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SUBJECT: Preparation of Thorium Oxide From ORNL Thorex Thorium Nitrate

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AEC RESEARCH AND DEVELOPMENT REPORT

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1.0 INTRODUCTION

Thorium recovered by the ORNL Thorex process must be converted to either metallic thorium or thorium oxide prior to reuse in a reactor. The current procedure for the conversion includes precipitation as the oxalate, calcination to the oxide, fluorination, and reduction of the fluoride to thorium metal. Preliminary data were needed concerning the decontamination that could be obtained in converting Thorex thorium nitrate to the oxide and the fluoride, the magnitude of the biological hazard involved in conducting the precipitation and calcination in unshielded equipment, and the activity distribution during the subsequent processing steps.

Three runs were made for the conversion of Thorex thorium nitrate to the oxide and the fluoride; one run was made at ORNL on a pilot-plant-scale (C-47), in which the Thorex thorium nitrate was processed to thorium oxide, and two laboratory-scale runs (FMPC-2 and -3) were conducted at FMPC[1] in which the oxide was prepared from Thorex thorium nitrate and the oxide converted to the fluoride. The activity concentrations in the feed for run FMPC-2 were insufficient to permit accurate analytical determinations and data for this run are not included. In addition, two laboratory-scale control runs were made at FMPC using nonirradiated thorium nitrate as the starting material. This report summarizes the decontamination factors, activity distribution, and radiation exposures or intensities for Thorex thorium nitrate and natural thorium.

2.0 SUMMARY

Thorium nitrate, recovered from irradiated thorium metal processed in the ORNL Thorex Pilot Plant, was converted to thorium oxide by precipitating thorium oxalate and calcining the oxalate to the oxide. The oxide was then converted to the fluoride. In the pilot-plant-scale run (C-47) using thorium feed containing 356 gross gamma cts/min/mg, a gross gamma decontamination factor of 1.6 was observed for the oxide. In a laboratory-scale run (FMPC-3) using a thorium feed

1. Feed Material Production Center at Fernald, Ohio, operated by the National Lead Company of Ohio.

containing 1223 cts/min/mg, a gross gamma decontamination factor of 1.4 was observed for the fluoride. (Decontamination factors for protactinium-233, ruthenium, zirconium-niobium, and rare earth are shown in Tables 4-4 and 4-5.)

Approximately 1800 gal of acid waste will be produced per ton of thorium processed to the oxide. Neutralizing the waste with sodium hydroxide, followed by removal of the precipitated solids, reduced the activity level in the waste by a factor of 2. Approximately 0.2 curies of total activity (beta plus gamma) may be expected in the neutralized waste solution from the processing of one ton of Thorex thorium nitrate product containing about 1223 gamma cts/min/mg thorium. The activity observed in the neutralized waste from the processing of natural thorium nitrate was lower by a factor of 20. About 0.03 curies of gamma activity was observed in the feed prepared from natural thorium; the curies of gamma activity observed in the feed for run FMPC-3 was about 30 times greater (Table 4-6).

An operator received less than 30 mr of whole-body radiation exposure while conducting a 16-hr pilot plant run in unshielded equipment in which Thorex thorium nitrate was processed to the oxide. The exposure to personnel should vary with the irradiation level and cooling time of the Thorex feeds, with process fluctuations, and with the extent to which fission products adsorb on the equipment surfaces. Extended periods of operation using Thorex thorium nitrate product will be required to demonstrate the feasibility of using unshielded equipment.

3.0 EXPERIMENTAL PROCEDURE

Thorium oxide was prepared from thorium nitrate solution at ORNL and at FMPC by (a) the addition of oxalic acid, precipitating thorium oxalate, (b) filtering and washing the thorium oxalate cake with water, and (c) calcining the washed thorium oxalate to thorium oxide. The combined aqueous filtrates and washes from the FMPC runs were neutralized with caustic soda and filtered. For the conversion to the fluoride, the oxide prepared at FMPC was heated in the presence of hydrogen fluoride. No hydrofluorinations were conducted at ORNL. The flowsheet used for the production of thorium oxide and fluoride is given in Fig. 3-1.

The pilot-plant-scale run at ORNL was carried out in unshielded equipment. The radiation exposure was determined by monitoring a special film badge worn by the operating personnel; this exposure is indicative of the hazard involved in processing Thorex thorium product in equipment designed for processing non-irradiated thorium nitrate. The exposure to personnel would be expected to vary, however, as the irradiation level and cooling time of the Thorex feeds vary and as process fluctuations affect individual fission product decontamination factors.

