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ASPECTS OF DENSITY MANIPULATION
IN FABRICATION OF MIXED
(U, Pu) OXIDE FUEL PELLETS

M. J. Barr

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OF MIXED (U, Pu) OXIDE FUEL PELLETS

M. J. Barr

ABSTRACT

Density control in mixed oxide [(U, Pu)O₂] fuel pellets can be achieved by several ceramic processing techniques. Binder-lubricant (hydrocarbon) additions, calcination of blended oxides, and ball-milling parameters were evaluated with respect to degree of density change and modification of microstructure. Binder-lubricants evaluated included Carbowax, Sterotex, methyl cellulose, polyvinyl alcohol, and Acracowax. Calcination of blended oxides was done in air and in nitrogen at temperatures up to 1000°C. Mixing-grinding experiments evaluated the effect of time, techniques, and grinding media on density, homogeneity, and impurity level.

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ASPECTS OF DENSITY MANIPULATION IN FABRICATION
OF MIXED (U, Pu) OXIDE FUEL PELLETS

M. J. Barr

INTRODUCTION

Production of large quantities of mixed oxide $[(U, Pu)O_2]$ fuel to specific densities requires an investigation of factors influencing sintered pellet density. Density control in ceramic materials can be achieved using any of several processing techniques such as hydrocarbon addition, raw material modification, and sintering (or firing) temperature variation. This paper will evaluate factors affecting sintered density in mixed oxide $(U_{0.75} Pu_{0.25})O_2$ pellets using two of the aforementioned processing techniques. Various binder-lubricant (hydrocarbon) additions and two powder modification operations (calcination and ball milling) were evaluated with respect to their effect on density and microstructure. The sintering temperature and time were $1675 \pm 25^\circ C$ and 2 to 4 hours, respectively.

Many hydrocarbons act as both a binder and a die lubricant. Each hydrocarbon evaluated is specifically classified in this report according to its effect on the pressability of powders. The binder-lubricants selected were those commonly used in mixed oxide processing.

Calcination of blended oxides is a material treatment useful for removing excess moisture or volatile matter and for modifying particulate properties of starting materials. Blended uranium and plutonium oxide powders were calcined in air or in nitrogen at temperatures to $1000^\circ C$. The effects of calcination on powder, green pellet, and sintered pellet properties were determined by measuring tap density, surface area, green pellet density, pellet ejection pressure, sintered pellet density and percent diameter shrinkage. All test groups were sintered concurrently at $1675^\circ C$ for 2 hours.

Powder ball-milling variables such as time, media type, and technique were evaluated against changes in sintered pellet density, microstructure, and homogeneity. Various source raw materials were used to determine relative effects. All test groups were sintered at 1675°C using the same furnace and sintering cycle.

SUMMARY

The addition of pore-forming binder-lubricants such as polyvinyl alcohol, Sterotex, methyl cellulose and Acrawax was found to be an effective method of controlling sintered pellet densities in the 85 to 95 percent of theoretical density range. Density control over a smaller range (± 2 to 4 percent) was obtained by varying pressing and preslugging pressures. Calcination of blended oxides and mixing-grinding control appear promising for density control in the 90 to 95 percent of theoretical density range. Sintered pellet micrographs revealed differences in microstructure resulting from variations in milling and binder-lubricant type and percent addition.

EXPERIMENTAL PROCEDURE

BINDER-LUBRICANT ADDITION

Binder-lubricant additions (with the exception of methyl cellulose and Acrawax) were made to a blended and milled master batch of mixed ($\text{U}_{0.75} \text{Pu}_{0.25}$) O_2 powder. The UO_2 had been produced via the ammonium diuranate process. The PuO_2 was obtained from direct calcination of plutonium nitrate [considered a candidate PuO_2 source for mixed (U, Pu) oxide fuel]. A detailed characterization of both powders can be found in BNWL-1441.⁽¹⁾ The two powders were initially blended in a twin shell blender, then dry ball-milled 42 hours. Binder-lubricants were added by

hand either to wet slurry or by layering (multiple passes through a 20 mesh screen) and vigorous shaking. All powder test groups were pressed using a hand operated hydraulic press at 20,000 or 40,000 psi and sintered at approximately 1675°C for 4 hours.

Methyl cellulose and Acrawax additions were made to batches containing calcined oxalate source PuO_2 and either 93 percent enriched (U^{235}) or ceramic grade normal UO_2 . The relative effect of the binder-lubricant addition on density and microstructure can be observed through comparison with standard test groups.

CALCINATION OF BLENDED OXIDES

Ceramic grade normal UO_2 and calcined oxalate source PuO_2 were blended in a twin shell blender and dry ball-milled 12 hours. Powders were calcined in air or in nitrogen at 600, 800, and 1000°C. Pellets were pressed at 25,000 or 50,000 psi using a hand-operated hydraulic press. All pellet test groups were sintered at one time at 1675°C for 2 hours.

