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SAVANNAH RIVER LABORATORY MONTHLY REPORT

^{238}Pu FUEL FORM PROCESSES

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Pellets prepared by cold pressing and sintering (rather than by hot pressing) LASL and SRL-milled powders show that 1) fracture in hot-pressed and oxidized fuel is caused indirectly by reduction of PuO_2 by graphite, 2) fuel can be cold pressed and sintered up to 95% theoretical density without fracture and with uniform and potentially improved microstructures, and 3) there are differences in the homogeniety of LASL and SRL-milled powders. The subjects described are:

Several precipitations of Pu(IV) oxalate were performed which indicated that few problems might be expected for full-scale processing in H-Area B-Line. Acceptable PuO_2 feed can be produced from a wide range of precipitation conditions, conversion of Pu(IV) to soluble Pu(VI) does not increase excessively with age, and the morphology of the PuO_2 is maintained on scaleup. These observations are based on studies of the following:

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INTRODUCTION

This report is one of a series to summarize progress in the Savannah River ^{238}Pu Fuel Form Program; this program is supported by the ERDA Division of Nuclear Research and Application (DNRA).

Goals of the Savannah River Laboratory (SRL) program are: to provide technical support for the transfer of DNRA ^{238}Pu fuel form fabrication operations from Mound Laboratory to new facilities being built at the Savannah River Plant (SRP), to provide the technical basis for ^{238}Pu scrap recovery at SRP, and to assist in sustaining plant operations. This part of the program includes:

> Demonstration of processes and techniques, developed by the Los Alamos Scientific Laboratory (LASL) and Monsanto Research Corporation (MRC), for production at SRP, thereby providing the data upon which technical standards and operating procedures will be based.
>
> Technical Support to assist plant startup and to ensure continuation of safe and efficient production of high quality heat source fuel.
>
> Technical Assistance after startup to accommodate changes in product and product specifications, to assist user agencies in improving product performance, to assist SRP in making process improvements that increase efficiency and product reliability, and to adapt plant facilities for new products.

COLD-PRESSED AND SINTERED FUEL

$^{238}PuO_2$ fuel samples, including three pellets and three fragments, were fabricated by cold pressing and sintering milled powder, instead of by vacuum hot pressing. The cold pressing and sintering process was used to confirm that the fuel fracture and density limitations observed in the present PuFF process are associated with phase changes accompanying the reduction of $^{238}PuO_2$ by the graphite die used to hot press the fuel. Cold-pressed and sintered fuel showed none of the microcracks, grain-boundary separations, porosity stringers, and mixed-phase morphologies observed in all fuel hot pressed in graphite. These observations, in addition to the microstructural observations reported in January 1977 for $^{239}PuO_2$, support the desirability of developing techniques or die materials to minimize the PuO_2 reduction that occurs during hot pressing.

Density of fuel made by hot pressing in graphite is limited to 90-92% theoretical because of excessive fracture at higher densities. The January 1977 report suggested that this fracture limitation was probably caused by reduction of PuO_2 to a suboxide phase which, on reoxidation, imposed sufficient stresses to fracture the fuel. In screening experiments discussed in this report, crack-free $^{238}PuO_2$ with densities up to 95% were readily obtained by cold pressing and sintering milled powder. No binders, special procedures, or optimized conditions were used. Results of these experiments suggest that high-density fuel that is free of cracks (and hence is stronger) is obtained by cold pressing and sintering (or by hot pressing in noninteracting dies) LASL and SRL-milled powders. Dimensional variations inherent in the cold pressing and sintering process could be compensated for by redesign of the fuel size and shape. Cold pressing and sintering is routinely used for manufacturing UO_2 pellets for LWR fuel.

Microstructures obtained by sintering $^{238}PuO_2$ milled by LASL were considerably more uniform than those obtained by sintering $^{238}PuO_2$ milled at SRL. These microstructural differences are not expected to be so pronounced for the PuFF MHW process because milled powder is granulated and presintered before hot pressing. The different fabrication response of SRL-milled powder is presumably caused either by absorbed moisture and corresponding agglomeration during milling in the air-atmosphere boxes at SRL, or by the shorter milling time used by SRL (8 hr versus 32 hr).

Preparation of Samples

Table 1 shows the feed powders, precipitation conditions, and results of cold pressing and sintering three $^{238}PuO_2$ pellets and three pellet fragments. These pellets and fragments had been cold pressed and presintered between 1050 and 1300°C in earlier experiments to establish the effect of granule presintering temperature on granule density (April 1976 report, p 20 and Table 2). In the experiments reported here, the samples were reheated, as one batch in a ThO_2 boat, to 1530°C for 5-1/4 hr in flowing air. Three of the samples, Pellets CP-57, CP-71, and CP-72, were made from $^{238}PuO_2$ feed that was milled 8 hr at SRL. The three pellet fragments, CP-84, CP-87, and CP-89, were cold pressed at SRL from powder that was milled 32 hr at LASL and sent to SRL for characterization studies. No binders were used and all pellets were pressed at 58,000 psi to about 65% density. Some pellets were broken after cold pressing or presintering, so that only fragments were sintered at 1530°C. Samples with different presintering temperatures were selected to note any effect of the step-sintering (alternative sintering path) on final density and microstructure.

Crack-Free Microstructures

Figures 1-6 show the microstructures of the pellets and fragments after sintering at 1530°C. In all six samples, the microstructures represent typical advanced-stage sintering. The grains are uniformly sized and equiaxed. Porosity is rounded, relatively coarse, and occurs primarily in the grain triple boundaries.

In contrast to the microstructures of samples hot pressed in graphite (January 1977 report), there are no microcracks, grain-boundary separations, macrocracks, stringers of submicron porosity or eutectoid and proeutectoid structures indicative of graphite interaction. Etching to reveal grain boundaries (January 1977 report, p 29) required about 4 times longer for these samples than for those of hot-pressed fuel; a higher proportion of grain boundaries were etched. This etching response indicates that many of the so-called "grain boundaries" in fuel hot pressed in graphite are really grain-boundary separations, reflecting a generally weaker ceramic.

Potential for Advanced Fuel Forms

The considerably improved microstructure and higher densities of cold-pressed and sintered fuel formed the basis of the hypothesis that fuel made with this microstructure should be stronger and more fracture resistant at higher power densities than fuel hot pressed in graphite. The three crack-free and high-density microstructures obtained from LASL-milled powder are shown in Figures 4, 5, and 6. The density measured by quantitative metallography on several 750X photomicrographs was between 92 and 95% of theoretical (Table 1). These densities approximate those obtained by Potter on air-sintering unmilled $^{239}PuO_2$ under similar conditions.[1] Porosity size and distribution are similar for all three (Figures 4, 5, and 6), and the average grain size is between 5 and 7 μm (Table 1).

Cold-pressed and sintered fuel densities in the 92-96% TD range could probably be reproducible to better than ±2% if the process is optimized and controlled. The corresponding dimensional control would be about ±0.7%. The diameter of a half-inch fuel pellet would then vary within ±0.0035 in., which may be acceptable for some engineering designs.

Differences in Fabrication Response Between LASL and SRL-Milled Powders

The differences in fabrication response between the three LASL-milled powders and the three SRL-milled powders and the variation among the pellets made from SRL-milled powder indicate that there still remains an unknown factor during ball milling which, if controlled, could produce more uniformly milled powder. Cold pressing and sintering milled powder dramatizes these differences more than for the MHW process because the mixing effect of granulation and re-pressing in MHW production obscures the effect. Therefore, differences may not be important to MHW processing in the PuFF facility, particularly in the dry-atmosphere cells if moisture is the primary cause of the variation.

Except for a few cold-pressing laminations and an occasional lower-density spot, the cross sections of the fragments made from LASL-milled powder show similar uniform features and no density gradients. By contrast, the microstructures obtained from SRL-milled powders (Figures 1, 2, and 3) are quite different from those obtained when LASL-milled powder is used, and differ from one another. The cross sections exhibit more low-density spots and holes. The densities obtained from 750X photomicrographs are lower than those made from LASL-milled powder and ranged between 86 and 93% of theoretical (Table 1). Porosity and grain size distribution were quite different. Pellet CP-57 exhibits large (10-μm) grains and very coarse pores, perhaps attributable to the stainless steel impurity (from the ball mill) evident in the photomicrograph of the as-polished pellet (Figure 1). Pellet CP-71, Figure 2, shows a porosity more like those from the LASL powder, Figures 4-6, but the grain size of this 91%-dense pellet is quite small (2 μm). Pellet CP-72 in Figure 3 shows a relatively low-density structure (86% TD) featuring larger grains than for the pellet fragments made from LASL-milled powder, and the porosity heavily decorates the grain boundaries.

TABLE 1

Cold Pressing and Sintering Tests[a] on Milled $^{238}PuO_2$

SRP Production Number[b]	*SRL Run Number, Pellet Number*	*Mode Size of Milled Powder, μm*	*Presintering Temp, °C*	*Density, % Theoretical*			*Sintered Grain Size, μm*[e]
				Cold-Pressed[c]	*Presintered*[c]	*Sintered*[d]	
50HA275A	S-20-8, CPR,[f] CP-57[g]	1.95	1300	-	87.2	93	10
107HA792	S-30-8, CP-71[g]	2.30	1175	65.71	71.87	91	2
107HA792	S-30-8, CP-72[g]	2.30	1175	66.09	72.71	86	9
507HA350A/B	S-54-32, CP-84[h]	1.75	1050	66.2	*i*	94	5
507HA348A/B	S-53-32, CP-87[h]	1.50	1175	*i*	*i*	92	5
506HA330	S-52-32, CP-89[h]	1.75	1300	64.6	78.3	95	7

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[a] Powder was cold-pressed at 58,000 psi, presintered 3 hr in air, sintered 5-1/4 hr at 1530°C, in flowing air in ThO_2.

[b] The first digit indicates the last number of the year, and the next two digits, the number of the month of production of the run.

[c] Bulk density on intact pellets.

