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CONTROLLED PuO₂ PARTICLE SIZE FROM Pu(III) OXALATE PRECIPITATION

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ABSTRACT

PuO_2 powder with reproducible particle size and morphology can be produced by controlling precipitation variables affecting the initial supersaturation and final solubility of plutonium oxalate. Such feed powders with constant characteristics are essential for reproducible fabrication response and controlled microstructures in the manufacture of $^{238}\text{PuO}_2$ heat sources.

Calcination does not change the morphology or shape of the size distribution of the PuO_2 particles from that of the precipitated Pu(III) hydrated oxalate. For a given precipitation method, the size and morphology of the Pu(III) oxalate are determined by precipitation temperature, nitric acid concentration, plutonium concentration, and oxalate ion concentration. Functional relationships of these variables were developed to control and predetermine the size, extent of agglomeration, and dimensions of the PuO_2 particles over the range of these variables for PuO_2 production. This report describes statistically designed factorial experiments and characterization of PuO_2 by Coulter counter and scanning electron microscopy (SEM). These control factors were applied successfully in full-scale production.

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CONTROLLED PuO_2 PARTICLE SIZE FROM Pu(III) OXALATE PRECIPITATION

INTRODUCTION

Inert and stable heat generating shapes of dense $^{238}\text{PuO}_2$ ceramics are produced for isotopic power applications by hot-pressing granulated $^{238}\text{PuO}_2$.^{1,2} $^{238}\text{PuO}_2$ powder is produced by calcining precipitated Pu(III) oxalate.³ Bickford, Rankin and Smith^{4,5} have shown that variations in the particle size and particle dimensions of the PuO_2 powder cause wide variation in the density and microstructure of the fuel forms. Such variation can be accommodated by ball milling PuO_2 powder to the same particle size. However, this can only be done by adjusting milling time for each different calcined powder size. A more desirable approach is to produce calcined feed with reproducible size characteristics.

Previous work at Savannah River^{3,6,7,8} and elsewhere⁹⁻¹³ has shown that widely different particle morphologies and sizes can be obtained from oxalate precipitation depending on several factors. These include the valence of the plutonium in solution, the mixing sequence of plutonium nitrate and oxalic acid solutions, and the variables affecting initial supersaturation (nucleation rate) and final solubility (particle growth rate). Prior interest has been mainly on the filterability of the precipitate and not on powder characteristics for fabrication. The production process presently used at Savannah River is batch Pu(III) oxalate precipitation by adding plutonium nitrate solution into oxalic acid solution (reverse strike addition), filtration, and calcination of plutonium oxalate to plutonium oxide.⁷ Fabrication processes for heat source fuels have been developed at Los Alamos Scientific Laboratory (LANL)¹⁴ and Savannah River^{4-7,15} and the fuels qualified for application using $^{238}\text{PuO}_2$ produced by reverse-strike precipitation as the reference material. A new two-step direct-strike Pu(III) oxalate precipitation method (that produced large PuO_2 particles for direct hot pressing into fuel forms) was published previously.⁸

This report describes how the reverse strike precipitation variables that affect the solubility of $\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ control the particle size and morphology of calcined $^{238}\text{PuO}_2$. Quantitative relations are presented showing how predetermined sizes, particle dimensions, and amounts of agglomeration can be obtained by control of precipitation variables.

EXPERIMENTAL TECHNIQUES

Precipitation and Calcination

^{238}Pu and ^{239}Pu nitrate feed solutions were obtained for these experiments by eluting Pu(IV) from ion exchange columns used to separate plutonium from dissolved reactor targets.¹⁶ Concentrations were from 2 to 8 g Pu/L and 0.4 to 5M nitric acid. Batch precipitations were performed in the laboratory on a 1 g and 10 g scale and in production equipment on a 60 g to 100 g scale. Pu(IV) was reduced to Pu(III) with 0.05 mole excess ascorbic acid and stabilized from reoxidation with 0.05M hydrazine.³ Plutonium nitrate solution was added into 0.9M oxalic acid solution, so-called reverse strike precipitation.⁷ The excess oxalic acid concentration in the slurry after precipitation was 0.2M.

