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Thorium-Uranium Oxide during Fiscal Year 1960
TO: F. L. Culler, Jr.
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ABSTRACT

Test quantities of thorium (approximately 3800 lb of thorium oxide and 3200 lb of mixed thorium-uranium oxide) were prepared during FY-1960 for members of the Reactor Experimental Engineering Division (REED). For preparation of thorium oxide, the calcination temperature was varied from 650 to 1600°C. The surface area of the fired oxide ranged from 0.5 to 25 sq m/g and the mean particle size ranged from 1 to 8 microns. For preparation of mixed thorium-uranium oxide, the calcination temperature was varied from 1050 to 1225°C. The mixed oxide contained either 0.5, 3.0 or 8.0 weight per cent of uranium as requested with a mean particle size of 2.5 microns. The over-all losses of thorium and uranium were 19.4 per cent and 18.3 per cent respectively.

Four 1400 lb batches of thorium nitrate were dissolved to prepare solutions containing 300-350 g/liter of thorium for solvent extraction studies in the Chemical Technology Division and 2100 lb of dry, recovered waste thorium oxide was supplied to the ORNL Fuel Cycle Program.

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1.0 INTRODUCTION

The thorium oxide facility was operated to prepare experimental quantities of thorium oxide and thorium-uranium oxide for testing in aqueous slurries in high temperature loops by the Reactor Experimental Engineering Division. Experimental sized 150 lb batches were prepared on request.

The major objective was to prepare an oxide for use in a slurry which possessed the best combination of physical and chemical properties for future use in the blanket of a breeder type homogeneous reactor. The slurry must retain these properties after many hours of circulation in the test loop and should be easily resuspended after a test loop shutdown.

Individual batches of oxide were prepared by altering the process conditions to yield a product possessing the properties specified in the request. Generally particle size, size classification, surface area, and the maximum permissible concentration of impurities were specified for thorium oxide. In addition, for mixed oxide the percentage of uranium was also specified. These specifications were changed for succeeding orders as the test data were evaluated.

2.0 EQUIPMENT, PROCESS, AND SPECIFICATIONS FOR OXIDE PREPARATION

A detailed discussion of the plant and equipment, process description and process variables may be found in ORNL-2583, and therefore only a brief description will be presented in this report.

With the exception of high temperature calcination, all of the process steps were performed in the thorium oxide facility, Building 2528. Prior to FY-1960, the preparation of thorium oxide and thorium-uranium oxide was carried out in the east end of Building 3019. The equipment was moved to Building 2528 in May and June of 1959. Henceforth in this report, the words "new facility" refer to Building 2528 rather than to the initial location of the thorium oxide preparation equipment in Building 3019. Thorium nitrate tetrahydrate and oxalic acid were dissolved in separate stainless steel tanks. The oxalic acid was added to the thorium nitrate with constant agitation. The precipitated thorium oxalate was digested at 95°C, cooled, pumped onto a filter bed, washed with demineralized water to remove impurities and then calcined to the oxide at a temperature of 650°C. The oxide was transported to a gas furnace building located north of Building 3019 where the oxide was calcined at any desired temperature up to 1600°C. The high temperature calcined oxide was returned to the thorium oxide facility for classification to remove particles greater than 10 microns. The classified material was dried, sampled and packaged for shipment to REED.

2.1 Plant and Equipment

The thorium oxide facility contains stainless steel tanks for thorium nitrate dissolution and oxalate precipitation, oxalic acid make-up and calcined oxide classification. The thorium oxalate precipitate was filtered on a 4 by 4 ft bed. The filtrate was withdrawn from the bed into one of two vacuum catch tanks and sent to waste. Storage and product carts were used to store oxide in Amersil trays. Pneumatic-type liquid level and specific gravity instrumentation was used for the make-up tanks.

A Nash Hytor pump provides a vacuum source and off-gas for the make-up tanks with the discharge connected to the building off-gas system. To prevent air-borne contamination buildup, the facility is equipped with a once-through ventilation system which provides a flow of 3700 cfm of air, or approximately eight building air changes per hour. The air enters the building through a set of steam coils and is exhausted through a stack above the building. The exhaust blower is preceded by a bank of six Model 1G-1000 Cambridge absolute filters which in turn are preceded by a bank of six Model 3A-95 Cambridge roughing filters to prevent the loss of any air-borne thorium to the outside. The off-gas for the hoods, glove boxes, etc., is provided by a small blower which exhausts to the building filter system previously described. Off-gas for the electric furnace is provided by a Sutorbilt rotary positive displacement pump designed with 10 in. of water pressure drop on the suction side. The discharge from the Sutorbilt blower also enters the plenum chamber immediately ahead of the roughing filters.

The thorium oxalate precipitation tank is equipped with cooling coils which are supplied with Freon from a York compressor. A temperature controller supplies Freon as required to maintain the contents of the precipitation tank at the desired temperature during the oxalic acid addition. This tank is also supplied with steam and water coils to permit digestion of the precipitated oxalate or for additional cooling capacity.