[d] Quantitative metallography on typical areas at 750X.

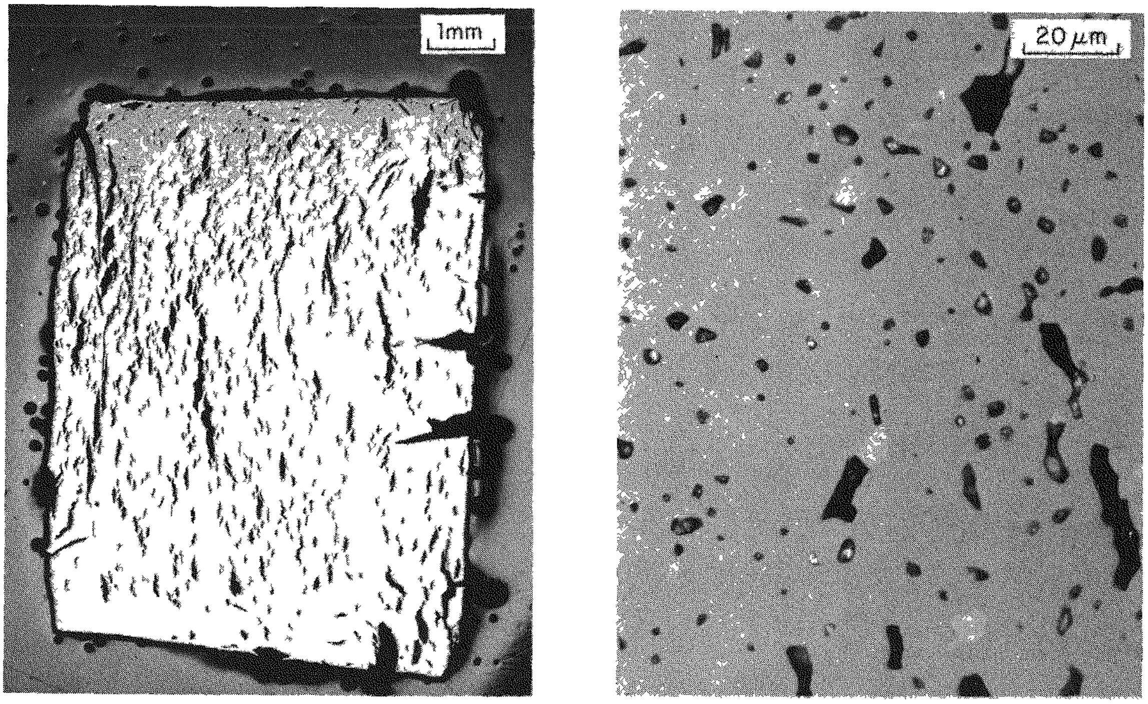
[e] Measured at 750X as the average uncorrected linear intercept.

[f] CPR = cold-pressed, granulated, and re-pressed.

[g] Milled 8 hr in SRL facilities.

[h] Milled 32 hr at LASL and shipped to SRL.

[i] Broken pellets.



Cross Section

As Polished

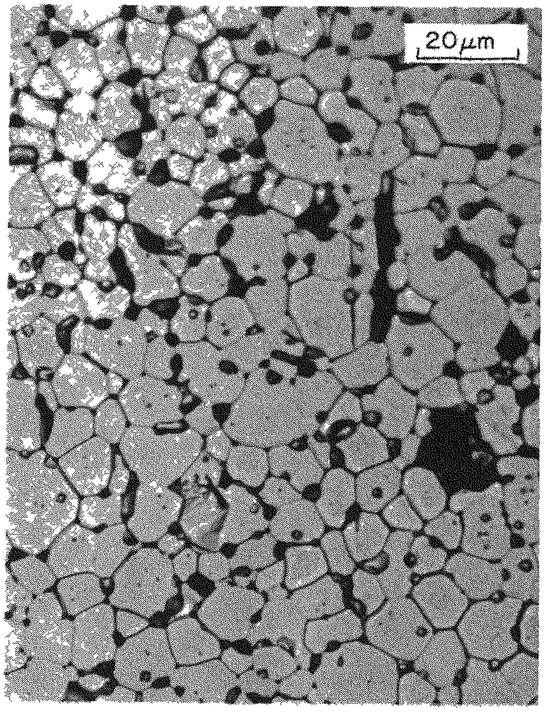


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FIGURE 1. Cold-Pressed and Sintered Pellet CP-57 Made from $^{238}PuO_2$ Granulated after 8 hr Milling

Cross Section

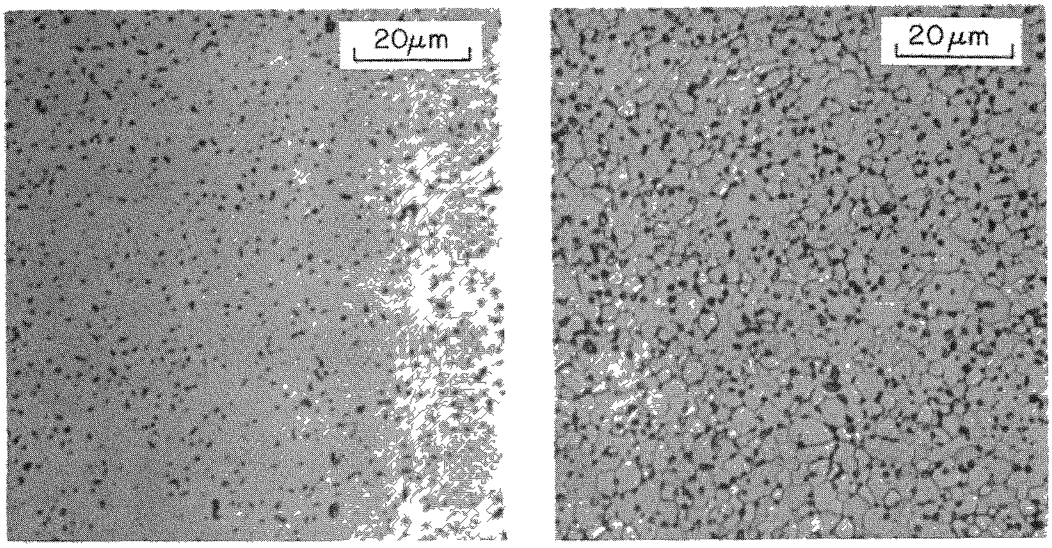

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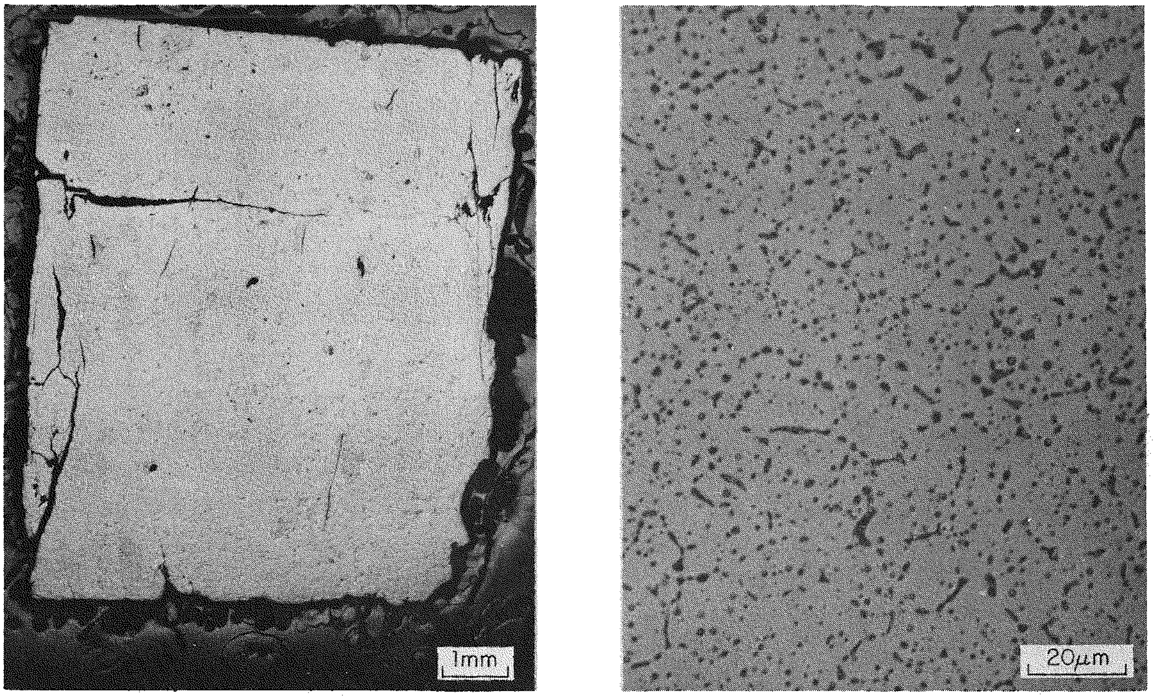
FIGURE 2. Cold-Pressed and Sintered Pellet CP-71 Made from $^{238}PuO_2$ Milled 8 hr at SRL



Cross Section

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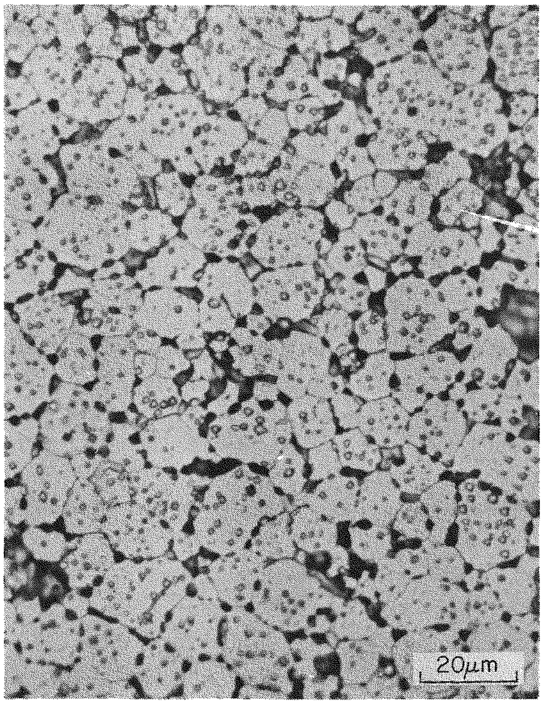

