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THE PREPARATION OF HIGHLY ENRICHED U_3O_8
FOR THE HIGH FLUX ISOTOPE REACTOR CORE

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METHOD OF PREPARATION

INTRODUCTION

Uranium fuel for the core of the High Flux Isotope Reactor (HFIR) was prepared in the form of a sintered U_3O_8 with a size range of 44 to 88 microns. The basic preparation method consisted of the precipitation of a solution of uranyl nitrate with hydrogen peroxide, followed by calcining and sizing operations. The process was essentially a batch-type operation utilizing laboratory-type equipment because of the geometry restrictions imposed by nuclear safety and the availability of the equipment from other oxide production programs. This report details the processing steps that were required to produce the material.

PROCESSING STEPS

Conversion of Uranium Metal Turnings to U_3O_8 and Dissolution in Nitric Acid

Uranium machine turnings were burned with oxygen to U_3O_8 in a water-cooled stainless steel burner. The construction material for the burner was Type 304L stainless steel, five-inch Schedule 40 pipe, with an overall length of 40 inches. The charge of turnings was limited to five kilograms. When burning was completed, the oxide was removed with a vacuum gulper system.

The U_3O_8 was dissolved in nitric acid to produce a concentration of approximately 250 grams of uranium per liter.

Precipitation of Uranyl Nitrate Solution with Hydrogen Peroxide

One kilogram of uranium as uranyl nitrate solution was transferred to the precipitator (Figure 1) and diluted to a concentration of approximately 8 percent. The pH of the solution was adjusted to 2.0 ± 0.1 with nitric acid or ammonium hydroxide.

Thirty percent hydrogen peroxide was added to the precipitator with sufficient ammonium hydroxide to control the pH at 2.0 ± 0.1 . The cooling water was adjusted to maintain temperature conditions in the range of $28 - 32^\circ C$. When the hydrogen peroxide no longer lowered the pH, an additional 500 milliliters was added and agitation continued for an additional 15 minutes.

The precipitated material was centrifuged in a Sharples Super Centrifuge and the cake was then transferred to platinum boats ($2''$ deep $\times$ $4\frac{1}{2}''$ $\times$ $8''$) (The peroxide filtrate contains a uranium concentration of 100 - 200 ppm and is economically recoverable.)

Calcining and Presizing

The boat of uranium peroxide (UO_4) was loaded into an electric resistance furnace and calcined for six hours at 800°C in an atmosphere of nitrogen. The boat contained approximately 500 grams of uranium.

The material was removed from the furnace in the form of agglomerated pieces and presized by rod milling and sieving to a size of 44 to 149 microns. The rod mill was a stainless steel container five inches in diameter by ten inches in length containing twelve 3/8-inch rods. The mills and sieves were limited to one-kilogram batches of U_3O_8 . Milling time was controlled at five minutes followed by a ten-minute sieving cycle in a standard laboratory eight-inch sieve. Syntron Vibrating Test Sieve Shakers were used for all sizing operations. The oversize oxide was recycled through the milling operation with the undersize being dissolved in nitric acid and recycled as feed for the peroxide precipitation step. A loss of approximately 5 percent was experienced in the sizing operation for the low-fire step.

Sintering and Final Sizing

Six kilograms of low-fired U_3O_8 (sized 44 to 149 microns) were loaded into a magnesium oxide crucible 5 1/2 inches in diameter by 9 1/2 inches high. The charge was placed in a Sentry Furnace (Figure 2) and heated in the ambient atmosphere at 1350°C for four hours followed with two hours at 1400°C . When the oxide had cooled to room temperature, it was milled and sized 44 to 88 microns with the same procedure as outlined for the low-fired material. A loss of approximately 30 percent was experienced in the sizing operation for the final product; however, the rejected material was also recycled as feed for the peroxide precipitation step.

The furnace used for this operation was Number 4 Sentry, 220-volt, single-phase resistance type with a power capacity of 22.5 kilowatts. A platinum lid was used to cover the crucible in the furnace.

