UNCLASSIFIED

OAK RIDGE NATIONAL LABORATORY

Operated By

UNION CARBIDE NUCLEAR COMPANY

UCC

POST OFFICE BOX P
OAK RIDGE, TENNESSEE

EXTERNAL TRANSMITTAL AUTHORIZED

ORNL
CENTRAL FILES NUMBER

CF-56-10-8

DATE: October 3, 1956
SUBJECT: Preparation of Standard OxideTO: Distribution
FROM: R. B. Gallaher and A. S. Kitzes

Photostat Price \$ 3.30

Microfilm Price \$ 2.40

Available from the
Office of Technical Services
Department of Commerce
Washington 25, D. C.

LEGAL NOTICE

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission

A. Makes any warranty or representation, express or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission to the extent that such employee or contractor prepares, handles or distributes, or provides access to, any information pursuant to his employment or contract with the Commission.

NOTICE

This document contains information of a preliminary nature and was prepared primarily for internal use at the Oak Ridge National Laboratory. It is subject to revision or correction and therefore does not represent a final report.

UNCLASSIFIED

420 001

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

PREPARATION OF STANDARD OXIDE

In order to facilitate correlation of the data obtained by the various groups associated with the HRP slurry program a certain set of conditions were specified for the preparation of a slurry which could be reproduced from time to time so that each group interested in working with thorium oxide would have available a similar material to use in relating their work with that done by other groups.

The following specifications were decided upon for the preparation of the "standard slurry".¹

1. The thorium oxide is to be prepared according to the procedure described in CF 56-1-50² and will meet the chemical and particle size analysis shown in Table I.
2. The powder is to be dispersed in distilled water at room temperature to give a slurry of 500 g Th/kg H₂O concentration.
3. This slurry is to be pumped 100 hours in the 200A loop at a temperature within the range of 150° to 200°C.

This report therefore covers only the preparation of the "standard slurry" according to the specifications set forth above. Included in the report are results of a few tests performed to determine the reproducibility of the specified method in preparing the "standard slurry".

Loop Operation

LO-12 oxide was used in preparing the "standard slurry". This batch of oxide was prepared from the oxalate precipitated from high purity thorium nitrate and fired at 800°C according to the recommended procedure.² The chemical composition of the oxide is shown in the first line of Table II.

TABLE I

SPECIFICATIONS FOR THORIUM OXIDE CHEMICAL ANALYSIS

(based on solids dried to constant weight at 200°C)

Th	87.2% minimum
CO ₃	0.3% maximum
SO ₄	100 ppm maximum
NO ₃	10 ppm maximum
Halides	10 ppm maximum
Fe-Cr-Ni(total)	50 ppm maximum
Si	10 ppm maximum
Al	10 ppm maximum
PO ₄	50 ppm maximum
Alkali metals	100 ppm maximum
Alkaline earths	1000 ppm maximum
Rare earths	50 ppm maximum

Particle Size Analysis 100% through 200 mesh screen

Size distribution from measurements of a 0.005 M Na₄P₂O₇ dispersion:

80% less than 10 microns

60% less than 4 microns

50% less than 2 microns

30% less than 1 micron

Nitrogen surface area: 15 to 20 m²/gm

Crystallite size by X-ray: 200 - 250 Å

UNCLASSIFIED

TABLE II

4

COMPLETE CHEMICAL COMPOSITION OF THORIUM OXIDES ON DRY BASIS

Sample	Th mg/g	Fe mg/g	Ni mg/g	Cr mg/g	Ti mg/g	SO ₄ mg/g	CO ₃ mg/g	Al mg/g	Si mg/g	Cu mg/g	Cl mg/g	F mg/g	PO ₄ mg/g	Mg mg/g	K mg/g	Na mg/g	Ca mg/g	Pb mg/g
LO-12*	873	<.005	<.005	<.005	--	<.10	2.2	.011	<.010	--	<.01	.04	<.020	.02	<.05	.12	<.05	<.02
200A-6-00**	865	.030	<.005	.016	<.02	.12	--	.04	<.01	<.005	<.01	<.01	<.02	<.01	<.03	<.03	<.05	<.02
200A-6-3***	867	.329	.058	.063	.06	<.10	1.8	.07	.022	<.005	.022	--	.15	<.01	<.03	<.03	<.05	<.02
200A-7-3***	870	.386	.070	.079	<.02	<.10	1.6	.11	.014	<.005	.028	.014	.04	<.01	<.03	<.03	<.05	<.02
200A-8-3***	863	.310	.056	.060	.08	<.10	0.56	.12	.01	<.01	<.01	<.01	.02	.03	<.03	<.03	<.05	<.02

* Original oxide.

** Slurry charged to loop. Oxide dried at 200°C to constant weight before analysis made.

*** Sample of slurry circulated at 200°C for 100 hours. Oxide dried to constant weight before analysis made.

420 004

UNCLASSIFIED

Prior to charging into the loop, the oxide was wet screened through a 200 mesh screen and then blended for 24 hours in a baffled stainless steel drum with a Lightnin' Mixer. The slurry containing 34-1/2 kg of thorium oxide was then pumped into the loop through the pressurizer fill point. At the same time, water was pulsafed through the back of the pump to prevent slurry from getting into the bearings.

