a period of 15 minutes. Excess oxalic acid is added to make the slurry 0.1 molar in oxalic acid. Following precipitation, the reaction products are chilled to $10^{\circ}C$ before discharge to the filter. Throughout the processing period, the reactor contents are stirred by means of an agitator. Heating and cooling are accomplished by circulating the reactor contents through a heater and a cooler. Each reactor is equipped with its own pump, heater, and cooler. A centrifugal pump is indicated on the flow sheet; however, to prevent damage to the plutonium oxalate crystals during the cooling cycle, it may be necessary to use a pump of gentler action, such as a diaphragm pump. The stainless steel reactor is a nominal 6 inches in diameter with a total capacity of 8 litres. The auxiliary equipment is also stainless steel. The reactors discharge to a common header for filtration.

Filtration

The plutonium oxalate slurry is fed to the basin of a rotary drum vacuum filter of safe geometry. Two filters operate in parallel, with one serving as a spare.

The filters are fed from a manifold which receives slurry from the precipitation reactors. Other types of filtration can be used and may eventually be proven superior. Batch filtration, using a filter boat which is then used as a container for calcination, as shown in the peroxide precipitation flowsheet is a feasible process. Other likely filtration processes are through filters and horizontal belt filters. The principal criterion for the selection of the best filtration process is probably involved with the ease of remote replacement, with reliability also being important. At this point, the rotary drum seems to be the best filtration process. It involves the least equipment and, thus, should require the least maintenance.

The plutonium oxalate cake is washed with two molar nitric acid which contains 0.05 $\underline{M}$ oxalic acid, a difference from the flowsheet. The washed, dewatered cake is cut off the belt with a "doctor" knife (or, shown in the Pu(III) flowsheet, is broken off over rolls) and falls into a hopper which feeds the screw calciner. The filtrate and wash solutions are vacuum transferred to filtrate storage through an in-line full-flow filter which acts as a backup filter in case of a belt failure on the rotary drum filter. The secondary filter is backwashed when required and the wash is recycled to the rotary drum filter.

Calcination

Calcination of the plutonium oxalate to plutonium oxide is performed in an electrically-heated screw calciner. The calcination temperature is 500°C. The calciner operates in tandem with a screwed cooler to cool the oxide to a reasonable temperature before discharge to a ball mill. A small air sweep through the equipment is provided to remove water vapor, gaseous reaction products, and fines. The air is preheated to reduce the load on the calcination heaters.

Grinding, Screening, and Packaging

The plutonium oxide from the calciner-cooler is passed through a ball mill where it is ground to specification particle size. According to some sources, grinding of oxide calcined from oxalate precipitate is unnecessary; grinding is included here as a worst case. The ball mill shown would be very small and probably would not have major maintenance problems. The overall impact of including it is probably small. The determination of a grinding requirement is a fruitful area for research if this process is selected as the primary one. After grinding the reduced oxide passes through a screen of specification mesh. It would be expected that very little material would fail to pass the screen as "overs." What overs exist will be collected in a canister for recycling to the grinder, as indicated on the flowsheet. The material passing the screen is canned, weighed, and sent to storage or shipping. Canning, weighing, shipping, and storage are the same for all processes under investigation and have no impact on process evaluation. These processing steps are not considered in detail.

Scrubbing

The equipment items: calciner-cooler, ball mill, screen, and canner hopper, are all interconnected and swept with air to minimize dusting of the process area with oxide. The air sweep accumulates water, reaction off-gases, and very fine dust particles. The off-gases are collected and passed through a cooler to reduce the temperature to a reasonable level, both for personnel protection and to reduce the operating temperature of the scrubber. The cooler outlet temperature is well above the dew-point of the off-gas, so that condensation and consequent corrosion of off-gas piping should not be a problem. The cooled off-gas goes to a venturi scrubber where it is contacted with a circulating liquid stream. A venturi scrubber is used because of its efficiency in removing very small particles. The scrubber discharge is liquid with entrained gas, and is passed to a packed column where the off-gases are separated from the liquid and entrained plutonium oxide particles. The cleaned off-gas is passed to the plant off-gas system, and the oxide-contaminated liquid is stored in vessels packed with boron-glass Raschig rings for further processing. The liquid from the scrubber is sampled and, if it is below discard limits, it is pumped to the waste treatment facility. If the liquid is above discard limits, it is sent to the filtrate receiver vessels for processing with the filtrate.