BALL-MILLING PARAMETERS

Ball-milling time, grinding media type, and the power charge-to-ball ratio were varied with raw materials of several sources. Homogeneity (determined by alpha-autoradiography) and sintered density were evaluated as a function of milling time and conditions. Milling conditions evaluated included:

- Twin shell mixing with subsequent wet slurry mixing
- Twin shell mixing with subsequent 8 and 20 hour dry milling
- Dry milling for 8, 20, and 40 hours
- Wet slurry milling for 2, 4, 8 and 16 hours using tungsten carbide (WC) cylinders.
- Wet slurry milling for 1, 4, 4, 8 and 16 hours using alumina (Al_2O_3) cylinders.

Test groups were pressed using a hand operated hydraulic press, then sintered at approximately 1675°C. Batch size and material variations are discussed later.

DISCUSSION OF RESULTS

BINDER-LUBRICANT ADDITION

The majority of binder-lubricant additions were made to a single blended and milled batch of mixed oxide powder. The results are summarized in Table 1 and in graphical form in Figure 1. Each binder-lubricant system evaluated is discussed as follows.

Milled Only. Milled powder was pressed using only a thin film of butyl stearate applied as a lubricant to the die cavity. The green pellet had adequate handling strength and edges appeared good. Approximately 10 seconds of dwell-time at pressure was used to completely outgas the pellets. The sintered density of approximately 94-1/2 percent TD defines the base for comparison. Figure 2 shows the appearance and microstructure of sintered pellets from Group 1 (milled only). The 500X micrograph in Figure 2 shows well-formed grains about 10 microns in diameter with small pores on grain boundaries. The larger interconnected microcracks which appear to pass through grains are believed the result of cooling stresses. Smaller microcracks evident within grains may be the result of second phase or of compositional differences (plutonium rich and low O/M areas). Light gray areas are grain pull-outs or voids filled with mounting resin.

Carbowax* Additions. Carbowax 20M was added to the milled powder in 1, 3, and 5 wt% quantities. The binder-lubricant was added as solution to obtain a wet slurry that was dried at 70°C and granulated through a 20 mesh screen before pressing.

* Carbowax 20M produced by Union Carbide Corporation

TABLE 1. Binder-Lubricant Effect on Mixed Oxide Green and Sintered Densities

Group	Binder-Lubricant System	Green Density,		Sintered Density, (a)	
		20,000 psi	40,000 psi	20,000 psi	40,000 psi
1	No Binder--no preslug	62.67	65.43	94.76	94.29
2	1% Carbowax--wet slurry	63.44	65.08	93.62	93.04
3	3% Carbowax--wet slurry	64.77	66.15	94.08	93.59
4	5% Carbowax--wet slurry	64.06	65.52	93.12	93.38
5	No Binder--20,000 psi preslug	64.18	66.54	94.55	94.23
6	No Binder--40,000 psi preslug	64.35	66.64	93.77	93.91
7	No Binder--60,000 psi preslug	64.82	66.76	92.66	94.31
8	1/4% PVA--wet slurry	62.40	65.53	94.42	94.73
9	1/2% PVA--1% Butyl-Stearate	63.48	66.32	93.49	93.21
10	1/2% PVA--3% Butyl-Stearate	64.22	66.54	93.70	94.17
11	1/2% PVA--5% Butyl-Stearate	65.22	66.96	93.49	93.81
12	1% PVA--wet slurry	58.74	62.06	90.67	90.94
13	3% PVA--wet slurry	57.77	61.12	85.03	86.27
14	5% PVA--wet slurry	56.73	60.09	79.83	81.79
15	0.3% Sterotex after 20,000 psi preslug	62.62	65.11	93.50	93.97
16	1% Sterotex--no preslug	60.41	63.01	90.90	90.57
17	3% Sterotex double 20,000 psi preslug	56.45	58.20	77.64	77.29
18	1/4% Methyl Cellulose--dry	62.79	65.11	93.50	93.18
19	1% Methyl Cellulose--dry	60.04	62.69	90.67	90.45
20	3% Methyl Cellulose--dry	54.84	57.38	81.24	80.85

(a) Percent of theoretical density based on 11.09 g/cm^3 and not corrected for O/M ratio.