A separate waste system consisting of a 2000-gal tank equipped with an agitator and a 500-gal black iron caustic storage tank is located north of the thorium oxide facility. All liquid waste except waste lost to building floor drains may be pumped from the process vacuum catch tanks to the 2000-gal waste tank. The waste was neutralized with 50 per cent caustic, which also aided in settling the suspended waste oxide. The tank is equipped with a drain standpipe located 18 in. above the bottom of the tank. The neutralized supernate above the level of the standpipe may be drained by gravity to the settling basin with essentially no discharge of thorium and uranium to the ORNL waste system.

2.2 Thorium Oxide Process

In a typical run, two drums of thorium nitrate tetrahydrate containing 200 lb net each were charged into the thorium dissolution precipitation tank by means of a fork lift truck. The material was usually badly caked and had to be "dug out" of the containers through ports inside the charging hood. Enough water was used to provide 117 gal of a 0.7 M thorium nitrate solution. Approximately 180 lb of chemically pure oxalic acid was added to demineralized water in a separate tank to form 257 gal of 0.7 M oxalic acid. Enough acid was used to provide an 8-10 per cent excess of oxalate ion above the stoichiometric amount required. The acid was pumped into the thorium nitrate make-up tank at a controlled rate (to provide the desired particle size) through a pipe which entered just above the agitator. The temperature was controlled by means of both Freon and water cooling coils. After the thorium oxalate was precipitated, the material was digested for 6 hr at 95°C.

Following the digestion step, the material was cooled and pumped onto a 4 by 4 ft filter bed covered with Dynel cloth as the filter medium. After the bed had reached a depth of some 8 in., a slight vacuum was applied

to the underside of the filter to remove excess nitric acid, oxalic acid and water. The product was then given three 25-gal warm water washes before the final drying was allowed to take place. The bed of thorium oxalate was then loaded by hand into Amersil trays 16-3/4 in. by 13-3/4 in. by 1-3/4 in. deep. The second half of the thorium oxalate solution was then pumped to the filter and the procedure was repeated. Some 24 trays were recovered from filtration of each half of the solution. The trays were loaded onto stainless steel racks inside a 2 by 3 by 4 ft deep electric furnace. After being fired at 650°C for 4 hr the material was cooled and the trays were unloaded by hand into a closed product discharge cart with glove ports into double plastic bags each of which contained some 10 kg of oxide.

The electric furnace product was then transported by truck from Building 2528 to the gas furnace building north of Building 3019 for the high temperature calcination step. Inside a hood, the product was loaded into eight Taylor crucibles, each 9 in. tall and 6-1/2 in. ID. Since 400 lb of thorium nitrate provided enough 650°C oxide to fill some 30 crucibles each run required four firings of the gas furnace to calcine oxide at temperatures above 1000°C. After high temperature calcination, the product was removed from the crucibles and then loaded into new plastic bags.

The material was then returned to Building 2528 for classification. The material was charged into the initial classification tank where the pH was adjusted to 2.6 with 2.0 M oxalic acid. The classified product was collected in a Tolhurst 12 in. Center-Slung centrifuge. After some 8-10 kg of material was collected in the centrifuge, the material was unloaded by hand into Amersil trays for drying in the electric furnace. After drying for 4 hr at 650°C in the electric furnace, the material was cooled and unloaded as previously described.

2.3 Thorium-Uranium Oxide Process

The thorium oxide was prepared in the usual manner by adding a batch of chemically pure oxalic acid at the desired concentration to thorium nitrate at the flow rate and temperature designed to provide the requested particle size. Uranium was added to the 650°C calcined thorium by depositing basic uranyl carbonate on the thorium in a slurry.

Ammonium diuranate prepared at the Y-12 plant was used as the raw material source of uranium for this preparation. A quantity of ammonium diuranate sufficient to provide the desired uranium-thorium atomic ratio for a batch was dissolved in 10 per cent excess ammonium bicarbonate to form an ammonium uranyl carbonate solution. To this solution, made up to 200 gal in a 300-gal stainless steel tank, was added the thorium oxide. The resultant slurry was heated to boiling and maintained close to 100°C (98-99°C) until all of the uranyl carbonate had deposited on the thorium and the excess ammonium bicarbonate had decomposed.

After all the uranium had been deposited onto the thorium, the slurry was cooled and filtered. The filter cake was washed and calcined for 4 hr at 650°C in the electric furnace. The mixed oxide was then fired in a gas furnace where it was calcined at the desired temperature for 4 hr. After being cooled, the gas furnace product was classified to remove the over-

sized particles (10 microns and over). The final step after classification was to dry the product for 4 hr at 650°C. After analysis indicated that the product met specifications, the product was packaged and shipped to the requestor.

2.4 General Specifications Required

The general specifications required for acceptable 1600°C thoria were divided into three categories: chemical composition, particle size, and surface area.