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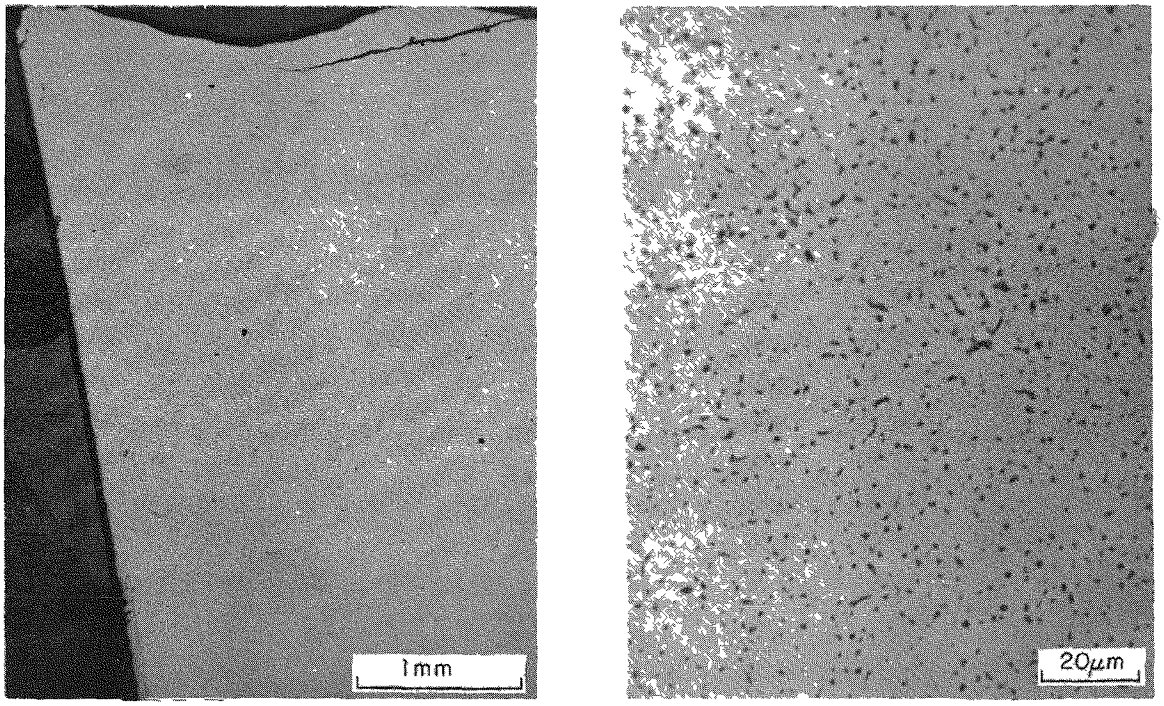
FIGURE 3. Cold-Pressed and Sintered Pellet CP-72 Made from $^{238}PuO_2$ Milled 8 hr at SRL



Cross Section

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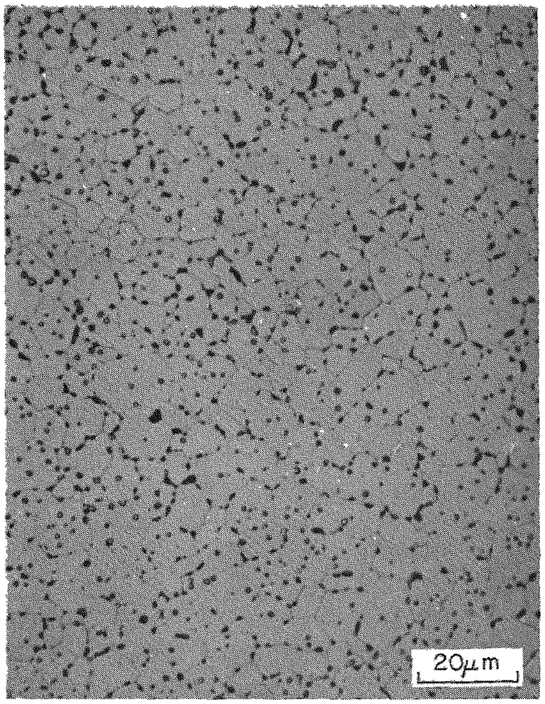

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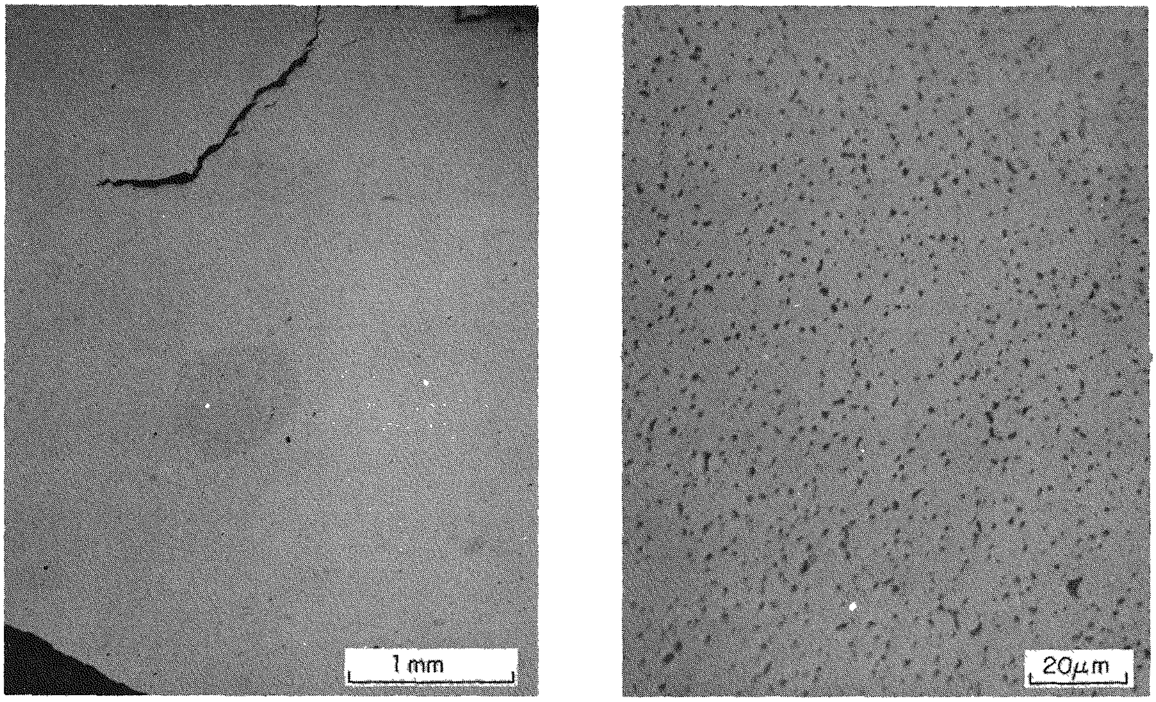
FIGURE 4. Cold-Pressed and Sintered Fragment CP-84 Made from $^{238}PuO_2$ Milled 32 hr at LASL