Filtrate Evaporation

The rotary drum filtrate and wash and scrubber liquid, if any, are collected in a manifold set of pencil tanks. The tanks are equipped so that filtrate can be drawn into some tanks by means of vacuum simultaneously with feeding the filtrate evaporator from other tanks. A small quantity of potassium permanganate ($KMnO_4$) is added to the solution. The $KMnO_4$ is not indicated on the flowsheet. The filtrate evaporator is fed by a metering pump and accomplishes a ten-to-one boildown by weight. Nitric acid of molarity 2.3 is the overhead product. The bottoms is 8.2 molar nitric acid and contains whatever plutonium or other solids are in the filtrate. The filtrate evaporator also accomplishes the destruction of the excess oxalic acid present in the filtrate. Nitric oxide and carbon dioxide are formed from the oxalic acid, and being noncondensables, are vented from the distillate condenser. The evaporator distillate is stored in a vessel filled with boron-glass Raschig rings, sampled, and if below discard limits, is piped to the waste treatment facility. The evaporator concentrate is cooled to a reasonable temperature, then recycled to the separations plant.

RESEARCH AND DEVELOPMENT

Minimize Number Of Process Trains For Direct Strike

Increased precipitation vessel volume and increased Pu feed concentration might reduce the number of precipitation vessels described in the process description

from 10 to 1. A slab tank 10.16 cm (4 inches) wide, 76.2 cm (30 inches) high, and 121.9 cm (48 inches) long would have 9.5 times more usable volume than the 8-litre precipitation vessel described. Such a slab tank, equipped with a circulation loop that includes a heater and a cooler, should provide the same plant capacity as the 10 reactors presently shown. To ensure adequate mixing in the slab tank, several nozzles connected to manifolds could be used. Solution from the circulation loop would be injected into the tank at several locations. Development work to determine proper baffling in the tank would be necessary to ensure adequate mixing.

The Pu feed concentration could be increased to more than 250 g of Pu per litre of solution. Laboratory scale work showed that feed concentrations up to 550 g of Pu per litre of solution were satisfactory[9]. However, for large batch sizes associated with the proposed 76-litre slab tank precipitation vessel, developmental work would be necessary to demonstrate the feasibility of 250 to 550-g of Pu per litre of solution feeds.

Cycle time for the precipitation vessel would also have to be determined. A 2-hour cycle time would allow a longer digestion time and sufficient Pu throughput to meet the 100 kg Pu per day plant requirement if batch size were greater than 8.5 kg Pu. This batch size would correspond to 35 litres of 250 g of Pu per litre of solution and 40.25 litres of 1.0 $\underline{M}$ oxalic acid.

Improve Filters and Calciners

Different types of filters and calciners should be investigated and improved. Factors to be considered are: amenability to automatic operation, ease of remote replacement, and amenability to assay for Pu accountability. The new safety standards will require remote operation. Equipment that was formerly acceptable under the old safety standards may not be acceptable in the future. Remote operation is especially important when one considers that the isotopes in recycled fuel grade Pu emit about 16 times more radiation to an operator's hand than ^{239}Pu in weapons-grade Pu.

In the future, pellet fabricators might want to reduce plant dust and its associated accountability problems; they may also want to reduce the number of processing steps. One way to do this would be to avoid milling in the pellet fabrication facility. In this case, precipitation parameters would have to be set to give oxalate particles of 1 μm diameter for adequate PuO_2-UO_2 blending. Particles of 1 μm are difficult to filter. They either pass through the conventional filter media or tend to blind it. Reverse osmosis and membrane filtration should be considered. G. D. White at ARHCO[21] has suggested that the oxalate slurry be centrifuged to separate the supernatant solution.

Special calciners would have to be developed to prevent these 1 μm particles from agglomerating. Another possible way to produce 1-μm PuO_2 in the conversion facility would be to grind the particles during calcination. A screw calciner could be developed for this.

Study Effect Of Continuous Process Parameters On PuO_2 Powder

The relationship between the precipitation and calcination parameters and product PuO_2 performance should be studied as suggested by G. D. White at Hanford. A set of conditions might be found that produce:

(a) A narrow particle size distribution with few if any particles in the respirable dust range (<4.0 μm).

(b) Particles of the proper size and shape which can be cold or hot-pressed directly to the desired theoretical density without pre-pressing and granulation.

(c) Particles with the proper surface area (1 to 5 m^2/g) so that their weight will be constant for at least 6 days. Continuous process PuO_2 is now about 40 m^2/g.

(d) Particles of stoichiometric PuO_2 which means less than 0.5 wt. % moisture content or less in weight after calcining at $950^\circ C$. Continuous process PuO_2 now has 2.5 wt. % moisture.

Alternatively, another set of conditions might be found which produces a product with the above properties except that the average particle size would be around 1 μm.