EFFECT OF BINDER-LUBRICANT ADDITION ON SINTERED DENSITY

FIGURE 1. Effect of Binder-lubricant Addition on Sintered Density

10X

500X

FIGURE 2. Micrographs of Pellets Fabricated
Using Milled Only Powder

Carbowax acts both as a binder and a die lubricant so separate lubrication of the die surface was not necessary. Pressure stabilization (complete outgassing) was obtained after about 7 seconds dwell. Green pellet appearance, edges, and handling strength appeared good. Data in Table 1 indicate that both green and sintered density appear highest at the 3 percent addition level. The addition of Carbowax appears to adversely effect sintered density by about 1 to 1-1/2 percent. Figure 3 shows the appearance and microstructure of sintered pellets from Group 3 (3 percent Carbowax addition). The 10X micrograph in Figure 3 indicates that the addition of Carbowax encourages the formation of open porosity, (compare the 10X micrographs in Figure 2 with that in Figure 3). The 500X micrograph in Figure 3 shows a high density region (between large pores) with relatively few pores at grain boundaries. The grains are about 20 microns in diameter. The ability of Carbowax to aid compaction through inter particle lubrication may be recognized by comparing 500X micrographs in Figures 2 and 3.

Preslug With No Binder. Milled powder was prepressed without binder to 20,000, 40,000 and 60,000 psi and the resulting pellets broken and sized by passing granules through a 20 mesh screen. The preslugged powder was then pressed at 20,000 or 40,000 psi, using only a thin film of butyl stearate on the die body. Green pellet appearance and strength were fair. However, pellet edges were susceptible to chipping. Data in Table 1 indicates that preslugging has little effect on green density. A consistent decrease in sintered density was observed when powder prepressed at high preslug pressures was pressed at 20,000 psi. The preslug pressures used did not appear to affect the sintered density of pellets pressed at 40,000 psi. Figure 4 shows the appearance and microstructure of sintered pellets from Group 7 (no binder--60,000 psi preslug). Preslugging to relatively high pressures (40,000 to 60,000 psi)

10X

500X

FIGURE 3. Micrographs of Pellets Fabricated
Using 3% Carbowax

10X

500X

FIGURE 4. Micrographs of Pellets Fabricated
Using no Binder, 60,000 psi Preslug

produces many granules that remain unbroken when compacted at lower pressures (15,000 to 20,000 psi). During sintering, these granules develop into regions of high density surrounded with interconnected voids and microcracks. The 10 and 500X micrographs in Figure 4 depict the extensive microcracks typical of preslugged (to high pressure) powder.

Polyvinyl Alcohol* Additions. All polyvinyl alcohol (PVA) additions were made using a wet slurry mix. The slurry was dried at 70°C and granulated through a 20 mesh screen. PVA is an excellent binder but has little lubricating effect. The die cavity was wiped with butyl stearate lubricant when powders containing 1/4, 1, 3 or 5 wt% additions of PVA were pressed. Butyl stearate was also added in 1, 3, or 5 wt% quantities to a basic batch containing 1/2 wt% PVA. Powder containing 1/2 percent PVA plus various additions of butyl stearate required essentially no dwell time and were the best appearing of all pellet groups produced. Figure 5 shows the appearance and microstructure of a sintered pellet from Group 13 (3 percent PVA), and Figure 6 shows a pellet from Group 10 (1/2 percent PVA plus 3 percent butyl stearate). The binding ability of PVA and the fact that it is a poor particle lubricant is evident in the micrographs shown in Figure 5. The extensive open porosity perpendicular to the direction of pressing force (10X micrograph) is indicative of poor intergranule lubrication, with the granules themselves being well bonded. The 500X micrograph in Figure 5 is of a dense area within a granule. Large resin filled voids are evident at the upper right corner and left edge of the micrograph.

Figure 6 includes micrographs of a pellet containing 1/2 wt% PVA plus 3 wt% butyl stearate--a good lubricant. The sintered density (93.5 percent theoretical) and microstructure compare well with pellets made using milled only powder (Figure 2) and made using 3 percent Carbowax (Figure 3).

* Polyvinyl alcohol produced under the trade name "Evanol" by E. I. duPont de Nemours, Inc.

10X

500X

FIGURE 5. Micrographs of Pellets Fabricated
Using 3% Polyvinyl Alcohol

10X

500X

FIGURE 6. Micrographs of Pellets Fabricated Using
1/2% Polyvinyl Alcohol Plus 3% Butyl Stearate

Sterotex* Additions. Sterotex powder was screened through a 100 mesh screen before mixing with milled and/or preslugged mixed oxide powder. The powder was preslugged at 20,000 psi before adding Sterotex at the 0.3 and 3 percent level. The 1 percent addition was added directly to the milled powder. Table 1 shows that the 0.3 wt% level (Group 15) green densities are comparable to Group 1. Dwell time necessary for pressure stabilization was less than 1 second. Sintered densities appear about 1/2 to 1 percent less than in Group 1. Sterotex is also a pore former and additions of 1 and 3 wt% lowered the sintered density by about 4 and 17 percent, respectively. Appearance and microstructure of sintered pellets produced using Sterotex (Group 15 and 16) are shown in Figures 7 and 8, respectively. The 10X micrograph in Figure 7 shows a relatively dense (93.5% theoretical density) pellet with well distributed porosity. The 500X micrograph shows this porosity to be interconnected by a series of microcracks. The structure is similar to but less severe than that shown in Figure 4, (no binder, 60,000 psi preslug). The addition of Sterotex to preslugged powder evidently improves granule-to-granule lubrication which results in improved compaction and relatively fewer microcracks.

