



**DRY — WAY PREPARATION OF THORIUM  
TETRAFLUORIDE**

*HELENO S. CORRÊA and EDUARDO C. COSTA*

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**INSTITUTO DE ENERGIA ATÔMICA**  
Caixa Postal 11049 (Pinheiros)  
CIDADE UNIVERSITÁRIA "ARMANDO DE SALLES OLIVEIRA"  
SÃO PAULO — BRASIL

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Heleno S. Corrêa and Eduardo C. Costa

Divisão de Engenharia Química  
Instituto de Energia Atômica  
São Paulo - Brasil

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# DRY - WAY PREPARATION OF THORIUM TETRAFLUORIDE

Heleno S. Corrêa and Eduardo C. Costa

## ABSTRACT

The dry-way preparation of ThF<sub>4</sub> via the action of anhydrous HF on ThO<sub>2</sub> has been studied. Batch hydrofluorinations were conducted in graphite boats at constant HF flowrate and constant feed gas temperature. Time, temperature and type of oxide were the variables studied.

Oxides prepared by calcining the oxalate at 400, 600 and 800°C, and by calcining the hydroxide at 600 and 800°C, as well as a sulfate-activated hydroxide, and the original oxalate and hydroxide, were hydrofluorinated at temperatures of 400, 500 and 600°C for 1 and 3 hours. Conversions were determined by the weight change of samples.

The highest conversions were obtained with the oxide derived by calcination of the oxalate at 800°C. Cross-plotting the experimental data in the form of time-temperature correlations at constant conversion allowed the determination of suitable combinations of time and temperature for a desired conversion level. Sintering of the tetrafluoride was observed at hydrofluorination temperatures higher than 525°C.

## 1. INTRODUCTION

Anhydrous thorium tetrafluoride is the starting material for the production of nuclear grade powder or massive thorium metal by calcium reduction. The widespread procedure adopted for the manufacture of anhydrous thorium tetrafluoride is the direct hydrofluorination of an oxide by the reaction



$$\Delta H_{298}^{\circ} \text{ } ^{\circ}\text{K} = - 43.8 \text{ Kcal/mol}$$

The reaction is generally conducted in the temperature range of 400-550°C at near atmospheric pressures.

In the past several other routes have been investigated, but there are two general groups into which they can be divided:

the dry and wet methods. The latter is of lesser importance and consists of the precipitation of a hydrated tetrafluoride from an aqueous solution followed by the elimination of the hydration water by heating in an anhydrous HF atmosphere<sup>1,2,3</sup> or in the presence of hydrofluorinating agents<sup>4,5</sup>.

In the dry method a thorium compound is directly reacted with a hydrofluorinating agent at high temperatures. In general, anhydrous HF<sup>1,2,6,7</sup> or Freon 12<sup>5,6</sup> are reacted with an oxide obtained by decomposition of the oxalate, hydroxide, sulfate or oxycarbonate. However attempts at the direct hydrofluorination of the oxalate and the hydroxide<sup>2</sup>, as well as the acetate<sup>8</sup>, have been reported.

Apparently the only work describing the hydrofluorination kinetics of this process is that of Lindstrom and Ellis<sup>7</sup>. In this work the reaction was followed spectrophotometrically by the measurement of interference films formed on the flat polished surfaces of single crystals of thorium dioxide at low pressures in the range of 218-327°C. Their results indicated diffusion control in this temperature range with the reaction rate proportional to the 1/2 power of both the HF partial pressure and the thickness of the ThF<sub>4</sub> layer, in remarkable agreement with the similar work previously conducted by Roberts and Ellis<sup>9</sup> on the hydrofluorination of polished continuous surfaces of uranium dioxide. The activation energy for this reaction obtained from an Arrhenius plot was ..... 6630 ± 280 cal/mol (75% confidence), which closely approximated the measured value of 6930 ± 140 cal/mol (90% confidence) reported previously<sup>9</sup> for the hydrofluorination of UO<sub>2</sub>.

The present work is not intended to supply data for kinetics studies, but to establish operating conditions for the preparation of thorium tetrafluoride. Our aims have been mainly focused on the determination of optimized conditions for a certain oxide in a two variable system: time and temperature. We have at-

tempted to establish optimal choices among oxides of different origins and graphical correlations between temperatures and corresponding times for desired conversion levels. The results herein referred to as optimal are related to our materials and setups, and strongly dependent on the preparation procedure and physical properties of the raw materials.

## 2. EXPERIMENTAL

### Apparatus

The experimental assembly is shown schematically in Fig. 1. The equipment consists principally of a gas feed unit, a reaction unit and an excess gas absorption unit. HF was fed directly from a heated cylinder through insulated lines into the tubular reactor (Fig. 2) and passed over graphite boats charged with the oxide. The reactor built from a 1 1/2" I.D. brass tube, nickel-plated throughout, had a water-cooled jacket in the jutting end to protect the Teflon-sealing gasket of the feeding port. Excess gases leaving the reactor were conducted through electrically heated 1/4" copper tubing lines into an absorption flask containing a 20% KOH solution. Unabsorbed gases were sucked by the water pump and flushed down the drain. Three graphite boats with a 7.7 cm<sup>2</sup> cross section were charged simultaneously in most of the runs.

### Reagents

All oxides studied were obtained from nuclear grade starting materials. Three of these oxides were obtained by calcining a thorium oxalate at 400, 600 and 800°C respectively and the remaining ones by calcining two different thorium hydroxides: hydroxide I and II. Hydroxide I was obtained by urea precipitation at 90°C of a thorium nitrate solution in the presence of formic acid, whereas hydroxide II was obtained under the same conditions in the presence of ammonium sulfate. The oxalate used was precipitated by