Maximum concentration of the chemical impurities for 1600°C calcined thoria were as follows:

<u>Impurity</u>	<u>Concentration, ppm</u>
Carbonate	500
Nitrate	10
Sulfate	100
Phosphate	100
Silicon	100
Halides (F + Cl)	10
Iron + Chromium + Nickel	50
Lead	10
Magnesium + Calcium	100
Sodium + Potassium + Lithium	100

The average particle size was to be between 2.6 and 3.5 microns. Batches outside these limits were acceptable provided they could be mixed with other runs to give the appropriate average particle size. In addition the weight fraction larger than 5 microns for any individual run could not exceed 5 per cent, the weight fraction above 10 microns could not exceed 0.1 per cent and the weight fraction smaller than 1 micron could not exceed 5 per cent. The surface area as determined by nitrogen absorption measurements was to be below 1.2 sq m/g.

3.0 FACILITY OPERATION DURING FY-1960

Approximately 3800 lb of thorium oxide and 3200 lb of mixed thorium-uranium oxide were prepared during FY-1960. The facility was operated 24 hr/day, 5 days/week. The particle size of thoria prepared ranged from 1 to 8 microns and the mixed oxide particle size was normally 2.5 microns. The calcination temperatures for thorium oxide covered the range of 650 to 1600°C. The calcination temperatures for mixed oxide covered a much smaller range, 1050 to 1225°C. The over-all product recovery was 80.6 per cent for the thorium charged and 81.7 per cent for the uranium charged to the facility.

3.1 Preparation of Thorium Oxide

A total of 1551 lb of thorium oxide with a mean particle size of 2.9 microns and calcined to 1600°C was prepared in nine runs as part of one campaign. The product from only one of the nine runs, DT-95, completely met all specifications (Table 3.1).

The chemical composition requirement was the only category which was not met on all of the nine runs. Particle size and surface area were within specifications in all cases. The requirement that the sum of iron, chromium and nickel metallic ions not exceed 50 ppm proved to be the most difficult to meet, although only the product from DT-89 contained more than twice (120 ppm) the maximum concentration. The phosphate requirement of no more than 100 ppm was exceeded on only two runs, DT-89 and DT-86, with 115 and 160 ppm PO_4^{3-} respectively. The run, DT-86, resulted in a high nitrate content (> 10 ppm) in the product. In spite of the chemical impurities, all of this material was accepted by the Reactor Experimental Engineering Division for evaluation in the test loops.

Sixteen special requests for thoria were filled during the year (Table 3.2). Particle size and calcination temperature were specified for each

Table 3.2. Summary of the Results of Special Thoria Preparations

Run No.	Calcination Temperature, °C	Weight ThO_2 Produced, lb	Mean Particle Size, microns	
			Requested	Actual
DT-60	1050	115.7	2.5	3.6
DT-61	650	179.0	3.5	4.5
DT-65	650	182.5	1.0	2.1
66	650	39.0	-	4.4
DT-78-65	650	58.3	10	6.3
DT-78-14	1400	48.5	10	7.9
DT-83-65	650	85.9	0.5	1.1
DT-83-14	1400	100.1	0.5	1.3
DT-96	650	149.3	2.5	2.6
DT-99	650	104.7	2.5	2.6
DT-94	1600	149.3	2.5	2.5
DT-97	1600	169.8	2.5	2.7
DT-100	800	203.7	a	0.90 to 2.6
DT-101	800	131.8	10	6.5
DT-102	800	197.0	< 1	1.15
DT-103	-	181.3	a	0.77 to 3.8

a. Particle size range greater than normal between 5 per cent and 95 per cent.

Table 3.1. Summary of Data from a Single Campaign

Run No.	Mean Particle Size, microns	Surface Area, sq m/g	Impurities, ppm									Weight ThO ₂ Produced, lb
			CO ₃ , %	Mg + Ca	Fe + Cr + Ni	PO ₄	SO ₄	Si	Halides	Pb	NO ₃	
DT-85	3.10	0.69	<.02	21	60*	80	10	<10	<10	<10	<10	148.2
DT-86	2.95	0.66	<.02	6	70*	160*	15	<10	<10	<10	28*	185.6
DT-87	2.80	0.66	<.02	25	75*	60	<10	<10	<10	<10	<10	178.1
DT-89	3.25	0.53	<.02	13	120*	115*	<10	<10	<10	<10	<10	165.1
DT-90	3.40	0.62	<.03	54	60*	95	<10	<10	<10	<10	<10	196.1
DT-91	3.10	0.60	<.03	57	55*	95	<10	<10	<10	<10	<10	176.7
DT-92	3.0	0.59	<.03	50	75*	60	<10	<10	<10	<10	<10	172.3
DT-93	3.2	0.56	<.03	25	59*	95	<10	<10	<10	<10	7	160.4
DT-95	2.65	0.59	<.05	2	50	95	<10	<10	<10	<10	<10	168.6

*Over specifications, which were: mean particle size, 2.6-3.5 microns; surface area, < 1.5 sq m/g; CO₃, 0.05 per cent; Mg + Ca, 100 ppm; sum of Fe, Cr and Ni, 50 ppm; PO₄, 100 ppm; SO₄, 100 ppm; Si, 100 ppm; halides, 10 ppm; Pb, 10 ppm; NO₃, 10 ppm.

batch of thorium. The control of particle size was dependent on the thorium nitrate and oxalic acid concentrations, the rate of mixing of the reagents, the precipitation temperature, the degree of agitation, the method of strike, and probably other uncontrolled factors.