In additions of 1 wt% or greater, the ability of Sterotex to form pores (with a lowering of sintered density) becomes evident. Both 10 and 500X micrographs in Figure 8 show larger pores than micrographs in Figure 7. The percent of theoretical density of the pellet shown in Figure 8 was about 90.6 percent.

Methyl Cellulose** Additions. Methyl cellulose powder was screened through a 100 mesh screen and added to as-milled powder (no preslug). Pellet green strength and appearance was good and edges appeared sharp. Both green and sintered densities

* Sterotex supplied by Capital City Products Company, Columbus, Ohio

** Methyl cellulose supplied by Fisher Scientific, Inc.

10X

500X

FIGURE 7. Micrographs of Pellets Fabricated
Using 0.3% Sterotex

10X

500X

FIGURE 8. Micrographs of Pellets Fabricated
Using 1.0% Sterotex

were affected by methyl cellulose additions with the 1/4, 1, and 3 wt% additions lowering the sintered density by about 1, 4, and 14 percent, respectively. Methyl cellulose is similar to Sterotex in that both possess lubricating and binder qualities. The appearance and microstructure of sintered pellets produced using methyl cellulose additions (Groups 18 and 19) are shown in Figures 9 and 10, respectively. The 10X micrographs in Figure 9 and Figure 10 shows the porosity induced through addition of methyl cellulose to be well distributed and similar to that formed with Sterotex. The 500X micrograph shows fewer microcracks and one can infer that a large percentage of the pores are closed. The 500X micrograph in Figure 10 indicates a pore structure similar to that shown in Figure 8--large pores interconnected by a series of microcracks.

Acrawax C* Addition. Quantities of Acrawax C were added to a 12 hour dry ball milled (Al_2O_3 cylinders) blend of Eldorado Normal UO_2 and 700°C calcined oxalate-source PuO_2 . As the raw material source, milling treatment, and sintering characteristics of this powder are different from the powder used in the aforementioned binder-lubricant studies, control groups containing no binder and 3 wt% Carbowax (wet slurry) were also prepared for comparison. Test pellets were pressed at 30,000 psi and sintered at 1650°C in argon--8% hydrogen for 4 hours. Table 2 lists green pellet ejection pressure, green density, and sintered density data.

The green pellet appearance of pellets containing Acrawax was very good. Lower ejection pressures indicate that Acrawax is a good die lubricant. Green and sintered densities indicate that percentages larger than 0.3 percent affect density to some

* Supplied by Glyco Chemicals Inc., 51 Weaver Street, Greenwich, Connecticut

10X

500X

FIGURE 9. Micrographs of Pellets Fabricated
Using 0.25% Methyl Cellulose (Dry)

10X

500X

FIGURE 10. Micrographs of Pellets Fabricated Using 1.0% Methyl Cellulose (Dry)

TABLE 2. Effects of Acrawax Addition on Mixed Oxide Pellet Properties

	No Binder	3% Carbowax	<u>Acrawax</u>		
			<u>0.3%</u>	<u>1%</u>	<u>3%</u>
Ejection Pressure at 30,000 psi Pressing Pressure (psi)	4400	4400	3600	3000	2200
Green Density at 30,000 psi Pressing Pressure (% TD)	50.14	51.28	49.18	48.36	46.83
Sintered Density (% TD)	93.61	92.42	92.58	88.34	83.04
Sintered Pellet Taper (mils)	2.0	1.5	1.5	1.0	1.0
Percent Diameter Shrinkage	20.0	19.5	19.9	19.2	18.9

NOTE: Percent of theoretical density is based on 11.09 g/cm^3 and is not corrected for binder content or O/M ratio.

degree. Figure 11 shows the porosity type and distribution of pellets containing 0.3, 1.0, and 3.0 wt% Acrawax. Porosity is essentially closed with few interconnecting microcracks. Additions of 1.0 and 3.0 wt% decrease density through the formation of closed pores with the number and average pore size increasing with higher weight percent additions.

Carbon Residue

The quantity of carbon remaining in sintered pellets from selected groups was also determined. Table 3 shows that essentially all hydrocarbon added plus the 250 ppm carbon present in the raw powder was removed (to the detectable limit ~ 50 ppm) during sintering.