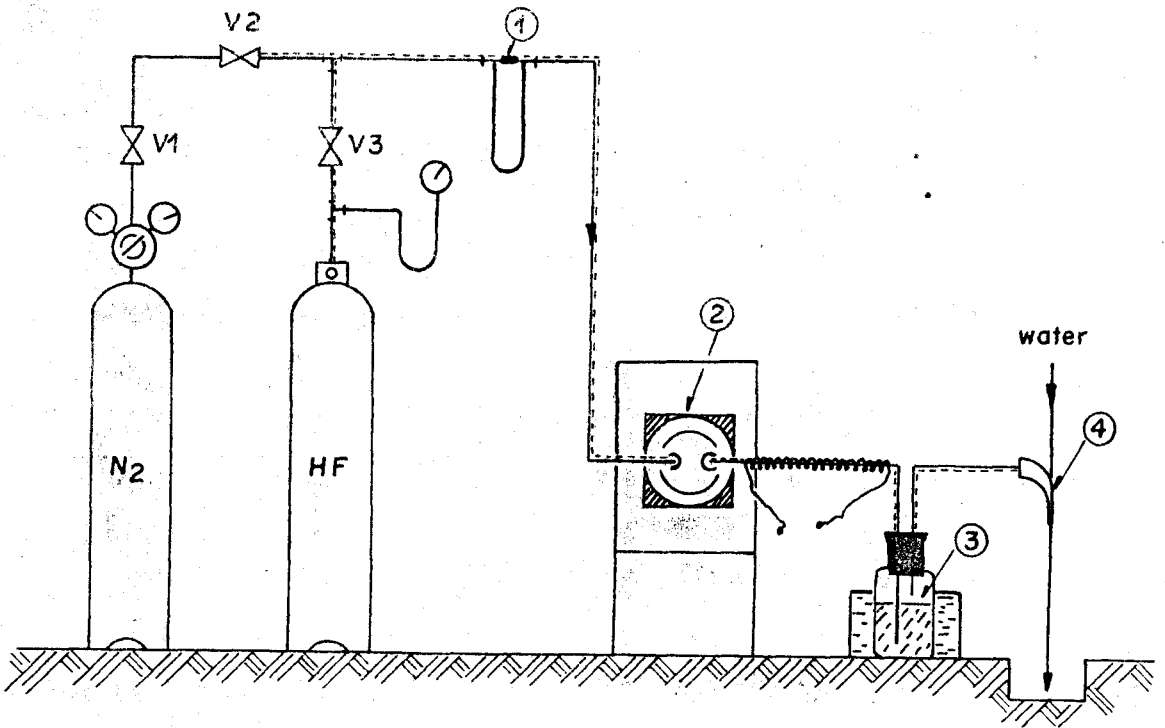


FIG. 1 Schematic diagram of the apparatus.

- ① - Flowmeter
- ② - Reactor
- ③ - KOH solution
- ④ - water pump

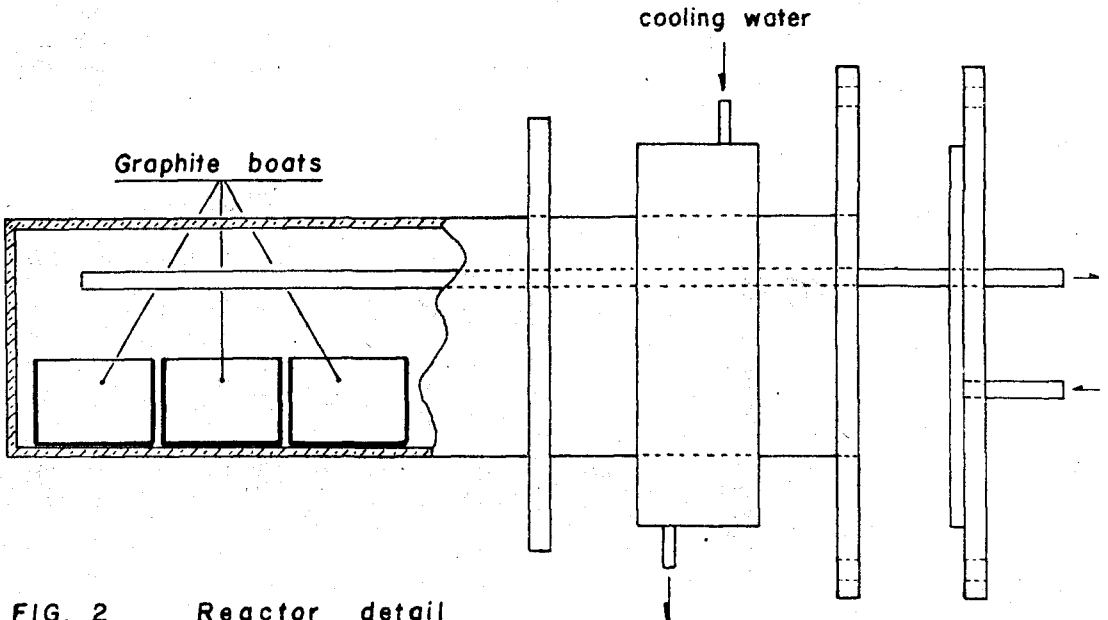


FIG. 2 Reactor detail

oxalic acid from a 50 g/l U, 1N HNO<sub>3</sub> solution at 25°C. All starting materials as well as the resulting oxides were free-flowing powders. Their physical properties are listed in Appendix C.

The choice of these different starting materials permitted the comparison between the hydrofluorination behavior of oxides of widely different surface areas (Cf. Table C.3, App. C). The introduction of the ammonium sulfate during the precipitation of hydroxide II, resulted after calcination at 800°C in an oxide of high surface area containing 2.65% SO<sub>4</sub><sup>=</sup>.

Anhydrous hydrogen fluoride (~ 99.9%) was used in all experiments. Water-pumped nitrogen (99.6 %) was used for purging and as a blanketing atmosphere in the cooling period.

#### Procedure

The graphite boats were charged to a depth of approximately 5 mm (~ 5 g sample of the oxide) with known weights of the dry powders, and loaded three at a time through the feed port of the reactor. The furnace was then switched on simultaneously with a nitrogen flow into the reactor and its temperature brought up to the desired level. At the beginning of a run the nitrogen flow was changed to an HF flow adjusted to approximately 60 cm<sup>3</sup>/min at 25°C, 1 atm. abs. At the end of a run the HF flow was changed back to the N<sub>2</sub> flow and the reactor and contents allowed to cool to room temperature. The weight change of the sample was measured and recorded.

### 3. DATA AND ANALYSIS

#### Qualitative Observations

In the cases of the oxides derived from the oxalate and from the sulfate-free hydroxide the reaction products showed surface cracks at random and indication of sintering only at high



temperatures, whereas the oxide derived from the sulfate-containing hydroxide showed signs of sintering even at the lower reaction temperatures. In the direct hydrofluorination of the oxalate and of the hydroxide I the resulting products had a grayish appearance due to the presence of residual carbon in the fluoride. In all cases a decrease in volume of the charge was observed.

### Experimental Data

The experimental data was correlated in the form of tables (tables A.1 to A.5, App. A) and plots of conversion vs. temperature and conversion vs. time. The experimental results for the oxides derived from the oxalate are shown in Figs. 3 to 7. The separate curves labeled A, B and C correspond to oxides derived from the same oxalate by prior calcination in air at 800, 600 and 400° C respectively.

Figures 9 through 13 show the data obtained from oxides A and B derived by calcination of hydroxide I at 800 and 600° C respectively.

In Figure 15 and 16 the data for the oxide derived from hydroxide II calcined at 800° C are given. Figures 17, 18 and 19 show the data for the direct hydrofluorination of the oxalate and hydroxide I.

