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ON THE
CHARACTERIZATION OF UO_2 POWDERS

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SUMMARY

A variety of UO_2 powders are being studied to determine the relationships existing between the physical and chemical properties of the powders and their sinterability.

During this quarter the main effort has been directed towards correlation of the particle size distribution of the powders with the sintered density of pellets. Particle size distribution measurements have been made on the virgin powders, ball milled powders and repulped green compacts. These measurements are related to the sintered densities of pellets.

The pressure applied during the green forming step of pellet production is shown to have a varied and considerable effect on particle size distribution.

I. INTRODUCTION

This report is the Fourth Quarterly Report on the Characterization of Uranium Dioxide Powders. It presents the progress made by United Nuclear Corporation under Contract AT-(40-1)-2699 for the period July 10, 1961 to October 10, 1961 (Report issued January 20, 1962). A broad spectrum of UO_2 powders are being characterized by physical and chemical means. The relationships that exist between the powder properties and ceramic performance are being investigated.

During this quarter the main effort has been directed toward a correlation of UO_2 powder particle size with the sintered density of pellets prepared from the powders. The change in powder sinterability brought about by ball milling is related to the change in the particle size distribution of the powders. The pressure applied during the green forming step of pellet production is shown to have a considerable effect on particle size distribution. The sintered density of pellets is compared with the particle size of pressed and reculped powders.

II. PARTICLE SIZE DISTRIBUTION AND SINTERABILITY OF UO_2 POWDERS

A. The Particle Size Distribution of the Virgin Powders

Particle size distribution measurements for twelve UO_2 powders in the virgin or as-produced state⁽¹⁾ were given in the last Quarterly Report. A qualitative correlation between the particle size distribution of the powders and sinterability was demonstrated.

B. The Effect of Ball Milling on Particle Size Distribution and Sinterability

Work has now been completed for particle size distribution on the powders after wet ball milling (twenty-four hours in acetone, air dried at room temperature). The range of 1 to 6 microns has been covered by means of a gravity sedimentation technique previously described⁽²⁾. A tabulation of these data, including the densities of pellets prepared from the oxides, is given in Table I.

(1) Detailed preparation procedures for the UO_2 powders are given in the Second Quarterly Report, Period Ending April 10, 1961. A schematic outline is included in the Appendix of the present report.

(2) Method described in Third Quarterly Report, Period Ending July 10, 1961.

TABLE I

PARTICLE SIZE DISTRIBUTION FOR UO_2 POWDERS VS. SINTERED PELLET DENSITIES

Type Oxide	Weight Percent Less Than Diameter (μ)						Pellet Density Geom.-g/cc
	1.0	1.5	2.2	3.0	4.3	6.0	
I (as-produced)	38	58	80	91	94	96	10.30
II (as-produced)	62	67	73	76	80	82	9.14
IIA (as-produced)	--	78	82	85	87	90	10.25
III (as-produced)	43	47	53	58	65	74	9.32
IIIA (as-produced)	45	58	77	94	98	98	10.65
IV (as-produced)	--	45	64	82	95	98	10.43
V (as-produced)	19	24	32	43	56	70	9.76
VI (as-produced)	44	48	53	60	68	79	9.58
VII (as-produced)	86	87	88	91	92	94	10.28
VIII (as-produced)	56	62	69	75	79	84	10.44
IX (as-produced)	33	38	46	53	64	74	8.57
X (as-produced)	33	38	46	54	64	71	8.26
I (after ball milling)	64	82	93	96	98	98	-
II (after ball milling)	69	79	83	92	96	99	9.96
IIA (after ball milling)	77	83	88	94	97	99	10.55
III (after ball milling)	56	65	76	85	93	98	10.51
IIIA (after ball milling)	68	78	90	98	100	100	10.67
IV (after ball milling)	56	70	84	92	98	97?	10.69
V (after ball milling)	47	53	73	85	95	99	-
VI (after ball milling)	42	54	74	82	93	98	10.44
VII (after ball milling)	81	84	87	90	92	95	10.58
VIII (after ball milling)	62	69	78	86	92	96	-
IX (after ball milling)	56	65	77	87	95	100	10.32
X (after ball milling)	51	62	76	87	96	99	10.11

Figure No. 1 shows the effect of ball milling on both the particle size distribution and the sinterability. Uranium dioxide powders, Types II, IX and X, in the virgin state were ceramically dead, i.e., pellet densities were only 79% to 83% of theoretical. After ball milling these powders gave pellets that were 91% to 94% dense. It is noted that the weight percent less than 6 micron correlates rather well with the sintered densities of the pellets.

A qualitative prediction of the ceramic performance can be made from the particle size distribution curve of an oxide regardless of the powder history. In Figure No. 2 four relatively active uranium dioxide powders are shown to give similar distribution curves. The four oxides differ not only in preparation method, but in treatment after preparation, i.e., Types I and IIIA were ceramically active as produced and IX and X were made active only after prolonged ball milling.