4.0 TABULATION OF RESULTS

A pilot-plant-scale run (C-47) was conducted at ORNL to prepare thorium oxide from Thorex thorium nitrate solution. Two laboratory-scale runs (FMPC-2 and -3) were conducted at FMPC to prepare thorium fluoride from Thorex thorium nitrate; data for run FMPC-2 are not included due to insufficient activity concentrations in the feed preventing accurate analytical determinations. The thorium nitrate used in the three runs was produced in the ORNL Thorex Pilot Plant from irradiated thorium metal. Also, two control runs were conducted at FMPC for comparison, using natural thorium nitrate procured from Lindsay Light Company.

The histories and compositions of the Thorex thorium nitrate solutions from which thorium oxide was prepared are summarized in Table 4-1.

4.1 Activity Distribution and Decontamination Factors

The activity distribution associated with the preparation of thorium oxide from Thorex thorium nitrate is presented in Tables 4-2 and 4-3. These data were determined for runs C-47 and FMPC-3, respectively.

Fig. 3-1

Flowsheet for the Production of Thorium Oxide and Thorium Fluoride

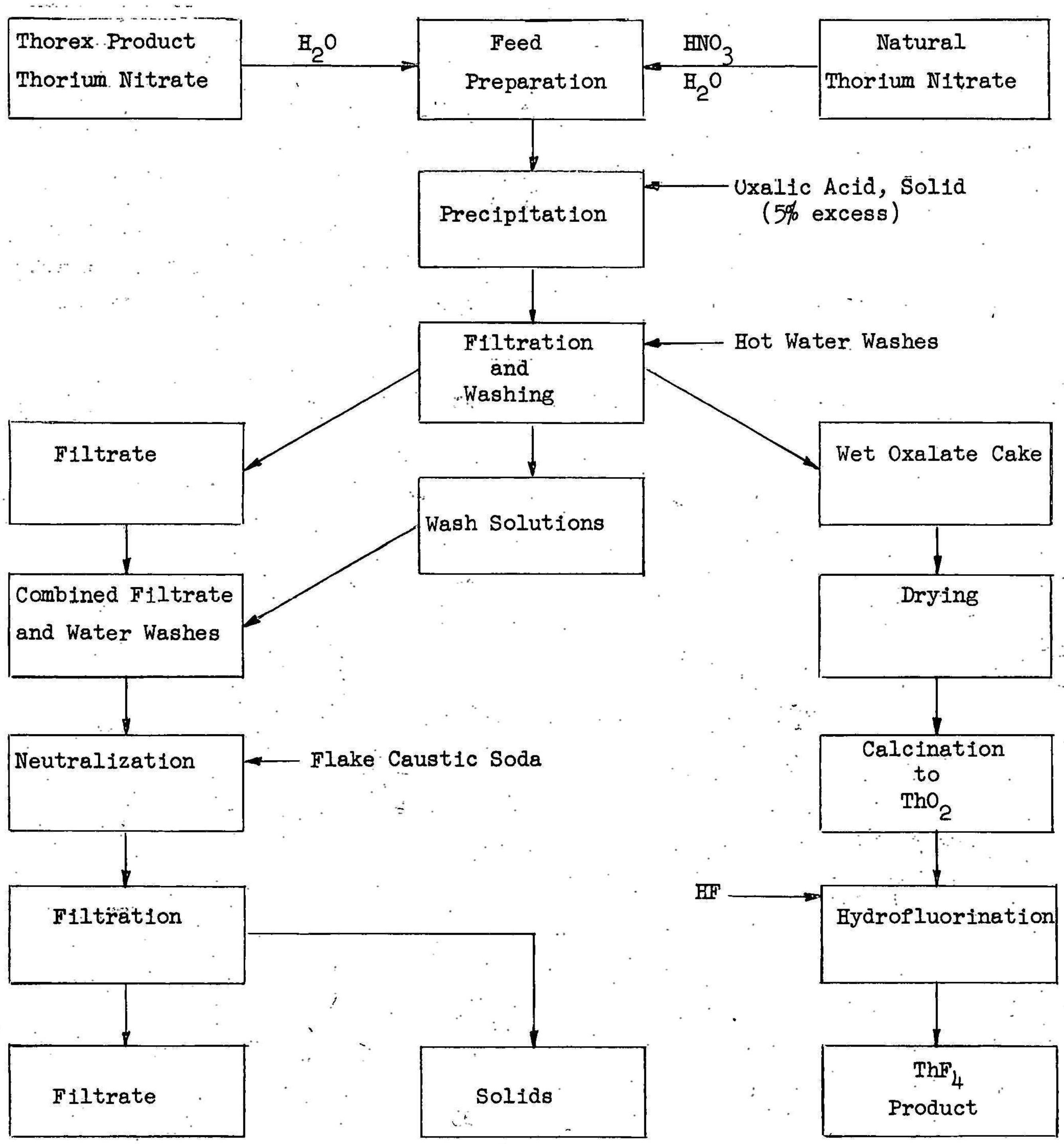

Table 4-1

Analyses and Histories of ORNL Thorex Thorium Nitrate Solutions

Used for Thorium Oxide Preparation

Run Number	C-47	FMPC-3
History of Thorium Slugs		
Cooling time, days	185	60-200
Grams U-233/short ton thorium	836	1400
Isolation date	4/22/55	9/7/55
Radiochemical Analyses, cts/min/mg		
Gross γ	356	1223
Pa γ	164	776
Ru γ	25	126
Nb-Zr γ	110	219
TRE β	61	45
Th-234 β	378	1350
Ionic Analyses		
Th, g/liter	423	542
U, ppm of thorium	-	3
HNO_3, N	-	1.3
PO_4, ppm of thorium	-	28
Spectrographic Analyses, ppm Th		
Al	27	165
Ca	18	6
Cr	13	640
Cu	2.1	1.5
Fe	95	128
Mg	4.7	-
Mn	2.1	-
Ni	18	17
Si	6.6	3.8
Na	5.6×10^3	110

Table 4-2

Activity Distribution in the Preparation of Thorium Oxide from ORNL Thorex Thorium Nitrate

(ORNL Pilot Plant-Scale Run C-47)

	Activity, cts/min/mg Th				
	Gross γ	Pa γ	Ru γ	Nb-Zr γ	TRE β
