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THE PREPARATION OF CONTROLLED PARTICLE SIZE U_3O_8 BY URANYL FORMATE PRECIPITATION AND CALCINATION

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PREPARED FOR THE U.S. DEPARTMENT OF ENERGY UNDER CONTRACT AT(07-2)-1

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by

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ABSTRACT

A conceptual process flowsheet for preparation of U_3O_8 by precipitating uranyl formate monohydrate with excess formic acid and calcining it was developed and demonstrated on a laboratory scale. The product U_3O_8 has a particle size distribution appropriate for fabrication of U_3O_8-Al fuel by powder metallurgy. The U_3O_8 particles are crystalline, do not exceed 150 µm in diameter, and have a narrow particle size distribution with most particles within the range of 44 to 150 µm. A ten-fold decontamination of uranium from low-level fission products during uranyl formate precipitation was demonstrated. Minimal variations in U_3O_8 particle size distribution as a function of various uranyl formate precipitation conditions were observed.

Preliminary tests demonstrated that calcination of uranyl formate monohydrate recovered from solution by evaporation to dryness did not produce U_3O_8 with the desired particle size distribution. Calcination of uranyl oxalate, uranous oxalate, or uranous formate also did not produce U_3O_8 with the appropriate particle size distribution.

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THE PREPARATION OF CONTROLLED PARTICLE SIZE U_3O_8 BY URANYL FORMATE PRECIPITATION AND CALCINATION

INTRODUCTION

At the Savannah River Plant (SRP), uranium fuels highly enriched in ^{235}U are periodically burned, reprocessed, and refabricated into new fuel. This recycle process leads to the accumulation of the nonfissile product ^{236}U, and each U-Al alloy fuel tube must therefore contain increasing amounts of total uranium to maintain the necessary ratio of neutron-induced fissions to nonfission neutron captures. On the basis of current cast alloying technology, the maximum uranium loading for fabricating reactor quality U-Al fuel tubes in the current design is limited to ∿30 to 35 weight per cent. If this alloying limit cannot be surpassed in the near future, increasing amounts of offsite ^{235}U will have to be blended with the SRP stockpile to achieve the desired reactivity.

Savannah River Laboratory (SRL) has developed process conditions and equipment for fabricating reactor-quality fuel tubes containing up to 60 wt % total uranium in a U_3O_8-Al powder metallurgy (PM) core. The U_3O_8 used for the PM development program was obtained by calcining UO_3 prepared at the Oak Ridge Y-12 Plant by thermal denitration of uranyl nitrate solution in a continuous-stirred bed denitrator.[1] The UO_3 has a particle size distribution in the range 150-600 μm (-30 to +100 mesh). Calcining UO_3 to U_3O_8 does not reduce particle size to the desired range; thus, the U_3O_8 must be ground for PM processing to achieve a particle size which matches that of aluminum powder. Elimination of the grinding operation is desirable because: (1) grinding is a slow operation, (2) grinding generates many undesirably fine particles, (3) grinding presents a potential for contamination releases during equipment maintenance and (4) it is difficult to eliminate U_3O_8 powder buildup in the grinder; the result could be a cross-mixing of variable composition ^{235}U feeds and therefore variable ^{235}U content in the U_3O_8-Al blends. There is no reported denitration processing experience[1,2,3] that demonstrates that UO_3 particle size can be controlled reproducibly within the size range desired so as to eliminate grinding in the PM process.

Much effort has been made in the nuclear industry to develop methods to control oxide particle size distribution by controlling conditions for precipitating actinide compounds from solution. A brief review of reported studies include precipitation of ammonium diuranate[4] and ammonium uranyl carbonate[5] for preparing uranium dioxide fuel forms. The experimental approach described in this report is based on previous studies at SRL of plutonium and neptunium oxalate precipitations.[6,7,8] The studies demonstrated that calcined PuO_2 and NpO_2 particle morphology and size distribution are determined by the oxalate precipitation conditions. Thus, the concept of controlled precipitation of uranium oxalates or formates was investigated as the best method for producing calcined U_3O_8 of appropriate size distribution for the PM process without grinding. A new U_3O_8 process, when demonstrated to be compatible with PM process requirements, could be considered as an alternative to thermal denitration for recycle of enriched uranium at SRP.

IMPORTANCE OF U_3O_8 PARTICLE SIZE DISTRIBUTION

U_3O_8 is ground with a roll grinder to a particle size predominantly in the range of 44-150 μm (-100 to +325 mesh US Standard) for the PM process. The particle size distribution is controlled because (1) particles or agglomerates larger than 150 μm (+100 mesh) tend to form large hard particles that can penetrate the tube cladding and cause undesirable hot spots with possible localized melting of the fuel tube during irradiation, (2) oxide containing more than 40 wt % of fines (particles smaller than 44 μm, or -325 mesh) is more susceptible to fission-gas blistering during irradiation, and (3) the particle size distribution of the U_3O_8 between -100 and +325 (150 to 44 μm) must match the particle size distribution of the aluminum powder to obtain a sufficiently homogenous U_3O_8-Al blend for isostatic compaction.

The desired U_3O_8 particle size distribution was established empirically from blending studies of ground U_3O_8 and T-108 aluminum powder. Average particle size distributions of the powders are plotted in Figure 1. Tests also showed that the ground U_3O_8 could be blended with T-101 aluminum powder. Since T-101 aluminum has a significantly lower particle size distribution than T-108 aluminum (Figure 1), these tests demonstrate that some variability in matching particle size of the powders to be blended can be tolerated without affecting the homogeneity of the U_3O_8-Al blends. T-101 aluminum powder was used for fabricating all fuel tubes during the PM development program.

URANYL FORMATE PRECIPITATION

Laboratory studies have demonstrated that calcination of uranyl formate monohydrate precipitated from solution by increasing the concentration of formic acid yields U_3O_8 with a particle size distribution appropriate for PM process requirements (see Preliminary Tests). Physical characteristics of U_3O_8 powder

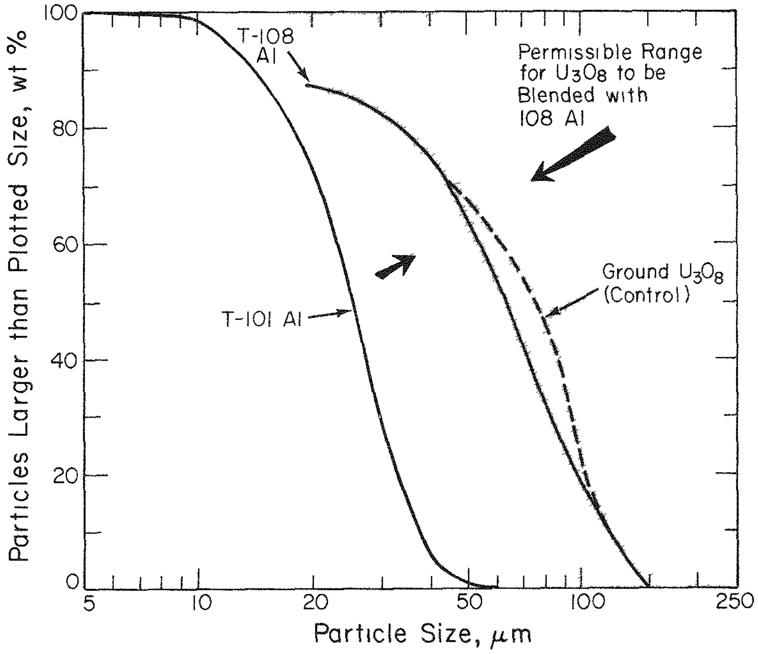

FIGURE 1. Particle Size Distributions of Ground U_3O_8 and Aluminum Powders used in Powder Metallurgy Process. Particle size of: U_3O_8 by sonic sifter, aluminum by Coulter Counter.

prepared by this method include: (1) no large particles, (2) crystalline particle morphology, and (3) a narrow particle size distribution which closely matches that of aluminum powder. These characteristics should provide the following advantages for the PM process:

- Elimination of grinding and sieving operations.
- Ready preparation of homogeneous U_3O_8-Al powder blends.

Solubility Data

The solubility of uranyl formate in aqueous formic acid at 25°C decreases with increasing formic acid concentration (Figure 2).[9] Solubility data at elevated temperature (>25°C) have not been published, but preliminary data from SRL have shown that solubility increases with increasing temperature. The composition of the solid phase precipitated from a saturated solution varies with formic acid concentration. At low acid concentration, a mixture of uranyl formate monohydrate [$UO_2(HCOO)_2 \cdot H_2O$] and a basic formate salt [$UO_2(OH)(HCOO) \cdot H_2O$] is precipitated. At high acid concentrations, pure uranyl formate monohydrate is precipitated.