Reactants were mixed by a paddle stirrer rotating at ~500 rpm in a small metal or glass precipitator with four equally spaced baffles. Temperatures of the feed solutions and the precipitation slurry were measured and held constant between 20 and 70°C with heaters or water-cooling jackets. Reactants were added at a constant rate over a period of 12 min. Precipitates developed promptly, permitting filtration within 5 min after addition of plutonium nitrate was completed. Plutonium oxalate precipitates were calcined in air at 735°C for 2 hr. Calcined $^{238}\text{PuO}_2$ contains typically 3,000 ppm total of Th, Np, U, and Am; 150 ppm each of Ca, Fe, and Si; 20 to 50 ppm each of Al, Ni, and Cr and <10 ppm of other cations.

Characterization

Log normal distributions of mass particle size were measured with a Coulter counter⁷ using 30 and 140 μm apertures on ultrasonically dispersed slurries in "Isoton" (a saline electrolyte provided by Coulter Electronics) solution. Accuracy was confirmed using calibrated latex spheres and scanning electron microscopy on analyzed powders. Mass mode size, rather than median or mean size, was used for correlation since mode size could be determined for the distribution of individual particles in bimodal distributions. Computed median and mean sizes usually represented total data averages for bimodal distributions that are combinations of distributions of individual particles and their agglomerates.

The extent of agglomeration in powders was determined using a log-normal plot of cumulative weight percent versus equivalent spherical diameter. The agglomeration index is the weight percent of particles in the population of larger size particles in the bimodal distribution. The index was read from log normal plots at

the first indication of curvature from the linear curve representing the distribution of smaller individual particles. In this manner, overlapping size distributions with different modes were resolved.

Powders were characterized by scanning electron microscopy¹⁷ and particle dimensions were measured (from photomicrographs) as the average dimension in the largest particles.

All measurements and graphical data were reduced and prepared with a Hewlett-Packard Model 9830 calculator with plotter. Statistically designed experiments were performed to develop correlations between morphological properties of calcined powders and precipitation parameters. A generalized linear regression code¹⁸ was used to establish the correlations and fit the data to a Taylor series expansion.

RESULTS AND DISCUSSION

Characteristics of Powders

Morphology

$\text{Pu}_2(\text{C}_2\text{O}_4)_3 \cdot 10\text{H}_2\text{O}$ crystals precipitate as monoclinic laths (Figure 1) isomorphous with crystals of La(III) and Ce(III) oxalates investigated optically by Wylie¹⁹. The lath crystals exhibit anisotropic growth along the principal axes with growth rate ratios among the axes between factors of five to ten. Layered growth was observed at high precipitation temperatures (large laths) parallel to the 001 face and perpendicular to the 001 direction indicative of rapid and pulsating growth in the Z direction.

Very little crystal branching was observed (Figures 1 and 2). This indicates that the rate-limiting step is the intrinsic growth rate of the oxalate crystals, and not the diffusion of solute to the crystal.²⁰ The behavior is consistent with the large supersaturation and the large entropy of precipitation. (The ratio of plutonium concentration in the feed to that in the final slurry varied between 50 and 1,500 for the range of variables in this work based on solubilities measured by Burney and Porter²¹.) The absence of dendritic growth and the rate limiting step of intrinsic crystal growth are the principal reasons that predetermined, uniform, and reproducible powder size and morphology can be obtained by controlling only the precipitation variables.

Calcined 1000°C

As-Precipitated

FIGURE 1. Effect of Calcination on $^{238}\text{PuO}_2$ Morphology

Delamination in
[100] orthopinacoid plane from
loss of interstitial
layers of water

Porosity associated
with water loss

"Mud flats" from
shrinkage on [010]
clinopinacoid plane

FIGURE 2. Effect of Calcination of Plutonium Oxalate
on PuO_2 Morphology

Effect of Calcination

Morphology of the particles and the shape of the size distribution are preserved on calcination even though large molar ratios of H_2O , CO_2 , and CO are evolved from the crystals (Figure 1). Conversion to PuO_2 without disintegration is attributed to the escape of water preferentially along $[100]$ planes in the crystal.¹⁹ Figure 2 shows the existence of rows of bubbles in the $[100]$ faces and the tendency to delaminate. About a one-third linear shrinkage occurs on calcination to PuO_2 at 735°C as determined from particle size measurements. Evidence of shrinkage is shown in Figure 2 by the "mud flats" on the other faces of the laths.