Summary of Binder-Lubricant Addition Experiments

As-milled mixed oxide powders generally feed poorly into semiautomatic presses and the powder condition must be modified

10X

0.3% Acrawax

250X

10X

1.0% Acrawax

250X

10X

3.0% Acrawax

250X

FIGURE 11. Micrographs of Pellets Fabricated Using Acrawax

TABLE 3. Carbon Analysis of Sintered Pellets

<u>Group</u>	<u>Binder-Lubricant System</u>	<u>Carbon, ppm</u>
1	Milled Only	<50
3	3% Carbowax--wet slurry	<50
4	5% Carbowax--wet slurry	<50
11	1/2% PVA--5% butyl-stearate	<50
12	1% PVA--wet slurry	<50
13	3% PVA--wet slurry	<50
14	5% PVA--wet slurry	<50
17	3% Sterotex double 20,000 psi preslug	80
20	3% methyl cellulose--dry	60
--	0.3% Acrawax	60
--	1.0% Acrawax	<50
--	3.0% Acrawax	<50

in some manner. The formation of granules by preslugging or binder addition is a useful technique; however, granule size and technique used will affect processing time, pressing efficiency, and green and sintered pellet physical properties to some degree. Table 4 compares the average sintered density, pellet uniformity (min-max diameter), and percent diameter shrinkage of the majority of groups tested. Comparison of the average diameter variation in Table 4 shows that batches containing no binder with preslugged powder (Groups 5, 6, and 7) were the most uniform followed by batches containing small quantities of methyl cellulose (Group 18), Sterotex (Groups 15 and 16), and PVA (Group 8). Higher percentages of PVA (Groups 13 and 14) lead to severe diameter variation. The variation in these groups is believed the result of firmly bonded granules and poor intergranule lubrication.

The effect of various binder-lubricants on sintered density is also shown in Figure 1. Generally, all binder-lubricants evaluated had some effect on sintered density. Small amounts (1/4 to 1/3 percent) of Sterotex, methyl cellulose, and Acrawax

TABLE 4. Binder-Lubricant Effect on Mixed Oxide Sintered Pellet Properties

Group	Binder-Lubricant System	Average Sintered Density (a)	Average Diameter Variation (mils)		% Diameter Shrinkage	
			20,000 psi	40,000 psi	20,000 psi	40,000 psi
1	Milled Only	94.52	1.3	1.2	13.6	12.4
2	1% Cartowax--wet slurry	93.33	1.3	2.2	13.5	12.7
3	3% Carbowax--wet slurry	93.83	1.2	1.5	13.4	12.6
4	5% Carbowax--wet slurry	93.25	1.1	1.2	13.8	13.2
5	No Binder--20,000 psi preslug	94.39	0.7	0.5	13.0	12.0
6	No Binder--40,000 psi preslug	93.84	0.3	0.7	12.7	11.8
7	No Binder--60,000 psi preslug	93.48	0.3	0.9	12.1	11.7
8	1/4% PVA--wet slurry	94.57	1.1	0.8	13.8	12.5
9	1/2% PVA--1% butyl stearate	93.35	1.5	1.5	13.5	12.3
10	1/2% PVA--3% butyl stearate	93.93	1.5	1.3	13.4	12.5
11	1/2% PVA--5% butyl stearate	93.65	1.5	2.2	13.0	12.6
12	1% PVA--wet slurry	90.80	2.2	2.1	15.0	13.8
13	3% PVA--wet slurry	85.65	4.1	4.7	14.2	12.5
14	5% PVA--wet slurry	80.81	5.1	6.5	13.8	12.2
15	0.3% Sterotex after 20,000 psi preslug	93.73	0.5	1.0	13.4	12.5
16	1% Sterotex--no preslug	90.73	0.6	0.6	14.0	12.5
17	3% Sterotex double 20,000 psi preslug	77.46	2.0	2.4	15.7	11.2
18	1/4% methyl cellulose--dry	97.34	1.0	0.5	14.4	12.5
19	1% methyl cellulose--dry	90.56	1.0	1.2	14.0	12.8
20	3% methyl cellulose--dry	81.04	1.0	1.0	13.9	12.5

(a) Percent of theoretical density is based on 11.09 g/cm³ and is not corrected for O/M ratio.

as well as larger percentages of Carbowax and PVA-butyl stearate combination decreased sintered density by about 1 percent theoretical. The addition of 1 wt% of Acrawax, PVA, Sterotex, or methyl cellulose decreased sintered density by about 4 percent and 3 wt% additions of PVA, methyl cellulose (wet), or Acrawax decreased sintered density approximately 10 percent.

A review of sintered pellet micrographs shows that Sterotex, Acrawax, and methyl cellulose decrease density via a "space filling" effect whereby a void is formed when the binder lubricant is driven off. PVA affects density by forming hard granules which compact poorly because of a lack of intergranule lubrication. Small quantities (<1/2 percent) of binder lubricants can be considered as pressing aids with benefits in areas of compaction, green pellet ejection, and green strength exchanged for a small decrease in sintered density.