Figure 20 shows the pyrolysis curves for a hydroxide and an oxalate<sup>10</sup>. It can be seen from this figure that the hydroxide studied was completely decomposed into the oxide at the calcination temperatures used, whereas the oxalate was only partially decomposed at 400° C (oxide C), but completely decomposed at the temperature of 600 and 800° C since a 5 hr calcination period was employed in all cases.

### Analysis of the Data

The analysis of figures 3 to 7 indicate that the end con-

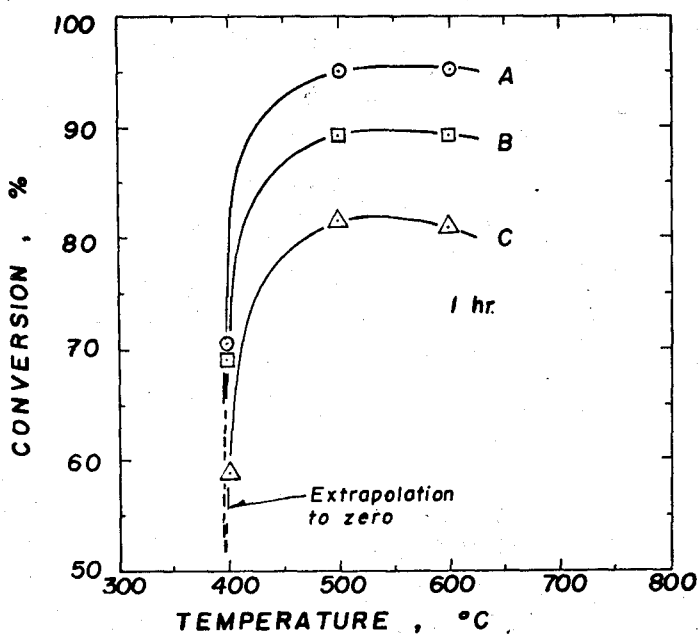


FIG. 3 Conversion vs. Temperature Curve  
Reaction Time: 1 hr.  
Oxides From the Oxalate

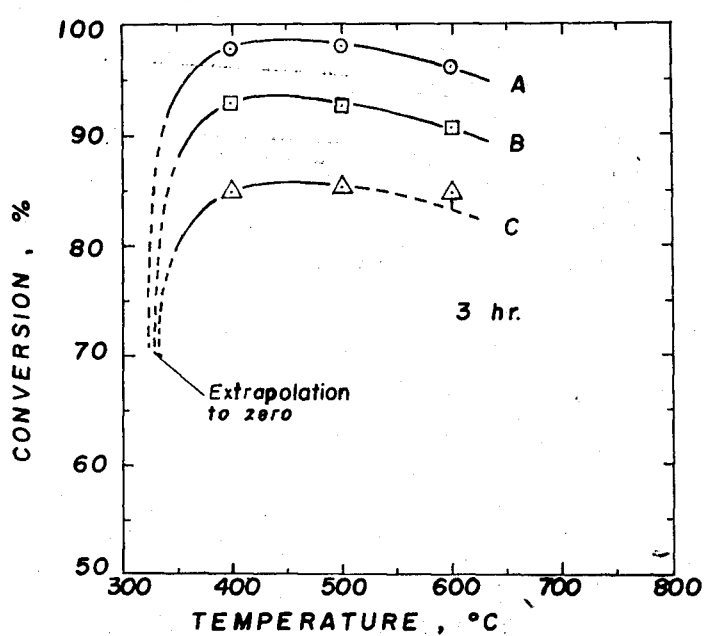


FIG. 4 Conversion vs. Temperature Curve  
Reaction Time: 3 hr.  
Oxides From the Oxalate

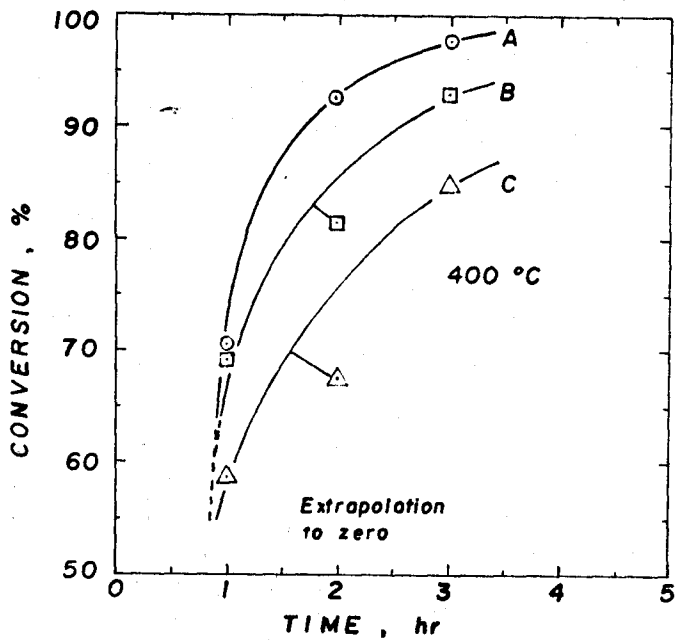


FIG. 5 Conversion vs. Time Curve  
Reaction Temperature : 400 °C  
Oxides From the Oxalate

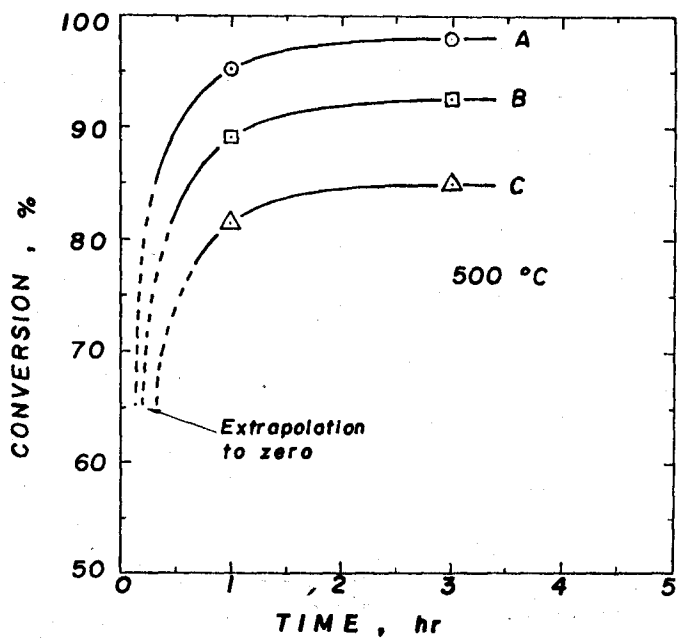


FIG. 6 Conversion vs. Time Curve  
Reaction Temperature : 500 °C  
Oxides From the Oxalate