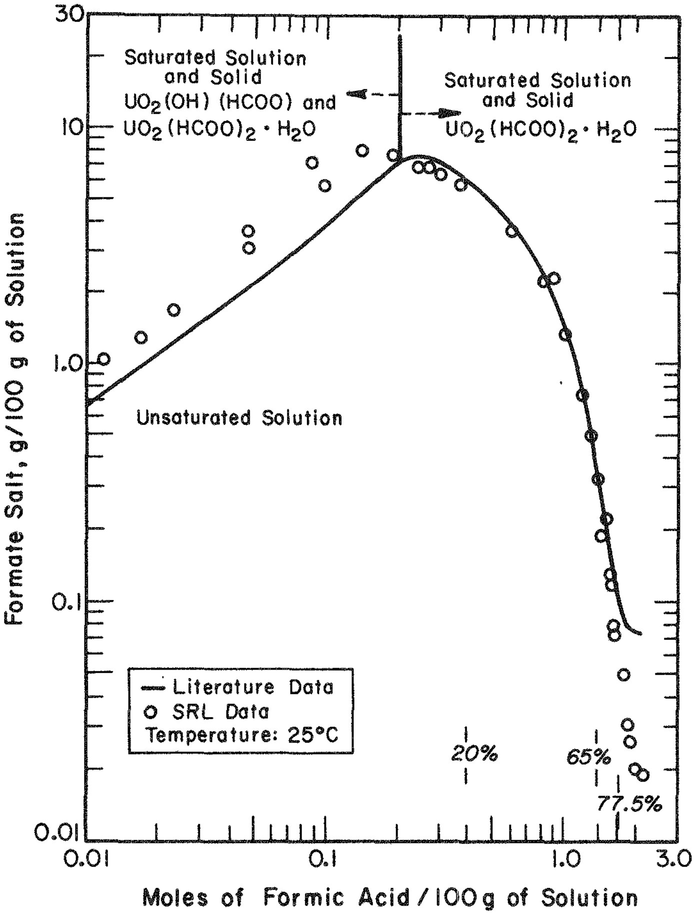

FIGURE 2. Solubility of Uranyl Formate in Aqueous Formic Acid

Because the method of increasing formic acid concentration provides for higher uranium recovery as a single solid phase, that method for recovering the salt was chosen for experimental studies. Recovered salts were identified by x-ray diffraction and thermogravimetric analysis.[10-13]

Conceptual Process Flowsheet

A conceptual flowsheet (Figure 3 and Table 1) has been developed for preparation of enriched U_3O_8 by precipitation and calcination of uranyl formate monohydrate for the PM process. Daily process capacity is expected to be ∿30 kg of enriched uranium to meet requirements for processing of 10,000 kg U/year. Nuclear safety will be maintained by proper sizing of the process equipment as well as mass and concentration limits when applicable. All formic acid solution would be prepared from commercially available technical grade (90%) formic acid.

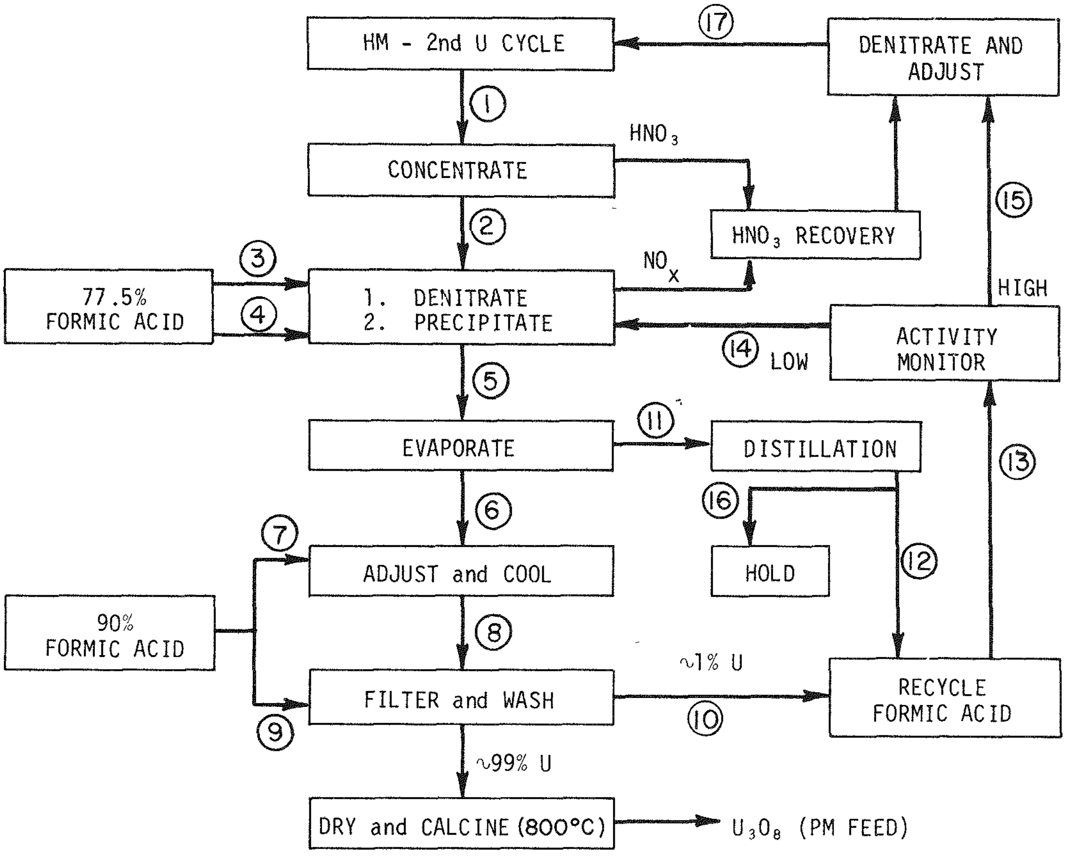

FIGURE 3. Conceptual Process for Preparation of U_3O_8 by Uranyl Formate Precipitation

Principal steps are:

- Denitration of uranyl nitrate solution by formic acid
- Precipitation of uranyl formate monohydrate by increasing the concentration of formic acid
- Evaporation of uranyl formate monohydrate slurry.
- Filtration to recover uranyl formate monohydrate cake.
- Recycling of filtrate solution containing soluble uranium.

TABLE 1

Description of Process Streams[a] in Conceptual Process Flowsheet of Figure 3[b]

	Process Stream																
	1	*2*	*3*	*4*	*5*	*6*	*7*	*8*	*9*	*10*	*11*	*12*	*13*	*14*[c]	*15*	*16*	*17*
Volume, L	6000	120	100	515	∿700	∿255	105	∿355	70	425	∿440	∿190	615	615	615	∿140	?
Meter Rate, (mole)/(min)(L feed)			0.7	1.27			Rapid		Rapid						0.7		
U, g/L	5	250			∿15	<10		<1		<1			<1	<1	<1		2-3
HNO_3, M	0.5	2															3-5
Formic Acid, wt %			77.5	77.5	∿65	69	90	∿76	90	∿79	∿62	∿77	77.5	77.5	77.5	77	

---

[a] Volumes and formic acid concentrations are approximate, based on mass balance calculations and experimental data. These volumes would be refined in future studies.

[b] 30 kg U/day process capacity.

[c] Process Stream 14 is split into two streams equivalent to Process Streams 3 and 4.

Denitration

The concentrated uranyl nitrate solutions from the second uranium solvent extraction cycle of the enriched uranium process (HM process at SRP) is denitrated by metering 77.5% formic acid (19.9M) to the hot (≥90°C) feed solution. Equipment and procedures for safe denitration of 10-liter batches of nitric acid (4 to 16M) by formic acid have been demonstrated previously.[14] Three or four 10-liter denitrators operating on 3 to 4 cycles per day would provide the needed process capacity; use of large-capacity denitrators may be feasible, but has not been demonstrated. The suggested formic acid metering rate of 0.70 moles/(min)(liter of feed), about five times faster than the maximum rate recommended in Reference 14, has been used on a laboratory scale to denitrate the 2M HNO_3 feed with no evidence of an uncontrolled reaction (i.e., no foaming). Thus, the primary considerations in determining the formic acid metering rate should be off-gas capacity for handling evolved NO_x vapor and minimization of any possible equipment pressurization. The principal driving force for reacting all complexed nitrate in the feed solution is formation of the uranyl formate complex, which has a high stability constant ($\sim 10^3$). Digestion for one to two hours in the presence of excess formic acid generally ensures complete denitration. Although excess formic acid is added during denitration, its concentration is controlled to ∿0.3 moles per 100 gms solution so that uranyl formate monohydrate does not precipitate (Figure 2). Therefore, the addition rate of formic acid during denitration will not affect the particle size distribution of the subsequently precipitated salt.

Precipitation

Uranyl formate monohydrate is precipitated by metering 77.5% formic acid to the hot uranyl formate solution. Slow addition of formic acid during precipitation controls nucleation and growth of the crystalline particles, yielding the appropriate particle size distribution for PM requirements. After formic acid addition is completed, the solution acid concentration is ∿1.4 moles per 100 g solution. Cooling of the solution to 25°C at this stage would recover ∿95% of the uranyl formate salt (Figure 2). However, filtrate volume would be too large to recycle (see discussion under Evaporation).

Although the solubility of uranyl formate in formic acid solution at elevated temperatures has not been reported, it is estimated that precipitation with formic acid at 90°C yields a slurry containing more than 50% solid uranyl formate monohydrate.

Therefore, subsequent process steps must be designed to keep the slurry well mixed. Cake formation from settled solids at any stage of the process in which the uranyl formate monohydrate continues to precipitate (including evaporation and cooling) could favor particle agglomeration, thereby shifting the particle size distribution into an undesirably large range.

Evaporation

Batch evaporation of the slurry further increases the concentration of formic acid and reduces the volume containing soluble uranium to be recycled as 77.5% formic acid. If the slurry were not evaporated, adjustment of the filtrate to the required recycle formic acid concentration using 90% formic acid would increase the recycle volume above the required formic acid feed volume. This would increase uranium loss because all the filtrate could not be recycled as formic acid feed.