ADVANTAGES AND DISADVANTAGES

Advantages

1. Operating Experience with Recycled Fuel Grade Pu

The plutonium(IV) oxalate process is the only conversion process studied in this series of reports that has operating experience with recycled fuel grade plutonium. Alkem in Hanau, West Germany has fabricated more than 3,000 kg of thermal reactor recycled fuel[32].

2. Precipitation Process with Least Number of Steps and Equipment

Compared to the other precipitation conversion processes, the plutonium(IV) oxalate process has fewer processing steps. This means that the cost to build, operate and maintain this process would be less. Fewer processing steps and less equipment means that the number of remote systems required for remote

maintenance and automated operation would be fewer. However, all the direct
denitration processes require even fewer steps and equipment than the PU(IV)
oxalate process.

3. High Decontamination Factor

It is expected that decontamination of plutonium nitrate feed from Purex solvent
extraction won't be necessary. However, the nitric acid and oxalic acid might
corrode the storage vessels and introduce impurities of Fe, Cr, and Ni into the
plutonium solutions. The decontamination factors of Pu(IV) oxalate are quite
high as discussed by Crocker and Hopkins[19] for the continuous process and by
Kuhn and Koch[22] for Alkem's direct strike method. By contrast, direct deni-
trated PuO_2 might pick up corrosion products from the hot denitration vessel
walls.

4. High Theoretical Density Mixed Oxide Pellets

As discussed earlier in this report, EBR and LWR fuels require mixed oxide
pellets to have 93 to 96% theoretical density (TD). Both Alkem's direct strike
and Hanford's continuous process Pu(IV) oxalate-prepared PuO_2 can be blended
with UO_2 to produce the desired theoretical density. However, direct strike
Pu(III) oxalate PuO_2 from both SRL and LASL does not produce as dense pellets
as Pu(IV) oxalate PuO_2. The same pellet fabrication process that produces
93 to 94% TD pellets from Pu(IV) oxalate PuO_2, produces only 85 to 88% TD
pellets from Pu(III) oxalate PuO_2[26]. However, pellet fabrication procedures
for Pu(III) oxalate PuO_2 can be modified to produce 90% TD pellets as required
for FFTF fuel[26]. But it is unknown at this time if Pu(III) oxalate PuO_2 can
give 93 to 96% TD mixed oxide pellets.

In earlier work, PuO_2 from oxalate was compared with PuO_2 from batch direct
denitration (prepared on laboratory scale) and PuO_2 from oxidized metallic
Pu[33]. The oxalate PuO_2 gave mixed oxide pellet densities which were less
than direct denitrated PuO_2, which in turn, were less than oxidized matel PuO_2.

No data have been reported on the percent TD of mixed oxide pellets from fluid
bed or screw calciner direct denitrated PuO_2, or from peroxide perpared PuO_2.

Disadvantages

1. Hazardous Hydrogen Peroxide Used for Valence Adjustment

For the most part, the products and reactants in the plutonium(IV) oxalate
process are stable; however, hydrogen peroxide is used for valence adjustment,
and can become explosive if not handled properly.

2. More Steps and Equipment than Direct Denitration Processes

Even if the precipitation vessel volume were increased so that only one vessel
rather than 10 were necessary, the precipitation process still requires filtra-
tion units and a precipitation vessel. These items are not required by the
direct denitration processes.

3. Dissolution in HNO_3 Leaves 0.06% Pu Undissolved

Without using corrosive fluoride ions, mechanically mixed oxides which have
been dissolved in hot nitric acid leave 0.06% Pu undissolved. This 0.06% is
for optimal blending using small 1-μm PuO_2 particles. Less than optimally
blended mixed oxides can leave as much as 10% Pu undissolved. By comparison,
sol gel produced U-Pu oxide completely dissolves without fluoride. Also, U-Pu
oxide which has been prepared by U-Pu hydroxide coprecipitation dissolves
completely without fluoride, as shown in most recent work[3].

4. Dust Problems with Mechanically Mixed Oxides

Dust problems seem to be unavoidable with all the conversion processes to pre-
pare PuO_2 for mechanically mixed oxides. Dust occurs when PuO_2 is prepared and
when PuO_2 is blended with UO_2. By contrast, processes for sol-gel vibrapacked
rods minimize dust.