Particle Size Distribution

Typical mass particle size distributions of calcined PuO_2 are shown in Figure 3. The log normal statistics suggest no decrepitation on calcining or fracture on stirring. The size distributions of both plutonium oxalate and PuO_2 are usually bimodal, representing a distribution of individual lath particles and a distribution of agglomerates of laths (Figures 3 and 4).

The mass size distribution obtained from the Coulter counter does represent the bulk properties of the powder sufficiently to correlate with the fabrication response of the powders.⁵

The population distribution measured with the Coulter counter, from which mass distribution is computed, is limited to particles with equivalent spherical diameter $>0.6\text{ }\mu\text{m}$. However, based on the portion of the population distribution that is measurable between 0.6 and $140\text{ }\mu\text{m}$ and on SEM observations, the mode size for a population distribution (rather than mass distribution) is about 0.3 to $0.4\text{ }\mu\text{m}$. But the particles less than $0.6\text{ }\mu\text{m}$ do not represent sufficient mass to alter the usefulness of the Coulter counter measurements.

Precipitation response was correlated with mass mode size of the distribution of individual particles. Mode size is the most probable size in the histograms (Figure 3). Mean size, median size, and standard deviation were also computed for the entire bimodal distribution; but, because these properties are characteristic of the combined distribution of both individual and agglomerated particles, correlations with precipitation variables were not particularly useful.

Agglomeration

The extent of agglomeration was measured with an agglomeration index taken from log normal plots (Figure 3). The actual amount of

FIGURE 3. Mass Particle Size Distribution of PuO_2

agglomerates is proportional to, and somewhat larger than, this index. By varying the ultrasonic dispersion time, it was shown that the agglomerate size distribution was broken down into the same distribution as for individual particles. Based on this result and SEM studies (Figures 4 and 5), agglomerates were shown to be loosely packed assemblages up to 400 μm in diameter comprised of individual lath particles. Agglomeration indices then were measured as the residual weight percent agglomerate after 1.5 min of dispersion.

Surface Area and Crystallite Size

Both surface area and crystallite size of PuO_2 within the particles are a strong function of calcining temperature.⁶ The relatively high surface area and its strong inverse temperature dependence are associated with fine porosity generated within the particles by escaping H_2O , CO_2 , and CO during calcination. Surface area and crystallite size are both largely independent of particle size and morphology. A calcination temperature of 735°C for 2 hr in air was used for all experiments to ensure complete conversion to PuO_2 and preserve sufficient sintering potential for subsequent fabrication.

Screening Experiments

Particle Size Dependence

A number of experiments were performed by Bickford, Rankin and Smith to show that variation in particle size and particle dimensions caused variable fabrication response.^{4,5} In this work, screening tests were performed using a variety of precipitation and calcination conditions to show that the precipitation variables alone account for the size and dimensions of the particles. At these high supersaturations, precipitation is self-nucleating and not affected by mechanical or scale factors.

These screening experiments showed that particle size could be predetermined by controlling precipitation temperature, nitric acid concentration, plutonium concentration, and oxalic acid concentration. Figures 6 and 7 show that the particle size of PuO_2 increases with the temperature of the precipitation slurry in an Arrhenius relation. All three dimensions of the laths increase with precipitation temperature. Figure 8 shows that PuO_2 particle size increases with increasing nitric acid concentration in the plutonium feed solution. Figure 9 shows that particle size decreases with increasing plutonium concentration above room temperature, but is rather insensitive to plutonium concentration at room temperature. Figure 10 shows that particle size decreases with increasing oxalate concentration.

FIGURE 4. Effect of Ultrasonic Dispersion on Particle Size Distribution

FIGURE 5. Effect of Ultrasonic Dispersion on Particle Size Distribution from Spherulite Agglomerates

22°C

40°C

67°C

FIGURE 6. Effect of Precipitation Temperature on PuO_2 Morphology

* Numbers are precipitation run numbers in Table 2.