Feed	356	164	25	110	61
Oxalate	253	--	1	24	60
Oxide	227	158	1	20	60

Table 4-3

Activity Distribution in the Preparation of Thorium Oxide from ORNL Thorex Thorium Nitrate

(FMPC Laboratory-Scale Run FMPC-3)

	Activity, cts/min/mg Th								
	Gross γ	Ru γ	Nb-Zr γ	Nb γ	Zr γ	Gross β	Pa γ	TRE β	Sr β
Feed	1223	126	219	112	48	1783	1121	45	0.22
Unwashed oxalate cake	1035	348	158	47	54	1829	847	44	-
Washed oxalate cake	871	< 1	114	27	47	1582	619	42	-
Dried oxalate cake	930	< 1	123	33	53	1678	548	43	-
Thorium oxide	990	< 1	126	32	57	1788	661	43	-
Hydrofluorinated cake	865	< 1	112	23	55	1100	510	44	-
Filtrate[a]	199	123	83	75	0.7	57	9.4	0.19	-
Wash[a]	43	28	19	18	0.24	13	2.2	0.06	-
Filtrate + wash[a]									
Before neutralization	254	152	105	94	1.5	74	9	0.22	< 0.1
After neutralization	97	0.37	78	1.8	0.2	15	17	0.01	-
Filtrate solids[a]	130	141	10	0.9	0.2	49	4.3	0.20	0.4

a. Based on thorium in feed.

The decontamination factors observed in the preparation of thorium oxide in runs C-47 and FMPC-3 are presented in Tables 4-4 and 4-5.

Table 4-4

Decontamination Factors for Thorium Oxide Prepared at ORNL

(Run C-47)

Step	Decontamination Factors				
	Gross γ	Pa γ	Ru γ	Nb-Zr γ	TRE β
Oxalate	1.4	-	>25	4	1.0
Oxide	1.6	1.0	>25	5	1.0

Table 4-5

Decontamination Factors for Thorium Fluoride Prepared at FMPC

(Run FMPC-3)

	Decontamination Factors							
	Gross β	Pa β	TRE β	Gross γ	Ru γ	Nb-Zr γ	Nb γ	Zr γ
Oxalate	1.1	1.9	1.0	1.3	>126	1.8	3.4	1
Oxide	1.0	1.7	1.0	1.2	>126	1.7	3.4	1
Fluoride	1.6	2.2	1.0	1.4	>126	2.0	4.9	1

4.2 Waste Disposal

The activities (in curies) observed in the product and the waste streams during the preparation at FMPC of thorium oxide from Thorex and natural thorium nitrate are presented in Table 4-6. The activity of the combined filtrate and wash produced in the oxalate precipitation step can be reduced about a factor of 2 by neutralizing with caustic soda and removing the precipitated solids. Approximately 1800 gal of neutralized waste is produced per ton of thorium processed.