CONCLUSIONS

Plutonium(IV) nitrate $[Pu(NO_3)_4]$ and oxalic acid $(H_2C_2O_4)$ can be combined in
different ways to precipitate plutonium(IV) oxalate hexahydrate $[Pu(C_2O_4)_2 \cdot$
$6H_2O]$ of different sizes and shapes. The oxalate particles retain their
original size and shape as they decompose to plutonium dioxide (PuO_2) during
calcination. Oxalic acid can be added to a solution of $Pu(NO_3)_4$ (direct strike),
or $Pu(NO_3)_4$ can be added to $H_2C_2O_4$ (reverse strike). $Pu(NO_3)_4$ and $H_2C_2O_4$ can
be added simultaneously, but as spearate streams, to the bottom of a precipi-
tation vessel while vessel contents overflow to a rotary drum filter (contin-
uous process). Continuous process is like a combination of direct and reverse
strike as evidenced by its PuO_2 particles, Table IV.

Particles less than 4 μm are considered respirable dust and are undesirable
from a safety viewpoint. Direct strike PuO_2 particles larger than 4 μm can
be made from $[Pu(NO_3)_4]$ of 1 to 500 g Pu per l. But, reverse strike PuO_2
particles larger than 4 μm require dilute $[Pu(NO_3)_4]$ of 5 g Pu per l. This is
a disadvantage because: feed from Purex solvent extraction would have to be
diluted, process and waste volumes would be increased, and Purex feed could not
be concentrated to minimize storage space. The continuous process needs develop-
mental work on the precipitation parameters to avoid PuO_2 particles less than
4 μm. Therefore, direct strike was selected for the process description and
equipment flow diagrams in this report.

TABLE IV.   Plutonium(IV) Oxalate Precipitation Process.

Process	Particle Configuration	Particle Size
direct strike	rosettes	20 μm
reverse strike	square prisms	3 μm at 25 g Pu/l 17 μm at 5 g Pu/l
continuous	rosettes, square prisms and thin plates	90% <9 to 12 μm 50% <5 μm

REFERENCES

1. The Generic Environmental Statement On The Use Of Recycle Plutonium in Mixed
    Oxide Fuel In LWR's. Volumes 1, 2, 3, and 4. WASH-1327. United States
    Atomic Energy Commission. Washington, D. C. August, 1974.

2. C. S. Caldwell. Babcock and Wilcox. Lynchburg Research Center. Lynchburg,
    Virginia. Private Communication. May 6, 1977.

3. I. N. Taylor. General Electric. San Jose, California. Private Communication.
    May 10, 1977.

4. D. E. Rasmussen. Hanford, Engineering Development Laboratory. Richland,
    Washington. Private Communication. May 16, 1977.

5. W. L. Nicholson, Jr. "The Plutonium Dioxide Dissolution Problem For LWR
    Plutonium Recycle And LMFBR Fuels: Fabrication and Reprocessing Problems
    and their Resolution." ORNL-TM-5903. Oak Ridge National Laboratory. Oak
    Ridge, Tennessee. July 1977.

6. M. C. Thompson. Savannah River Laboratory. Aiken, South Carolina. Private
    Communication. October 27, 1976.

7. R. E. Lerch. "Dissolution Of Unirradiated Mechanically Blended, Sol Gel,
    And Coprecipitated Mixed Oxide Fuel." HEDL-TME 72-67. Hanford Engineering
    Development Laboratory. Richland, Washington. June 1972.

8. C. S. Caldwell. "Development Of Plutonium Bearing Fuel Materials." NUMEC
    P-80. Nuclear Materials and Equipment Corporation. Apollo, Pennsylvania.
    September, 1961.

9. J. F. Facer, Jr. and K. M. Harmon. "Precipitation Of Plutonium(IV) Oxalate." HW-31186. Hanford Atomic Products Operation. Richland, Washington. March 30, 1954.

10. E. V. Bemden. "Fuel Fabrication-An Overview." Belgonucleaire S. A. Dessel, Belgium. 1976.

11. D. Vollath, H. Elbel and H. Fiedler, "Calculations of In-Pile Behavior of Carbide Fast Breeder Fuel Pins by Means of Saturn-1." Fuel and Fuel Elements For Fast Reactors, Volume II. International Atomic Energy Agency. Vienna, Austria. Page 85. 1974.

12. K. P. Louwrier, K. Richter, G. Kramer, and M. Lebrun. "Preparation Of A Highly Reactive Plutonium Dioxide Powder For Plutonium-Uranium-Carbide And Nitride Fuel." Journal of Nuclear Materials Volume 61. Page 219. 1976.

13. P. M. French. Westinghouse Electric Corporation. Cheswick, Pennsylvania. Private Communication. May 4, 1976.

14. "^{238}Pu Fuel Form Processes, Monthly Report." DPST-77-128-1. Savannah River Laboratory. Aiken, South Carolina. January, 1977.