FIGURE 7. Effect of Temperature on Mode Size and Agglomeration

* Numbers are precipitation run numbers in Table 2.

FIGURE 8. Effect of Nitric Acid Concentration on Mode Size and Agglomeration

* Numbers are precipitation run numbers in Table 2.

FIGURE 9. Effect of Plutonium Concentration on Mode Size and Agglomeration

* Numbers are precipitation run numbers in Table 2.

FIGURE 10. Effect of Oxalate Concentration in Final Slurry on Mode Size

Agglomeration Dependence

Agglomeration has an inverse Arrhenius dependence on precipitation temperature (Figure 7). Above 50°C, the calcined powder is largely free of agglomerates. The exothermic formation of the agglomerates, their morphology as loose-stacked laths, and the size distribution of the component laths imply that agglomerates are formed by coalescence of individual laths already formed, probably because of the high number density of laths in the highly supersaturated solution. (Based on Coulter counter measurements and calculations using measured equivalent spherical diameters, the number density of precipitate crystals was calculated to be between 10^6 and 10^8 particles/cc with an average separation of 10 to 100 Å in the slurry. These numbers imply heterogeneous nucleation of laths and high probability of collisions which could form agglomerates.) Larger particles at higher temperatures imply fewer particles and, hence, less potential to agglomerate. If agglomerates are formed as dendrites or nucleated as agglomerate clusters, rather than coalesced from separately formed laths, they would have endothermic temperature dependence as for particle size. Agglomeration is shown in Figures 7, 8, and 9 to have a dependence on other precipitation variables inverse to that for particle size.

Baker and Bergougnou²² developed a model for this kind of agglomeration-controlled growth at high supersaturations that exhibits many of the properties observed for agglomeration of plutonium oxalate: pH dependence, increased mean size with increasing agglomeration and increasing rate of generation of unit particles, log normal size distribution, and SEM appearance. In their model, agglomerates develop by collision and adherence of unit particles rather than by deposition of solute ions.

The soft agglomerates of lath particles were reduced on ball milling as effectively as individual lath particles and are not a significant factor in fabrication response. However, when a uniform distribution of coarse porosity is required in the PuO₂ ceramic body, precipitation conditions can be selected to obtain entirely agglomerated feed (Point C in Figure 11). This can be presintered to obtain granulated PuO₂ directly for subsequent consolidation.^{6,8} In this manner, mechanical granulation by milling, cold-pressing, and comminution can be avoided.⁸

Spherulites were formed (Figure 5) when nitric acid concentration in the feed was increased up to 5M or the nitric acid concentration was constant throughout the mixing. Under these conditions of lower initial supersaturation and higher solubility, growth rate is so rapid that initially formed nuclei grow several laths at once from a common site rather than nucleating additional individual laths. Spherulites were not a significant morphology within the range of temperature and concentrations of interest for fabrication, however.

Point G: 0.7M $[H^+]$, 45°C
Mode = 5.7 μm

Point E: 1.8M $[H^+]$, 45°C
Mode = 12 μm

Point H: 0.7M $[H^+]$, 22°C
Mode 3.5 μm

Point F: 1.8M $[H^+]$, 22°C
Mode = 4.7 μm

FIGURE 11a. Mode Size and Morphology for Several Precipitation Conditions (Plane GEFH Figure 12)

Point I: 0.7M $[H^+]$, 45°C
Mode = 3.5 μm

Point B: 1.8M $[H^+]$, 45°C
Mode = 7.5 μm

Point C: 0.7M $[H^+]$, 22°C
Mode = 1.7 μm

Point D: 1.8M $[H^+]$, 22°C
Mode = 2.5 μm

FIGURE 11b. Mode Size and Morphology for Several Precipitation Conditions (Plane IBCD Figure 12)