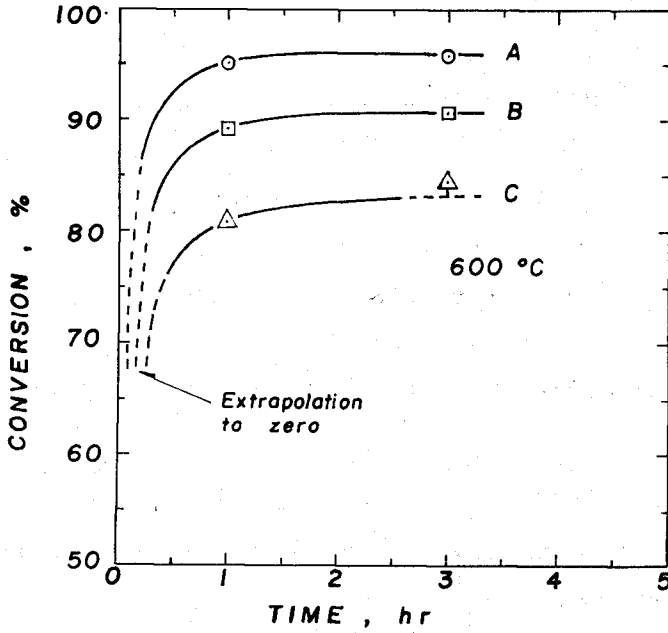


FIG. 7 Conversion vs. Time Curve  
Reaction Temperature: 600 °C  
Oxides From the Oxalate

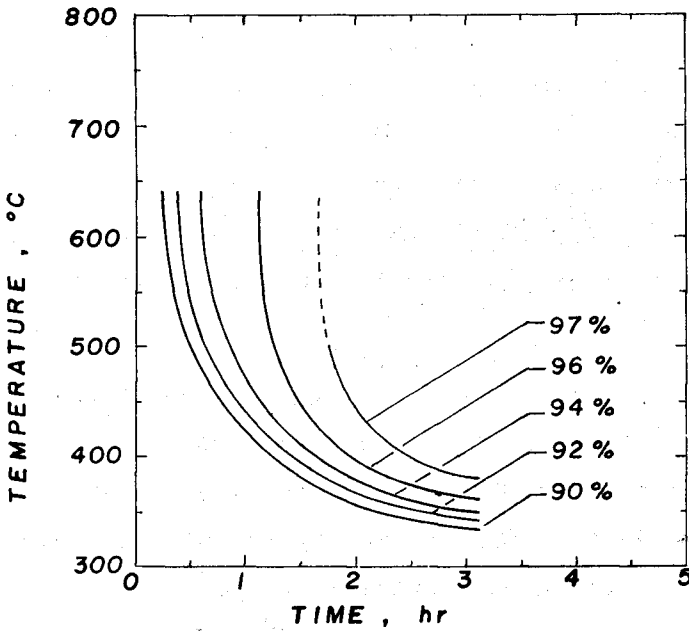


FIG. 8 Temperature - Time Correlation  
at Constant Conversion  
Oxide A From the Oxalate

version increases directly with the calcination temperature of the oxalate in the temperature range studied. The highest conversion of 98.1% was observed with oxide A. Sintering of the tetrafluoride was responsible for the falling conversion at temperatures above approximately 525°C. To better visualize the relationship between time and temperature, the data in these plots were unified in the form of a time-temperature plot shown in Fig. 8. This Figure indicates that conversions higher than 97% can be obtained by suitable combinations of time and temperature chosen from this plot.

Figures 9 through 13 for the hydrofluorination behavior of the oxides derived from hydroxide I, also indicated an increased end conversion with increasing calcination temperature of the hydroxide. The highest observed conversion in this case was 98.2%. However, now, sintering plays a major rôle in the hydrofluorination behavior of these oxides and end conversions above 525°C are a measure of the competing processes of reaction and sintering, the latter tending to decrease the porosity of the product layer thus hindering the gas diffusion into the sample. Sintering is particularly important at initial times at high temperatures as evidenced by a comparison between Figures 9 and 10. After the initial temperature surge on the external surface of the sample the slow diffusion process sets in which finally raises the conversion in time. Cross-plotting the data in these graphs resulted in the correlation shown in Fig. 14.

In Figures 15 and 16 the data for the oxide obtained from hydroxide II indicated strong sintering of the fluoride above 500°C, to such an extent that conversion levels at anytime at 600°C were lower than at 400°C. This is accounted for by the high surface area of the oxide ( $14.5 \text{ m}^2/\text{g}$ ) and consequent sintering. The highest conversion attained in this case was 94.0% at 500°C for 3 hours.

The direct hydrofluorination of the oxalate (Figs. 17 and 18)

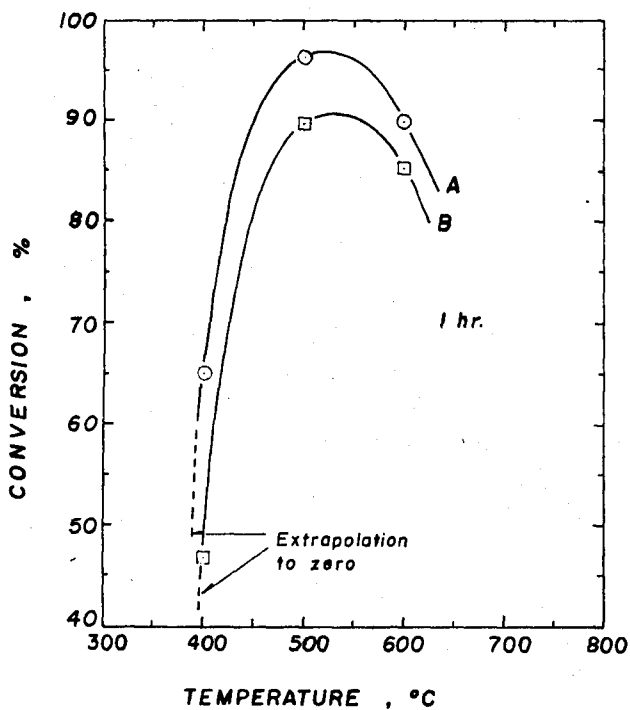


FIG. 9 Conversion vs. Temperature Curve  
Reaction Time : 1 hr  
Oxides From the Hydroxide I