CALCINATION OF BLENDED OXIDES

Several characteristics were measured to determine the effect of blended oxide calcination on particulate properties. Tap density, B.E.T. surface area, green density of pellets pressed at 25,000 and 50,000 psi, and pellet ejection pressure are presented in Table 5. The decrease in ejection pressure with 800 and 1000°C calcination temperature indicates a morphological change in the powder. This change is also supported by higher green densities in Groups 6 and 7. The lower densities evident in Groups 3 and 4 are the result of U_3O_8 formation during the air calcination. The percent of theoretical density quoted was not corrected for this effect (theoretical density of U_3O_8 is 8.3 g/cm^3).

Table 6 contains sintered pellet data. The similarity in sintered densities obtained with forming pressures of 25,000 and 50,000 psi for Groups 1 and 2 is consistent with previous experience with pellets formed from as-milled or as-mixed powders. The differences in sintered densities obtained as a result of

TABLE 5. Effects of Blended Oxide Calcination on Powder and Green Pellet Characteristics

Group	Treatment	Tap Density, g/cm ³	Surface Area, m ²	Green Density, ^(a)		Ejection Pressure,	
				25,000 psi ^(b)	50,000 psi ^(b)	25,000 psi ^(b)	50,000 psi ^(b)
1	Vee Blended Only	1.6	6.4	47.50	53.21	3600	6100
2	12 hr. Dry Ballmill	2.9	10.5	51.61	56.19	3600	6100
3	600°C Air Calcine	2.9	4.4	46.31	51.10	2800	5300
4	1000°C Air Calcine	2.5	6.1	49.07	52.58	2200	3300
5	600°C-N ₂ Calcine	3.3	<1.0	50.86	56.08	3600	7200
6	800°C-N ₂ Calcine	3.2	1.0	55.19	59.37	2200	3900
7	1000°C-N ₂ Calcine	3.9	<1.0	66.45	69.75	1100	1900
8	600°C Air Reactivation	3.1	<1.0	60.69	64.09	1400	3300

(a) Percent of theoretical density is based on 11.09 g/cm³ theoretical is not corrected for nonstoichiometry or binder percentage.

(b) Cold forming pressure

**TABLE 6. Effects of Blended Oxide Calcination
on Sintered Pellet Characteristics**

Group	Treatment	Diameter Variation, (max-min in mils)		Sintered % TD, (a)		Δ Sintered, % TD (a)	% Diameter Shrinkage,	
		225,000 psi ^(b)	50,000 psi ^(b)	25,000 psi ^(b)	50,000 ^(b)		25,000, psi ^(b)	50,000 psi ^(b)
1	Vee Blended Only	3.0	2.0	89.2	88.9	-0.3	19.5	16.4
2	12 hour Dry Ball Mill	2.0	2.0	91.8	91.8	0.0	18.6	16.3
3	600°C Air Calcine	0.7	0.2	89.1	91.7	2.6	21.4	19.4
4	1000°C Air Calcine	0.5	0.7	91.0	93.2	2.2	18.9	18.1
5	600°C--N ₂ Calcine	1.0	1.0	87.1	91.3	4.2	18.8	16.8
6	800°C--N ₂ Calcine	0.3	0.2	86.4	90.2	3.8	15.6	14.9
7	1000°C--N ₂ Calcine	ND ^(c)	ND	72.6	76.4	3.8	4.35	4.50
8	600°C Air Reactivation	ND	ND	72.2	76.7	4.5	7.44	7.61

(a) Percent theoretical density is based on 11.09 g/cm³ as theoretical and is not corrected for O/M ratio. The O/M ratio of all pellet groups was approximately 1.95.

(b) Cold forming pressure

(c) No measurable difference

the two forming pressures (Groups 3 through 8) indicate that sintered density is affected by forming pressure when blended powders are calcined. This effect varies with the calcining temperature and is believed due to granule aggregation or pre-sintering and the effect of pressing pressure on those aggregates.

Micrographs of sintered pellets (Figures 12 and 13) show that calcining atmosphere affects sintered pellet microstructure. Figures 12 and 13 indicate that calcination of blended powder (milled but not preslugged) to 600°C or higher produces granules or aggregates that maintain their identity through subsequent compaction and sintering. Granule identity is more obvious in sintered pellets using powder calcined in nitrogen. The U_3O_8 formed during air calcination is believed a contributor to improved sinterability (compare Group 4 sintered density with Group 7 sintered density in Table 6) and more uniform microstructure (compare micrographs of sintered pellets from Groups 4 and 7). Recalcination of Group 7 powder in air (observe Group 8 data) did not modify granule characteristics sufficiently to affect either sintered density or microstructure. Micrographs of Group 8 sintered pellets (not shown) were essentially identical to those from Group 7 pellets.