Insensitivity to Other Process Variables

Tests were made to establish that variations in primary and secondary nucleation factors had negligible effects. Concentration and rate variables, as well as nucleation from fragmented crystals, seed crystals in heels, suspended matter, equipment, and scale of operation were tested. Because plutonium supersaturations were very high in the range of interest, plutonium oxalate nucleation was expected to be heterogeneous, rapid, and self-nucleating. Agitation rate was varied from 150 rpm to 1,100 rpm without measurable variations in size and morphology. With no agitation, however, smaller particles were produced that were difficult to filter. Addition rates were varied from 20%/min to 1%/min without significant effect. Digestion time at 23°C was varied from 0 min to 60 min without significant effect, implying rapid ripening of particles. Seed crystals of plutonium oxalate and suspended oxalic acid particles in supersaturated oxalic acid solution did not affect size and morphology. Precipitations in glass and metal equipment on a 1 g, 10 g and 60 g scale were the same. No differences were noted between ^{239}Pu and ^{238}Pu , demonstrating radiolytically formed gases or nuclear radiation had no effect. Consequently, precipitation at high supersaturation is spontaneously self-nucleating. Size and morphology, then, are determined only by the initial supersaturation (nucleation) and the final solubility (growth).

The effect of calcination rates and temperature were evaluated to show that rate of conversion of plutonium oxalate to PuO_2 was not significant. PuO_2 particle size distribution and shape (SEM) were unchanged when plutonium oxalate was placed into a hot furnace (735°C) or the temperature rise to 735°C was programmed at 2°C/min. Rapid heating and various holding times at 180°C and 350°C where first water then oxalate are removed also had no effect. Calcination at 1,100°C was required before the particle size distribution showed sintering as a reduction in fines and increased mode size.

Correlation With Precipitation Variables

Statistical Design and Responses

The screening tests established that PuO_2 particle size and extent of agglomeration were determined by the precipitation temperature, nitric acid concentration in the feed, plutonium concentration in the feed, and final oxalate concentration in the mixed slurry. Statistically designed experiments at constant 0.20M oxalate concentration in the slurry were performed to determine the correlation among these precipitation variables.

The experimental results from a three-factor, two-level factorial analyses are shown in Figure 12. Both mass mode size and agglomeration index show the general correlations with precipitation variables noted above. Surfaces at constant mass mode size are shown at 4.5 and 6.0 μm . Particle size is presently being controlled between these limits in $^{238}\text{PuO}_2$ production. Surfaces of constant mode size intersect the body diagonal (Line CE) of the parameter space. This diagonal represents nearly the maximum rate of change of solubility of plutonium oxalate with the variables.^{21,22} Mode size increases along line CE along with increasing solubility. Alternatively, agglomeration decreases with increasing solubility along this line so that agglomeration has the inverse dependence on precipitation variables as does mode size. The SEM photographs (Figure 11a) for the front face (EFHG) and (Figure 11b) for the back face (BDGI) of Figure 12 show visually these variations in particle size and morphology.

Effect of Oxalate Concentration

Varying final oxalate ion concentration in the mixed slurry causes variation in particle size and agglomeration in the same direction as does plutonium concentration, but with 1-1/2 times the effect. Figure 9 shows the decrease in particle size with increasing oxalate ion concentration with the precipitation temperature and plutonium and nitric acid concentrations held constant. The rate of size change at 0.20M excess oxalate is 1.5 times the rate of size change with plutonium concentration for similar conditions, as shown in Figure 13. Such a dependence is expected if size is dependent on final solubility since the molar ratio of oxalate to plutonium in plutonium oxalate is 1.5. Because it was convenient to fix the oxalate to plutonium ratio for production of $^{238}\text{PuO}_2$, the parametric studies in this work were performed at or normalized to a constant 0.20M excess oxalate ion concentration in the final slurry.

Functional Relationships for Size and Agglomeration

Functions relating mass mode size, agglomeration index and lath dimensions to precipitation variables were established (Table 1) based on 53 ^{239}Pu and ^{238}Pu precipitations in the range $20 < T < 70^\circ\text{C}$, $2.0 < \text{Pu} < 8.0 \text{ g/l}$, and $0.4 < A < 2.2\text{M}$. Eleven terms of a Taylor series were selected as a compromise between quality of the fit (number of excess degrees of freedom) and accuracy of the data points. Attempts to fit the data to a function with theoretical basis, such as $1/T$ and $\ln$ concentration terms, were not successful.