SUMMARY

Sixteen kilograms of oxide were sampled as a batch after blending in an eight-quart Patterson-Kelley blender. A cross-blending operation was performed on nine to ten batch lots to provide good homogeneity of the oxide. A yield of 85 percent was experienced for the program when comparing the feed material with the product produced. Chemical and physical test data are detailed in the Appendix.

Figure 1. PRECIPITATION EQUIPMENT.

Figure 2. SINTERING FURNACES

APPENDIX

TEST DATA

Figure A-1 is a photomicrograph showing the physical shape of the U_3O_8 particles; Figure A-2 is a photomicrograph of a metallurgical specimen.

Table A-1 summarizes the chemical and physical data of the two blends of U_3O_8 .

Figure A-1. PHOTOMICROGRAPH SHOWING THE PHYSICAL SHAPE OF THE U_3O_8 PARTICLES (100X)

Figure A-2. PHOTOMICROGRAPH OF METALLURGICAL SPECIMEN SHOWING THE PHYSICAL CONDITION OF THE U_3O_8 PARTICLES. (100X)

Table A-1
CHEMICAL AND PHYSICAL DATA

	Blend 1	Blend 2
Uranium Content (wt%)	84.614	84.602
Isotopic Analysis (wt%)		
U-234	1.00	1.00
U-235	93.18	93.16
U-236	0.35	0.33
U-238	5.47	5.51
Surface Area (krypton BET determination - M^2/gm)	0.050	0.047
Density (toluene pycnometer - gms/cc)	8.23	8.24
UO_2 (X-ray diffraction - %)	< 1	< 1
Fluorine (ppm)	< 1	< 1
Spectrographic (ppm on U_3O_8 basis)		
Al	2	7
B	< 0.1	< 0.1
Ba	< 2	< 2
Be	< 0.01	< 0.01
Ca	< 10	< 10
Cd	< 0.1	< 0.1
Co	< 1	< 1
Cr	< 2	4
Cu	10	8
Fe	20	20
K	< 6	< 6
Li	< 0.2	< 0.2
Mg	3	8
Mn	< 1	< 1
Na	< 1	< 1
Ni	5	4
P	< 100	< 100
Si	< 10	< 10
V	< 1	< 1
Stoichiometry (by difference calculation)	U_3O_8 8.015	U_3O_8 8.021
Syntron Sieve Analysis (100- gram sample - %)		
+170	0.0	0.2
-170 +200	18.9	14.2
-200 +230	14.1	15.6
-230 +270	30.1	28.7
-270 +325	32.5	35.8
-325	4.4	5.5

The analytical data for the individual batches comprising Blends 1 and 2 are summarized in Tables A-2 and A-3.

Table A-2
BLEND 1
(Component Batches)

	Batch Number								
	169346	169349	169407	169410	169412	169414	169416	169422	169355
gms U/gm	84.6522	84.659	84.623	84.628	84.669	84.660	84.621	84.655	84.668
U-234	0.97	0.99	0.97	1.00	1.00	1.01	0.97	1.00	1.00
U-235	93.20	93.14	93.20	93.14	93.19	93.09	93.18	93.13	93.16
U-236	0.31	0.32	0.30	0.32	0.34	0.39	0.36	0.35	0.36
U-238	5.52	5.55	5.53	5.54	5.47	5.51	5.49	5.52	5.48
Al	< 1	2	3	6	1	3	4	3	1
B	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ba	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Be	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Ca	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Cd	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Co	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Cr	2	< 2	< 2	6	< 2	7	4	5	< 2
Ni	4	4	3	8	4	4	2	6	4
Fe	15	20	20	50	30	60	50	75	15
Cu	6	8	6	10	6	8	5	20	8
K	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6
Li	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Mg	< 2	5	15	15	8	30	3	10	6
Mn	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Na	1	< 1	< 1	2	< 1	< 1	< 1	2	< 1
P	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100
Si	< 10	< 10	12	12	< 10	10	< 10	< 10	10
V	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
F	< 1	< 1.4	< 1	< 1	< 1	< 1	< 1	< 1	< 1
UO ₂	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%
% -325	4.1	6.1	6.5	5.2	5.9	4.9	6.3	5.2	5.1
Density	8.23	8.23	8.25	8.23	8.24	8.25	8.25	8.26	8.26
Surface Area	0.049	0.049	0.048	0.051	0.049	0.052	0.051	0.055	0.056
Kgs U ₃ O ₈	16.3	16.2	16.2	16.6	16.6	16.6	16.5	16.5	16.6
Screen Size									
+170	0	0	0.2	0	0.5	0	0.2	0.2	0
-170 +200	21.4	17.3	15.7	9.0	25.5	18.5	18.4	18.8	13.0
-200 +230	20.8	19.3	24.0	20.4	18.6	18.1	21.8	19.7	21.9
-230 +270	14.6	15.7	12.5	18.0	13.7	15.6	13.6	17.5	14.4
-270 +325	39.1	41.6	41.1	47.4	35.8	42.9	39.8	38.6	45.6
-325	4.1	6.1	6.5	5.2	5.9	4.9	6.3	5.2	5.1