Cross Section As Polished

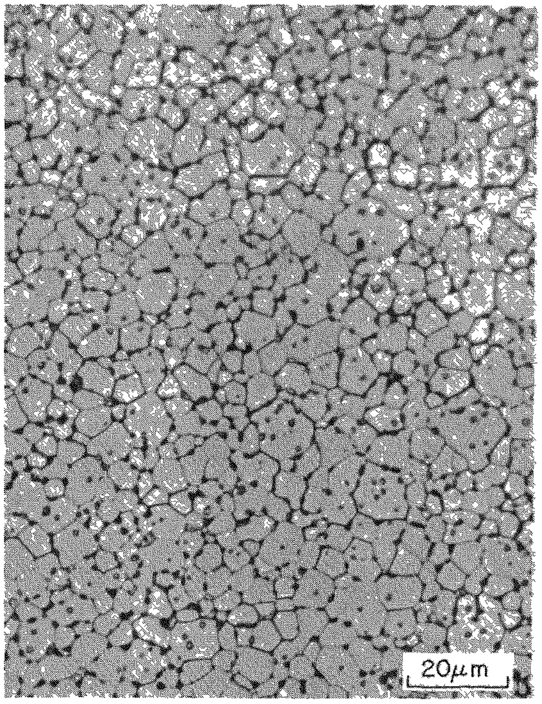


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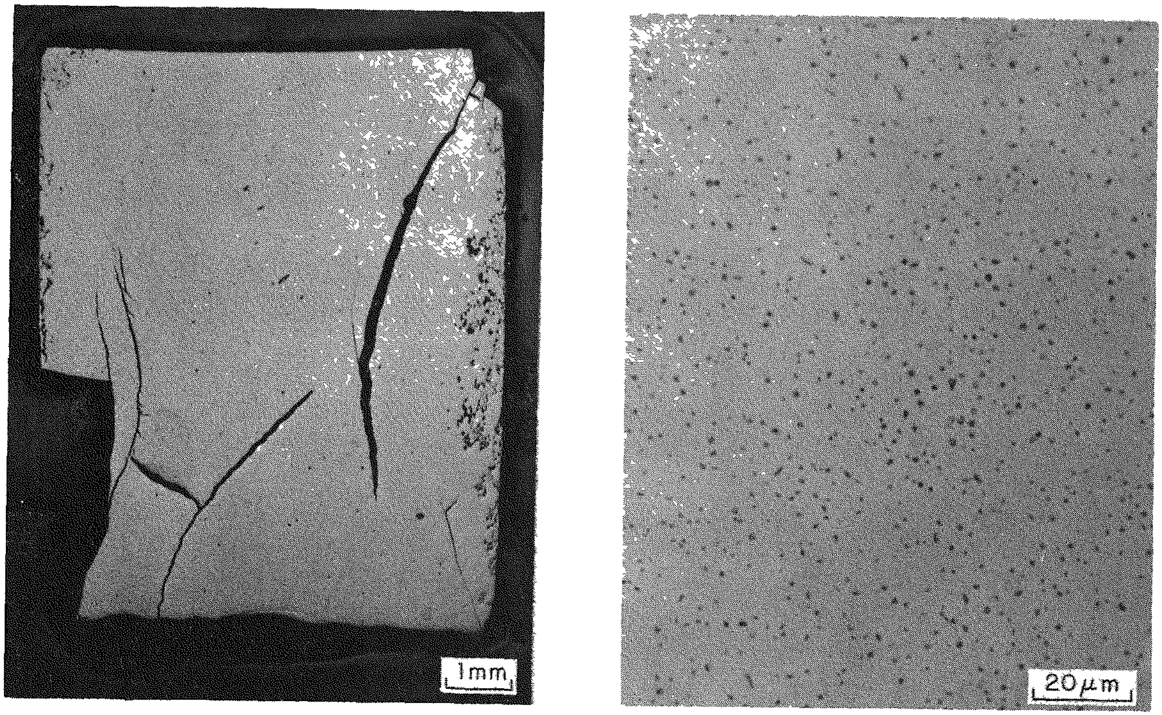
FIGURE 5. Cold-Pressed and Sintered Fragment CP-87 Made from $^{238}PuO_2$ Milled 32 hr at LASL



Cross Section

As Polished

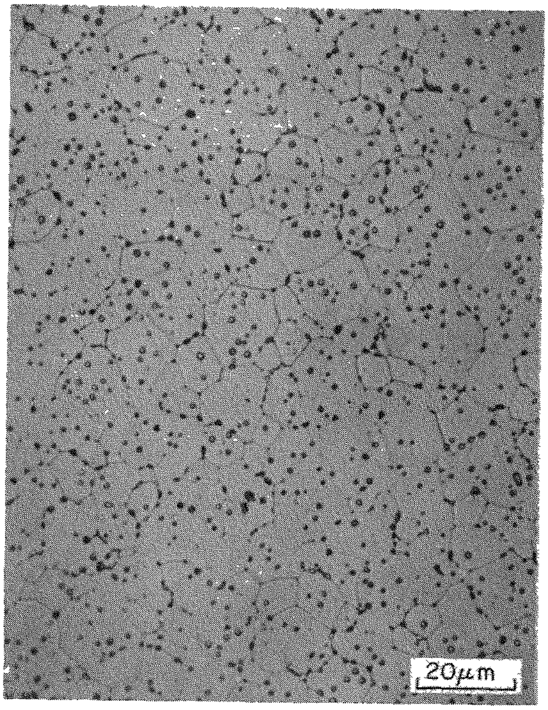


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FIGURE 6. Cold-Pressed and Sintered Fragment CP-89 Made from $^{238}PuO_2$ Milled 32 hr at LASL

The cross section at lower magnifications of Pellet CP-57 (Figure 1) is not comparable to the others because in this case the milled powder was granulated after one cold compaction, then recompacted as granules. The severe pressing laminations shown for Pellet CP-57 would cause some concern should they occur in cold compaction or hot pressing in the PuFF facility, because of possible effects on shard size distribution and on the structure of MHW sphere. The laminations are indicative of little bonding between granules. The microstructure at high magnification in Figure 1 can be compared, however, to those of other pellets and shows coarser features than those of the other pellets.

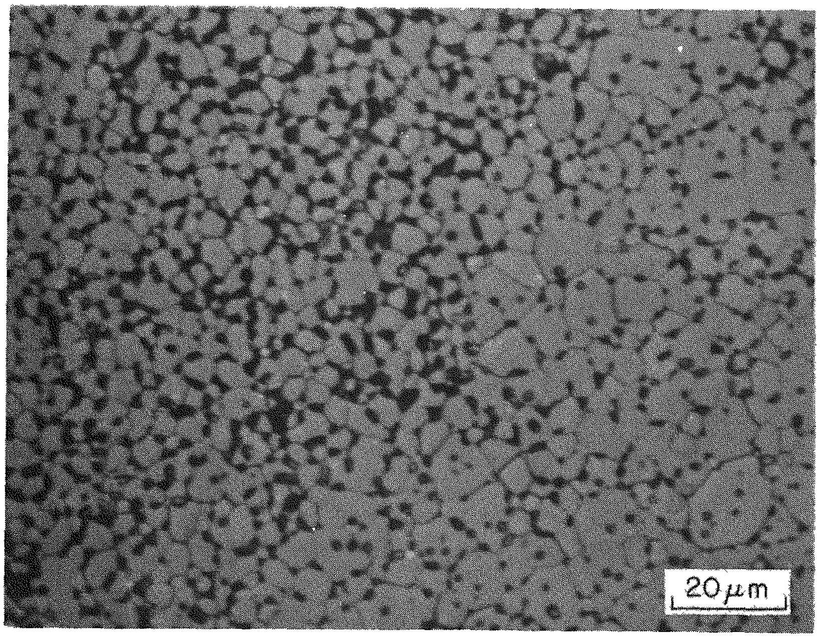
Low-density spots occur in all six samples, but are considerably more abundant in pellets sintered from SRL-milled feed. These density variations can be caused by trapped gas, moisture, or other impurities. The contrast in these low-density and normal areas are shown in Figure 7a. As expected, the lower-density area has a correspondingly smaller grain size.

Figure 7b shows a sliver of high-density PuO_2 in a lower-density matrix. Such slivers were minor features of all six samples, but were significantly more abundant in pellets made from SRL-milled powder. High-density slivers have been observed frequently (December 1974 report, Figure 12 and October 1976 report, Figures 12 and 15) and were associated with milling. The slivers are attributed to the flaked powder that has been caked to the surface of the ball mill during milling and subsequently scraped from the wall of the mill. The higher abundance of high-density slivers in SRL-milled powder may again reflect the higher water content in air-atmosphere boxes and a correspondingly higher agglomeration rate.

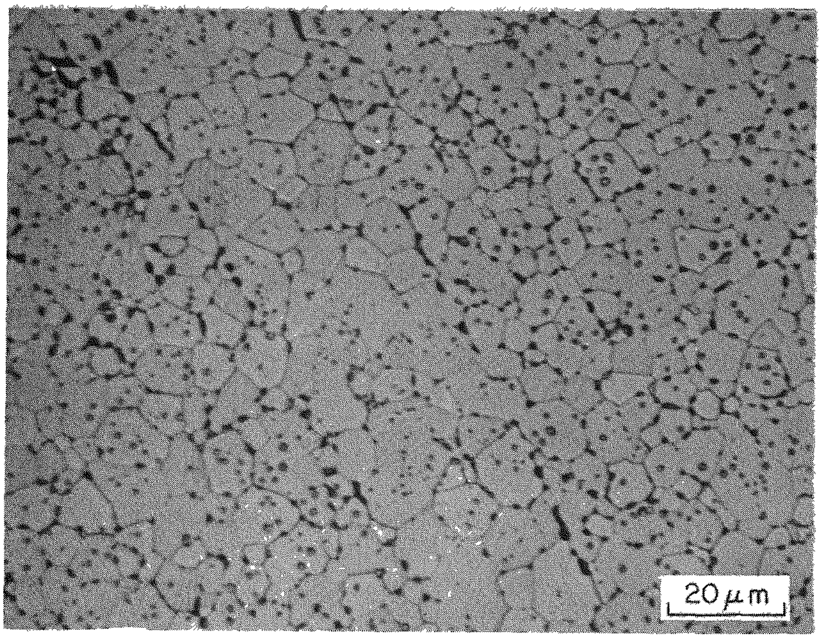
DIRECT FABRICATION OF $^{238}PuO_2$

Six Pu(IV) reverse-strike oxalate precipitations were performed using both ^{238}Pu and ^{239}Pu. Results of these precipitations, combined with those of previous studies, lead to the following conclusions concerning production of $^{238}PuO_2$ feed in H-Area B-Line for direct fabrication of fuel forms:

- In contrast to their effects on the present Pu(III) oxalate precipitation, varying precipitation temperature, nitric acid concentration, and Pu/oxalate ratio do not have nearly so large an effect on the particle size distribution and morphology of calcined PuO_2 obtained from Pu(IV) oxalate precipitations. Consequently, specifications of precipitation conditions for Pu(IV) oxalate precipitation need not be so restrictive.



a. Low Density-High Density Interface



b. Sliver of Packed Milled Powder

FIGURE 7. Microstructural Variations in Cold-Pressed and Sintered $^{238}PuO_2$ Made from Milled Feed. Pellet CP-84, Etched

- Decreasing precipitation temperature from 35°C to 25°C decreases particle size somewhat, but more importantly for packing uniformity during fuel fabrication, the particles are more nearly cubic at the lower temperature and only a single particle morphology exists.

- When hydrogen peroxide is used to convert any Pu(VI) formed during aging in nitrate solution back to Pu(IV), the resulting oxalate precipitate is too fine, poorly formed, and of mixed Pu(III) and Pu(IV) valence (October 1976 report). However, recent work shows that PuO_2 powder size and morphology are unaffected by valence adjustment with peroxide if excess peroxide is removed by heating the plutonium nitrate solution 1-1/4 hr at 60-70°C before oxalate precipitation.

- Analyses of filtrates for soluble ^{238}Pu show that even after aging the nitrate solution for 4 months, little, if any, additional soluble Pu(VI) is formed. The plutonium content of the filtrate is not greatly affected by age of the solution, valence adjustment, or precipitation conditions. For these reasons, a significant increase in plutonium recycle (once-through loss) is not expected, and valence adjustment will probably not be required for Pu(IV) oxalate precipitation in H-Area B-Line.