The azeotropic composition of aqueous formic acid (77.5%) was chosen as a recycle feed to denitration and precipitation steps because the azeotrope can be prepared by simple evaporation. However, batch evaporation of the slurry solution to the azeotropic composition would reduce the volume by more than 90% and could cause particle agglomeration. Therefore, evaporation is considered complete after a 60 to 65% volume reduction. The final slurry volume is controlled so that downstream addition of 90% formic acid produces the required formic acid recycle volumes and composition.

Filtration

Before filtration, the slurry is cooled to ambient temperature to maximize recovery of uranyl formate monohydrate. About 99% of the initial uranium charge is recovered as uranyl formate monohydrate by filtration at a formic acid concentration of ∿1.7 moles per 100 g solution (Figure 2). The filter cake is washed with fresh 90% formic acid to remove entrained formic acid which contains low levels of beta-gamma activity (from ^{95}Zr and ^{95}Nb in the feed from the solvent extraction process). The wash does not dissolve a significant quantity of precipitated uranyl formate monohydrate because of the high concentration of formic acid. However, the wash is collected with the filtrate to recycle any dissolved uranium and to adjust the final formic acid concentration to 77.5% in the filtrate. The filter cake is then dried and calcined in a static bed under a controlled oxygen atmosphere at 800°C to produce a free-flowing U_3O_8 powder.

Recycle

The filtrate, which contains about 1% of the initial uranium charge, is monitored for beta-gamma activity and recycled either back to the denitrator and precipitator stages (low activity) or back to the solvent extraction process (high activity). The high-activity limit for recycle to solvent extraction would depend on establishment of permissible exposure levels from gamma activity in both the solid uranyl formate monohydrate product and the recycle filtrate which would not be hazardous to process personnel. Minimum uranium decontamination factors of about 10 for ^{95}Zr and ^{95}Nb can be expected by precipitating the uranium from the feed solution based on experimental studies discussed on p 18.

Activity carried with precipitated uranyl formate monohydrate could be further reduced by pumping the concentrated uranyl nitrate feed through a silica gel bed before denitration; however, studies would be required to ensure that contact with silica gel would not increase silicon contamination of the precipitated uranyl formate monohydrate above essential material specifications. Activity in the recycled filtrate also might be reduced by silica gel treatment, but the effect of formic acid on bed operation has not been determined.

Recycle of the formic acid filtrate to solvent extraction requires that uranyl nitrate solution be prepared. Excess HNO_3 will be added to the filtrate to destroy all formic acid, including complexed formate ion.

A fractional distillation column is proposed in the flowsheet to recover formic acid from the distillate obtained from the batch evaporator. Actual inclusion of the column would be determined by the economics of using recovered formic acid versus fresh formic acid feed. Fractional distillation would yield enough 77% formic acid to (1) adjust the filtrate to the volume required for recycle, and (2) provide fresh feed volume for denitration and precipitation when the filtrate is recycled to solvent extraction. Thus, after startup, the only process steps which would require fresh formic acid feed (about 20 to 30% of total formic acid introduced to the process) would be feed adjustment and cake washing.

Laboratory Tests of Flowsheet

Two laboratory-scale tests to simulate the recommended process have been completed. These tests were run with the initial feed at about 1/100 of the proposed process scale (85 mL vs. 10L). Flowsheet conditions are summarized in Table 2. The precipitated solid was identified as uranyl formate monohydrate from x-ray diffraction patterns. Although experimental problems in the batch evaporation stage for Sample 1 caused deviations from specified flowsheet conditions, the precipitate was readily recovered by the conceptual precipitation/evaporation process. Also, formic acid metering rates for Sample 1 were lower than the recommended flowsheet rates. Absence of foaming during denitration at either of the two experimental metering rates indicates that the higher metering rate can be used safely for denitration if the offgas system can readily accommodate the NO_x evolution.

The particle size distribution of uranyl formate monohydrate and the corresponding U_3O_8 (Table 3 and Figure 4) were measured by sonic-sifter and mechanical sieving (see Experimental section for explanation of sieving method). The lack of significant difference between U_3O_8 particle size distributions for Samples 1 and 2 shows that the higher formic acid metering rate during precipitation of Sample 2 did not significantly change the particle size distribution of the calcined oxide.

TABLE 2

Laboratory Tests of Conceptual Flowsheet: Conditions for Precipitation of Uranyl Formate Monohydrate from Aqueous Uranyl Nitrate with Formic Acid

	Measurements for		*Conceptual Flowsheet*
	Sample 1[a]	*Sample 2*	*Design Value*
Feed Rate of 77.5% Formic Acid, (moles formic acid)/(min)(liter of uranyl nitrate solution)			
To denitrator[b]	0.36	0.70	0.70
To precipitator	0.63	1.27	1.27
% Formic Acid in Condensate from Evaporation of Uranyl Formate Monohydrate Slurry	56	62	∿62
Composition of Filtrate from Uranyl Formate Monohydrate Slurry			
Formic Acid, %	72	80	∿78
Uranium, g/L	1.32	0.56	0.71
% Recovery of Solid Uranyl Formate Monohydrate	98.5	99.2	∿99

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a. Evaporation problems reduced condensate volume, causing formic acid concentrations to deviate from flowsheet design values.

b. Uranyl nitrate feed to denitrator:
Composition: 250 g U/L, 2M HNO_3
Volume: 170 mL (Sample 1), 85 mL (Sample 2).

TABLE 3

Particle Size Distribution of U_3O_8 Prepared According to Conceptual Flowsheet

			Wt % of Particles in Size Range						
Sample	*Powder*	*Sieving Method*[a]	*<44 μm (fines)*	*44 to 53 μm*	*53 to 74 μm*	*74 to 88 μm*	*88 to 105 μm*	*105 to 150 μm*	*>150 μm*
1	UFH[b]	Mechanical	21.7	← - - - - - -		78.1[c]	- - - - - - - - →		0.2
	U_3O_8	Mechanical	50.8	← - - - - - -		49.1[c]	- - - - - - - - →		0.05
	U_3O_8	Sonic	10.4	21.0	18.2	22.0	15.7	12.6	0.02
2	UFH[b]	Mechanical	40.4	← - - - - - -		56.0[c]	- - - - - - - - →		3.6
	U_3O_8	Mechanical	55.5	← - - - - - -		42.4[c]	- - - - - - - - →		2.0
	U_3O_8	Sonic	14.6	11.3	10.5	9.9	13.5	36.4	3.6

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[a] See Experimental section for description.

[b] Uranyl formate monohydrate.

[c] Total for 44 to 150-μm range.

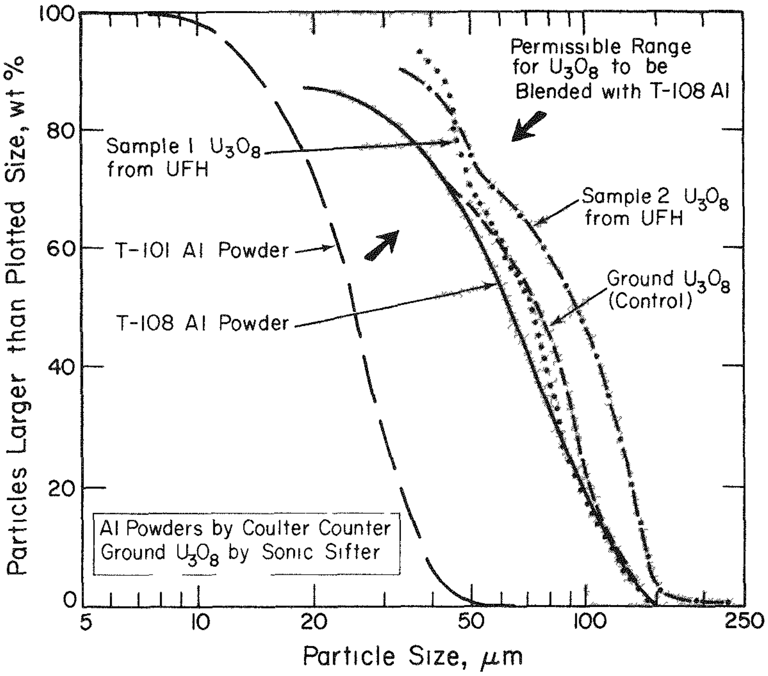

FIGURE 4. Particle Size Distribution of U_3O_8 Prepared According to Conceptual Flowsheet. (Particle size of: U_3O_8 by sonic sifter, aluminum by Coulter Counter.)

Sonic-sifter sieving is one of the methods utilized for determining particle size distributions of ground U_3O_8 to provide controlled blending conditions in the PM process. Thus, direct comparisons can be made of sonic sifter data for U_3O_8 obtained by calcining uranyl formate monohydrate and for U_3O_8 obtained by grinding calcined UO_3. From the measured particle size distribution (Figure 4), the U_3O_8 obtained by calcining uranyl formate monohydrate prepared according to the recommended process is an appropriate candidate for blending tests with either T-108 or T-101 aluminum powder.

Decontamination of Uranium from Fission Products

The enriched uranyl nitrate feed for the U_3O_8 process from solvent extraction generally contains less than one μCi of beta-gamma activity, primarily ^{95}Zr and ^{95}Nb, per gram of uranium. Currently, the solution is shipped to the Oak Ridge Y-12 Plant where a third solvent extraction cycle concentrates the solution and reduces fission product activity before thermal denitration.[1] Specifications for recycled enriched uranium metal shipped from Y-12 to SRP establish the maximum acceptable fission product activity as 0.05 μCi/g U. Therefore, depending on the feed activity, solvent extraction at Y-12 must achieve minimum decontamination factors ranging from 2 to 20.