Table A-3
BLEND 2
(Component Batches)

	Batch Number									
	169348	169405	169408	169411	169413	169415	169350	169357	169359	169360
gms U/gm	84.672	84.682	84.657	84.703	84.637	84.698	84.656	84.606	84.653	84.676
U-234	0.96	0.95	0.99	0.98	1.00	1.04	0.99	0.94	1.01	1.01
U-235	93.19	93.16	93.18	93.18	93.12	93.09	93.15	93.17	93.12	93.16
U-236	0.31	0.27	0.30	0.32	0.35	0.36	0.34	0.33	0.36	0.31
U-238	5.54	5.62	5.53	5.52	5.53	5.51	5.52	5.56	5.51	5.52
Al	2	5	3	5	2	3	4	1	1	1
B	< 0.1	< 0.1	< 0.1	< 0.1	0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1
Ba	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2	< 2
Be	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01
Ca	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10
Cd	< 0.1	< 0.1	< 0.1	< 0.1	0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1
Co	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
Cr	< 2	4	< 2	6	4	4	5	< 2	2	2
Ni	5	8	3	6	4	6	6	5	2	2
Fe	15	30	30	55	80	60	75	25	40	45
Cu	8	7	6	10	25	6	15	10	4	4
K	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6	< 6
Li	< 0.2	< 0.2	0.3	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2	< 0.2
Mg	8	10	7	6	12	30	10	8	4	4
Mn	< 1	1	< 1	< 1	< 1	2	< 1	< 1	< 1	< 1
Na	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
P	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100	< 100
Si	10	15	< 10	10	< 10	< 10	< 10	15	< 10	12
V	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
F	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
UO ₂	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%	< 1%
% -325	4.4	5.4	7.9	8.4	5.4	6.0	6.3	4.9	4.1	4.1
Density	8.26	8.27	8.22	8.22	8.26	8.23	8.27	8.27	8.26	8.26
Surface Area	0.048	0.049	0.049	0.045	0.052	0.054	0.057	0.052	0.048	0.054
Kgs U ₃ O ₈	16.3	16.3	16.2	16.5	16.5	16.5	16.6	16.6	16.3	16.7
	Screen Size									
+170	0	0.2	0	0	0.2	0	0	0	0.1	0.1
-170 +200	20.0	24.8	18.3	10.3	17.7	16.3	12.3	12.6	21.0	18.8
-200 +230	19.3	17.0	19.3	22.2	20.6	20.5	19.6	15.7	11.8	14.7
-230 +270	14.9	14.6	13.9	15.3	14.8	13.5	16.2	27.8	29.2	28.0
-270 +325	41.4	38.0	40.6	43.8	41.3	43.7	45.6	39.0	33.8	34.3
-325	4.4	5.4	7.9	8.4	5.4	6.0	6.3	4.9	4.1	4.1