As shown in Table 2, the multiple correlations for mass mode size and agglomeration index are 98.0% and 96.8%, respectively.

FIGURE 12. Factorial Analysis of ^{238}Pu Oxalate Precipitation

FIGURE 13a. Effect of Temperature on Mode Size for Several Different Feed Compositions

FIGURE 13b. Effect of Temperature on Agglomeration for Several Different Feed Compositions

TABLE 1

Relation Between PuO_2 Powder Properties and Precipitation Variables for Reverse Strike Pu(III) Oxalate Precipitation

Variables	a_0	A, M a_1	P, g/l a_2	T, °C a_3	AP a_4	AT a_5	PT a_6	APT a_7	A^2 a_8	P^2 a_9	T^2 a_{10}	Multiple Correlation	Standard Error	Correlation Coefficient		
														A	P	T
Mode size μm	8.9213	-6.206	-0.05710	-0.2483	- 0 -	0.18927	0.00090636	-0.0068855	1.3727	-0.007048	0.002799	98%	0.50 μm	0.42	-0.36	0.77
Lath length μm	15.981	18.733	-0.99239	-0.44942	1.5641	0.21104	0.03204	-0.0047162	5.6325	-0.11211	0.0032318	82.8%	3.6 μm	0.10	-0.39	0.68
Lath width μm	-4.7673	15.218	-1.3388	-0.039982	-0.052873	0.049701	-0.0048357	-0.0054381	-6.1282	0.1577	0.001941	83.5%	1.2 μm	0.09	-0.25	0.72
Lath thickness μm	1.2005	-3.2745	0.3312	-0.01818	0.0062695	0.044509	0.0040028	-0.0032992	1.0297	-0.037931	-0.00022941	86.7%	0.18 μm	0.52	-0.17	0.50
Agglomeration Index, wt %	143.74	-96.77	3.5561	-3.5345	1.2481	1.2277	- 0 -	-0.13251	12.817	-0.18622	0.02153	96.8%	5 wt %	-0.44	0.54	-0.69

$$\text{Variable} = a_0 + a_1 A + a_2 P + a_3 T + a_4 AP + a_5 AT + a_6 PT + a_7 APT + a_8 A^2 + a_9 P^2 + a_{10} T^2$$

A = initial nitric acid concentration (molar, M) in the Pu nitrate feed

P = Pu concentration (grams/liter, g/l) in the feed

T = temperature (°C) in the precipitation solution

(oxalic acid concentration for all tests = 0.2M excess in the final slurry)

TABLE 2

Experimental Data Relating PuO₂ Particle Size, Agglomeration, and Lath Dimensions to Precipitation Variables^a

Isotope Sample	Observed Responses					Variables		
	Mode μm	Agg. Index wt %	Length μm	Width μm	Thickness μm	HNO ₃ M	Pu g/L	Temp °C
Two-Level Factorial Analysis								
238 A	3.8	22	b	b	b	1.2	4.0	33
238 B	7.8	12	11.5	3.2	0.7	1.8	8.0	48
238 C	2.2	65	3.4	1.1	0.2	0.7	8.0	25
238 D	2.8	57	7	1.1	b	1.8	8.0	25
238 E	12	1	25	6.3	1.5	1.8	2.0	48
238 F	4.9	13	10	2.0	0.4	1.8	2.0	25
238 G	5.1	8	21	4.1	0.25	0.7	2.0	48
238 H	3.7	28	12	1.2	b	0.7	2.0	25
238 I	3.9	19	8.5	3.3	0.4	0.7	8.0	48
238 J	5.7	13	205	3.4	0.5	1.1	5.0	42
Two-Level Factorial Analysis								
238 A-1	4.0	25	9	2.3	0.5	1.1	5.0	35
238 R	4.3	28	9	2.3	0.5	1.1	5.0	35
238 B-1	4.6	14	10	1.7	0.8	1.0	6.0	40
238 C-1	c	c	8.5	1.7	0.2	1.4	4.0	30
238 D-1	3.0	30	8.4	1.6	0.2	1.0	4.0	30
238 E-1	6.0	13	10	2.2	0.8	1.4	4.0	40
238 F-1	2.4	35	7.5	2.5	0.2	1.0	6.0	30
238 G-1	4.8	25	10	2.5	0.5	1.0	4.0	40
238 H-1	3.9	33	6.5	1.2	0.3	1.4	6.0	30
238 I-1	5.3	18	11	2.5	0.5	1.4	6.0	40
Additional Individual Samples								
239 P-10	4.9	c	9	2.0	0.45	1.1	5.0	35
239 S-10	6.9	70	b	b	b	0.7	8.0	22
239 1	4.2	50	b	b	b	0.7	4.2	25
239 16	4.5	40	9	1.9	0.3	1.2	4.2	25
239 15	6.3	19	b	b	b	2.2	4.2	25
239 12	3.0	68	b	b	b	0.4	4.1	25
239 4	c	45	b	b	b	1.2	7.3	25
239 6	6.2	18	13	6.0	0.7	1.2	4.1	43
239 7	13	4	25	8.7	0.9	1.2	4.1	70
239 13	4.4	13	14	3.5	b	1.2	3.9	33
239 14	3.7	27	b	b	b	1.2	4.0	25
239 18	4.6	29	b	b	b	1.2	2.0	25