Decontamination of uranium from fission products during precipitation of uranyl formate monohydrate was measured, using the same parameters listed in Table 2 for Sample 2. Mixed fission products from SRL solvent extraction studies were added to the feed to adjust the activity of Sample 3 (0.69 μCi of ^{95}Zr and ^{95}Nb per gram of uranium) to approximately that of recent product solutions (0.80 μCi/g U) as shipped to Y-12. The higher activity of the feed for Sample 4 (3.16 μCi/g U) approximates the expected increase in activity after several recycles of the formic acid filtrate. Solution activities were measured by gamma pulse-height analysis; the activity of solid uranyl formate monohydrate was determined by dissolving a known weight in formic acid solution before analysis.

Decontamination factors ranging from 7 to 90 for various fission products were obtained when uranyl formate monohydrate was precipitated (Table 4). The combined ^{95}Zr, ^{95}Nb activity in Sample 3 was reduced from 0.69 μCi/g U in the solution to 0.072 μCi/g U in the solid; Sample 4 activity was reduced from 3.16 μCi/g U in the solution to 0.149 μCi/g U in the solid. The average decontamination factor for ^{95}Zr, ^{95}Nb, about 10, indicates that purification of uranyl nitrate feed by a third solvent extraction cycle could be eliminated if uranyl formate monohydrate precipitation were used for onsite recycle of enriched uranium.

TABLE 4

Decontamination of Uranium by Precipitation as Uranyl Formate Monohydrate

	Fission Product Activity, (dis)/(min)(g uranium), in				*Decontamination Factor for*	
Fission Product	*Feed[a] for*		*UFH[b] from*			
	Sample 3	*Sample 4*	*Sample 3*	*Sample 4*	*Sample 3*	*Sample 4*
^{95}Zr	7.51×10^5	3.03×10^6	4.95×10^4	1.42×10^5	15.2	21.3
^{95}Nb	7.85×10^5	3.99×10^6	1.12×10^5	1.89×10^5	7.0	21.1
^{103}Ru	1.76×10^6	5.55×10^6	2.36×10^5	5.35×10^5	7.5	10.4
^{106}Ru	2.96×10^6	1.21×10^7	4.13×10^5	1.35×10^6	7.2	9.0
^{137}Cs	2.96×10^5	1.41×10^6	4.32×10^4	1.56×10^4	6.9	90.4
^{144}Ce	3.81×10^6	1.68×10^7	2.75×10^5	3.64×10^5	13.8	46.2

---

a. 21.25 g uranium in feed.

b. 19.90 g uranium recovered as uranyl formate monohydrate.

Although the decontamination factor for all measured fission products increased as the feed activity increased, the total activity of several nuclides (Ru, Zr, Nb) carried with the solid also increased. The greatest increases in decontamination were observed for Cs and Ce, indicating that these nuclides are carried with the solid by adsorption rather than precipitation.

Fission product mass balances show about a 50% loss of ^{95}Zr and ^{95}Nb in precipitating uranyl formate monohydrate. This loss is probably due to adsorption by the glass-fritted filter rather than to experimental error, particularly since all other nuclides exhibited good mass balance. Anomalous precipitation and adsorption behavior for ^{95}Zr and ^{95}Nb in acid solutions has been reported previously.[15] The possible loss of ^{95}Zr and ^{95}Nb to the glass equipment indicates the need for studies of the behavior of ^{95}Zr and ^{95}Nb with steel-fritted filters (expected process equipment).

Effect of Changes in Process Conditions on Particle Size Distribution

Several studies of the effect of changes in process conditions on the particle size distribution of precipitated uranyl formate monohydrate were completed before development of the conceptual flowsheet. Therefore, the final formic acid concentration was not adjusted by the evaporation procedure. However, more than 95% of the uranium was precipitated in all tests, even when the filtrate contained less formic acid (about 65%) than specified by the flowsheet (about 78%). This demonstrates that increasing the concentration of formic acid by evaporation has only a small effect on total uranium recovery; evaporation is primarily important for maintaining required filtrate recycle volumes.

Small changes were made in the following conditions (as summarized in Table 5) to reflect possible variations during actual processing:

- Uranium concentration in feed.
- Formic acid feed rate to denitration stage.
- Formic acid feed rate to precipitation stage.
- Precipitation temperature.
- Final solution temperature.

TABLE 5

Changes in Process Conditions to Test Effects on Particle Size Distribution of U_3O_8

	Sample						
	5[a]	*6*	*7*	*8*	*9*	*10*	*11*
Uranyl Nitrate Feed							
Concentration, g U/L	207	217	217	217	217	227	197
Volume, mL	200	200	200	200	200	300	220
Formic Acid Feed Rate (moles formic acid)/(min)(liter of uranyl nitrate solution)							
To denitrator	0.35	0.35	0.35	0.35	0.35	0.24	0.32
To precipitator	0.63	0.50	0.71	0.63	0.63	0.42	0.58
Solution Temperature, °C							
During precipitation	90	90	90	90	95	90	90
Final	25	3	3	25	25	25	25
Filtrate Volume, mL (approx.)[a]	800	800	800	800	800	900	820
% Formic Acid (approx.)	68	68	68	68	68	62	68
g U/L	1.86	1.13	ND	ND	ND	ND	ND
% Recovery of Solid Uranyl Formate Monohydrate (minimum)	97	98	98	97	97	95	97

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[a] No evaporation before filtration.

The particle size distributions of the calcined U_3O_8 product (Table 6) changed very little as a result of the imposed process changes. However, the measured particle size distribution for these samples are smaller than the distributions reported for the samples obtained from the conceptual flowsheet design (Samples 1 and 2 in Table 3). These results demonstrate that some variability in the particle size distribution of uranyl formate monohydrate can occur during precipitation. The observed variability is not correlated with any of the studied process changes.

The particle size distributions for some of the U_3O_8 powders also were measured with a Coulter Counter (see Experimental section for description of technique). The particle size distributions for U_3O_8 measured by this technique (Figure 5) indicate: (1) a narrow size distribution and (2) little reduction of size by ultrasonic dispersion.

Those powders which contain more than 40 wt % of the particles less than 44 μm generally have more than 99 wt % of the particles larger than 10 μm. This narrow distribution is advantageous because the radiation stability (resistance to fission-gas blistering of cladding) of U_3O_8-Al fuel compacts made with U_3O_8 prepared from uranyl formate monohydrate is expected to be better than that of compacts made with ground U_3O_8, where about 2 to 10 wt % of the particles are smaller than 10 μm.

The observation that the powder particle sizes are not reduced by ultrasonic dispersion indicates that powders should maintain their particle size distributions throughout mechanical processing operations. This observation is consistent with the discrete crystalline particle morphologies of U_3O_8 powders prepared from uranyl formate monohydrate, as discussed in the following section.

The particle size distribution of most U_3O_8 powders prepared from uranyl formate monohydrate generally falls between the particle size distributions of T-101 and T-108 aluminum powders. Because ground U_3O_8 powder blends homogeneously with either of these aluminum powders, U_3O_8 powder prepared from uranyl formate monohydrate also should blend homogeneously with either aluminum powder.

The measured uranium concentrations in the filtrates from Samples 5 and 6 (Table 5) show that cooling the solution to near 0°C before filtration increases uranium recovery only slightly, about 1% for specified process conditions.

TABLE 6

Effect of Variable Process Conditions[a] on Particle Size Distribution of U_3O_8

		Wt % of Particles in Size Range						
Sample	*Sieving Method*[b]	*<44 µm (fines)*	*44 to 53 µm*	*53 to 74 µm*	*74 to 88 µm*	*88 to 105 µm*	*105 to 150 µm*	*>150 µm*
5	Sonic	19.8	22.8	41.8	14.2	1.11	0.22	0.06
6	Sonic	80.5	7.0	8.4	2.7	1.11	0.22	<0.01
7	Sonic	46.8	18.4	21.7	7.3	3.5	2.1	0.2
8	Sonic	58.4	18.0	18.7	3.3	1.0	0.6	<0.01
9	Sonic	48.7	22.3	22.3	4.7	1.3	0.6	0.14
10	Mechanical	39.9	←		58.9[c]		→	0.26
11	Mechanical	44.6	←		50.4[c]		→	<0.1

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a. Described in Table 5. See Table 3 for particle size distributions at conceptual flowsheet design values.

b. See Experimental Section for description.

c. Total for 44 to 150-µm range.

