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DISSOLUTION OF THORIUM IN MIXTURES OF HNO_3 AND HF

by

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ABSTRACT

Laboratory measurements of rates of dissolution of thorium in mixtures of nitric and hydrofluoric acids show that thorium can be dissolved with practicable time cycles in large-scale processing. The corrosion of stainless steel during the dissolution of thorium is acceptable, except that when the thorium is coated with Al-Si alloy, frequently used as a bonding material for aluminum cans, severe local corrosion of the stainless steel occurs at areas of contact with residual Al-Si. This contact corrosion does not occur when the cans are hot-press-bonded to the thorium without Al-Si.

CONTENTS

LIST OF TABLES AND FIGURES

DISSOLUTION OF THORIUM IN MIXTURES OF HNO_3 AND HF

INTRODUCTION

Neutron irradiation of thorium to produce U^{233} is the basis for a thermal breeder power reactor. The buildup of fission product poisons prevents complete conversion of the thorium. Removal of the fission products and separation of the fissionable U^{233} from the residual thorium by aqueous processing methods analogous to the Purex process require that the irradiated thorium be dissolved in nitric acid. Previous studies have shown that thorium can be dissolved in nitric acid if HF is present to catalyze the reaction.(1) This report describes laboratory study of the HF-catalyzed dissolution of thorium with nitric acid, with the objectives of obtaining data for predicting the performance of the dissolving process on a large scale and determining the severity of corrosion of stainless steel equipment by the HF.

SUMMARY

The rates of dissolution of thorium in mixed solutions of nitric and hydrofluoric acids were measured and used for calculating dissolving times on a large scale. The calculated times were well within the range of practical operability.

The general corrosion of stainless steels 304L and 309Cb by the dissolving solutions was acceptable, 10 mils per year or less, but when the thorium was bonded to aluminum cans with Al-Si alloy and spots of residual Al-Si adhered to the thorium after alkaline dissolution of the cans, extreme attack, 5 inches per year, of the stainless steel occurred at spots in contact with the residual Al-Si. This localized contact corrosion was not observed with thorium fuel elements that were canned by hot-press bonding the aluminum to the thorium without Al-Si.

DISCUSSION

EXPERIMENTAL PROCEDURES

Rates of dissolving were measured by immersing cylindrical elements of thorium, of measured weight and area, in the dissolving solutions, and removing and weighing the elements after measured periods of dissolution. Decreases in area of the elements were calculated from the losses in weight, on the basis of the experimental observation that the cylinders dissolved 30% faster at the ends than at the longitudinal surface.

The solutions were analyzed after each period of dissolution. The concentrations of thorium were measured by titration with disodium ethylenediamine tetraacetic acid at pH 2.8, with sodium alizarin sulfonate as indicator.(2) The concentrations of acid were measured by titration to pH 7.3 with sodium hydroxide, with potassium oxalate added to prevent interference by the thorium. Hydrofluoric acid was separated by distillation from a sulfuric acid solution, and was measured by titration with a solution of thorium nitrate with sodium alizarin sulfonate used as an indicator.(3)

Rates of corrosion of stainless steel were determined by the loss of weight of coupons of measured area. The corrosion rates were averaged over the entire area of the coupon, except when the attack was obviously nonuniform.

PRELIMINARY STUDIES

The first thorium elements used in the dissolution tests were cylinders to which aluminum cans were bonded with Al-Si alloy. Two methods were tested for dissolving these elements. In an integral dissolution method, the aluminum can, the Al-Si, and the thorium were dissolved in a single solution of nitric acid that contained both mercuric nitrate to catalyze dissolution of the aluminum,and fluoride to catalyze dissolution of the thorium. In the second method, the aluminum can and Al-Si were first dissolved with a solution of NaOH and $NaNO_3$; this solution was drained and rinsed from the thorium, and the thorium was then dissolved in a solution of HNO_3 and HF. In preliminary tests with integral dissolution, the attack on the Al-Si bonding alloy by the mixed solution of Hg^{++}, HF, and HNO_3 was very slow and the final solution contained an objectional amount of solid silicon. The two-step process was faster and yielded a product solution relatively free of solids. It was therefore selected as the basis for the remainder of the study.

Scouting experiments with uncanned thorium showed that the most desirable initial concentration of nitric acid was 10M HNO_3 or less, and that 0.05 to 0.1M HF was sufficient to catalyze the reaction. Nitric acid at concentrations of 12M or greater yielded solutions from which thorium nitrate precipitated at room temperature. The results of these tests are shown in Table I. The composition of the gas evolved during dissolution was 85% NO, 7.6% N_2, 3.5% H_2, 2.1% H_2O, and less than 1% of NO_2, N_2O, and O_2. An average of 5.22 ±0.22 mols of acid was consumed per mol of thorium dissolved.

TABLE I

Effect of HNO_3 Concentration on Dissolver Product Solution

Initial thorium 170 to 190 g; 36 to 39 cm^2 surface
Dissolved at boiling temperature of solution

Initial Dissolving Solution			Dissolution	Product Solution	
HNO_3, M	HF, M	Volume, ml	Time, hr	Th, M	HNO_3, M
8	0.12	200	4.5	1.68	1.37
10.4	0.05	400	8	1.86	1.60
10.3	0.1	400	8	2.18	0.35
12.4	0.1	400	8	2.58(a)	0.50
14	0.1	250	7.5	2.56(a)	2.41

(a) $Th(NO_3)_4$ precipitated when solutions were cooled to 30°C.