In the facility the degree of agitation and the method of strike could not be changed. Therefore the two principle variables used to control the particle size were the concentrations of thorium nitrate and oxalic acid and the rate of addition of oxalic acid to thorium nitrate. The precipitation temperature also was controlled to some degree; however, the heat removal capacity of the York compressor obtained from salvage was insufficient to maintain the temperature of the combining oxalic acid and thorium nitrate solutions at 20°C during the entire precipitation. A study of the control of particle size may be found in CF-59-1-101 dated January 22, 1959 by K. O. Johnsson and C. V. Ellison.

3.1.1 Preparation of Small Particles. To manufacture oxides with a particle size of 0.5-1 micron, 0.87 M oxalic acid and 0.87 M thorium nitrate were made up with the acid 8 per cent in excess of the stoichiometric amount required. The oxalic acid was added to the thorium nitrate at the maximum rate permitted by the equipment, 24 gpm at an initial thorium nitrate solution temperature of 20°C. Runs DT-83 and DT-102 were batches prepared in this manner. One-half of DT-83 was calcined at 650°C, which resulted in a classified product thorium with a mean particle size of 1.1 microns. The other half of DT-83, calcined for 4 hr at 1400°C, produced thorium with a mean particle size of 1.3 microns. DT-102, prepared six months later, using the same procedure and calcined at 800°C resulted in a classified thorium with a mean particle size of 1.15 microns. The initial run, DT-65, to produce a particle size of 1 micron resulted in a thorium with a mean particle size of 2.1 microns; however, the equipment at that time provided a maximum addition rate of only 9 gpm.

Direction of strike is another factor important to particle size. A direct strike is defined as the addition of oxalic acid into the thorium nitrate (normal procedure) and a reverse strike is the addition of thorium nitrate into the oxalic acid. A reverse strike, other variables remaining the same, should produce smaller particles. In general, agglomerates are formed in the reverse strike procedure which must be broken up to form true particles. Unless the agglomerates were broken up in the classification step, particle size analyses showed the apparent mean particle size to be larger than those formed in a direct strike. Due to the pressing need to operate the facility and the extra expense involved, the necessary additional piping was not installed in the new facility to allow a reverse strike on a pilot plant scale. Therefore, the effect of this particular variable on particle size control could not be tested on large scale operations.

3.1.2 Preparation of Large Particles. To prepare oxides with a requested mean particle size of 10 microns two variables, concentrations of the oxalic acid and the thorium nitrate and the oxalic acid addition rate into the thorium nitrate, were changed. The concentration of the raw materials was reduced to 0.5 M from 0.87 M and the addition rate of the oxalic acid was 1.5 gpm compared to 24 gpm required for small particle size thorium. The precipitation was made at 30°C rather than 20°C as another aid to insuring that large particles were precipitated. Run DT-78, made to

prepare thorium as described above with a mean particle size of 10 microns, resulted in particle sizes of 6.3 microns for one-half of the oxalate calcined at 650°C and 7.9 microns for the other half calcined at 1400°C. A repeat preparation, DT-101, resulted in thorium with a mean particle size of 6.5 microns for 800°C calcined thorium. From these studies of the preparation of both small and large sized particles it was concluded that desired particle sizes between 1 and 8 microns could be prepared with confidence in the results.

3.1.3 Preparation of Ceramic Grade Thorium. For ceramic grade thorium, a wide range of particle sizes was requested. Runs DT-100 and DT-103, typical examples of this type of preparation, were made with the oxalic acid and thorium nitrate at a concentration of 0.87 M. The initial rate of addition of oxalic acid was held at 8 gpm for 5 min at which time the rate was increased to the maximum of 24 gpm for approximately 15 min; the rate was gradually decreased to 2 gpm over the final 18 min required to complete the precipitation. The temperature of the thorium nitrate was 70°C and the temperature of the oxalic acid was 20°C immediately prior to the beginning of the strike. When the flow of oxalic acid was increased to 24 gpm, both the refrigeration coils and the cooling coils in the oxalate precipitation tank were placed in operation. The heat removal capacity of these coils was such that the initial solution temperature had dropped from 70°C to 43°C 9 min after the oxalic acid addition began.

Immediately following the completion of the acid addition, both the Freon to the refrigeration coils and the water supply to the cooling coils were shut off. The precipitated oxalate was allowed to digest for 45 min at a temperature of 43°C; the solution was cooled to 30°C, filtered, washed with room temperature demineralized water, and calcined for 2 hr at 800°C. Of the material prepared in Run DT-100, 95 per cent had a particle size of less than 2.6 microns and 5 per cent had a particle size of less than 0.9 microns. Similar values for Run DT-103, a repeat of DT-100, were 3.8 and 0.8 microns, respectively. For normal material (one specified mean particle size) for example DT-96, a 2.9 micron material, the particle size range in the 5 to 95 per cent fraction was from 1.7 to 4.0 microns. No results from loop tests with this material have been received.