After charging the loop with slurry, water was pumped through the same opening until the liquid level in the pressurizer was 30 in. above the fill point giving a total wetted volume of 76 liters at room temperature. No difficulties were encountered in any of the loading operations.

The system was then checked for leaks with 1200 psi helium especially around the pump main flange since this joint was not seal welded for these low temperature runs.

If the pressure checks proved satisfactory and no leaks were found, 50 psig of oxygen was added and the pressurizer heaters turned on. Circulation was started and the loop heaters turned on when the system pressure reached 1000 psig.

The slurries were circulated at 200°C and 1400 psig for 100 hours; the purge flow to the back of the pump was maintained at 20 cc/min.

Samples were taken from the pump suction sampling station approximately 6, 24, 48 and 100 hours after the loop temperature reached 200°C. After 100 hours of circulation at 200°C, the loop was cooled to room temperature according to the recommended procedure. When the loop temperature dropped below 100°C and the system pressure decreased to approximately 500 psig two one-liter samples and one four-liter sample were drawn from the suction sample point. The slurry was then drained into a stainless steel drum and the loop was washed several times by circulating the supernatant liquid decanted from the slurry.

The pump and the loop were not disassembled between runs.

Preparation of "Standard Slurry"

Three batches of standard slurry were prepared in runs 200A-6, 200A-7 and 200A-8 by following the procedure just described. These runs will be described as a single run because of the similarity in operation. Differences, however, are pointed out when pertinent.

In each run, the loop temperature varied between 200° and 204°C during the 100 hours of circulation. The pump requirements varied slightly during the run. There was a 7 to 10% decrease both in the pump power and in the current requirements. The power decreased from about 11 to about 10 kw and the current requirements decreased from about 1.50 to about 13.9 amps during the 100 hours of operation at 200°C.

At the end of each run, the solids were easily drained from the loop. In run 200A-6, distilled water in addition to the supernatant liquid was used to fill the loop for the washing operations as there was insufficient supernatant liquid available from the first run for circulation during the washing operation.

In runs 200A-7 and 200A-8, only supernatant liquid from the run and the previous run was used in the washing operations. The slurry from each run was drained into a separate barrel and then all three batches were blended with a Lightnin' Mixer prior to distribution.

Results

Analytical data for the samples taken during each run are presented in Table III. In addition to chemical data, the operation conditions of the loop and the pump power requirements, recorded at the time the samples were taken, are also listed. Sample 200A6-00 represents the slurry which was charged to

UNCLASSIFIED

TABLE III

CIRCULATION OF ThO_2 SLURRIES AT 200°C WITH WESTINGHOUSE 200A PUMP

- a) Chemical Data
 b) Pump Requirements
 c) Loop Operating Conditions

CHEMICAL DATA												Pump Requirements			Loop Operating Conditions	
Sample	Time	Solids							Filtrate			amps	kw	Purge flow to back of pump cc/min.	Temp °C	Press psig
		Th mg/g Slurry	Fe mg/g Slurry	Ni mg/g Slurry	Cr mg/g Slurry	Ti mg/g Slurry	SO_4 mg/g Slurry	pH	pH	SO_4 ppm	Cond. $\mu\text{hos} \times 10^5$					
200A-6-00	0	450	0.016	<0.005	0.008	<0.02	0.065	--	--	--	0.76	--	--	--	--	--
-0	15.4	316	0.045	0.007	0.016	<0.02	<0.100	8.6	8.6	9	4.4	15.0	10.7	20	201	1400
-1	22.6	353	0.053	0.010	0.021	<0.02	<0.100	9.0	9.4	18	2.0	15.0	10.5	20	201	1400
-2	46.9	370	0.104	0.016	0.024	0.02	<0.100	9.8	9.7	<10	7.8	14.4	10.3	20	201	1400
-3	101.2	337	--	--	--	--	--	--	8.6	10	0.75	13.9	9.9	20	201	1400
200A-7-0	7.5	324	9.019	<0.005	<0.005	<0.02	<0.10	9.1	8.5	<5	--	15.5	11.3	20	200	1400
-1	26.0	357	0.052	0.006	0.012	<0.02	<0.10	9.8	9.1	<5	--	14.9	10.6	20	201	1400
-2	50.5	384	0.088	0.015	0.021	0.02	<0.10	8.8	7.0	<5	--	14.4	10.3	20	200	1400
-3	101.0	369	--	--	--	--	--	--	6.5	<5	--	13.8	9.9	20	201	1400
200A-8-0	7.5	393	0.023	<0.005	0.006	<0.02	<0.10	8.1	8.9	<5	2.8	15.4	11.1	20	200	1400
-1	25.4	410	0.048	0.015	0.009	<0.02	<0.10	8.0	7.9	<5	8.2	14.6	10.6	20	203	1400
-2	49.3	368	0.070	0.021	0.012	<0.02	<0.10	7.6	7.3	<5	1.4	14.6	9.8	20	200	1400
-3	101.3	388	--	--	--	--	--	--	5.6	19	4.5	14.2	10.0	20	200	1400

UNCLASSIFIED

the system at the start of each run. In addition, the results of the complete chemical analysis for this sample and for the samples, 200A6-3, 200A7-3 and 200A8-3, taken at the end of 100 hours of circulation are shown in Table II. These analyses were determined after the samples were dried at 200°C to constant weight.