15. "^{238}Pu Fuel Form Processes, Monthly Report." DPST-76-128-11. Savannah River Laboratory. Aiken, South Carolina. November, 1976.

16. E. L. Christensen and W. J. Maraman. "Plutonium Processing At The Los Alamos Scientific Laboratory." LA-3542. Los Alamos Scientific Laboratory. Los Alamos, New Mexico. April 1969.

17. P. M. Brown and W. H. Reas. "The Replacement of Hydriodic Acid by Hydrogen Peroxide or other Reducing Agents." HW-22434. Hanford Works, General Electric Company. Richland, Washington. November 15, 1951.

18. R. L. Beede. "Continuous Plutonium(IV) Oxalate Precipitation, Filtration, And Calcination Process." HW-45700. Hanford Atomic Products Operation. Richland, Washington. September 27, 1956.

19. H. W. Crocker and H. H. Hopkins, Jr. "Conversion Of Plutonium Nitrate To Plutonium Tetrafluoride Via The Continuous Oxalate-Fluoride Method." HW-SA-2880. Hanford Atomic Products Operation. Richland, Washington. January 25, 1963.

20. G. D. White. Atlantic Richfield Hanford Company. Richland, Washington. Private Communication. February, 1977.

21. G. D. White. Atlantic Richfield Hanford Company. Richland, Washington. Private Communication. January 28, 1977.

22. K. D. Kuhn and K. H. Koch. "Description Of A Conversion Facility For Plutonium Nitrate." _Kerntechnik 15 Nr. 6._ Page 257. 1973.

23. K. H. Koch. Alkem GmbH. Hanau, Degessa, West Germany. Private Communication April 5, 1977 and May 23, 1977.

24. P. K. Smith, G. A. Burney, D. T. Rankin, D. F. Bickford, and R. D. Sisson, Jr. "Effect Of Oxalate Precipitation On PuO_2 Microstructures." DP-MS-76-34. Savannah River Laboratory. Aiken, South Carolina. August 24, 1976.

25. "^{238}Pu Fuel Form Processes, Monthly Report." DPST-77-128-3. Savannah River Laboratory. Aiken, South Carolina. March 1977.

26. D. E. Rasmussen. Hanford Engineering Development Laboratory. Richland, Washington. Private Communication. May 16, 1977.

27. J. D. Moseley and R. O. Wing. "Properties Of Plutonium Dioxide." RFP-503. Rocky Flats, Division, Dow Chemical Company. Golden, Colorado. August 1965.

28. J. M. Cleveland. _The Chemistry Of Plutonium._ Gordon and Breach Science Publishers. New York, New York; London, England; and Paris, France. Pages 84, 110, 111, 112. 1970.

29. R. E. Connick and W. H. McVey. "The Peroxy Complexes Of Plutonium(IV)." Paper 4.12. _The Transuranium Elements Research Papers, IV-14B._ McGraw Hill Book Company. New York, New York. Page 445. 1949.

30. L. H. Taylor. Atlantic Richfield Hanford Company. Richland, Washington. Private Communication. May 13, 1977.

31. C. S. Caldwell and O. Menis. "Development Of Plutonium Bearing Fuel Materials." NUMEC P-90, Progress Report. Nuclear Materials and Equipment Corporation. Apollo, Pennsylvania. December 31, 1961.

32. P. Funke, W. Lins, V. W. Schneider. "Production Of Mixed-Oxide Fuel For Fast Reactors." _Fuel & Fuel Elements for Fast Reactors, Volume II._ International Atomic Energy Agency, Vienna. Page 397. 1974.

33. M. J. Barr. "Evaluation Of Mixed U, Pu Oxide Sintering Variables And PuO_2 Powder Source." HEDL-TME 72-140. Hanford Engineering Development Laboratory. Richland, Washington, January, 1971.

I L L U S T R A T I O N S

Pu(IV) Oxalate

Flow Sheet & Material Balance
(2 sheets)