- A 15-g ^{239}Pu(IV) oxalate precipitation at 25°C showed the same PuO_2 particle morphology as 1-g precipitations, indicating relative insensitivity to scale.

Effect of Precipitation Conditions on Size and Morphology of PuO_2 Powder

In the experiments described in this section the precipitation conditions for Pu(IV) oxalate were modified to obtain smaller and more nearly cubic particles that might be hot-pressed more easily without preferred orientation in the microstructure. This change in particle morphology is desirable, but not essential, if it can be readily obtained by minor changes in the H-Area B-Line finishing operations. A second objective was to evaluate the effects of varying precipitation conditions on particle size and morphology to determine the range of control. These experiments demonstrated the relative insensitivity of the Pu(IV) oxalate process, in contrast to Pu(III) oxalate precipitation. Pu(IV) oxalate precipitation can apparently tolerate a much wilder range of temperature, acid, and plutonium concentrations and still produce a satisfactory product.

All previous precipitations have been performed at 35°C, 5 g Pu/L, and 1.2M HNO_3 in the feed, and addition into 0.9M $H_2C_2O_4$

to a final 0.20M excess of oxalate in the slurry. These tests produced nearly square plate-like particles for the most part, with some rounded particles, with a particle size of 15-20 μm (Table 2). These particles have been used satisfactorily in hot-pressing experiments as shown, for example, in the January 1977 report. However, these particles are relatively thin and tend to align on compaction. Further, a feed batch would sometimes contain large rounded plates and/or smaller square plates in bimodal distributions (Sample T-40 in Table 2 and Figure 3 in the November 1976 report).

Table 2 lists the results of precipitation tests of Samples T-2A, T-2B, T-2C, and 44. Particle size distributions are shown in Figure 8 and morphologies are shown in Figure 9. Sample 44 (Table 2) showed that larger particles of one morphology and with unimodal size distribution were obtained at 50°C, but were unacceptably thin (October 1976 report).

On the basis of the dependencies noted for Pu(III) oxalate precipitation, a lower precipitation temperature was expected to produce smaller particles because of lower solubility; also, increasing nitric acid concentration increased particle thickness preferentially [relative to other two dimensions (Table 1 of March 1976 report)] and, hence, might be helpful in producing more nearly cubic particles during Pu(IV) oxalate precipitation. Finally, Louwrier, et al.[2] found that more nearly cubic particles, 2 to 3 μm on an edge, were obtained at room temperature, higher nitric acid concentrations, and higher (25 g/L) plutonium concentration. On the basis of Pu(III) behavior and the reasonable operating limits of the present H-Area B-Line capability, the precipitation conditions shown in Table 2 for Samples T-2A, T-2B, and T-2C were selected for testing.

Samples T-2A and T-2B, which were precipitated at 25°C, 5 g Pu/L, and different nitric acid concentrations, showed nearly the same unimodal particle size distribution and morphology (Figures 8 and 9). Decreasing the precipitation temperature decreased the particle size only a little to the 10-15 μm range, but produced prismatic, rather than platy, particles without the bimodal character frequently obtained from higher-temperature precipitations. The average square dimension decreased from about 20-30 μm to 10-20 μm, a linear factor of about 2 or an area factor of 4. However, the thickness increased about a factor of 3 (Figure 9 versus Figure 3 of the November 1976 report), so that equivalent spherical diameter was not decreased greatly. No rounded plates or flared-edge agglomerated particles were observed at this lower temperature.

Recent, unreported results indicate that these prismatic particles have about the same fabrication response as large particles obtained at 35°C. Because of similar fabrication response, both prismatic and platy particles are probably acceptable for direct fabrication of fuel from H-Area B-Line product. Consequently, precipitation conditions between 20 and 40°C, and between 1.0 and 2.0M HNO_3 are probably acceptable.

The conditions for Sample T-2C (Table 1) were similar to those used by Louwrier.[2] As shown in Figure 9, this powder is considerably less desirable. The square prisms are smaller, poorly formed, and agglomerated, and a broad distribution of fines is evident (Figure 8).

The relative insensitivity of PuO_2 characteristics to precipitation conditions may be associated with the delayed nucleation of the precipitate. In contrast to the immediate precipitation of Pu(III) oxalate, precipitation of Pu(IV) did not occur until after considerable addition and mixing had been completed. Nucleation seems to be delayed until the concentrations of plutonium, nitric acid, and oxalic acid are more nearly representative of the completed addition; hence, variations in solubility conditions were not as great as when initial portions were mixed. The delayed precipitation reflects the fact that Pu(IV) is initially strongly complexed by oxalate and remains in solution. Addition of more feed increases the nitric acid concentration and decreases the oxalic acid concentration by dilution so that the solubility of Pu(IV) oxalate decreases causing precipitation. The equilibria are:

$$H^+ + C_2O_4^{2-} = HC_2O_4^-$$

$$Pu(C_2O_4)_2(s) + xC_2O_4^{2-} = Pu(C_2O_4)_{2+x}^{x2-} \text{ (solution)}$$

Conversion of Pu(IV) to Soluble Pu(VI) Oxalate

Some Pu(IV) may convert to Pu(VI) during aging of ^{238}Pu nitrate solution. Pu(VI) oxalate is soluble and might cause increased losses of plutonium to the filtrate, which is recycled for recovery. The purpose of these tests was to determine the extent of Pu(VI) conversion and to determine whether hydrogen peroxide could be used to reduce Pu(VI), if formed, to Pu(IV) before precipitation.

Plutonium Valence Adjustment with Hydrogen Peroxide

Samples T-1A and T-1B (Table 2) represent ^{238}Pu(IV) oxalate precipitation with and without a plutonium valence adjustment by H_2O_2 addition prior to oxalate precipitation. The results, described in the October 1976 report, showed that unacceptable PuO_2 size and morphology were obtained when peroxide was added for

TABLE 2

Precipitation Conditions and PuO_2 Characteristics of Pu(IV) Oxalate Precipitates Calcined at 735°C for 2 hr in Air

	Test of Precipitation Conditions				*Valence Adjustment Tests*			
Sample No, Plutonium Isotope	*T-2A,* ^{239}*Pu*	*T-2B,* ^{239}*Pu*	*T-2C,* ^{239}*Pu*	*44,* ^{239}*Pu*[a]	*T-1A* ^{238}*Pu*[a]	*T-1B,* ^{238}*Pu*[a]	*T-1C,* ^{238}*Pu*	*T-1D* ^{238}*Pu*
Precipitation Conditions								
Aging Time, days[c]	-	-	-	-	1	1	120	120
H_2O_2 Added	No	No	No	No	Yes	No	Yes	No
Temp, °C	25	25	25	50	35	35	35	35
HNO_3 Conc, M[d]	1.1	2.0	1.5	1.2	1.2	1.2	1.3	1.3
Pu Conc, g/L[d]	5	5	10	5	5	5	5	5
$H_2C_2O_4$ Conc, M[e]	0.9	0.9	0.5[f]	0.9	0.9	0.9	0.9	0.9
Scale, g Pu	1	1	1	1	1	1	1	1
Excess H_2O_2[g]	-	-	-	-	Not removed	-	Removed	-
Pu Conc in filtrate, mg/L	45	20	15	-	40	45	25	20
PuO_2 Characteristics								
Particle Size Distribution								
Mode, µm	11.0	11.5	-	18.0	11.2/29.0	12.5/34	18.0	17-25
Median, µm	10.8	12.3	14.4	17.0	11.8	13.6	17.5	17.6
Mean, µm	11.7	13.6	14.2	17.9	16.3	15.6	17.2	17.8
Std Dev, µm	4.9	5.2	5.9	7.8	13.1	9.5	4.8	7.9
Modality	uni	uni	bi	uni	tri	bi	uni	bi
Wt % <2 µm	0	0	0	1	∿5	∿2	0	0
Packing Density, % TD								
Pour[h]	-	-	-	-	-	-	-	-
Tap[h]	-	-	-	-	-	-	-	-
Appearance	Small square prisms	Small square prisms	Poorly formed square prisms plus fines	Large square plates	Poorly formed plates plus fines plus mixed valence	Square prisms plus rosettes (trace)	Small square prisms plus rosettes (trace)	Small round plates plus smaller square prisms

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a. Data from October 1976 report.

b. Data from June and November 1976 reports.

c. After elution from anion exchange resin.

d. Concentration in plutonium nitrate feed solution.

e. Concentration in oxalic acid solution before adding plutonium nitrate.

f. Plus 3M HNO_3.

g. Excess peroxide removed by heating 1-1/4 hr at 60-70°C before precipitation.

h. For 735°C calcining temperature.

TABLE 2 (Continued)

	Fabrication Experiments		
Sample No, Plutonium Isotope	*T-40*, ^{239}Pu[b]	*T-50* ^{239}Pu[b]	*U-10*, ^{239}Pu
Precipitation Conditions			
Aging Time, days[c]	-	-	-
H_2O_2 Added	No	No	No
Temp, °C	35	35	25
HNO_3 Conc, M[d]	1.2	1.2	1.1
Pu Conc, g/L[d]	5	5	5
$H_2C_2O_4$ Conc, M[e]	0.9	0.9	0.9
Scale, g Pu	10	10	15
Excess H_2O_2[g]	-	-	-
Pu Conc in filtrate, mg/L	40	40	-
PuO_2 Characteristics			
Particle Size Distribution			
Mode, µm	23	13.8	17.5
Median, µm	19.1	13.8	16.0
Mean, µm	19.2	15.7	16.6
Std Dev, µm	8.1	8.7	5.8
Modality	bi	uni	uni
Wt % <2 µm	0	0	0
Packing Density, % TD			
Pour[h]	24.9	22.7	29.3
Tap[h]	31.5	31.8	33.6
Appearance	Round plates	Square plates	Small square prisms

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[a] Data from October 1976 report.

[b] Data from June and November 1976 reports.

[c] After elution from anion exchange resin.

[d] Concentration in plutonium nitrate feed solution.