Settling rates and settled bed densities for the three batches of standard slurry are shown in Table IV. Parts of the four-liter sample were used to obtain these data.

Particle size distributions were obtained from parts of the one-liter sample taken at the end of the run (200A6-F, 200A7-F and 200A8-F) for each batch of standard slurry and these data are shown in Table V. Two methods were used to determine the particle size distributions. In one method, the solids were dispersed in 0.005 M $\text{Na}_4\text{P}_2\text{O}_7$ with mild agitation. In the second method, the solids were dispersed with a Waring Blendor in xylene using oleic acid as the dispersant.

The particles were found to be spherical in the three batches of oxide, when examined under an optical microscope. The spheres varied in diameter from 8 to 30 microns, with an estimated average diameter of approximately 15 microns. Photographs of the spheres found in the slurry from 200A-7 are shown in Fig. 1.

Pseudo shear diagrams for the three batches of "standard slurry" are shown in Fig. 2. The data were obtained at room temperature using a tube 0.0985" in diameter and 8.031 feet long in the low temperature viscometer.⁴ These slurries exhibit a rather unique behavior in that the extrapolation of the data indicates that they have little or no yield stress. The maximum variations in the data are $\pm 5\%$ and, in part, these variations are the result of differences in the solids concentrations in the effluent from the viscometer tube.

TABLE IV

SEDIMENTATION DATA FOR "STANDARD SLURRY"

<u>Run</u>	<u>Settling Rate</u> <u>(cm/sec)</u>	<u>Settled Bed Density</u> <u>(g Th/kg H₂O)</u>
200A-6	0.22 $\pm$ 0.02	3970
200A-7	0.18 $\pm$ 0.02	3160
200A-8	0.13 $\pm$ 0.02	3100

TABLE V

SEDIMENTATION PARTICLE SIZE DISTRIBUTIONa) Solids Dispersed in 0.005M $\text{Na}_4\text{P}_2\text{O}_7$ with air sparging

Apparent Stokes Diameter Microns	Amount less than stated size (wt%)			
	200A-6-00**	200A-6-F***	200A-7-F	200A-8-F
25.60	95.5	96.3	99.0	98.3
14.75*	84.0	88.0	89.0	84.0
11.44*	73.5	80.0	79.5	70.0
9.57*	63.0	71.8	70.0	56.0
8.52*	52.5	63.5	60.5	42.0
7.70*	42.0	55.6	51.0	28.0
7.10	31.8	47.9	41.8	14.8
5.11	20.5	43.2	41.3	12.2
4.20	19.4	42.7	41.3	11.9
3.66	18.2	42.2	41.3	11.7
3.00	16.0	42.0	41.3	11.7
2.60	13.7	41.7	41.0	11.4
2.03	10.3	41.3	40.6	11.4
1.84	9.2	40.8	40.1	11.4
1.65	8.0	40.4	39.7	11.2
1.50	6.9	39.9	39.2	11.2
1.40	6.9	39.9	39.2	11.2
1.30	5.8	39.5	38.8	10.9
1.20	4.6	39.5	38.8	10.9
1.10	4.6	39.2	38.8	10.9
1.00	4.2	39.2	34.6	10.7
0.90	3.8	38.2	34.4	10.6
0.80	3.0	37.7	34.0	10.5
0.70	2.4	37.0	33.5	10.3
0.60		35.5	33.0	10.0

b) Solids dispersed in xylene with Waring Blendor

	Amount less than stated size (wt%)				
	7 μ	5 μ	3 μ	2 μ	1 μ
Screened 10-12	98%	87%	74%	55%	29%
200A-6-3	99	97	95	59	32
200A-7-3	98	96	89	81	61
200A-8-3	97	96	90	84	72

* Data interpolated by G. W. Leddicotte

** Material charged to loop

*** Part of one-liter sample taken at end of 100 hours circulation at 200°C

Fig. 1 Spherical Particles of ThO_2 Found in Run 200A-7.
Magnification - 800x

Fig 2. Pseudo-Shear Diagrams

Conclusions

From the results obtained so far, it appears that the three slurries prepared in runs 200A-6, 200A-7 and 200A-8 are nearly identical in chemical composition (Table II) and in physical appearance when observed under a microscope. In addition, identical pseudo shear diagrams were obtained for the three batches of slurry. On the other hand, the three batches of slurry do not appear identical if the sedimentation and the particle size data are compared.

REFERENCES

1. R. B. Korsmeyer, Letter to Slurry Program Committee, January 1, 1956.
2. W. E. Carr, Pilot Plant Preparation of Thorium Oxide, ORNL CF-56-1-50, (January 4, 1956).
3. D. G. Thomas, Personal Communication.
4. R. H. Nimmo, Letter to D. G. Thomas, July 17, 1956.