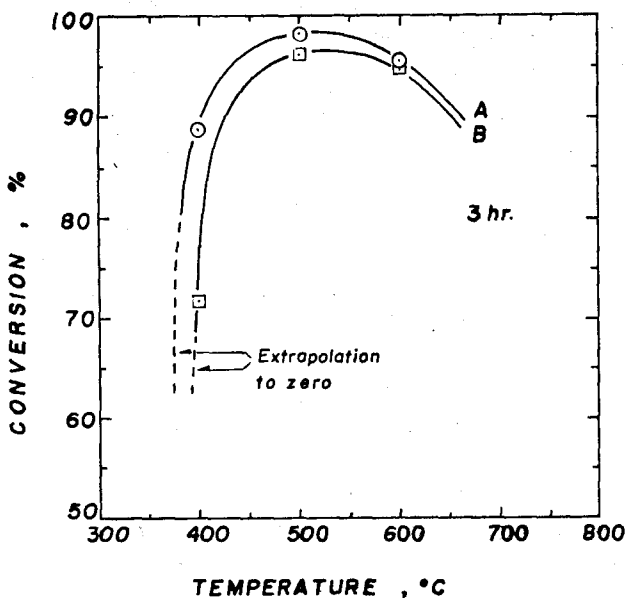


FIG. 10 Conversion vs. Temperature Curve  
Reaction Time : 3 hr  
Oxides From the Hydroxide I

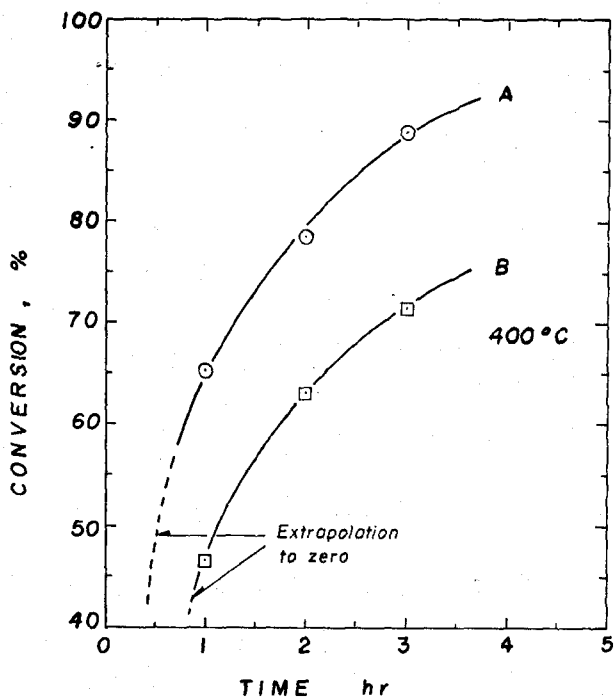


FIG. 11 Conversion vs. Time Curve  
Reaction Temperature : 400 °C  
Oxides From the Hydroxide I

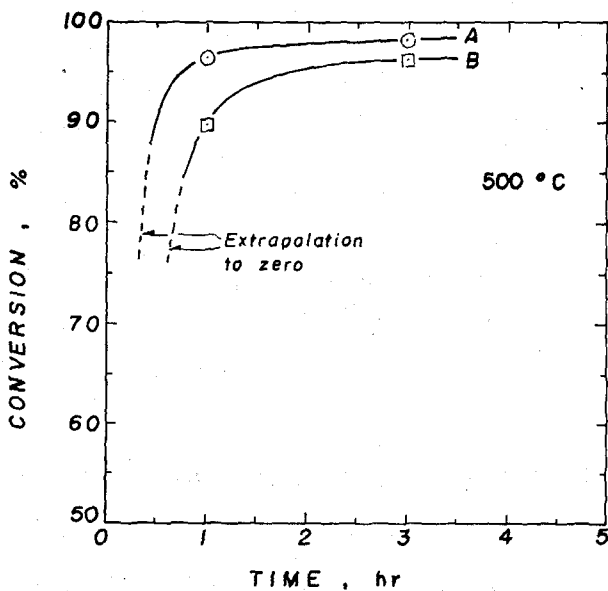


FIG. 12 Conversion vs. Time Curve  
Reaction Temperature : 500 °C  
Oxides From the Hydroxide I

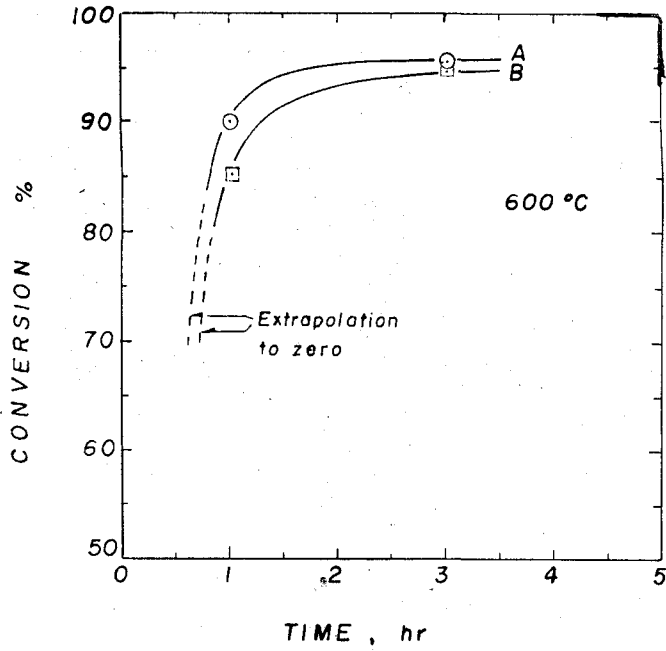


FIG. 13 Conversion vs. Time Curve  
Reaction Temperature : 600 °C  
Oxides From the Hydroxide I

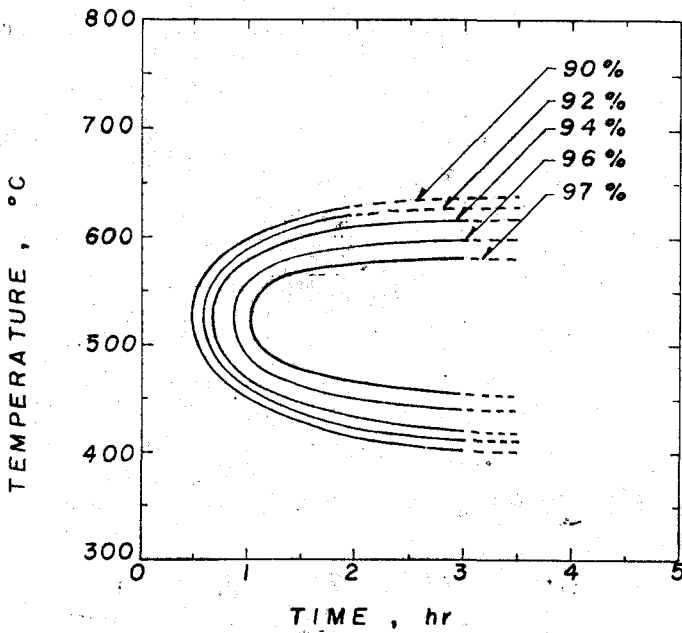


FIG. 14 Temperature - Time Correlation  
at Constant Conversion  
Oxide A From the Hydroxide I