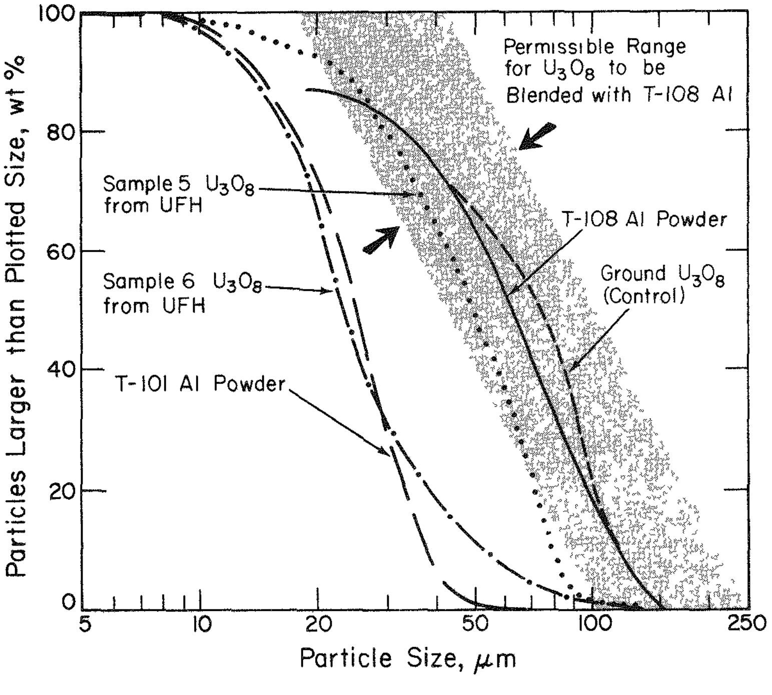

FIGURE 5. Coulter Counter Determination of Particle Size Distribution of U_3O_8 Prepared by Calcination of Precipitated Uranyl Formate Monohydrate. (All particle size distributions by Coulter Counter except ground U_3O_8 by sonic sifter)

Particle Morphology

Scanning-electron-microscope photomicrographs show that uranyl formate monohydrate is precipitated as distinct crystalline particles (Figure 6). The crystals are large (generally >10 μm) and have smooth surfaces. Precipitation of the salt does result in some particle agglomeration, but the particle size distribution generally is observed to be between 25 and 150 μm in agreement with sieving data.

Calcining the uranyl formate monohydrate to U_3O_8 does not significantly reduce the particle size or alter the large particle morphology of the original salt (Figure 7). At high magnification (5000X), the crystal surfaces exhibit a definite grainy texture. This grainy surface texture results from the growth of small crystalline domains of U_3O_8 within the larger crystals during calcining. These U_3O_8 domains are believed to contribute to the particle porosity which is important to radiation stability of the fuel. Matching of the formate prepared oxide porosity to the porosity of the currently used oxide (prepared from UO_3) should be possible by varying either temperature or time of calcining.

In contrast to the formate-based U_3O_8 particles, the particles of enriched U_3O_8 prepared by grinding calcined UO_3 from the thermal denitration process are composed of agglomerates of small crystals of about 1-μm size (Figure 8). These agglomerates have a broad size distribution with many particles observed as falling in the 1 to 10-μm size range.

PRELIMINARY TESTS

The following sections describe preliminary tests made with several uranium salts to determine a candidate salt for preparing U_3O_8 with the desired particle size distribution. These early studies identified uranyl formate monohydrate as the most promising method for preparing U_3O_8 and led to the studies described in the previous sections.

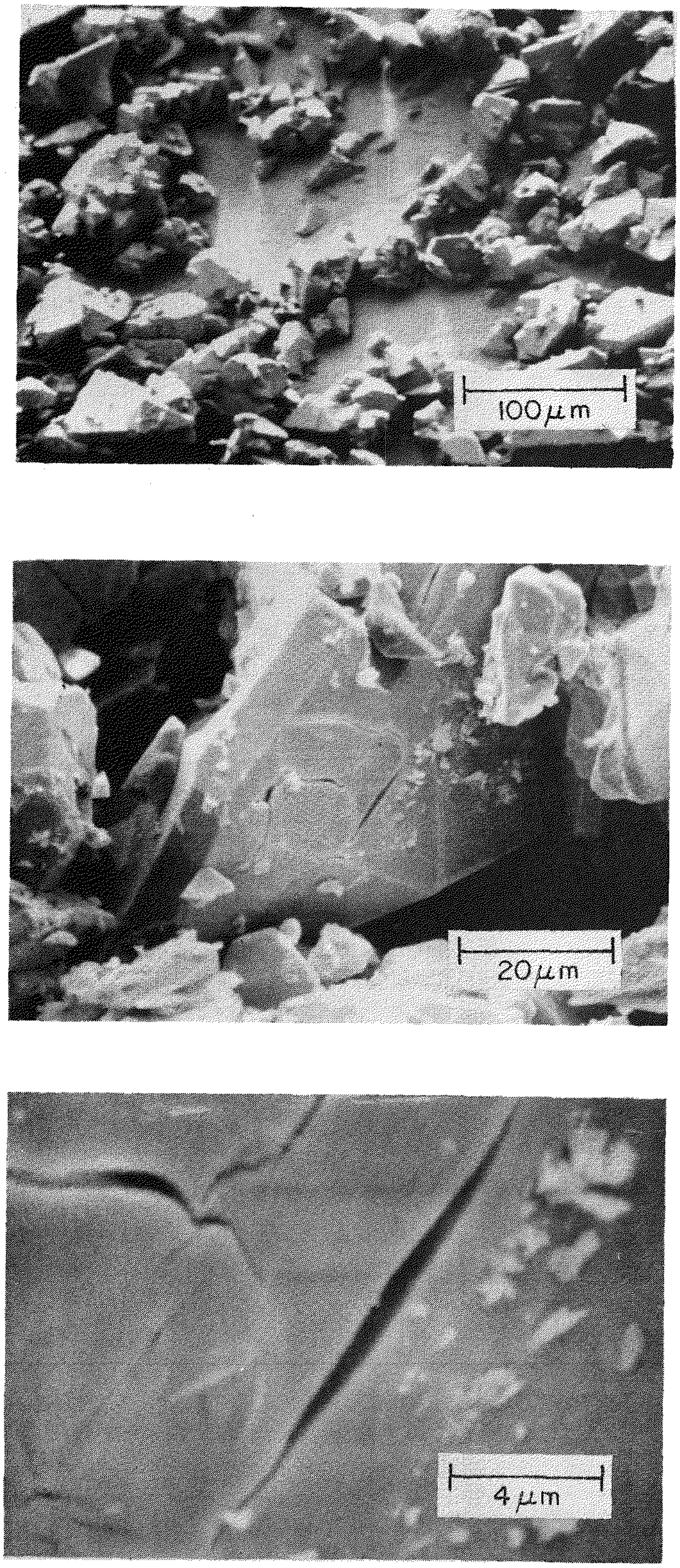

FIGURE 6. Scanning Electron Photomicrographs of Uranyl Formate Monohydrate Crystals Precipitated from Aqueous Formic Acid

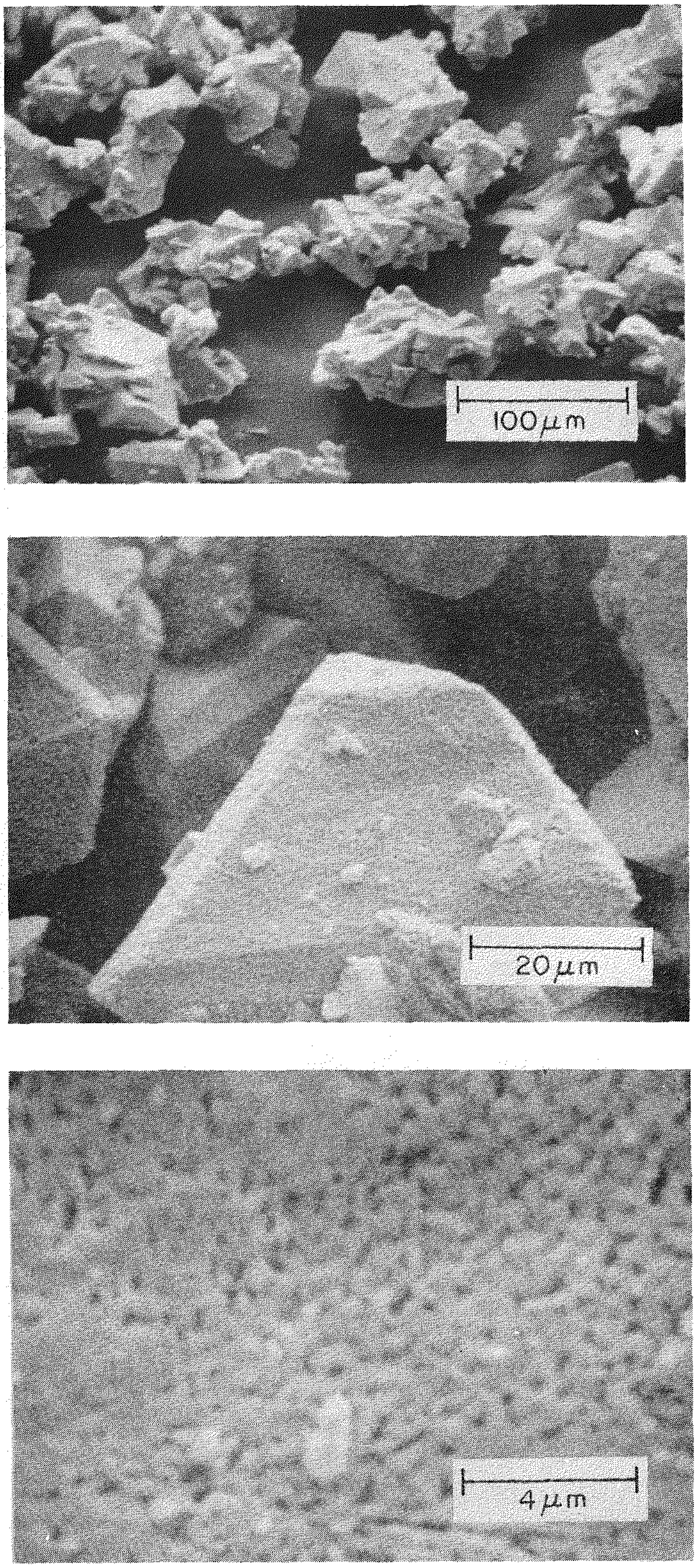

FIGURE 7. Scanning Electron Photomicrographs of U_3O_8 Prepared by Calcining Precipitated Uranyl Formate Monohydrate (cf. Figure 6)