3.1.4 Other Preparations. Run 66 was prepared to simulate a preparation made some months prior to the start of FY-1960. In this preparation, oxalic acid crystals were added by hand to the thorium nitrate solution. The thorium oxalate was digested for 1 hr at 70°C, filtered, and calcined at 650°C. Of the 100.5 lb of thorium initially present, only 33.5 lb of thorium as thorium oxide was recovered. Since there was no information available on previous runs of this type, the expected yield of oxide from this type of preparation was not known and no results of the testing of this material by the requestor were available.

The remaining orders were for particle sizes in the 2.5 micron range with calcination temperatures ranging from 650 to 1600°C. These particles were prepared by using the appropriate concentrations and flow rates to produce the desired particle size. As experience was gained on each run, the ability to produce the required particle size improved, especially for 2.5 micron material. The reasons for the inability to prepare less than 1 micron material have already been discussed.

3.2 Thorium Uranium Oxide

The term "regular mixed oxide" was defined by members of the Reactor Experimental Engineering Division as follows: "It will have a nominal particle size of 2.5 microns, a cut-off aimed at 5 microns and no measurable content of particles above 10 microns in size. The percentage of uranium to thorium will be on a weight percentage basis, the thorium oxalate prior to calcination will be digested for 6 hr at 95°C, and after the uranium is added to the pure thorium, the mixture will be calcined at the maximum temperature which does not produce sintering."^a The orders for mixed oxide were 0.5, 3 and 8 weight per cent of uranium and the original request from the Reactor Experimental Engineering Division was for a total of 3725 lb of mixed oxide.

By December 1, 1959, ten batches of mixed oxide had been prepared and shipped to the Reactor Experimental Engineering Division (Table 3.3).

Table 3.3. Mixed Oxide Prepared

Run No.	Mean Particle Size, microns		Surface Area, sq m/g	U, wt %	Th, wt %	Gross Wt., lb
	Requested	Actual				
MO-62	2.5	3.7	0.9	8.0	80.0	165.2
MO-63	2.5	3.6	0.9	7.4	80.4	175.3
MO-64	2.5	3.3	1.3	7.2	80.4	184.6
MO-67	2.5	2.2	2.1	2.6	85.3	140.7
MO-68	2.5	2.1	1.8	0.5	86.6	151.5
MO-69	2.5	2.3	6.3	0.5	87.5	177.5
MO-71	2.5	3.0	0.8	2.6	85.9	147.4
MO-72	2.5	2.8	0.9	2.5	85.6	159.2
MO-73	2.5	2.5	1.3	2.5	85.6	149.4
MO-74	2.5	2.3	1.7	2.0	85.9	178.2

Specifications for chemical impurities, which were identical to those for thorium oxide, were met without difficulty. Particle sizes produced were large compared to the particle size of 2.5 microns requested for several runs, regardless of the uranium to thorium ratio required, but approached specifications as experience was gained from each preparation. The uranium to thorium ratio and the surface areas of these mixed oxide products were acceptable for all runs. All of these preparations were calcined at 1050°C for 4 hr.

^aLetter to D. E. Ferguson from R. N. Lyon, May 25, 1959, subject--
"ThO₂ Production Requirements for REED."

In December, 1959, the Reactor Experimental Engineering Division cancelled all remaining requests for mixed oxide due to the lack of integrity of the thorium-uranium oxide. Regardless of the weight per cent uranium none of the oxides prepared and tested prior to the cancellation date maintained their original mean particle size but rapidly broke up into smaller particles as the materials were circulated in test loops. It was decided at the time of cancellation by the Reactor Experimental Engineering Division to specify 1050°C calcination for 8 per cent, 1100°C for 3 per cent, and 1225°C for 0.5 per cent uranium in the mixed oxide. Therefore the product of run MO-69, a 0.5 per cent uranium mixed oxide was returned to the Thorium Oxide facility for recalcination at 1225°C as compared to the original calcination temperature of 1050°C. The material sintered and as a result was no longer useful. After an unsuccessful study was carried out to determine the correct calcination temperature and atmosphere which would produce mixed oxide with lasting integrity, there was no further interest by the Reactor Experimental Engineering Division in testing mixed oxides.

When the remaining requests for mixed oxide were withdrawn, ten additional runs were stopped at various steps of preparation and the material was placed in storage. In Table 3.4 the material on hand is listed.

Table 3.4. Mixed Oxide on Hand^a

Run No.	Gross Wt., lb	U, wt %	Calcination Temp., °C	Classified
MO-69	177.5	0.5	1225	No ^b
MO-70	172.7	0.5	1225	No ^b
MO-75	157.1	3.0	1050	Yes
MO-76	212.7	8.0	1050	Yes
MO-77	168.8	3.0	1100	No
MO-79	187.0	8.0	1050	No
MO-80	176.2	3.0	1100 ^c	No
MO-81	165.5	3.0	Not calcined	No
MO-82	168.7	3.0	Not calcined	No
MO-84	193.5	3.0	Not calcined	No

^aThis material is presently stored in Building 7019, ORNL.