In general, the effects of calcining blended oxide are dependent upon the temperature and atmosphere used. Data in Table 5 also indicate that:

- Calcining at 1000°C in air has much less effect on the final sintered density than calcining at 1000°C in nitrogen.
- A 600°C recalcining in air of powder calcined in N_2 at 1000°C did not change the sintered densities.
- A calcining temperature of about 800°C in nitrogen appears optimum to obtain densities near 90% theoretical density.
- Surface area and green density data indicate that particulate properties of $(U_{0.75}Pu_{0.25})O_2$ powders are significantly changed by 800°C or greater calcining temperatures.

Group 2 - 250X

Group 2 - 500X - Etched

As-Ball Milled

Group 3 - 250X

Group 3 - 500X - Etched

600°C Air Calcination

Group 4 - 250X

Group 4 - 500X - Etched

1000°C Air Calcination

FIGURE 12. Micrographs of Pellets Fabricated Using As-Ball Milled Powder and Powder After Air Calcination

Group 5 - 250X

Group 5 - 500X - Etched

600°C Nitrogen Calcination

Group 6 - 250X

Group 6 - 500X - Etched

800°C Nitrogen Calcination

Group 7 - 250X

Group 7 - 500X - Etched

1000°C Nitrogen Calcination

FIGURE 13. Micrographs of Pellets Fabricated Using Powder After Nitrogen Calcination

- The diameter variation (taper or hourglassing) is significantly reduced with calcination. The decrease in diameter variation and increase in green densities may be the result of aggregation and improved packing efficiency during compaction.

BALL-MILLING PARAMETERS

Effect on Sintered Density

Experiments involving ball-milling time, grinding media type and quantity used UO_2 and PuO_2 powders from several sources. Generally, UO_2 and PuO_2 powders were initially blended in a twin shell blender and further mix-milled in a rubber-lined ball mill. The mix-milling operation was usually done dry; however, wet slurry milling was also evaluated. Experiments were designed to determine the effect of mixing and grinding conditions on sintered pellet homogeneity, density, and microstructure. Table 7 summarizes the data.

The term "wet milling" in Table 7 is used to describe a condition where a ball mill is loaded to a weight ratio of grinding media to powder charge of between 2 and 4. The term "wet mixing" describes a condition where five to seven large (3/4 inch diameter) tungsten carbide cylinders are used with varied quantities of powder. In both situations, water equivalent to approximately one-third of the powder weight would be added to the mill.

Data in Table 7 show that twin shell blending and wet mixing produce sintered pellets between 88 and 90% of theoretical density. The difference in grinding efficiency of Al_2O_3 cylinders (density of 3.8) and WC cylinders (density of 15.6) is really apparent when Groups 2I, J, K and L are compared with Groups 2E, F, G and H. Wet grinding produces sintered densities 2 to 4 percent greater than equivalent dry grinding time (compare Groups 2E, F, G and H with Groups 2B and 2C).

TABLE 7. Green and Sintered Density Versus Mixing-Grinding Treatment

Group	Material Source	Treatment	% Theoretical Green Density ^(a)	% Theoretical Sintered Density ^(a)
1	Burned Plutonium Metal and United Nuclear UO ₂			
1A		2 hour twin shell blend (dry)	55	90
1B		Wet mix with Carbowax	56	89
2	Calcined Plutonium Oxalate and Eldorado UO ₂			
2A		2 hour twin shell blend	50	90
2B		8 hour dry ball mill (WC)	55	93
2C		20 hour dry ball mill (WC)	57	94
2D		4 hour wet mix with Carbowax	54	93
2E		2 hour wet mill (WC)	52	90
2F		4 hour wet mill (WC)	53	94
2G		8 hour wet mill (WC)	54	97
2H		16 hour wet mill (WC)	56	96
2I		1 hour wet mill (Al ₂ O ₃)	52	88
2J		4 hour wet mill (Al ₂ O ₃)	53	90
2K		8 hour wet mill (Al ₂ O ₃)	53	91
2L		16 hour wet mill (Al ₂ O ₃)	54	93
3	Calcined Plutonium Nitrate and Eldorado UO ₂			
3A		4 hour wet mill (Al ₂ O ₃)	53	90
3B		10 hour wet mill (Al ₂ O ₃)	54	92
4	Calcined Plutonium Oxalate and 93% Enriched UO ₂			
4A		8 hour dry mill (WC)	65	93
4B		20 hour dry mill (WC)	68	95
4C		40 hour dry mill (WC)	68	95
4D		40 hours dry + 4 hours wet (WC)	67	96

(a) Green and sintered density and based on a theoretical density of 11.09 g/cm³ and are not corrected for binder content or O/M ratio. Pressing pressure was 40,000 to 50,000 psi, except for Group 4D (30,000 psi).