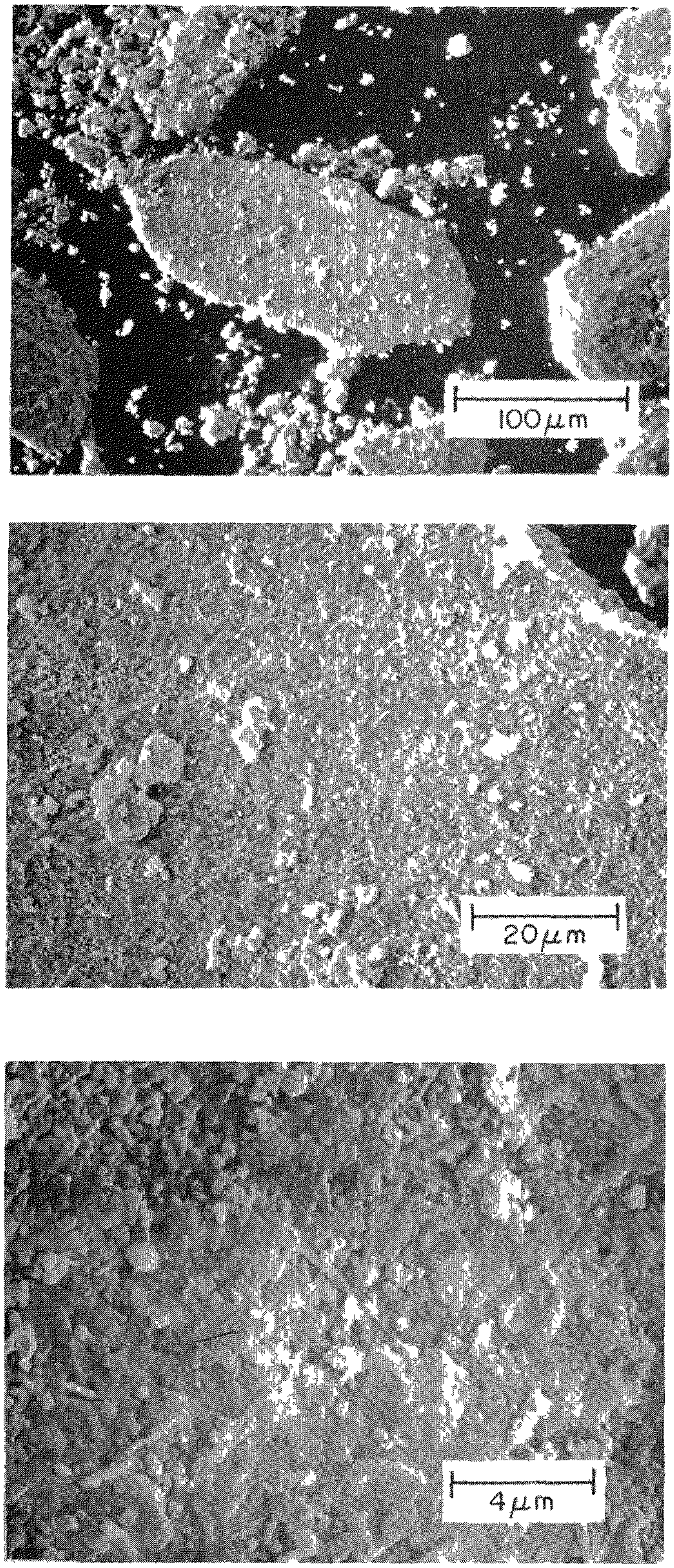

FIGURE 8. Scanning Electron Photomicrographs of Ground U_3O_8 Prepared by Calcination of Enriched UO_3

Uranyl Formate

For the preliminary tests, unsaturated uranyl formate solutions were evaporated to dryness (100% recovery of the uranium salt). Evaporation without any agitation produced a hard precipitate cake that yielded an undesirable number of large particles when broken up. Mechanical or manual stirring during evaporation failed to eliminate all cake formation, although particle size distribution was improved (Tables 7 and 8). Several samples which were filtered from a partly evaporated and stirred uranyl formate slurry (∿20% of initial solution volume remaining) had a variable particle size distribution (Samples C and D) and a high proportion of undesirably large particles. Evaporation concentrates both uranium and formic acid in solution. Those conditions favor nucleation at the surfaces of existing crystals and result in undesirable large agglomerates. This agglomeration mechanism is supported by scanning-electron-photomicrographs of the uranyl formate salt recovered from a partially evaporated solution and the corresponding calcined oxide (Figure 9).

Stirring of the uranyl formate salt during calcination clearly breaks down the large particle agglomerates. The U_3O_8 particle size was reduced to a distribution which more closely matches the T-108 aluminum size distribution than does U_3O_8 powder calcined in a static bed (Samples B' and C' in Table 8; also see Figure 10). However, stirring did not eliminate large particles.

Static-bed calcining with a rapid temperature rise to 800°C resulted in only a small reduction in the U_3O_8 particle size distribution of the parent formate salt (Sample B vs. Sample B" and Sample C vs. Sample C"). A slow temperature rise through the thermal decomposition temperatures of the uranyl formate salt reduced U_3O_8 particle size significantly (Samples A vs. Sample A" and Sample D vs. Sample D'). However, slow calcining did not eliminate large particle agglomerates. These results show that uranyl formate salt having the desired particle size distribution (i.e., prepared by precipitation as discussed in previous sections) should be calcined in a static bed by rapidly increasing temperature in order to minimize any reduction in particle size.

The U_3O_8 powders prepared from uranyl formate recovered by evaporation procedures contained undesirable large particles. However, the general match of particle sizes with both ground U_3O_8 and T-108 aluminum powders was considered to be close enough to identify uranyl formate as the candidate uranium salt for preparing U_3O_8 for the PM process. These tests led to a study of uranyl formate solubility in aqueous formic acid solutions. This resulted in the successful precipitation tests for recovering uranyl formate of appropriate particle size which were described in a previous section.

TABLE 7

Experimental Conditions for Preparation and Calcination of Uranyl Formate Salt by the Evaporation Method

Sample	*Salt Recovery Procedure*	*Calcination* Rate to 400°C	Rate to 800°C	*Stirring*	*Product*
A	Manual stirring	-	-	-	Formate salt
A'	during evaporation	Slow	-	5 rpm	UO_{2+x}[a]
A"		Slow	Rapid	None	U_3O_8
B	Mechanical stirring	-	-	-	Formate salt
B'	during evaporation	Slow	Rapid	5 rpm	U_3O_8
B"		Rapid	Rapid	None	U_3O_8
C	Filtered from slurry	-	-	-	Formate salt
C'	after partial evaporation	Rapid	Rapid	5 rpm	U_3O_8
C"		Rapid	Rapid	None	U_3O_8
D	Filtered from slurry	-	-	-	Formate Salt
D'	after partial evaporation	Slow	Rapid	None	U_3O_8

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a. Substoichiometric Oxide supported by x-ray diffraction pattern.

TABLE 8

Particle Size Distributions for Uranyl Formate Salts and Calcined Oxides from Experimental Conditions of Table 7

Sample	*Sieve Analysis*	*Wt % of Particles in Size Range* <44 µm (fines)	44 to 53 µm	53 to 74 µm	74 to 88 µm	88 to 105 µm	105 to 150 µm	>150 µm
U_3O_8, control	Sonic	28.3	8.3	10.9	15.3	16.7	20.5	0.0
A	Mechanical	13.1	←		65.0[a]		→	21.9
A'	Mechanical	43.4	←		49.5[a]		→	7.1
	Sonic	39.9	14.7	18.3	8.1	5.1	7.5	7.5
A"	Mechanical	35.6	←		51.6[a]		→	12.8
	Sonic	31.6	18.1	17.9	7.9	5.2	7.4	11.9
B	Mechanical	11.1	←		37.7[a]		→	51.1
B'	Mechanical	34.7	←		51.3[a]		→	14.0
	Sonic	28.3	12.7	13.8	8.8	7.6	13.8	15.0
B"	Sonic	16.0	12.0	11.0	5.1	3.6	8.0	44.4
C	Mechanical	0.4	←		32.3[a]		→	67.4
C'	Mechanical	34.5	←		53.6[a]		→	11.8
C"	Mechanical	17.1	←		28.7[a]		→	54.2
D	Mechanical	13.2	←		72.6[a]		→	14.2
D'	Mechanical	28.7	←		62.8[a]		→	8.5