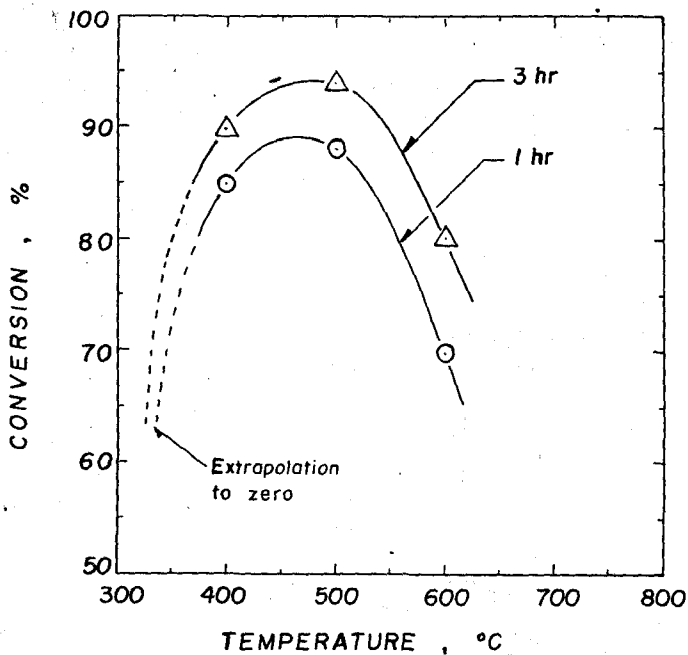


FIG. 15 Conversion vs. Temperature Curve  
Oxide A From the Hydroxide II

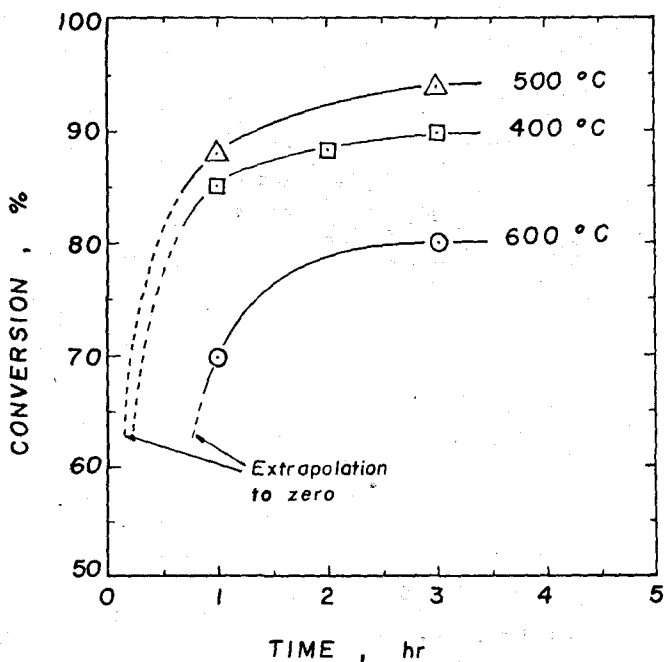


FIG. 16 Conversion vs. Time Curve  
Oxide A From the Hydroxide II

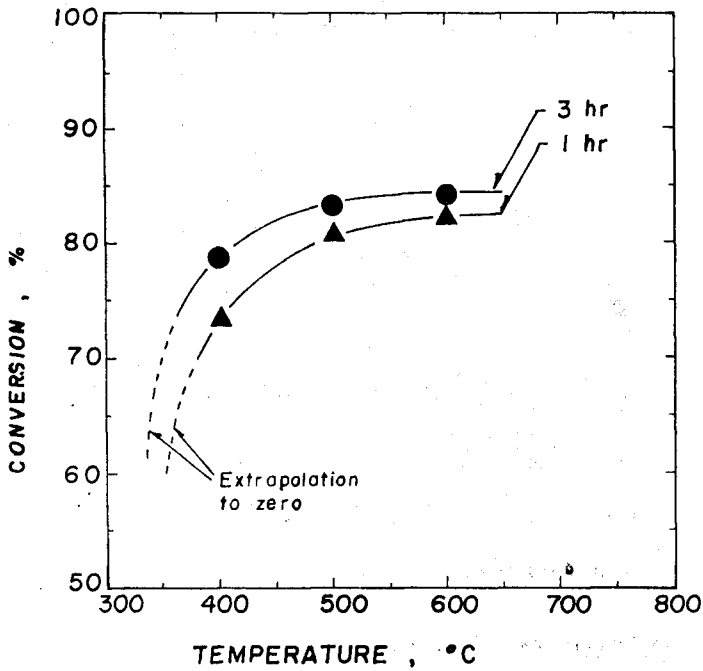


FIG.17 Conversion vs. Temperature Curve.  
Direct Hydrofluorination of the Oxalate.