Effect on Impurity Level

Analyses of milled powder show that contamination from grinding media is related to grinding efficiency. Table 8 shows that wet milling with WC media added excessive quantities of tungsten into the powder. Aluminum and tungsten impurity levels after dry milling with WC* and wet milling with Al_2O_3 are acceptable.⁽²⁾

TABLE 8. Contamination by Grinding Media

<u>Milling Time, hours (wet)</u>	<u>Impurity Level (a)</u>	
	<u>Aluminum, ppm</u>	<u>Tungsten</u>
0	20	0
1	50	Not Determined
2	50	0.24% (2400 ppm)
4	100	2.1%
8	200	3.6%
16	500	5.3%

(a) The media to powder charge ratio was not constant and increased with the increase in time.

The excessive tungsten pickup is a result of the high ratio of grinding media weight-to-powder charge weight. Standard practice is to fill ball-mill jars to 40 or 50 percent of their volume with grinding media. Sufficient powder is then added to cover the media. This "rule-of-thumb" produced a media-to-powder charge weight ratio of 5/1 to about 12/1 at the 16 hour level (the procedure was to remove a portion of powder at specific times while maintaining the same quantity of grinding media). The media-to-powder charge ratios used for Al_2O_3 evaluation were controlled from 1/1 to a maximum of 5/1. Additional wet-milling-experiments with WC indicated that impurity pickup is considerably

* Data not shown.

reduced when low media to powder ratios ($<3/1$) are used, and the wet slurry is relatively thick. (No viscosity values are available.)

Microstructure of pellets sintered to about 90 percent theoretical density is shown in Figures 14 (milled with Al_2O_3 media) and 15 (milled with WC media). The micrographs indicate that sintered pellet microstructure is influenced by media type, with larger grains produced when powder is milled with Al_2O_3 . The WC impurity may act as a grain growth inhibitor; however, the grain size appeared relatively insensitive to milling time. Sintering conditions were indentical.

Effect on Homogeneity

Milling efficiency and/or time will also effect sintered pellet homogeneity. Figure 16 shows the variation produced with no milling (twin-shell blend only), 8 hour dry mill, and 20 hour dry mill. This series of alpha-autoradiographs indicates that moderately good homogeneity can be obtained with 8 hours of dry ball milling. The effect of wet milling on homogeneity can be seen by comparing Figure 16 with Figure 17. Figure 17 indicates that excellent homogeneity can be obtained in a relatively short time using the wet-milling-technique.

10X

500X

FIGURE 14. Micrographs of Pellets Fabricated
After 4 Hours Wet Milling Using
 Al_2O_3 Media

10X

500X

FIGURE 15. Micrographs of Pellets Fabricated
After 2 Hours Wet Milling Using WC Media

Twin Shell Blender

Dry Ball Milled
8 Hours

Dry Ball Milled
20 Hours

FIGURE 16. Effect of Dry Milling on Mixed Oxide Homogeneity

2 Hour Wet Slurry Ball Mill
WC Media

4 Hour Wet Slurry Ball Mill
 Al_2O_3 Media

FIGURE 17. Effect of Wet Milling on Mixed Oxide Homogeneity

CONCLUSIONS

The following conclusions are drawn from this study:

1. The addition of a pore forming hydrocarbon is an effective technique for density control within the 85 to 95 percent theoretical density range. The addition of about 1 wt% of polyvinyl alcohol, Methocell, Sterotex, or Acrawax lowers the theoretical density of ball-milled powder by about 4 percent of theoretical density.
2. Calcination of blended oxides in nitrogen can be used for density control on the 85 to 90 percent theoretical density range.
3. Mixing-grinding control can be used to control densities in the 89 to 90 percent theoretical density range. However, the range of control and density obtained is sensitive to starting raw material characteristics.
4. Wet milling generally produces a higher sintered pellet density and superior homogeneity per unit time than dry milling; however, impurity introduction when wet milling with WC media may become excessive.
5. Sintering 2 to 4 hours at 1650°C in Ar-8% H₂ effectively removes carbon to approximately the 50 ppm level.

RECOMMENDATIONS

Variations in processing equipment, source and consistency of raw materials, and process batch size will also affect sintered density. The techniques discussed herein may still be applied. However, the base sintered density and degree of change will be affected by the aforementioned variables. Additional process experiments using production materials and processing equipment are suggested to determine the extent and controllability of density change.

Sintered pellet microstructure and porosity size and distribution are modified by processing variations. When variations in density are desired, the effect on microstructure and porosity must be considered.

The wide range of microstructures and porosities possible with normal processing (including density control) may affect thermal conductivity, gas retention and release, pellet swelling, diffusion rates, and possibly pellet integrity. In view of this, the effect of microstructure and porosity on fuel pellet performance must be taken into consideration in property evaluations and design requirements.

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