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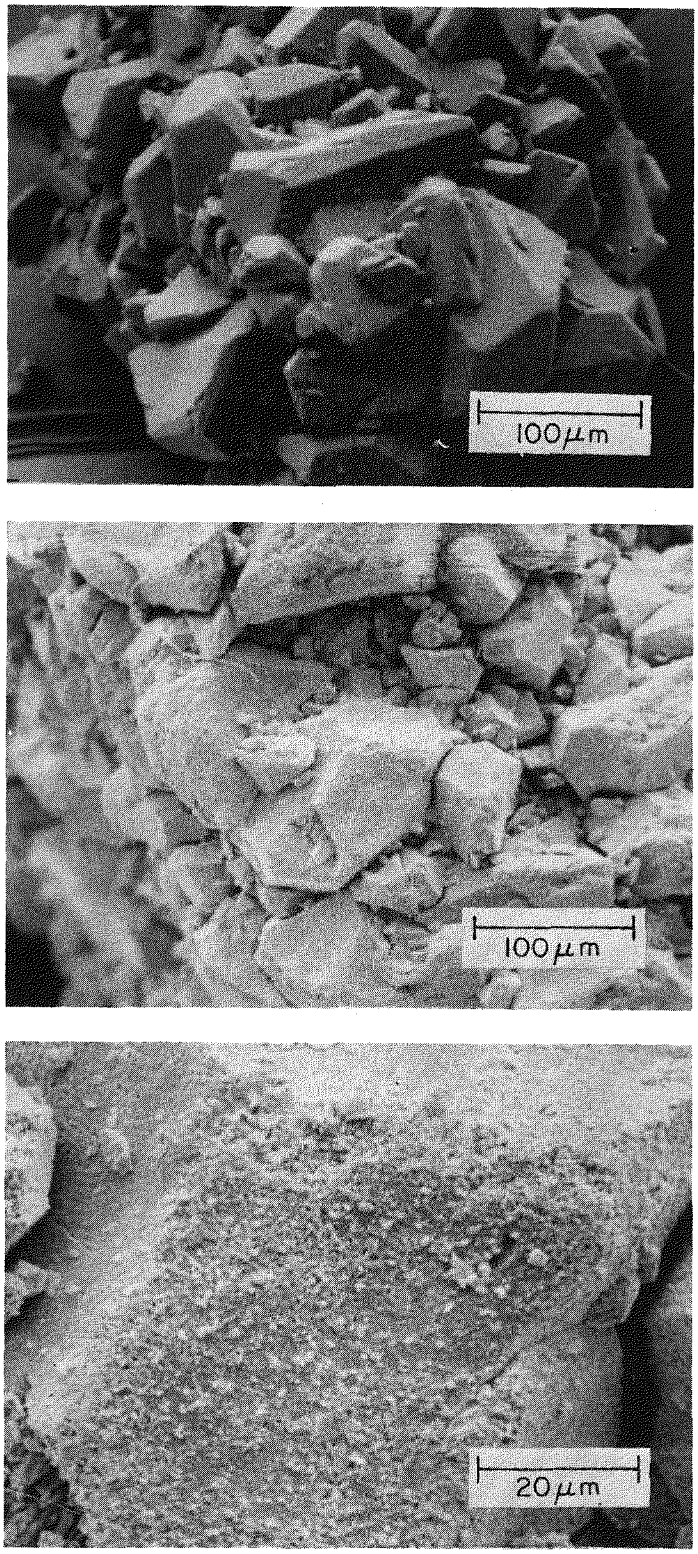
a. Total for 44 to 150-µm range.



a. Uranyl Formate

b. U_3O_8

c. U_3O_8

FIGURE 9. Scanning Electron Photomicrographs of Uranyl Formate Salt and Corresponding Calcined U_3O_8 as Recovered by Partial Evaporation

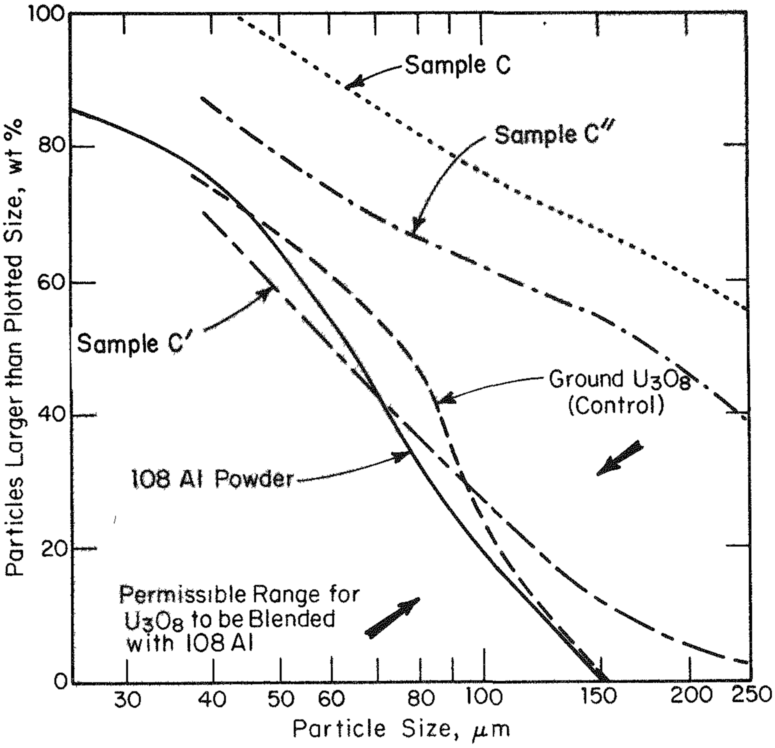


FIGURE 10. Effect of Stirring During Calcination of Uranyl Formate Salt on Particle Size Distribution of U_3O_8

Uranyl Oxalate

Uranyl oxalate, $UO_2(C_2O_4) \cdot nH_2O$, was prepared by rapid addition of an oxalic acid solution to uranyl nitrate solution at room temperature. A free-flowing powder was recovered by evaporating solvent from the slurry solution while stirring. Filtration of the precipitate from the slurry solution was tried, but yielded a hard precipitate cake after drying.

Table 9 summarizes the conditions used in preparing several lots of uranyl oxalate and the measured particle size distribution of the corresponding U_3O_8 products. Particle size distribution matched poorly with that of the ground U_3O_8 (control) sample. Varying precipitation and calcining conditions did not significantly improve the particle size distribution. No further studies were made of uranyl oxalate preparation for this program.

TABLE 9

Preparation Conditions for Uranyl Oxalate and Particle Size Distribution of U_3O_8 Product

Sample	*Uranyl Nitrate, g/L*	*Oxalic Acid, M*	*Powder Moisture Level*	*Calcining Rate to 400°C*	*Calcining Rate to 800°C*
E	300	0.5	Moist	-	Rapid
F	300	0.75	Oven dried	-	Slow
G	300	0.75	Air dried	Rapid	Rapid

	Particles in Size Range, wt %[a]						
Sample	*>150 μm*	*105-150 μm*	*88-105 μm*	*74-88 μm*	*53-74 μm*	*44-53 μm*	*<44 μm (Fines)*
E	40.5	6.5	2.7	2.9	4.1	3.4	39.9
F	67.7	24.8	6.5	0.5	0.0	0.0	0.4
G	73.1	9.6	5.8	3.4	2.5	2.5	3.2
Control (Ground U_3O_8)	0.0	20.5	16.7	15.3	10.9	8.3	28.3

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[a] Particle size by sonic sifter method.

Uranous Oxalate

Uranous ion, U(IV), was prepared by reduction of uranyl ion with Rongalite (sodium formaldehyde sulfoxylate).[16] Rongalite reduces uranyl ion to U(IV) without coprecipitating with the added oxalate. The reduction kinetics depend on nitric acid concentration and temperature.[17] Stable uranous ion solutions were prepared at 45 and 55°C by adding solid Rongalite to uranyl nitrate in 2M HNO_3. Uranous oxalate, $U(C_2O_4)_2 \cdot nH_2O$, was prepared by a slow direct strike addition of oxalic acid solution to the uranous solution. The low solubility of uranous oxalate allowed 100% recovery of the salt by filtration.

Table 10 summarizes the conditions used in preparing uranous oxalate and the measured particle size distribution of the corresponding oxides. Distributions were generally poorly matched with the control sample (ground U_3O_8). The large proportion of fines is attributed to the very low solubility of the complex. Although oxalic acid was slowly metered into the stirred, hot uranium solution (conditions expected to increase particle size), the high local concentration at the added drops of oxalic acid and the rapidity with which uranous oxalate forms apparently produced a high proportion of small crystals.

TABLE 10

Preparation Conditions for Uranous Oxalate and Particle Size Distribution of Calcined U_3O_8 Product

Sample	*Solution Temp, °C*	*Oxalic Acid Addition Rate, mL/min*	*Powder Moisture*	*Calcining Rate to 400°C*	*Calcining Rate to 800°C*
H	45	3	Oven dried	-	Slow
J	45	3	Air dried	Rapid	Rapid
K	55	3	Moist	Rapid	Rapid
L	55	1.5	Air dried	Slow	Rapid
M	25	Hydrolysis of methyl oxalate	Air dried	Rapid	Rapid

	Particles in Size Range, wt %[a]						
Sample	*>150 μm*	*105-150 μm*	*88-105 μm*	*74-88 μm*	*53-74 μm*	*44-53 μm*	*<44 μm (Fines)*
H	22.8	0.8	0.5	0.8	0.9	3.9	70.3
J	0.2	0.2	0.3	0.3	0.5	0.7	97.8
K	13.1	3.0	2.9	2.5	2.4	3.5	72.6
L	14.0	1.7	0.5	0.8	0.7	3.1	79.1
M	0.9	0.6	0.6	0.7	1.2	2.4	93.5
Control (Ground U_3O_8)	0.0	20.5	16.7	15.3	10.9	8.3	28.3

---

[a] Particle size by sonic sifter method.