C. Particle Size Distribution in the Sub-Micron Range

Particle size measurements by gravity sedimentation techniques become less accurate at the low end of the range and the method is not usually used below one micron. Centrifugal sedimentation methods greatly reduce the settling time and thus avoid the adverse effects of convection currents and diffusion on sub-micron particles. Such methods are useful in the range 0.1 - 1 micron.

A centrifugal sedimentation method described by Boyd⁽³⁾ was used to study the sub-micron particle size distribution of the UO_2 powders. As described in Boyd's procedure, the diameter of the particles is calculated using the Svedberg-Nichols equation together with corrections based on Oden's method of tangential intercepts.

No relationship was found between particle size distribution of powders in the range 0.1 - micron and sinterability. It was concluded that particle size distribution measurements made by gravity sedimentation (i.e., 1 to 10 micron range) afforded sufficient information. Studies in the sub-micron range were discontinued.

III. EFFECT OF PRESSING PRESSURE ON UO_2 POWDER CHARACTERISTICS

A. Experimental

In order to study the effect of the cold compacting step on powder characteristics, the twelve UO_2 lots under study were pressed and repulped as follows:

(3) C. M. Boyd, H. P. House, and Oscar Menis, "Analytical Chemistry in Nuclear Reactor Technology," TID-7568 (Pt. 3), April 1, 1959.

Fig. No. 1 Particle Size Distribution for UO_2 Powders (Before and After Ball Milling).

Fig. No. 2. Particle Size Distribution of UO_2 Powders (Comparison of Active As-Produced Powders With Dead Powders Activated by Ball Milling)

Green pellets were pressed, without binder, to the same pressures to be used later in the cold pressing step for the final sintered pellets. The die was lightly dusted with Esterotex lubricant to obtain a more equal distribution of pressing pressure and better punch release. These fragile pellets were repulped by dispersing a slurry containing about 70 grams of the pressed powder in 150 ml of water using a low speed Waring Blender for five minutes. The slurry was then dried for several days at 45°C. The soft lumps from the dried slurry were broken down by lightly working the sample between two pieces of plate glass. The repulping process described is no more violent than the subsequent dispersion treatment used for particle size measurements and it is believed that the fundamental particle characteristics of the pressed powders are retained.

Particle size distribution measurements and Fisher Sub-Sieve size determinations were carried out on the pressed and repulped powder.

B. Discussion and Results

From the data presented thus far under Contract AT-(40-1)-2699, and also from related work that has been reported in the literature considerable effort has been extended towards correlating the virgin powder characteristics, e.g., surface area, oxygen to uranium ratio, particle size and DTA-TGA curves. Unfortunately, these relationships are, so far, not considered to be sufficiently definitive to adequately predict sinterability. This is true even in an ideal situation where the powder comes from the same general preparative route and the pellets are prepared under similar conditions. The relationships become even more obscure when attempts are made to predict the activities of powders made from widely differing preparation methods and the activities are defined by the sintered densities of pellets obtained from any one of a number of possible pelleting procedures.

Standing between the mass of virgin powder characteristics, on the one hand, and the final sintering operation on the other is the cold pressing operation. This compacting step (often 50 TSI or greater) has an unpredictable effect on the powder characteristics depending on the hardness and morphology of the agglomerates. Since the powder, after cold compacting, is actually what the sintering furnace "sees", it was deemed necessary at this point to investigate the powders after pressing and careful repulping. The pressed and repulped powder characteristics should be more directly traceable to sinterability than the characteristics of the virgin powders.

The effect of the green compacting pressure and particle size distribution is demonstrated by the curves depicted in Figure No. 3.

EFFECT OF GREEN PRESSING ON PARTICLE SIZE DISTRIBUTION

FIGURE NO. 3

The oxide powder Type V, produced by a single oxidation and reduction of sintered pellets, is ceramically dead. Powder Type IV, produced from sintered pellets by four oxidation-reduction cycles, is an active powder. The results obtained for the ball milled powders is included for purposes of comparison. The data show that the green compacting step does have a pronounced effect on the particle size. It is interesting to note that the prepressing had an even greater effect than ball milling on the particle size of the active powder. This effect was noted for the other active powders.

The twelve UO_2 powders under study have been pressed and repulped in the manner² described and particle size distribution measurements compared with the sintered densities of pellets prepared from the virgin powders. The data are given in Table II and depicted in Figure No. 4. The pellet densities are shown in decreasing order and their relation to the distribution curves is apparent. Only Type VIII gives a pressed powder particle size that does not fall in line with its relative position in the sinterability rankings.

Fisher Sub- Sieve size measurements show the appreciable effect of the pressing step on the agglomerate size. The results given in Table III compare the agglomerate diameters of the virgin powders, the pressed and repulped powders, and the ball milled powders. The Fisher Sub-Sieve size measurements of the pressed powders show a better correlation with the pellet densities than was obtained from measurements of the virgin powder.