[e] Concentration in oxalic acid solution before adding plutonium nitrate.

[f] Plus 3M HNO_3.

[g] Excess peroxide removed by heating 1-1/4 hr at 60-70°C before precipitation.

[h] For 735°C calcining temperature.

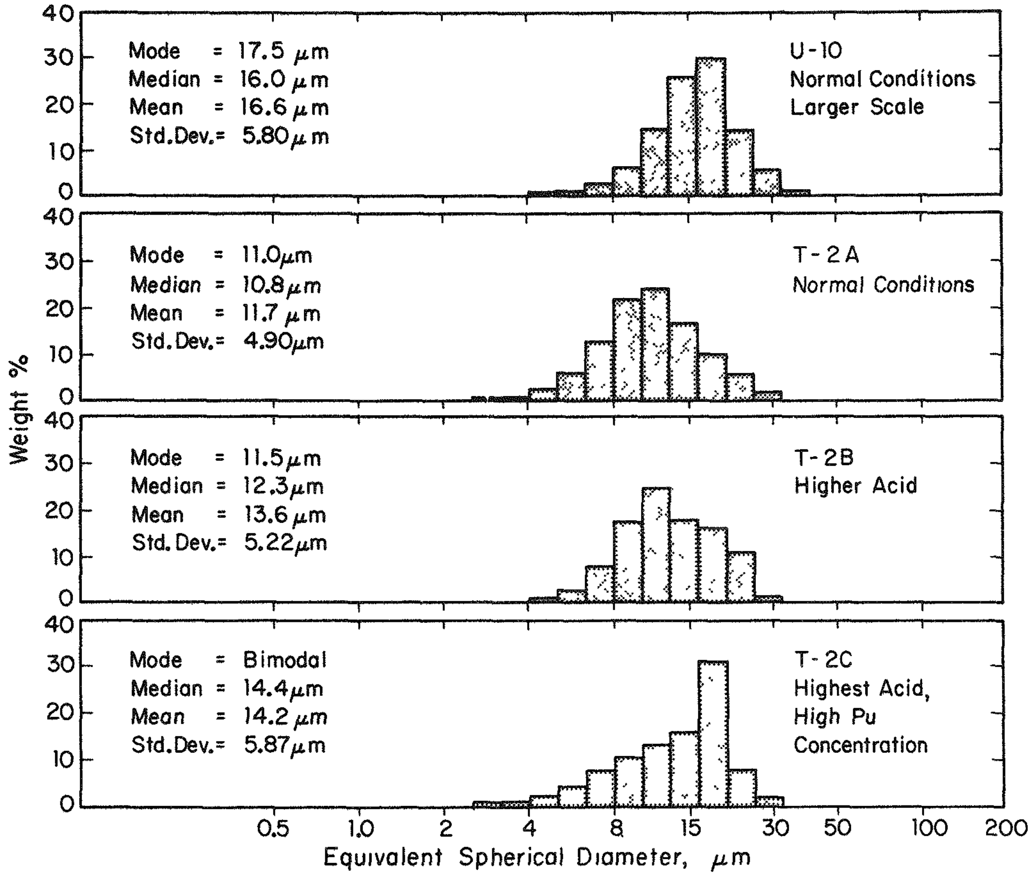
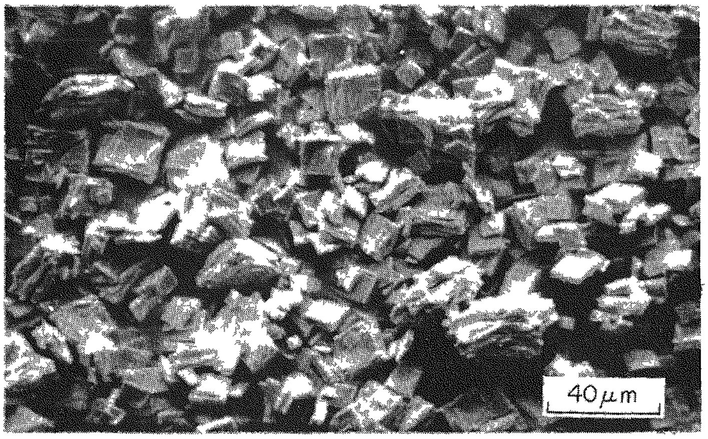
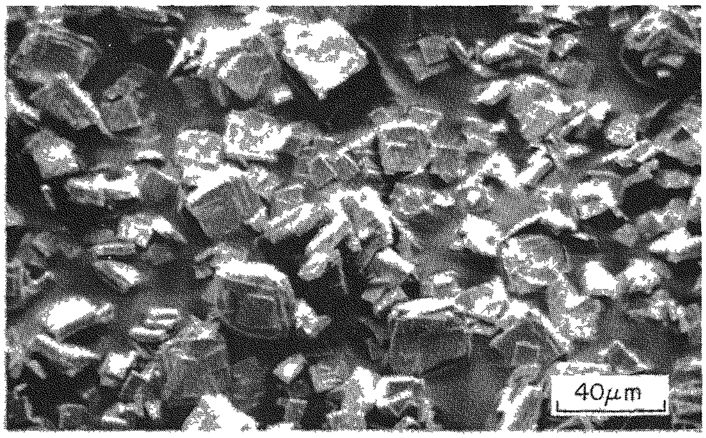


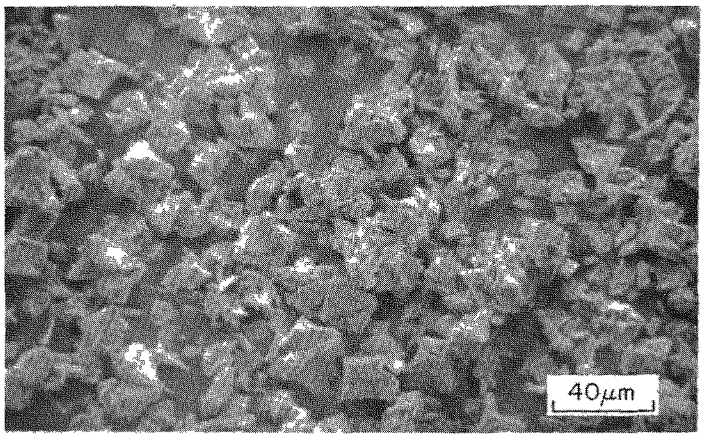
FIGURE 8. Mass Particle Size Distribution of $^{239}PuO_2$ from Pu(IV) Oxalate Precpitations by Varying Nitric Acid Concentration at 25°C



SEM 629 Sample T-2A
$1.1M$ HNO_3, 5 g Pu/L



SEM 630 Sample T-2B
$2.0M$ HNO_3, 5 g Pu/L



SEM 632 Sample T-2C
$1.5M$ HNO_3, 10 g Pu/L,
$3M$ HNO_3 in $0.5M$ $H_2C_2O_4$

FIGURE 9. SEM Photomicrographs of $^{239}PuO_2$ from Pu(IV) Oxalate Precipitations under Various Precipitation Conditions at 25°C

plutonium valence adjustment. Fines, poorly developed square plates, and needle-shaped particles of Pu(III) oxalate were formed (Figure 7 of the October 1976 report).

Samples T-1C and T-1D (Table 2) represent a repeat of experiments for preparing Samples T-1A and T-1B after 120 days' feed storage, except that Sample T-1C was heated about 1-1/4 hr at 60-70°C after peroxide addition and before oxalate precipitation to remove excess peroxide and to oxidize any Pu(III) to Pu(IV). Figures 10 and 11 show the results of removing excess peroxide.

The particle size distribution and morphology for both Sample T-1C and the control, Sample T-1D, were generally similar to the results obtained in all other Pu(IV) precipitations at 35°C. Consequently, excess peroxide can be removed by heating to obtain an acceptable product.

As shown in Figure 11, the control (Sample T-1D) showed a bimodal mix of large rounded plates and smaller square plates typical of Samples T-20, T-30, and T-40, all precipitated at 35°C (June and November 1976 reports). In contrast to Sample T-1B in the earlier pair of experiments (identical conditions, except for age of the nitrate feed solution), Sample T-1D yielded no rosette particles as a minor constituent. On the other hand, Sample T-1C, with H_2O_2 added for plutonium valence adjustment, and Sample T-1B, without H_2O_2, gave the same particle size distribution and morphology: square plates plus a trace amount of rosettes. These observations show the effectiveness of removing excess peroxide by heating prior to precipitation.

Extent of Pu(VI) Formation

To determine amounts of plutonium remaining in solution [as Pu(VI)], filtrates from the precipitations outlined in Table 2 were analyzed. As shown in Table 2, the concentration of plutonium in the filtrate is typically 40 mg Pu/L, even after 120 days' aging. This concentration compares favorably to filtrate concentrations of 10 to 20 mg Pu/L for Pu(III) oxalate precipitations. Consequently excessive Pu(VI) formation is not expected, and recycle of soluble plutonium in filtrates will not be inordinately higher for Pu(IV) precipitations.

Note (Table 2) that the expected decrease in plutonium concentration in the filtrate is observed as acid concentration increases in Samples T-2A, T-2B, and T-2C, which is consistent with the relationship between oxalate solubility and acid concentration described above.