TABLE 2, Contd

Isotope Sample	Observed Responses					Variables		
	Mode	Agg. Index	Length	Width	Thickness	HNO ₃	Pu g/L	Temp
	μm	wt %	μm	μm	μm	M		°C
Additional Individual Samples, Contd								
239 19	b	50	b	b	b	1.2	8.0	25
238 20	3.1	30	b	b	b	1.2	6.25	33
238 21	4.1	23	b	b	b	1.1	4.0	33
238 28	4.1	b	b	b	b	1.1	5.0	35
238 29	3.7	28	b	b	b	1.1	5.0	35
238 30	4.8	23	b	b	b	1.4	4.0	30
239 31	4.7	18	b	b	b	1.4	4.0	30
239 32	3.4	39	b	b	b	1.4	7.2	30
239 35	b	30	b	b	b	1.4	6.0	30
239 36	4.5	25	b	b	b	1.1	5.0	35
239 37	4.1	25	b	b	b	1.1	5.0	35
239 38	2.4	67	b	b	b	0.7	8.0	22
239 B-2	d	d	17	3.0		0.9	7.0	50
239 C-2	d	d	16	5.0	0.7	1.3	3.0	30
239 D-2	d	d	6.5	2.6	0.25	0.9	3.0	30
239 E-2	d	d	13.5	5.0	0.45	1.3	3.0	50
239 F-2	d	d	5	1.4	0.2	0.9	3.0	30
239 G-2	d	d	16	5.0	0.4	0.9	3.0	50
239 H-2	d	d	8	2.2		1.3	7.0	30
239 I-2	d	d	10	3.2	0.4	1.3	7.0	50
239 A-2	d	d	13	6.2	0.4	1.1	6.0	40

a. Excess oxalate in final slurry for all precipitations is 0.2M.

b. Indistinct SEM photomicrographs or no SEM analysis.

c. Deleted for $\Delta > 2\sigma$.

d. Foreign material mixed in precipitate.

These functions predict mode size and agglomeration index to 0.5 μm and 5 wt %, respectively. The correlation coefficients show the dependencies noted. Precipitation temperature is the strongest factor. In contrast to its affect on mode size, plutonium concentration has a larger effect on agglomeration than does nitric acid concentration. The variation in mass mode size and agglomeration versus precipitator temperature is shown in Figures 13a and 13b for several plutonium and nitric acid concentrations. Mass mode size varies from 1 to 20 μm throughout the parameter space and agglomeration index varies from 0 to 100 wt %.

Functional Relationships for Dimensions

The dimensions of the particles exhibit different dependencies on precipitation variables in the above tests. Other work^{4,5} has shown that milling and fabrication response might depend not only on mass mode size but also on the aspect ratios of the laths dimensions and their thickness. For this reason, the dimensions (mass distributed) of the laths were also correlated with precipitation variables using measurements on SEM photomicrographs. The functions and correlation parameters are shown in Tables 1 and 2. The quality of the fit was lower due to measurement accuracy. Multiple correlations between 83% and 87% were obtained.