Table 4-6

Activity Distribution in the Preparation of Thorium Oxide at FMPC from ORNL Thorex and Natural Thorium Nitrate

(Curies/Ton Thorium Processed)

	Thorium Nitrate Feed		Thorium Oxide		Filtrate and Wash[c]			
					Before Neutralization		After Neutralization[b]	
	Natural[a]	Thorex	Natural[a]	Thorex	Natural[a]	Thorex	Natural[a]	Thorex
		FMPC-3		FMPC-3		FMPC-3		FMPC-3
Gross γ	0.025	0.98	0.016	0.78	0.009	0.02	0.005	0.01
Pa γ	-	0.57	-	-	-	-	-	-
Ru γ	-	0.099	-	<0.0007	-	0.0012	-	0.0011
Nb-Zr γ	-	0.176	-	0.099	-	0.008	-	0.00077
Nb γ	-	0.093	-	0.025	-	0.007	-	7×10^{-6}
Zr γ	-	0.038	-	0.045	-	0.00001	-	1.3×10^{-6}
Gross β	0.10	6.46	-	7.19	0.02	0.298	0.01	0.195
Pa β	-	3.22	-	2.46	-	0.036	-	0.051
Sr β	-	0.0008	-	-	-	<0.0003	-	-
TRE β	-	0.16	-	0.16	0.032	0.00088	-	0.0008

a. Natural thorium procured from Lindsay Light Company.

b. Filtrate after precipitated solids were removed.

c. Not determined for run C-47.

4.3 Radiation Levels

In run C-47, 51.7 kg of thorium (as thorium nitrate) was converted to thorium oxide in unshielded pilot-plant-scale equipment. Hence, the radiation exposure to personnel in this run should be indicative of the hazard involved in processing Thorex thorium nitrate product in unshielded equipment.

The gross gamma activity of the 1.82 M Thorex thorium nitrate solution was 356 cts/min/mg Th. The maximum radiation reading at contact with the precipitator during agitation of the mixture was 14 mr/hr; at working level the reading was 1.5 mr/hr. The maximum reading 18-in. above the unwashed oxalate cake was 20 mr/hr. After the oxalate cake had been washed and the free moisture removed by vacuum, a reading of 88 mr/hr was obtained 2 ft above the edge of the cake; this position was approximately at the working level for an operator scooping the oxalate from the filter into trays. The trays were loaded by hand into a furnace.

During the entire experiment (precipitation, filtration, washing, scooping oxalate into trays, loading trays into the furnace, removing trays from the furnace, and unloading the trays) the operator wore a special film badge to measure whole-body radiation. At the conclusion of the experiment, the film badge showed no significant radiation above background. The probable total radiation exposure of the operator was less than 30 mr (the lower limit of sensitivity of the film for such a period of time).

A summary of the radiation intensities determined in the FMPC laboratory-scale runs, using Thorex thorium nitrate and the control run in which natural thorium nitrate was processed, is presented in Table 4-7.

Table 4-7

Radiation Intensities in the FMPC Laboratory-Scale Preparation of Thorium Oxide From ORNL Thorex and Natural Thorium Nitrate

(Activity in mr/hr through container walls)

(Monitored by a paper shell cutie-pie)

	Natural Thorium[a]				Irradiated Thorium[b]			
	At Contact		At 6-in.		At Contact		At 6-in.	
	$\beta + \gamma$	γ	$\beta + \gamma$	γ	$\beta + \gamma$	γ	$\beta + \gamma$	γ
Feed Solution	3	3	0.9	0.7	4	1.5	2	1
Oxalate Slurry	0.9	0.9	0.6	0.4	2.5	1.5	1	0
Oxalate Cake[c]	4	4	0.6	0.6	1	0	0.2	0
Filtrate and Wash	0.2	0.2	0.1	0.1	0.25	0.25	0.2	0.2
Neutral Filtrate	0.1	0.1	0.1	0.1	0.4	0.2	0.2	0.1

a. Natural thorium nitrate procured from Lindsay Light Company.

b. ORNL Thorex thorium nitrate solution.

c. Through the wall of a Buchner funnel.

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