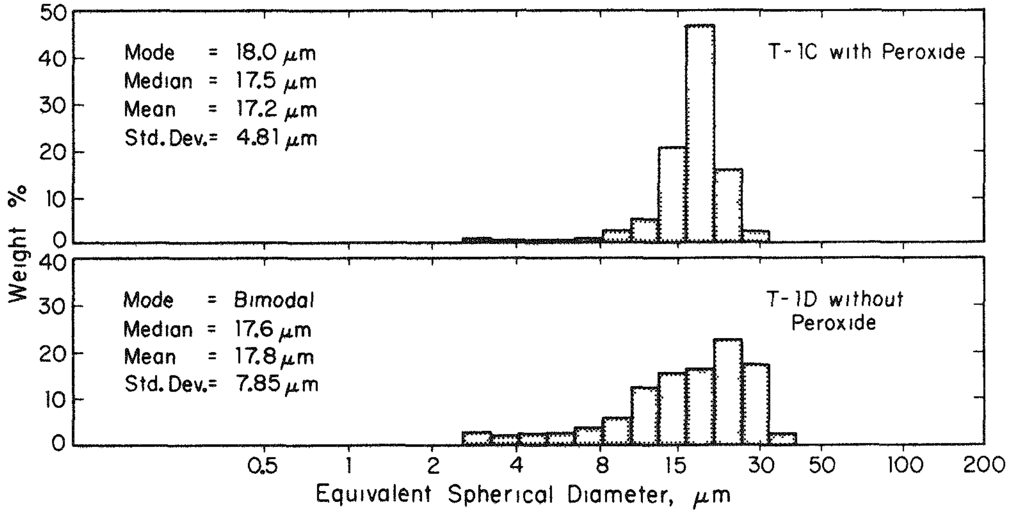
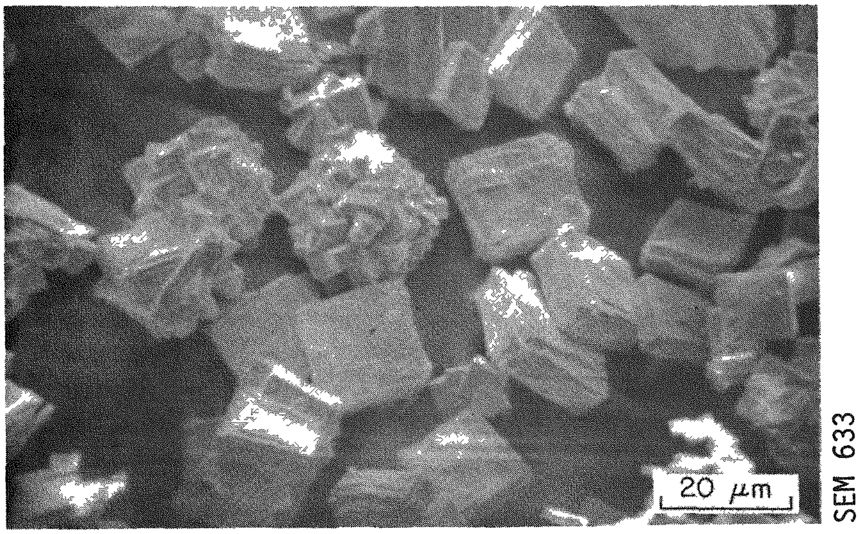
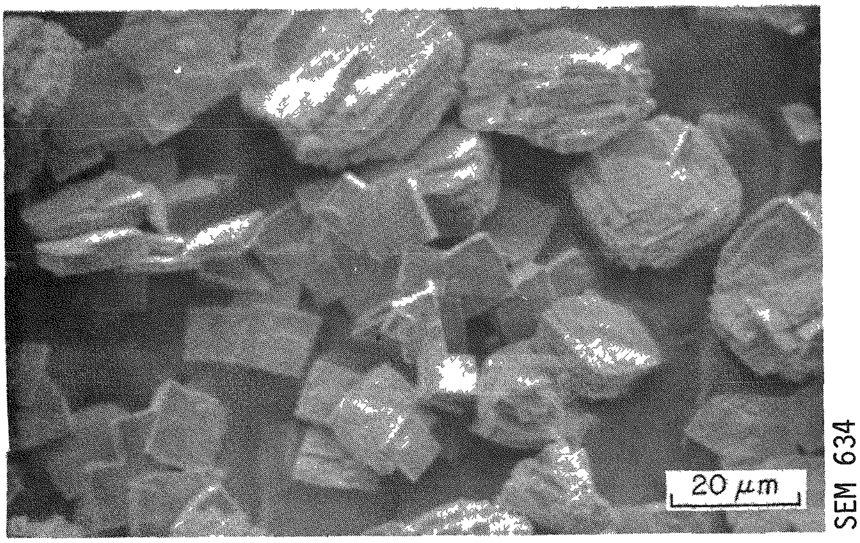


FIGURE 10. Mass Particle Size Distribution of $^{238}PuO_2$ Obtained from Pu(IV) Oxalate Precipitations with and without Pu Valence Adjustment by Hydrogen Peroxide Addition. Excess peroxide was removed by heating for 1-1/4 hr at 60-70°C.



Sample T-1C. H_2O_2 Added, Excess Removed by Heating Prior to Precipitation



Sample T-1D. No H_2O_2 Added

FIGURE 11. SEM Photomicrographs of $^{238}PuO_2$ Obtained from Pu(IV) Oxalate Precipitations with and without Pu Valence Adjustment by Hydrogen Peroxide Addition

Effect of Precipitation Scale on PuO_2 Morphology

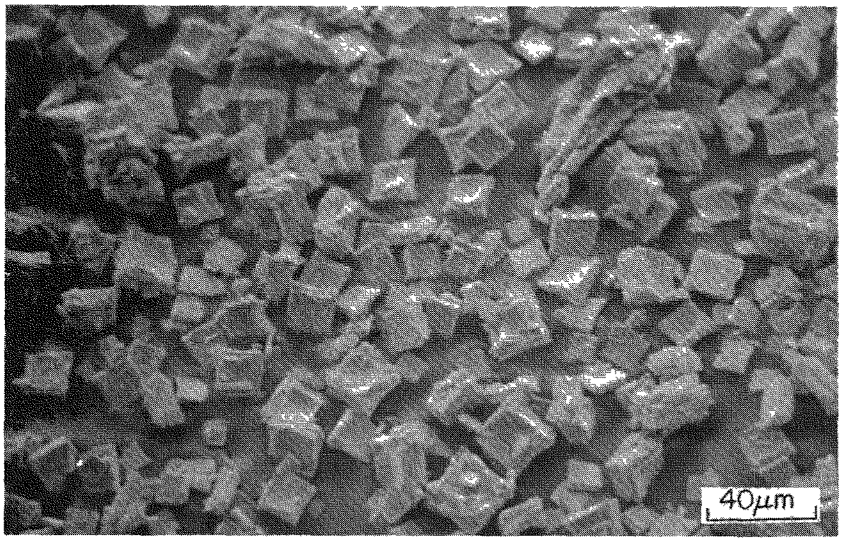
A 15-g sample of Pu(IV) oxalate (Sample U-10) was precipitated at 25°C to obtain sufficient $^{239}PuO_2$ for fabrication tests of the smaller, more nearly cubic, prismatic particles. Previous precipitations on an 8 to 10-g plutonium scale at 35°C showed the same particle size and morphology as for the 1-g scale tests at 35°C. In H-Area B-Line precipitations, batches of 60 g of plutonium oxalate are used.

Table 2 and Figures 8 and 12 show that, in the precipitation of 15 g of Sample U-10, particles were somewhat larger than, but of the same unimodal distribution and morphology as particles from 1-g precipitations. Even though the measured mode size is larger than for Sample T-2A, the size shown by SEM in Figure 12 seems to be about the same. No rounded plates, agglomerates, rosettes, or fines were produced. The particles of Sample U-10 are relatively thicker than those produced at 35°C, as desired. These results indicate that H-Area B-Line production could be scaled up with little difficulty.

CHARACTERIZATION OF STANDARDIZED $^{238}PuO_2$ PRODUCTION

Twelve additional production lots of standardized H-Area B-Line $^{238}PuO_2$ have been characterized for particle size distribution, morphology, and packing density. On the average, these lots had smaller particle sizes, less mature lath morphology, and higher packing densities than for the 61 runs analyzed previously (compare with February, April, May, and October 1976 reports). However, except for Run 608HA573 of Lot HL369, the size and morphology were within the ranges previously documented.

The size of $^{238}PuO_2$ feed should be large enough to be ball milled to nearly spherical particles and constant enough so that ball milling conditions are the same for each B-Line production batch. Size variation had previously been associated with varying fabrication response. Previous work (1975 and 1976 reports) has shown that particle size and morphology can be controlled by controlling oxalate precipitation conditions, particularly precipitation temperature. SRP improved the control of precipitation conditions in 1975 and began the production of "standardized" $^{238}PuO_2$ by controlling the feed temperature to 30-40°C, the plutonium concentration between 4 and 6 g/L, and the nitric acid concentration between 1.4 and 1.6M, and by maintaining a constant oxalate-to-plutonium ratio. By using these conditions since November of 1975, SRP has produced feed with a mass mode size between 4.2 and 6.0 μm, well developed lath morphology, and tapped packing densities between 2.0 and 2.2 g/cc.



SEM 655

FIGURE 12. SEM Photomicrograph of $^{239}PuO_2$ Obtained from Large-Scale (15 g) Pu(IV) Oxalate Precipitation at 25°C. Sample U-10

The characteristics of the lot samples outlined in Table 3 and Figure 13 are generally within the ranges stated above; however, there is a decided and undesirable trend towards smaller feed powders. The average mass mode size for the 12 lots is 4.6 μm, relatively low for the 4.2 to 6.0 μm range of earlier samples. The average tap density is 2.30 g/cc, higher than the 2.0 to 2.2 range of earlier samples and consistent with the presence of smaller particles. Finally, although no samples contained the submicron fines that were observed in 15% of the previous analyses (October 1976 report), SEM analysis indicated generally less mature lath particles (April 1976 report, Figure 2). Runs 607HA555, 607HA558, and particularly Run 608HA573 showed the same kind of fines described in Figure 3 of the October 1976 report as fill and bridging material in agglomerates. The small mode size, finer particle size distribution, and higher tap density for these three lots all generally correlate to confirm a smaller feed.

In recent months LASL has occasionally found smaller-than-normal particle sizes for other H-Area B-Line runs and has had to compensate by reducing the ball-milling time from 36 hr to 24 hr. These findings by both laboratories on oxide powder produced at SRP during the summer of 1976 could be explained by one or more of the following causes: 1) precipitation temperature too low, 2) acid concentration too low, and 3) plutonium concentration too high. SRP data indicate that the plutonium concentration was occasionally higher than 6 g/l during that period.