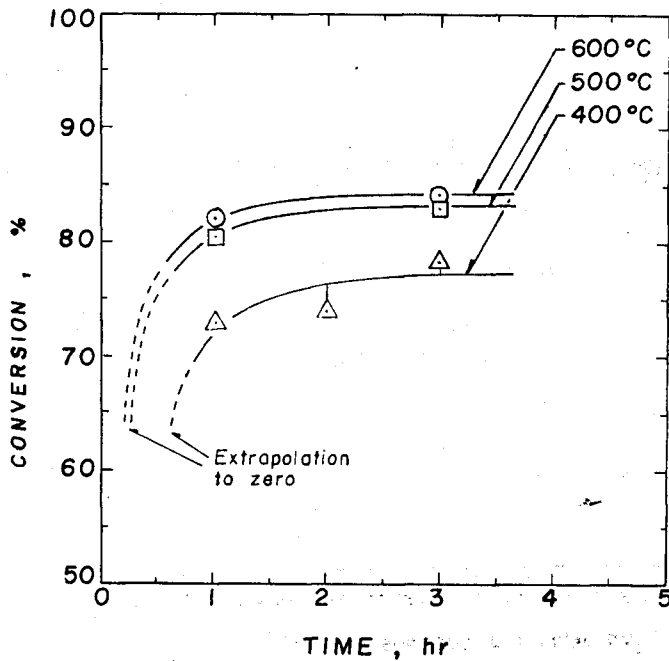


FIG.18 Conversion vs. Time Curve  
Direct Hydrofluorination of the Oxalate

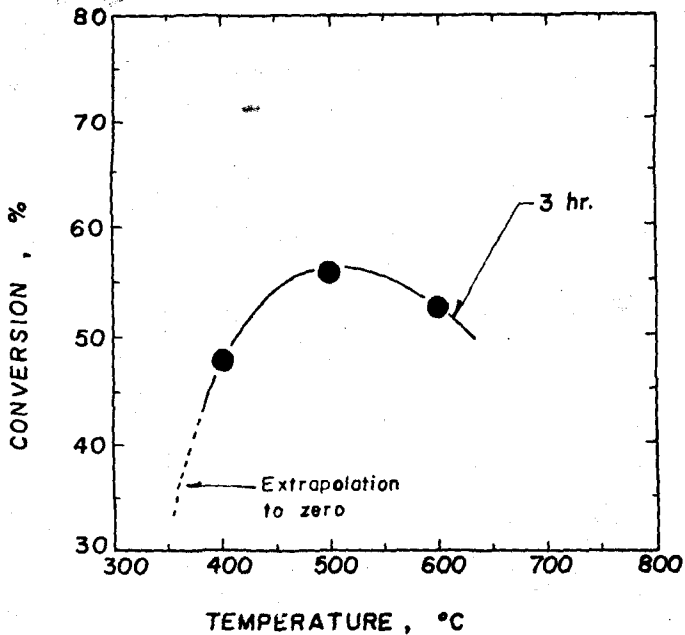


FIG.19 Conversion vs. Temperature Curve.  
Direct Hydrofluorination of the Hydroxide I

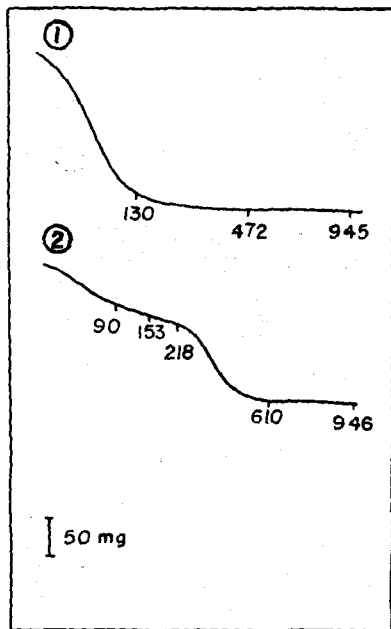


FIG.20 Pyrolysis curves of thorium derivatives (10)

- ① Hydroxide via gaseous ammonia.
- ② Oxalate

and of hydroxide I (Fig. 19) gave poor results. The light-gray color of the resulting products in both cases indicated the presence of residual carbon which probably inhibited the reaction.

#### 4. CONCLUSIONS

The oxide obtained by calcining the thorium oxalate in air at 800°C (oxide A) was by far the best starting material among all of the compounds studied. Besides the ease of preparation of the mother oxalate, this oxide gave satisfactory end conversions and little sintering upon hydrofluorination. Conversions higher than 98% can be obtained with this oxide by hydrofluorination at 500°C for 2 hours. It is believed that all end conversions reported in this work are a lower limit for the measured values, since there was some hydrolysis of the product upon cooling due to the presence of traces of water in the nitrogen fed to the reactor.

From the data for the hydrofluorination of the oxides derived from hydroxide I and II the importance of the sintering behavior in the hydrofluorination process was evidenced. A comparison between the specific areas of the different oxides calcined at 800°C (Table C.3, App. C) indicated that the lower the specific area, the lower the extent of sintering of the fluoride layer, in agreement with expected results. In all cases, at hydrofluorination temperatures above 525°C, there was a drop in conversion due to sintering of the product.

The presence of sulfate in the hydroxide markedly increased the surface area of the resulting oxide. However this had a negative effect upon its hydrofluorination behavior due to the increased sintering.

#### 5. NOMENCLATURE

$F_1$  ThO<sub>2</sub> content in any compound, mass fraction

- $F_2$   $\text{Th}(\text{SO}_4)_2$  content in any compound, mass fraction  
 $m_i$  initial mass of the sample, g  
 $m_f$  final mass of the sample, g  
 $M$  molecular weight, g/g-mol  
 $t_f$  hydrofluorination time, hr  
 $t_f^0$  hydrofluorination temperature, °C  
 $X$  fractional conversion of any material to  $\text{ThF}_4$

#### RESUMÉ

On a étudié la préparation par voie sèche du  $\text{ThF}_4$  anhydre par l'action du HF gazeux sur le  $\text{ThO}_2$ . Les fluorurations ont été mises au point dans un réacteur discontinu en bateaux de graphite à un débit de HF et température constants. Le temps, la température et la provenance de l'oxyde ont été les variables étudiées.

Les oxydes préparés par la calcination de l'oxalate à 400, 600 et 800 °C, par la calcination de l'hydroxyde à 600 et 800 °C, et par la calcination à 800 °C d'un hydroxyde contenant du sulfate, aussi bien que l'oxalate et l'hydroxyde originaux ont été soumis à l'action du fluorure d'hydrogène à des températures de 400, 500 et 600 °C par périodes de 1 et de 3 heures. Les conversions ont été mesurées par la variation de poids des échantillons.

Les conversions les plus élevées ont été celles obtenues avec un oxyde provenant de la calcination de l'oxalate à 800 °C. La corrélation des données expérimentales sous la forme de graphiques de temps contre température à conversion constant ont permis la détermination des combinaisons de temps et températures pour des niveaux de conversion choisis. À des températures supérieures à 525 °C on a observé frittage partiel du tetrafluorure.

#### RESUMO

A preparação via seca do  $\text{ThF}_4$  pela ação do HF anidro sobre o  $\text{ThO}_2$  foi estudada. As fluoretações foram feitas em um reator descontínuo em botes de grafite a um fluxo constante de HF à temperatura constante. O tempo, a temperatura e a origem do óxido foram as variáveis estudadas.

Óxidos preparados pela calcinação do oxalato a 400, 600 e 800 °C, pela calcinação do hidróxido a 600 e 800 °C e pela calcinação a 800 °C de um hidróxido contendo sulfato, juntamente com o oxalato e hidróxido originais foram fluoretados nas temperaturas de 400, 500 e 600 °C por 1 e 3 horas. A conversão foi determinada pela variação de peso da amostra.

As conversões mais elevadas foram obtidas com o óxido preparado pela calcinação do oxalato a 800 °C. Correlação dos dados experimentais na forma de gráficos de tempo vs. temperatura à conversão constante permitiram a determinação de combinações adequadas de tempo e temperatura para um nível de conversão desejado. Indícios de sinterização do tetrafluoreto foram observados à temperaturas de fluoretação superiores a 525 °C.