Equipment	Description
D-1 FEED STORAGE VESSELS	STAINLESS STEEL, SLAB TANKS, 10,000 L CAPACITY
P-1A&B CIRCULATION PUMP	CANNED STAINLESS STEEL 15 GPM
P-13A&B FEED PUMP	GEAR PUMPS SST, 0.3 GPM
A-1 A,B,C,D,E,F,G,H,I,&J AGITATOR	SST, TURBINE TYPE, 300 RPM
R-1A,B,C,D,E,F,G,H,I&J PRECIPITATOR	6" ID. CAPACITY 8L, SST
P-5A,B,C,D,E,F,G,H,I&J PUMP	SST, CANNED, 5GPM
E-1A,B,C,D,E,F,G,H,I&J HEATER	SST, SHELL & TUBE DUTY = 2500 BTU/HR
E-2A,B,C,D,E,F,G,H,I&J COOLER	SST, SHELL & TUBE DUTY = 7500 BTU/HR.
FL-1A&B FILTER	CONTINUOUS ROTARY DRUM VACUUM FILTER, POLYPROPYLENE CLOTH, SST SHELL & ACCESSORIES
E-5A&B CALCINER	SCREW CALCINER SST, DUTY = 50,000 BTU/HR CAPACITY = 12 #/HR OF Pu O2 ELEC. HEATED
E-6A&B COOLER	SCREW COOLER, SST, DUTY = 658 BTU/HR CAPACITY = 12 #/HR OF Pu O2
ME-1A&B SCREW FEEDER	SST,
ME-2A&B BALL MILL	SST SHELL & INTERNALS, CAPACITY = 12 #/HR OF Pu O2
ME-3A&B SIEVE	SST, MOTOR DRIVEN SCREEN
E-3 AIR HEATER	CST, ELECT. HEATED DUTY = 5,000 BTU/HR.

PRECIPITATION REACTION
$$Pu(NO_3)_4 + 2H_2C_2O_4 + 6H_2O \longrightarrow Pu(C_2O_4)_2 \cdot 6H_2O \downarrow + 4HNO_3$$

CALCINATION REACTION
$$Pu(C_2O_4)_2 \cdot 6H_2O + \overset{\Delta}{\longrightarrow} PuO_2 + 4CO_2 + 6H_2O$$

NOTE ①
PRECIPITATION CYCLE:
TOTAL CYCLE TIME = 1 HR.
CHARGE R-1 WITH 3L FEED AND CIRCULATE AT 5 GPM
ADD 15g OF 50% H_2O_2
HEAT SOLUTION TO 50°C WITH E-3 OVER 10-MIN PERIOD
ADD 7.2L OF 1M $H_2C_2O_4$ OVER 15-MIN PERIOD
MAINTAIN TEMP AT 50°C DURING ADDITION
CHILL PRODUCTS TO 10°C BEFORE DISCHARGING TO FL-1 WITH E-4
FULL DAY LOAD REQUIRES 9.25 REACTORS OPERATING SIMULTANEOUSLY
MATERIAL BALANCE SHOWS FLOWS FOR COMBINED REACTORS ON CONTINOUS BASIS

NOTE ②
OVERS FROM SIEVE ARE COLLECTED IN CANNISTER FITTED WITH A
QUICK-CONNECT FITTING AT ME-3 & ME-2. MANIPULATOR TRANSFERS
FULL CANNISTER BACK TO ME-2 FOR RECYCLING OVERS.

NOTE: MATERIAL BALANCE VALVES ARE TOTAL FLOWS

BASIS: THROUGHPUT OF 100 KG Pu/DAY; OPERATION 24 HRS/DAY

STREAM GMS/HR COMPONENT	101	102	103	104	105	106	107	108	109	110	111	112	113	114	130	131	132
Pu(NO3)4	8,471		8,471			TRACE							TRACE				121
Pu(C2O4)2						7,222							217				
PuO2				4,718										TRACE			
H2O2								33									
H2C2O4						564			3,686				564				
H2O	15,186	11,125	26,311			58,984		33	32,640		69,264		126,119	38.6 LBS/HR	2,129		
HNO3	3,151		3,151			813					14,336		15,111		38		
CO & CO2															2,498		
AIR											32,991				32,991		
METAL IONS	169		169			169	42						127				
SULFUR	8		8			8							27				
HALOGENS (F&Cl)	1		1			1											
STEAM or BRINE						87 LBS/HR.										6,819 LBS/HR.	
TOTAL GMS/HR	26,986	11,125	38,111			67,761	4,760	66	36,326	32,991	83,600		142,165	38.6 LBS./HR.	37,656		6,819 LBS./HR.
Pu, GMS/L	250		150														
FLOW, L/HR	16.7	11.1	27.8		1600	68.8		0.065	40.9	25,483	76		132				
PRESS, PSIA	PUMP	SYSTEM	PUMP		30			SYSTEM	SYSTEM	STD	STD		SYSTEM		SYSTEM	SYSTEM	
TEMP, °C	AMBIENT	AMBIENT	AMBIENT					50°C	AMB	STD			10		190°C	-10°C	
MOLARITY	3N, HNO3		1.8 HNO3			1.7, HNO3 0.1M H2C2O4			1M H2C2O4		3N, HNO3		2.4N, HNO3				
BATCH QUANTITY			3L			7.4L		7ML	4.43L								
PHASE	LIQUID	LIQUID	LIQUID	VAPOR	LIQUID	LIQUID	SOLID	LIQUID	LIQUID	GAS	LIQUID		LIQUID	LIQUID	GAS	LIQUID	LIQUID