^bThis material was initially classified after calcining for 4 hr at 1050°C; however, it was not reclassified after calcination at the higher temperature.

^cApproximately 75% of the total had been calcined at 1100°C when the cancellation was received.

3.3 Losses

A total of 3200 kg of thorium was charged to the thorium make-up tank during 10.5 months of operation. Of this total 619 kg (19.35 per cent of

feed) was lost during the preparation of the oxides. The uranium loss during the manufacture of mixed oxides was 18.29 per cent, 52,362 g recovered from 64,083 g of uranium charged, (Table 3.5).

Table 3.5. Summary of Thorium and Uranium Losses

Run No.	Losses, %		Run No.	Losses, %	
	Th	U		Th	U
DT-60	8.01	-	MO-82	11.00	23.33
DT-61	5.53	-	DT-83	5.26	-
DT-62	16.89	1.24	MO-84	1.96 ^a	14.07
MO-63	11.42	16.26	DT-85	12.88	-
MO-64	6.80	13.90	DT-86	2.84	-
DT-65	2.13	-	DT-87	1.43	-
Run 66	66.5	-	DT-88	1.07	-
MO-67	23.95	22.94	DT-89	0.16 ^a	-
MO-68	17.74	0.86	DT-90	7.27 ^a	-
MO-69	2.71	13.43	DT-91	0.26	-
MO-70	5.23	4.41	DT-92	1.26 ^a	-
MO-71	20.98	21.17	DT-93	4.54	-
MO-72	14.95	20.27	DT-94	13.65	-
MO-73	20.21	27.87	DT-95	6.22	-
MO-74	4.54	25.54	DT-96	3.30	-
MO-75	16.31	32.99	DT-97	0.96	-
MO-76	7.51*	23.44	DT-98	7.95	-
MO-77	10.54	27.41	DT-99	5.30	-
DT-78	4.97	-	DT-100	5.78	-
MO-79	6.34	10.25	DT-101	1.46 ^a	-
MO-80	6.97	8.63	DT-102	12.95	-
MO-81	13.19	14.51	DT-103	6.80	-

^aIndicates a percentage gain. Where percentage gains are significant (above 2 per cent), material lost to the vacuum waste tanks had been recovered and credited to the run then in progress.

The major losses during the preparation of thorium oxide and thorium-uranium oxide occurred in the initial oxalate filtration step. Both nylon and Dynel cloth filter media were used to cover the 4 by 4 ft filter frame. The nylon failed rapidly in service and was replaced by Dynel after approximately 3 months. Since the Dynel cloth was available only in 38 in. widths two widths were sewn together using nylon thread in order to cover the filter frame. Three seams were sewn to insure a longer life of filter. After only two or three filtrations, the nylon thread failed presumably because of attack from 4 N nitric acid formed during the precipitation step. Thus oxalate was lost through the gaps where the stitching failed.

The other major loss occurred during the passage of the nitric acid and the subsequent water washes through the oxalate filter cake. Unless great care was taken when applying vacuum, solids were pulled through the cloth and lost to the waste system. The small particle size of the material produced also contributed to the filtration loss problem.

Another factor which contributed to the losses, although not as important as the first two factors cited, was that it was necessary to manually handle the thorium eight times during the preparation of each batch of thorium oxide. If the thorium oxide was used to make mixed oxide, the thorium-containing material was handled an additional three times. No special significance should be attached to any individual run loss since material "lost" during one run was often credited to the following run. In an experimental facility such as this, an over-all process loss of 19.3 per cent for thorium and 18.3 per cent for uranium is considered quite reasonable.

It is estimated that of the 619,000 g of thorium and 11,721 g of uranium losses, 97 per cent of these materials are stored in the 2000-gal stainless steel waste tank as a cake on the bottom of the tank below the 18 in. standpipe drain. The loss to the floor drains and to the settling basin is estimated to have been 18 kg of thorium and 0.3 kg of depleted uranium. The material in the waste tank could be recovered provided that the cake could be resuspended and recycled to the facility onto the filter bed. However, since sodium hydroxide was used as a neutralization agent attempts to recover the material were not made since the Na specification on all acceptable oxide was 100 ppm.

3.4 Additional Services Performed

3.4.1 Thorium Nitrate Tetrahydrate Dissolutions. During the year four 1400-lb batches of thorium nitrate tetrahydrate were dissolved to provide solutions containing 330-350 g/l thorium for Unit Operations solvent extraction studies. This procedure resulted in a saving of funds which would have been required to modify Unit Operations Section facilities to meet Health Physics requirements for handling dry thorium compounds and was a reasonable use of the facilities and supply of raw material in the thorium oxide facility.

3.4.2 Supplying Waste Oxide. In order to provide the ORNL Fuel Cycle Program with a minimum of 2000 lb of dried thorium oxide, sufficient thorium oxide slurry which had been used in the Reactor Experimental Engineering Division's loops and stored as waste oxide was transported from Y-12 storage to the thorium oxide facility. The supernate covering the settled oxide was removed and the wet oxide was loaded by hand into Amersil trays for drying in the electric furnace. One week was required to load and dry an estimated 2600 lb of wet oxide at 400°C in the facility's furnace. A total of 2106 lb of dry oxide was sampled, bagged, and placed in 55-gal stainless steel drums to be fused by an outside company for eventual use in laboratory compaction studies.