The equations in Table 1 predict PuO_2 lath dimensions to 3.6 μm in the 3 to 30 μm length range, 1.2 μm in the 1.0 to 10 μm width range, and 0.18 μm in the 0.1 to 1.5 μm range for thickness of the laths. The correlation coefficients show the same general trends of lath dimensions with precipitation variables as for mass mode size (Table 3). However, the magnitude of the dependencies are different for each lath dimension. For example, nitric acid concentration has a large effect on thickness, but little effect on length and width. The temperature dependence at 1.5 M HNO_3 and 5 g Pu/L is shown in Figure 14a.

The anisotropy of the growth of each dimensions is shown in Figure 14b. Ratios of the PuO_2 dimensions (length/thickness, length/width, and width/thickness) are plotted versus nitric acid concentration at 35°C and 5.0 g Pu/L in the feed. Up to 50-fold variation in the ratios was observed throughout the parameter space. This could cause a large variation in ball milling response at constant milling time and cause variable packing on subsequent consolidation.

Applicability In Production

All these relations were found to hold for $^{238}\text{PuO}_2$ production on a 60-100 g ^{238}Pu scale of precipitation. Many production batches have been precipitated using these relations to control

TABLE 3

Control of PuO_2 Characteristics by Pu(III) Oxalate Precipitation

	<u>Range</u>	<u>Error</u>	<u>Correlation Coefficients</u>		
			<u>Temp.</u>	<u>Nitric Acid</u>	<u>Pu Conc.</u>
Mode Size, μm	1 - 20	0.50	0.77	0.42	-0.36
Agglomeration, wt %	0 - 100	5.0	-0.69	-0.44	0.54
Length of Lath, μm	3 - 30	3.6	0.68	0.10	-0.39
Width of Lath, μm	0.5 - 8	1.2	0.72	0.09	-0.25
Thickness of Lath, μm	0.1 - 1.5	0.18	0.50	0.52	-0.17

Applicability: Temperature, 20 to 60°C
 Nitric Acid, 0.7 to 2.0M
 Pu Conc., 2.0 to 8.0 g/l
 Oxalic Acid, 0.20M in slurry

FIGURE 14a. Effect of Temperature on PuO_2 Lath Dimensions

FIGURE 14b. Effect of Nitric Acid Concentration in Precipitation Feed on the Ratios of PuO_2 Crystal Dimensions

mass mode size between 4.0 and 6.0 μm . Lath dimensions are controlled to 8 to 15 μm length, 1 to 4 μm width, and 0.5 to 1.0 μm thickness. This product has exhibited reproducible fabrication response using constant parameters both at SRP⁴⁻⁶ and at Los Alamos Scientific Laboratory.

One should be able to predetermine and control particle size characteristics for PuO_2 obtained from other oxalate precipitation techniques as well.⁸ For example, in mixed oxide fuel for light water reactors, relatively large rosette aggregates of $^{239}\text{PuO}_2$ are obtained by precipitating Pu(IV) oxalate with direct strike mixing using higher plutonium concentrations in the feed.⁹ Once control functions are established, characteristics of these particles can be preselected for optimum blending with UO_2 . In general, the size characteristics of many oxides can be predetermined and controlled for systems in which precipitation is self-nucleating.

CONCLUSIONS

Preselected and constant size characteristics of PuO_2 feed powders can be obtained for any desired fabrication process by controlling precipitation parameters. Pu(III) oxalate precipitated by adding Pu(III) feed into oxalic acid produces bimodal, log-normal distributions of monoclinic lath particles and loosely bound agglomerates. These particles can be calcined to PuO_2 without disintegration and produce high surface area lath particles of the same bimodal distribution. The particle size and lath dimensions of the PuO_2 particles and their agglomerates are determined solely by the precipitation factors affecting final solubility of Pu(III) oxalate: precipitation temperature, nitric acid concentration, and plutonium and oxalate concentrations.

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