Slow release of oxalate ion in a homogenous acid solution through hydrolysis of dimethyl oxalate was considered as a technique to improve particle size distribution of the uranous oxalate. Methyl oxalate was added as a 0.4M solution to a stirred uranous ion solution at ambient temperature. A slow hydrolysis reaction over four hours did not result in complete precipitation of uranous oxalate as evidenced by a green supernate. The precipitate was filtered and the solution filtrate was heated to 50°C. This resulted in complete precipitation of the uranium salt. The uranous oxalate precipitates were combined and calcined to U_3O_8. The particle size distribution of the U_3O_8 prepared by this method did not change significantly (Sample M) with respect to U_3O_8 prepared from direct-strike oxalic acid precipitation of uranous oxalate.

Particle size distribution of uranous oxalate-based U_3O_8 measured by the Coulter Counter method (Figure 11) closely matches the particle size distribution of T-101 aluminum powder. However, the size distribution is much lower than T-108 aluminum powder which represents the optimal size distribution for the PM process. Therefore, no further studies were made of uranous oxalate precipitation for this program.

Uranous Formate

Attempts were made to prepare uranous formate, $U(HCOO)_4 \cdot nH_2O$, by adding concentrated formic acid to uranous solution. A light green uranium solid was recovered at ∿70% yield by filtration. X-ray diffraction patterns revealed that the solid was an amorphous formate salt; no distinguishable crystalline peaks were observed which could be attributed to uranous formate.[10] Table 11 summarizes the preparative conditions for the amorphous formate salt and the measured particle size distributions of the calcined U_3O_8. Size distribution matched poorly with that of the control sample because too many large particles were present.

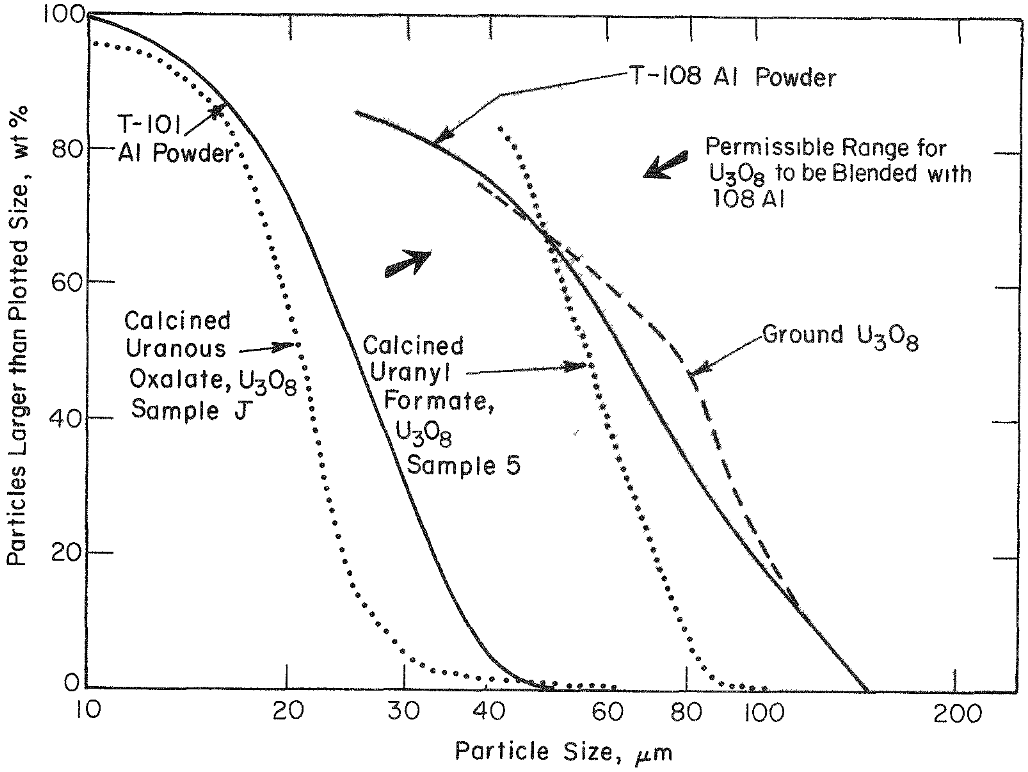

FIGURE 11. Coulter-Counter-Measured Particle Size Distribution of Calcined U_3O_8 Prepared from Uranous Oxalate. (Calcined uranyl formate distribution by sonic sifter.)

TABLE 11

Preparation Conditions for Uranous Formate and Particle Size Distribution of Calcined U_3O_8 Product

Sample	*Formic Acid Addition Rate*	*Powder Moisture*	*Calcining Rate to 400°C*	*Calcining Rate to 800°C*
N	Rapid	Air dried	-	Slow
P	Rapid	Air dried	-	Slow

Sample	*Particles in Size Range, wt %*[a]						
	>150 μm	*105-150 μm*	*88-105 μm*	*74-88 μm*	*53-74 μm*	*44-53 μm*	*<44 μm (Fines)*
N	81.2	5.5	2.0	1.9	2.9	2.1	4.3
P	82.1	3.4	1.0	5.3	6.8	0.0	1.2
Control (Ground U_3O_8)	0.0	20.5	16.7	15.3	10.9	8.3	28.3

---

a. Particle size by sonic sifter method.

Scale-up for preparation of large quantities of uranous formate would be difficult because the formic acid denitration reaction would have to be well controlled to maintain uranium as U(IV). Uranous ion is reoxidized to uranyl ion during rapid denitration of the solution. No further studies on preparation of the uranous formate salt were made for this program.

EXPERIMENTAL

Formic Acid Concentration

All formic acid solutions were prepared from commercially available, technical grade (90%) formic acid. Total free acid concentration was determined by titration with sodium hydroxide.[18] In some cases, absolute formic acid concentration was determined by a redox titration procedure with potassium permanganate.[18] The correction to the total free acid concentration in the technical grade acid was determined to be approximately two volume per cent by this procedure. Gas chromatographic analysis also showed approximately two volume per cent acetic acid as a contaminant.

Uranium Concentration

Absolute uranium concentrations of standard solutions were determined by a colorimetric determination of the uranyl thiocyanate complex. Most other uranium solution analyses were made by neutron activation analysis with a ^{252}Cf source. Absolute uranium concentration by this method was determined by reference to a standard solution. Depleted uranium was used in all tests described in this report.

Calcination Procedures

The prepared uranium salts were calcined in air in a muffle-furnace. Several samples were calcined by raising the temperature to 400°C at the maximum heating rate of the furnace (approximately 10°C per minute, holding at 400°C for 2 to 3 hours, and/or rapidly increasing temperature to 800°C and holding for 4 hours. This procedure is referred to as the rapid calcining rate in Tables 7, 9, 10, and 11. Some uranyl formate samples in Table 7 were calcined by heating slowly at about 0.5°C per minute through two temperature ranges (160 to 200°C and 350 to 400°C) and then rapidly to 800°C. The specified temperature ranges correspond to dehydration of uranyl formate monohydrate and decomposition of uranyl formate, respectively, as determined by thermogravimetric analysis. The slow calcining procedure described for other uranium salts in Tables 9, 10, and 11 generally involved heating the sample at approximately 3°C per minute to either 400°C or 800°C.

Several samples were stirred during calcining by modifying the furnace to accept a motor driven quartz glass paddle stirrer. Slow stirring speeds of $\sim$5 rpm were used to determine whether particle agglomeration could be reduced reproducibly by mechanical agitation during conversion to U_3O_8.

Particle Size Measurement

The particle size distribution of the uranium salts and calcined oxides were determined either by sonic sifter analysis, by mechanical sieving analysis, or by the Coulter Counter method.

Sonic Sifter

The apparatus consists of several sieves of decreasing mesh size (range bracketed by 100 mesh to 325 mesh U. S. standard sieves). A powder sample is vibrated for fifteen minutes by a vertical oscillating column of air and repetitive mechanical pulse. The weight of oxide retained by each sieve is used to calculate the weight per cent of particles in a given mesh size range.

The sonic sifter procedure is the preferred method for determining particle size distribution because it is one of the methods currently used for determining size distribution of ground U_3O_8 in the PM process. However, mechanical sieving is more convenient, and results by that method generally agree well with sonic sifter data (Table 8).

Mechanical Sieving

The particle size distribution is determined by mechanically vibrating the powder through specified sieves (60, 100, and 325 mesh U. S. standard) with an autoshaker and weighing the powder retained by each sieve.

Coulter Counter

The Coulter Counter method is a standard technique for measuring particle size.[19,20] To use this method all particles larger than 62 μm (+230 mesh) are separated from the powder to be measured. The remaining fine powder is ultrasonically dispersed in an electrolyte solution before determining the particle size distribution. The Coulter Counter data then are adjusted to include the particle size distribution of the particles larger than 62 μm as determined by sonic sifter sieving.

The Coulter Counter method has the advantage of measuring the particle size distribution below the 44-μm limit (-325 mesh) of the sieving methods. The Coulter Counter data were generally in agreement with sieving data over the size ranges where data overlap occurred. This indicated that any particle agglomerates were not breaking down into smaller particles during the ultrasonic dispersion procedure for sample preparation.

ACKNOWLEDGMENTS

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