TABLE II

PARTICLE SIZE DISTRIBUTION OF UO_2 POWDERS WHICH HAVE BEEN PRESSED AND REPULPED
VS.
PELLET DENSITIES

Type Oxide	Press- ing Pressure (TSI)	WEIGHT PERCENT LESS THAN DIAMETER (μ)							Pellet* Density, Geom.-g/cc
		10.4 μ	7.2 μ	5.8 μ	4.1 μ	2.8 μ	2.0 μ	1.4 μ	
I	41	--	--	--	100	99	95	87	10.30
II	53	95	92	90	86	82	78	70	9.14
IIA	66	97	94	93	91	89	86	82	10.25
III	62	100	98	91	82	74	68	62	9.32
IIIA	66	--	--	--	--	100	98	95	10.65
IV	50	--	--	--	100	98	92	84	10.43
V	50	94	85	81	69	58	47	36	8.76
VI	48	100	97	94	86	80	74	69	9.58
VII	50	96	93	91	90	88	87	85	10.28
VIII	50	98	92	90	84	80	75	70	10.44
IX	52	100	96	90	77	64	54	46	8.57
X	60	96	92	85	75	63	52	42	8.26

* Pellets prepared using 1% PVA, 0.5% Sterotex, dewaxing temperature 900°C under steam and H_2 , firing temperature 1650°C under cracked ammonia for four hours.

PARTICLE SIZE DISTRIBUTION OF REPULPED COMPACTS

FIGURE NO. 4

TABLE III
FISHER SUB-SIEVE SIZE DETERMINATIONS

Type UO ₂ Oxide	Virgin Powder (d ₅₀)	Pressed and Repulped Powder (d ₅₀)	Ball Milled Powder (d ₅₀)	Sintered* Pellet Density, Geom.-g/cc
I	0.88	0.79	0.85	10.30
II	6.10+	0.89	0.70	9.14
IIA	5.10+	0.65	0.54	10.25
III	2.58	0.86	0.73	9.32
IIIA	0.54	0.54	0.49	10.65
IV	0.96	0.82	0.77	10.43
V	2.27	2.10	0.95	8.76
VI	2.35+	1.03	0.75	9.58
VII	8.15+	1.90+	0.55	10.28
VIII	0.87+	0.76	0.49	10.44
IX	2.16	1.12	0.73	8.57
X	3.19+	1.19	0.70	8.26

*Pellets were prepared from a granulation of the virgin powders with 1% polyvinyl alcohol. They were pressed to a green density of 6.5 g/cc and fired in cracked ammonia at 1650°C for four hours.

+The values obtained for the agglomerate diameter of these powders did not level off to a minimum as the porosity setting was decreased to the practical limit of the apparatus.

OUTLINE OF PREPARATION METHODS*

UO ₂ TYPE		PREPARATION SCHEME			
I	UF ₆	<u>organic reduction</u> →	UF ₄	<u>pyrohydrolyze</u> Steam - H ₂ →	UO ₂
II	UF ₆	<u>super dense process</u> →	ADU	<u>reduction</u> cracked NH ₃ →	UO ₂
IIA	UF ₆	<u>dense process</u> →	ADU	<u>reduction</u> cracked NH ₃ →	UO ₂
III	UF ₆	<u>fluffy process</u> →	ADU	<u>reduction</u> cracked NH ₃ →	UO ₂
IIIA	UF ₆	<u>super fluffy process</u> →	ADU	<u>reduction</u> cracked NH ₃ →	UO ₂
IV	UF ₆	→ ADU →	UO ₂	→ sintered UO ₂ pellets → <u>oxidation-reduction cycle four times</u> →	UO ₂
V	UF ₆	→ ADU →	UO ₂	→ sintered UO ₂ pellets → <u>oxidation-reduction one cycle</u> →	UO ₂
VI	UO ₂ (NO ₃) ₂	<u>denitrate</u> →	UO ₃	<u>reduction</u> → UO ₂ → HF → UF ₄ → <u>pyrohydrolyze</u> steam - H ₂ →	UO ₂
VII	UO ₂ (NO ₃) ₂	<u>dense process</u> →	ADU	<u>reduction</u> cracked NH ₃ →	UO ₂
VIII	UO ₂ (NO ₃) ₂	<u>fluffy process</u> →	ADU	<u>reduction</u> cracked NH ₃ →	UO ₂
IX	UO ₂ (NO ₃) ₂	<u>pot denitrated</u> →	UO ₃	<u>reduction</u> cracked NH ₃ →	UO ₂
X	UO ₂ (NO ₃) ₂	<u>fluid bed denitrate</u> →	UO ₃	<u>reduction</u> cracked NH ₃ →	UO ₂

* Detailed procedures given in First Quarterly Report (Period Oct. 10, 1960 through Jan. 10, 1961).