TABLE 3

Characteristics of Standardized $^{238}PuO_2$ Production

			Particle Size, μm			*Packing Density, g/cc*		
Lot	*Run*[a]	*SRL No.*	*Mode*	*Median*	*Mean*	*Pour*	*Tap*	*SEM Morphology*
362	606HA534	S-86	4.7	5.43	9.01	1.42	2.30	Laths
363	607HA536	S-87	5.5	5.05	6.72	1.32	2.25	Laths
364	607HA542	S-88	4.6	4.52	7.17	1.34	2.10	Laths
365	607HA546	S-89	5.4	5.53	8.18	1.31	2.30	Laths
366	607HA555	S-100	4.2	4.06	7.09	1.40	2.32	Laths plus fines in agglomerates
367	607HA558	S-101	4.3	3.45	4.75	1.55	2.60	Laths plus fines in agglomerates
368	608HA565	S-102	4.5	4.66	7.77	1.11	2.01	Laths
369	608HA570	S-103	4.7	4.49	7.08	1.43	2.29	Laths
369	608HA573	S-104	3.0	3.00	4.28	1.65	2.62	Laths plus fines in agglomerates
370	608HA574	S-105	4.9	4.79	6.18	1.38	2.30	Laths
371	609HA577	S-107	5.4	4.98	5.72	1.14	2.10	Laths
372	609HA582	S-106	4.5	4.13	5.39	1.50	2.35	Laths

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[a] The first digit indicates the last number of the year, and the next two digits indicate the number of the month of production of the run.

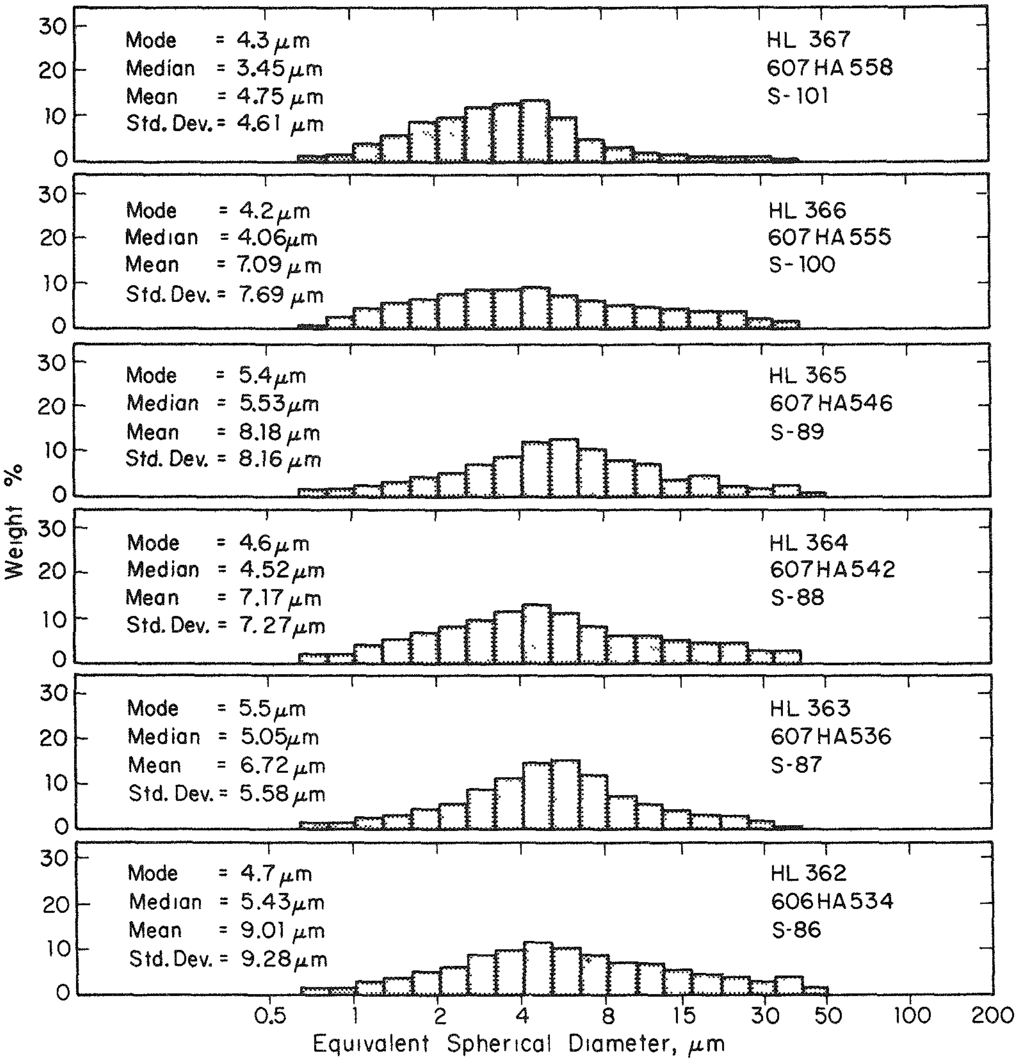

FIGURE 13. Mass Particle Size Distributions of Standardized $^{238}PuO_2$ Production (Samples S-86 to S-107)

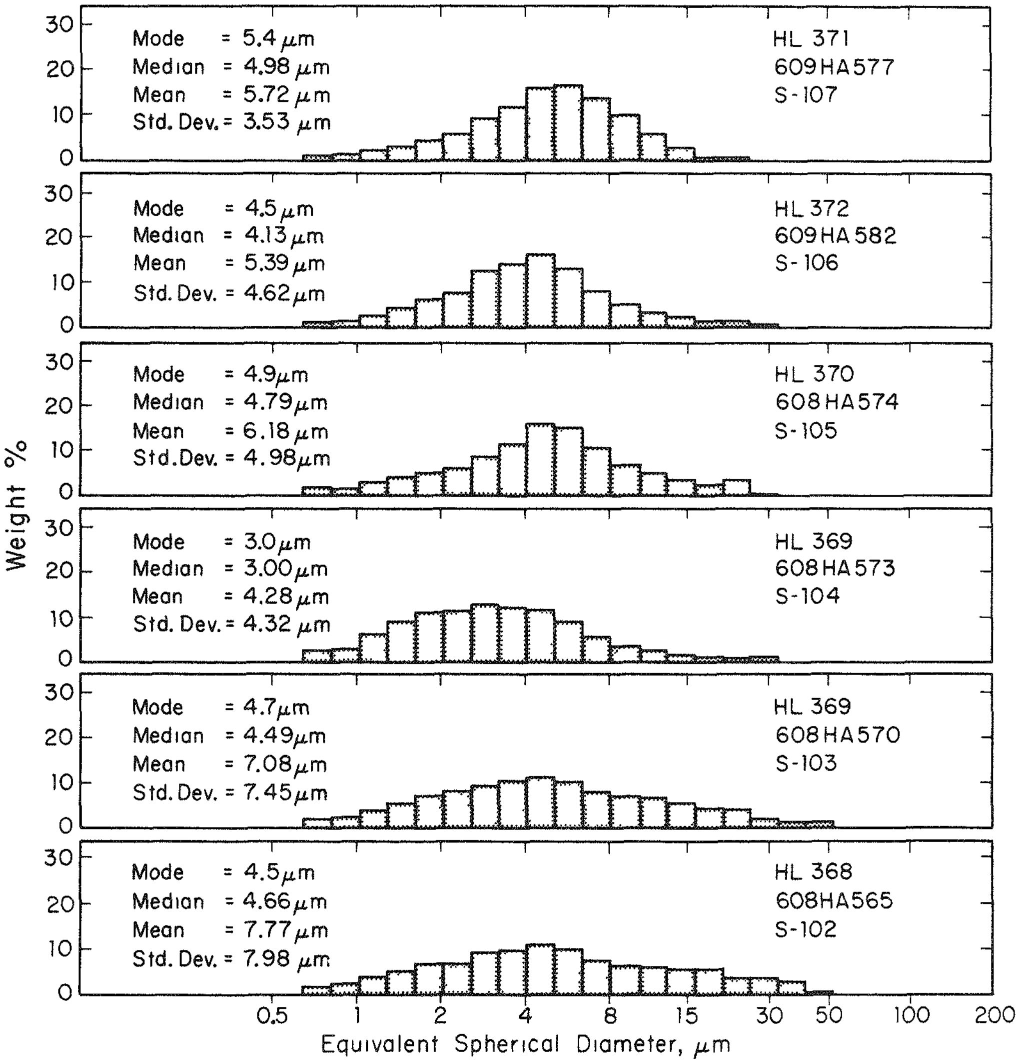

FIGURE 13. (Continued)

EXPERIMENTAL FACILITIES

PLUTONIUM EXPERIMENTAL FACILITY

All major equipment items have been installed in the PEF. Checkout of individual pieces of equipment and equipment systems has begun. Checkouts will continue as equipment or systems are completed. The evacuable transfer locks were tested and found to be leak free. The primary cooling loop on the chilled water system has been tested, and the secondary cooling loop is being tested. Checkout of the hot press will begin when the chilled water system is operational.

The status of the PEF projects is as follows:

Project Number	*Title*	*% Completion*
1374	Hot Press Facility	98
1489	Unit Operations Equipment	91
1505	Hot Press	84
4604	Sintering Furnace	68

OFFSITE SCRAP RECOVERY

Processing of offsite scrap in H-Area B-Line continued throughout the month of February. A total of 702.0 g ^{238}Pu was charged to the recovery dissolvers. The inventory of 80% ^{238}Pu offsite scrap totals 10,105.0 g and includes 5,275.0 g from LASL, 4,601.7 g from Mound Laboratory, and 228.3 g from miscellaneous sources.

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1. P. E. Potter. "Studies of the Sintering Behavior of Plutonium Dioxide." *J. Nucl. Mater. 15*, 100 (1965).

2. 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." *J. Nucl. Mater. 61*, 219 (1976).