ME-4	ME-5	D-5	P-6A&B	D-6A&B	P-7A&B	P-8A&B	D-7A&B	E-7A&B	E-8A&B	P-10A&B	D-10	P-11
CANNER	BALANCE	FILTRATE RECEIVER	PUMP	EVAPORATOR	PUMP	PUMP	VESSEL	REBOILER	CONDENSER	PUMP	SEPARATOR	PUMP
		SST, GEOMETRICALLY SAFE, CAPACITY 1200L	SST, GEAR PUMP,	SST, GEOMETRICALLY SAFE, 100L/HR.	SST, 6GPM CANNED	SST, 0.5 GPM GEAR PUMP	SST, FILLED W/ BORON-GLASS RR, 25L CAPACITY	SST, SHELL & TUBE DUTY=360,000 BTU/HR.	SST, SHELL & TUBE DUTY=306,000 BTU/HR.	SST, 15GPM CANNED	SST, CONTACTOR FILLED W/ PALL RINGS, RESERVOIR FILLED W/BORON-GLASS RR, CAPACITY=1,200 FT³/HR.	SST, GEAR 0.2 GPM

D-11A&B	P-12A&B	B-1	D-12	FL-2	E-4	E-9	J-1	D-9A&B
SCRUBBER BTMS STORAGE	PUMP	BLOWER	VACUUM TRAP	POLISH FILTER	OFF-GAS COOLER	BOTTOM COOLER	VENTURI SCRUBBER	DISTILLATE RECEIVER
SST, FILLED W/BORON-GLASS RR, 200L	SST, GEAR, 1 GRM	SST & FRP, 20 SCFM	SST, 5" ID x 24" HIGH	IN-LINE FILTER SST, 5" ID CASE, POLYPROPYLENE ELEMENT	SST, SHELL & TUBE DUTY=6000 BTU/HR.	SST, SHELL & TUBE DUTY=343 BTU/HR.	SST, CAPACITY=20 SCFM 0.1 GPM WATER	SST, FILLED W/BORON-GLASS RASCHIG RINGS, 2000 L EACH

OXALATE KILL REACTION

$$H_2C_2O_4 + 2HNO_3 \xrightarrow{\Delta} 2H_2O + 2CO_2 + 2NO_2$$

CONT. FROM SHT. 1

STREAM GMS/HR COMPONENT	116	117	115	119	120	121	122	123	124	125	126	127	128	129	130	113	132	133	134	135
Pu(NO3)4										TRACE 4						TRACE			TRACE	
Pu(C2O4)2																217	121		4	
PuO2	TRACE							TRACE							TRACE					
H2O2																				
H2C2O4																564			564	
H2O	2,129	132,421	34	17,000 LBS./HR.	1,948		2,088	2,270	134,691	883			294 LBS./HR.		2,129	127,994			126,119	19 LBS./HR.
HNO3	38	19,727			TRACE			38	19,765	613					38	15,111			15,111	
CO & CO2 or CO2 & NO2	2,498		1,125		2,498										2,498					
AIR	32,991				32,991										32,991					
METAL IONS									127							127			127	
SULFUR									27							27			27	
HALOGENS (F & Cl)									4							4			4	
STEAM or BRINE				381 LBS./HR.																
TOTAL GMS/HR	37,656	142,148	1,159	17,000 LBS./HR.	37,437	381 LBS./HR.	2,088	2,308	154,456	1,658			294 LBS./HR.		37,656	144,044			141,956	19 LBS./HR.
Pu, GMS/L									<10⁻³	3.1						0.93			0.03	
FLOW, L/HR	30,675	142	748		33,419		2.1	2.3	155	1.2						134			132	
PRESS., PSIA	SYSTEM	PUMP	SYSTEM		SYSTEM	30	PUMP	SYSTEM							SYSTEM	SYSTEM			SYSTEM	
TEMP. °C	50°C	40°C	40°C	20	42.5°C		27	AMB	AMB				20°C		190°C	10			10	20
MOLARITY		2.3N, HNO3							2.2, HNO3	8.2N, HNO3						2.4N, HNO3			2.4N, HNO3	
BATCH QUANTITY																				
PHASE	GAS	LIQUID	VAPOR	LIQUID	GAS	VAPOR	LIQUID	LIQUID	LIQUID	LIQUID			LIQUID		GAS	LIQUID	LIQUID	LIQUID	LIQUID	LIQUID