3.4.3 Calcination and Classification. DF-18, an oxide previously prepared, was returned from the Reactor Experimental Engineering Division to be fired for 4 hr at 1500°C and reclassified. The request was made on

January 11, 1960, with the material to be returned to the Reactor Experimental Engineering Division by January 20, 1960. The scheduled activities of the facility were interrupted long enough to carry out this request and the material was returned in time to meet the Reactor Experimental Engineering Division's schedule for the material.

4.0 APPENDIX - DETAILS OF PRODUCT

In FY-1960, 66 lots of material were delivered for research purposes at X-10 and Y-12 (Table 4.1). One lot was shipped off-site. These shipments represent a total of 5,173 kg of material containing 3,238 kg of thorium and 27.45 kg of uranium.

Table 4.1. Product Shipment Data for FY-1960

Shipping Date	Material or Run No.	Total Weight, kg	Thorium Weight, g	U-238 Weight, g	U-235 Weight, g	Total U, wt % ^a	Mean Particle Size, microns	Calcination Temp., °C	Classified	Shipped To	Location
7-5-59	DT-58	5.50	4,813	-	-	-	2.05	650	Yes	R. L. Pearson	X-10
8-5-59	TNT-Crystals	1.63	660	-	-	-	-	-	-	W. T. McDuffee	X-10
8-17-59	ThO ₂	136.12	119,202	-	-	-	-	-	-	A. C. Neeley	Y-12
8-19-59	DT-15	2.30	2,021	-	-	-	2.10	1600	Yes	C. E. Schilling	X-10
8-19-59	MO-57	2.13	1,680	170.2	0.37	10.0	1.80	1050	No	C. E. Schilling	X-10
8-19-59	DT-58	2.28	1,995	-	-	-	2.05	650	Yes	C. E. Schilling	X-10
8-25-59	DT-60	52.46	46,102	-	-	-	3.60	1050	Yes	P. R. Kasten	Y-12
8-25-59	DT-61	81.17	69,417	-	-	-	4.50	650	No	P. R. Kasten	Y-12
8-25-59	DT-65	82.76	71,918	-	-	-	2.10	650	No	P. R. Kasten	Y-12
8-25-59	Run 66	17.73	15,212	-	-	-	4.40	650	No	C. S. Morgan	Y-12
9-3-59	MO-62	74.92	59,936	6,031	16.89	8.0	3.65	1050	Yes	F. N. Peebles	Y-12
9-16-59	MO-63	79.52	63,950	5,900	15.93	8.0	3.65	1050	Yes	F. N. Peebles	Y-12
9-22-59	DT-60	4.18	3,673	-	-	-	3.60	650	No	G. W. Parker	X-10
9-23-59	MO-64	83.74	67,344	6,004	15.01	8.0	3.35	1050	Yes	F. N. Peebles	Y-12
10-7-59	MO-67	63.81	54,430	1,665	4.16	3.0	2.20	1050	Yes	E. L. Compere	Y-12
10-12-59	MO-68	68.71	59,482	350	0.90	0.5	2.10	1050	Yes	P. R. Kasten	Y-12
10-20-59	MO-69	80.50	70,437	394	1.00	0.5	2.30	1050	Yes	E. L. Compere	Y-12
10-20-59	TNT-Crystals	8.67	3,510	-	-	-	-	-	-	C. E. Schilling	X-10
10-20-59	TNT-Crystals	22.17	8,913	-	-	-	-	-	-	C. E. Schilling	X-10
10-23-59	DT-20	20.20	17,736	-	-	-	-	1600	No	S. Clinton	X-10
10-28-59	DT-78	55.97	48,973	-	-	-	7.9	1400	No	D. Thomas	Y-12
10-29-59	TNT-Crystals	10.00	4,020	-	-	-	-	-	-	C. E. Curtis	Y-12

Table 4.1. Product Shipment Data for FY-1960 (Continued)