## 6. ACKNOWLEDGEMENTS

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8. APPENDIXAppendix A - Experimental and Calculated DataTable A.1Hydrofluorination data for oxides derived from the oxalate

$t_f^o$ (°C)	$t_f$ (hr)	Type of oxide	$m_i$ (g)	$m_f$ (g)	X (%)
400	1	A	5.0044	5.5952	70.8
		B	5.0034	5.5809	69.3
		C	5.0010	5.4910	58.8
	2	A	5.3357	6.1619	92.9
		B	3.9825	4.5253	81.8
		C	5.1882	5.7789	68.3
	3	A	4.0041	4.6565	97.8
		B	3.9552	4.5655	92.6
		C	4.0379	4.6096	85.0
500	1	A	5.0071	5.8003	95.0
		B	5.0227	5.7702	89.3
		C	4.9756	5.6513	81.5
	3	A	4.0968	4.7663	98.1
		B	4.3478	5.0191	92.6
		C	3.9723	4.5365	85.2
	1	A	5.0443	5.8441	95.1
		B	3.9883	4.5807	89.1
		C	4.0020	4.5362	80.1
	3	A	3.5160	4.0785	96.0
		B	4.0496	4.6606	90.5
		C	3.9647	4.5240	84.7

Table A.2

Hydrofluorination data for oxides derived from the hydroxide I

$t_f^o$ (°C)	$t_f$ (hr)	Type of oxide	$m_i$ (g)	$m_f$ (g)	X (%)
400	1	A	5.1699	5.7324	65.3
		B	5.1882	5.5918	46.7
	2	A	5.0915	5.7578	78.6
		B	5.0095	5.5371	63.2
	3	A	5.2821	6.0648	88.9
		B	6.0761	6.8012	71.6
500	1	A	5.2194	6.0579	96.4
		B	5.3604	6.1616	89.7
	3	A	5.7334	6.6718	98.2
		B	5.1718	6.0023	96.3
	1	A	5.1565	5.9304	90.0
		B	5.1613	5.8434	85.1
3	A	4.8714	5.6470	95.5	
	B	5.8702	6.7972	94.7	

Table A.3

Hydrofluorination data for the oxide derived from  
hydroxide II calcined at 800°C

$t_f^o$ (°C)	$t_f$ (hr)	$m_i$ (g)	$m_f$ (g)	X (%)
400	1	4.7392	5.4786	85.1
	2	5.0129	5.8279	87.9
	3	4.1746	4.8700	89.9
500	1	5.1082	5.9372	87.6
	3	5.2049	5.8700	94.0
600	1	5.0096	5.6576	69.8
	3	5.0670	5.8246	80.1



Table A.4

Direct hydrofluorination of the thorium oxalate

$t_f^c$ (°C)	$t_f$ (hr)	$m_i$ (g)	$m_f$ (g)	X (%)
400	1	4.1580	2.8240	73.1
	2	3.9676	2.8551	74.1
	3	4.3920	3.0709	78.8
500	1	4.6233	3.2127	80.6
	3	4.9684	3.4055	83.1
600	1	4.3663	3.0090	82.1
	3	4.6054	3.1405	84.0

Table A.5

Direct hydrofluorination of the hydroxide I

$t_f^o$ (°C)	$t_f$ (hr)	$m_i$ (g)	$m_f$ (g)	X (%)
400	3	5.5992	5.4276	47.7
500	3	5.0699	4.9090	55.9
600	3	5.8995	5.7083	52.5

Appendix B - Conversion calculations

The end conversion of a sample was calculated by performing a material balance on the boat contents as follows:

$$\begin{array}{l} \text{final weight} = \text{weight of} + \text{weight of} \dots\dots\dots (1) \\ \text{unreacted} \qquad \qquad \text{ThF}_4 \text{ produc} \\ \text{material} \qquad \qquad \qquad \text{ed} \end{array}$$

In mathematical form we can then write:

$$m_f = m_i(1 - X) + (m_i X F_1) \frac{M_{\text{ThF}_4}}{M_{\text{ThO}_2}} \dots\dots\dots (2)$$

or by rearrangement:

$$X = \frac{1}{\left[ F_1 \frac{M_{\text{ThF}_4}}{M_{\text{ThO}_2}} - 1 \right]} \left[ \frac{m_f}{m_i} - 1 \right] \dots\dots\dots (3)$$

In our calculations we considered three different cases , which were as follows:

Case 1 : The initial sample contained ThO<sub>2</sub> only (F<sub>1</sub> = 1).

$$X = 6 (m_f/m_i - 1) \dots\dots\dots (4)$$

Case 2 : The initial sample contained some Th(SO<sub>4</sub>)<sub>2</sub> (F<sub>1</sub> < 1).

Hence Eqn. 3 was of the form

$$X = \frac{1}{\left[ F_1 \frac{M_{\text{ThF}_4}}{M_{\text{ThO}_2}} + F_2 \frac{M_{\text{ThF}_4}}{M_{\text{Th}(\text{SO}_4)_2}} - 1 \right]} \left[ \frac{m_f}{m_i} - 1 \right] \dots\dots (5)$$

For the oxide studied the  $SO_4^{=}$  content was 2.65 %, therefore  $F_2 = 0.0585$  and Eqn. 5 reduced to

$$X = 5.4 (m_f/m_i - 1) \dots\dots\dots (6)$$

Case 3 : The sample consisted either of oxalate or hydroxide ( $F_1 < 1$ ). The assumption was then made that no unreacted oxide was present in the final sample, hence Eqn. 3 assumed the following forms

oxalate:  $X = 2.6 (1 - m_f/m_i) \dots\dots\dots (7)$

hydroxide:  $X = 16.2 (1 - m_f/m_i) \dots\dots\dots (8)$

Appendix C - Physical properties of the powders

Table C.1

Sieve analysis of the raw materials

U.S. Standard Sieve (mesh)		Thorium oxalate (%)	Thorium hydroxide I (%)	Thorium hydroxide II (%)
	+ 20	-	3.33	-
- 20	+ 65	89.00	3.97	22.00
- 65	+100	10.20	3.95	3.00
-100	+150	] 0.80	7.60	6.20
+150	+200		5.90	11.90
-200	+325		9.32	25.60
-325			69.96	31.30

Table C.2

Densities of the raw materials

Density (g/cm <sup>3</sup> )	Thorium oxalate	Thorium hydroxide I	Thorium hydroxide II
bulk	0.52	1.32	1.34
tap	0.72	1.49	1.56

Table C.3

Specific surfaces of the oxides obtained by  
calcining the raw materials at 800°C

	Raw material		
	Thorium oxalate	Thorium hydroxide I	Thorium hydroxide II
Specific surface (m <sup>2</sup> /g)	1.1	6.4	14.5