Stream notes: 126 — HI-LEVEL RECYCLE NORMALLY ZERO; 127 — HI-LEVEL RECYCLE NORMALLY ZERO; 129 — AS REQUIRED; 132 — INTERMITTANT FLOW; 133 — INTERMITTANT FLOW

Diagram labels:
- TO FL-1 (132)
- (133) 3N HNO3 BACKWASH
- FROM FL-1 SHT 1 (113)
- (134)
- FL-2 — FILTER ELEMENTS TO INCINERATION
- ME-4
- CV-1 — (107) — ME-5 — PRODUCT PuO2 TO STORAGE OR SHIPPING
- FROM SHT 1 (130) — E-4 — 10°C RISE CWR — 50°C — CWS (128)
- D-5
- P-6 A&B
- D-12 — (129) TO VACUUM SOURCE
- D-6 A&B
- E-8 A&B — 10°C RISE CWR — (119) CWS
- D-7 A&B — (115) TO VENT
- P-8 A&B — (117)
- E-7 A&B — (121) 15# STM — CONDENSATE
- P-7 A&B
- E-9 — 97°C — 20°C — (123) RECYCLE TO SEPARATIONS PLANT — 10°C RISE CWR — (135) CWS
- (116)
- (126)
- (127)
- (120) TO VENT — B-1
- D-9A&B — TO VENT — SAMPLE — P-10A&B
- J-1 — D-10 — (122) PW — P-11 — TO VENT
- D-11A&B — SAMPLE — P-12A&B — (123)
- (124) TO WASTE TREATMENT AND ACID RECOVERY

Pu (IV) OXALATE

BASIS: 100 KG Pu/DAY
250G Pu/L
3M IN HNO₃

H₂O 267L/DAY

FEED FROM PUREX
400 L/DAY
250G Pu/L
3M HNO₃

FEED STORAGE SLAB TANKS 10,000L TOTAL CAPACITY

50 % H₂O₂
≈ 7 ML/BATCH

IM H₂C₂O₄
4.43 L/BATCH

667L/DAY
150G Pu/L
1.8M HNO₃

BATCH PRECIPITATOR 3L BATCH VOL=8L RES TIME=1 HR #TRAINS=10

$Pu(NO_3)_4 + 2H_2C_2O_4 + 6H_2O \rightarrow Pu(C_2O_4) \cdot 6H_2O \downarrow + 4HNO_3$

BACKWASH
70 G Pu/DAY

1,651 L/DAY TOTAL
7.4L/BATCH
1.74M HNO₃
0.1M H₂C₂O₄

3N HNO₃
1,824 L/DAY

BACKWASH

POLISHING FILTER

FILTER

25G Pu/DAY
3,168 L/DAY
2.4M HNO₃

125 Pu/DAY
3,168 L/DAY
2.4M HNO₃

STORAGE 1,200 L GEOMETRICALLY SAFE

CALCINER 500°C COOLING 50°C

$Pu(C_2O_4)_2 \cdot 6H_2O \xrightarrow{\Delta} PuO_2 + 4CO_2 + 6H_2O$

AIR-611,592 L/DAY STP

BOTTOMS RECYCLE TO SEPARATIONS PLANT
25 G Pu/DAY
29 L/DAY
8.2M HNO₃

OFF GAS

$H_2C_2O_4 + 2HNO_3 \xrightarrow{\Delta} 2H_2O + 2CO_2 + 2NO_2$

H₂O
50 L/DAY
27°C

TO PLENUM
CO-18648L/DAY
CO₂-18648
AIR-611,592
H₂O-22,929
(STP)

OFF-GAS

EVAPORATION 10:1 BOILDOWN GEOMETRICALLY SAFE

SCRUBBER 43°C GEOMETRICALLY SAFE

GRINDER

TO PLENUM
CO₂-6720L/DAY STP
NO₂-6720L/DAY STP

3,408 L/DAY
2.3M HNO₃

OVERS

RECYCLE OF HI-LEVEL WASTE

55 L/DAY

DISTILLATE STORAGE 1,000L RASCHIG RING

BOTTOMS STORAGE 500L RASCHIG RING

SCREEN & PACKAGE

PuO₂ PRODUCT
113.2 KG/DAY

TO WASTE 3,720L/DAY
2.2 M HNO₃

DISTRIBUTION

INTERNAL

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   21   Library
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30 – 121   TID-4500, UC-83, Nuclear
           Converter Reactor Fuel
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