Shipping Date	Material or Run No.	Total Weight, kg	Thorium Weight, g	U-238 Weight, g	U-235 Weight, g	Total U, wt % ^a	Mean Particle Size, microns	Calcination Temp., °C	Classified	Shipped To	Location
11-10-59	MO-71	66.87	47,421	1,732	4.33	3.0	3.00	1050	Yes	E. L. Compere	Y-12
11-12-59	MO-72	72.20	61,818	1,776	4.44	3.0	2.80	1050	Yes	F. N. Peebles	Y-12
11-17-59	MO-73	67.77	57,980	1,653	4.13	3.0	2.55	1050	Yes	E. L. Compere	Y-12
12-2-59	MO-74	80.81	69,415	1,616	4.04	3.0	2.35	1050	Yes	C. S. Morgan	Y-12
12-3-59	MO-69	11.90	10,413	58.3	0.15	0.5	2.30	1050	Yes	O. C. Dean	X-10
12-4-59	MO-75	1.00	853	20.80	-	3.0	2.85	1050	Yes	O. C. Dean	X-10
12-4-59	MO-76	1.00	815	60.70	-	8.0	2.80	1050	Yes	O. C. Dean	X-10
12-4-59	MO-81	1.00	860	22.00	-	3.0	-	650	No	O. C. Dean	X-10
12-16-59	DT-60	5.50	4,832	-	-	-	3.60	650	No	O. C. Dean	X-10
12-18-59	DT-83	7.35	5,703	-	-	-	1.10	650	No	O. C. Dean	X-10
1-19-60	ADR-1	635.04	255,818	-	-	-	-	-	-	R. S. Lowrie	X-10
2-16-60	DT-85	67.21	58,835	-	-	-	3.1	1600	Yes	I. Spiewak	Y-12
2-16-60	DT-86	84.20	73,969	-	-	-	2.95	1600	Yes	I. Spiewak	Y-12
2-16-60	DT-87	80.77	70,859	-	-	-	2.80	1600	Yes	I. Spiewak	Y-12
2-16-60	DT-83	45.50	39,885	-	-	-	1.35	1400	No	D. Thomas	Y-12
2-16-60	DT-83A	39.06	34,013	-	-	-	1.10	650	No	D. Thomas	Y-12
2-29-60	TNT-Crystals	2.74	1,100	-	-	-	-	-	-	F. E. Seeley	Y-12
3-3-60	DT-89	74.88	65,670	-	-	-	3.25	1600	Yes	I. Spiewak	Y-12
3-3-60	DT-90	88.96	74,240	-	-	-	3.40	1600	Yes	I. Spiewak	Y-12
3-3-60	DT-91	80.16	70,380	-	-	-	3.10	1600	Yes	I. Spiewak	Y-12
3-16-60	DT-22	6.00	5,245	1.0	25.0 ^b	-	1.65	650	No	E. L. Compere	Y-12
3-17-60	DT-96	11.52	10,012	-	-	-	2.60	650	No	AERO Project Inc.	--
3-22-60	DT-92	78.18	68,611	-	-	-	3.00	1600	Yes	I. Spiewak	Y-12
3-31-60	ADR-2	635.04	255,818	-	-	-	-	-	-	R. S. Lowrie	X-10
4-1-60	TNT-Crystals	90.72	36,469	-	-	-	-	-	-	C. S. Morgan	Y-12
4-11-60	DT-93	72.91	63,797	-	-	-	3.20	1600	Yes	I. Spiewak	Y-12

Table 4.1. Product Shipment Data for FY-1960 (Continued)

Shipping Date	Material or Run No.	Total Weight, kg	Thorium Weight, g	U-238 Weight, g	U-235 Weight, g	Total U, wt % ^a	Mean Particle Size, microns	Calcination Temp., °C	Classified	Shipped To	Location
4-11-60	DT-95	76.49	67,089	-	-	-	2.65	1600	Yes	I. Spiewak	Y-12
4-20-60	DT-94	1.00	877	-	-	-	2.50	1600	Yes	F. Sweeton	X-10
4-25-60	LO-1-15 ^c	15.47	13,588	-	-	-	-	-	-	C. Curtis	Y-12
4-25-60	DT-55	46.28	40,671	-	-	-	2.20	1400	-	C. Curtis	Y-12
4-28-60	ADR-3	635.04	255,818	-	-	-	-	-	-	R. S. Lowrie	X-10
4-28-60	DT-94	1.62	1,421	-	-	-	2.50	1600	Yes	P. Haas	X-10
4-28-60	DT-100	3.80	3,328	-	-	-	1.35	800	No	C. E. Schilling	X-10
4-29-60	DT-100	10.00	8,758	-	-	-	1.35	800	No	C. Curtis	Y-12
5-5-60	DT-96	67.71	58,847	-	-	-	2.60	650	No	E. L. Compere	Y-12
5-5-60	DT-94	67.79	59,371	-	-	-	2.50	1600	Yes	E. L. Compere	Y-12
5-5-60	DT-97	77.02	67,662	-	-	-	2.70	1600	Yes	E. L. Compere	Y-12
5-5-60	DT-99	47.49	41,193	-	-	-	2.60	650	No	E. L. Compere	Y-12
5-6-60	ADR-4	635.04	255,818	-	-	-	-	-	-	R. S. Lowrie	X-10
5-10-60	DT-100	4.54	3,960	-	-	-	1.35	800	No	J. Shaffer	Y-12
5-25-60	DT-101	52.70	46,023	-	-	-	6.50	800	No	I. Spiewak	Y-12
6-22-60	DT-102	12.87	11,255	-	-	-	1.15	800	No	A. C. Neeley	Y-12
6-22-60	DT-102	45.43	39,729	-	-	-	1.15	800	No	I. Spiewak	Y-12
6-22-60	DT-102	1.97	1,723	-	-	-	1.15	800	No	S. Clinton	X-10
Totals		5,173.47	3,237,968	27,453.00	71.35						

^aPercentage requested.^bEnriched uranium; not included in totals.^cComposite samples from Runs LO-1 through LO-15.

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