DISSOLVING RATES

The dissolving rates of thorium were measured in solutions of the six compositions shown in Table II and Figure 1, which also present the smoothed data for dissolving rates. The rates of dissolving decreased exponentially with a linear increase in concentration of thorium in the solution. The following empirical equations define, within 10%, the dissolving rates for initial dissolving solutions of 10M HNO_3 and four concentrations of HF.

Initial HF, M	Dissolution Rate, R mg/(cm^2)(min)	Limits of Applicability, H^+, M
0.1	$1.1 \exp(0.603H^+) - 0.01 \exp(1.085H^+)$	0.5 to 10
0.075	$1.02 \exp(0.512H^+) - 0.75$	1.5 to 10
0.05	$0.95 \exp(0.50H^+) - 0.85$	1.0 to 10
0.01	$0.0127 \exp(0.693H^+)$	5 to 10

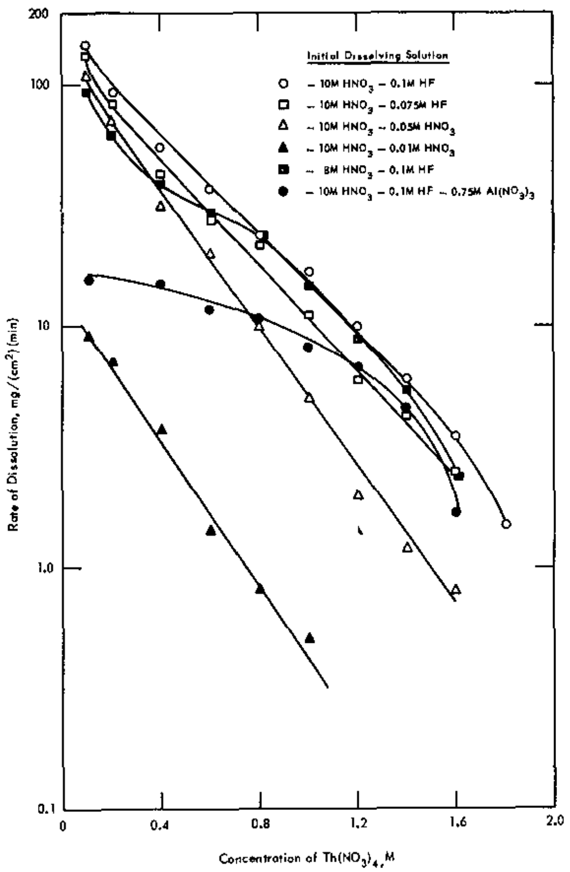

FIGURE 1 – DISSOLUTION OF THORIUM IN MIXTURES OF HNO_3, HF, $Al(NO_3)_3$, AND $Th(NO_3)_4$

TABLE II

Thorium Dissolving Rates

$mg/(cm^2)(min)$

Concentration of Thorium Dissolved, M	Rate of Dissolution in Solution of Indicated Initial Composition					
	10M HNO_3 0.01HF	10M HNO_3 0.05M HF	10M HNO_3 0.075M HF	10M HNO_3 0.1M HF	8M HNO_3 0.1M HF	10M HNO_3 0.1M HF 0.75M $Al(NO_3)_3$
0.1	9.0	115	132	148.0	95	15.4
0.2	7.05	70	85	92.5	63	
0.4	3.7	32	43	55.0	39.5	14.0
0.6	1.4	20	28	37	30.4	11.8
0.8	0.80	10	22.5	25	26	10.3
1.0	0.50	5	11	17	15	8.3
1.2		2	6	10	9	6.7
1.4		1.2	4.5	6	5.5	4.4
1.6		0.8	2.5	3.5	2.5	1.7
1.8				1.5		

CALCULATIONS OF TIME CYCLES

The time cycles for dissolution were calculated by use of the following model for the dissolving process:

1. Three cylindrical elements of thorium with aluminum cans are initially charged to the dissolver.
2. The cans are dissolved with NaOH-$NaNO_3$ and the solution is removed.
3. One-third of the thorium is dissolved and the solution is removed.
4. One-half of the remaining thorium is dissolved and the solution is removed.
5. Two more canned elements are charged, to restore the total thorium metal in the dissolver to the equivalent of three whole elements, and the cycle of Steps 2 through 5 becomes repetitive.

The times required for Steps 3 and 4 of the model process at 1/3 of the foregoing scale were calculated from the data of Figure 1 by incremental integration. The time required to dissolve the first 1/3 of the thorium in a one-element batch of 900 grams was calculated from the sum of the times necessary to dissolve six successive 50-gram increments of the thorium. Each of the six increments of time was calculated from the area of the element and the measured rate of dissolving at the proper concentration of solution:

$$\text{Minutes required to dissolve 50 g} = \frac{\text{50,000 mg}}{[\text{Rate, mg/(cm}^2\text{)(min)}][\text{Area, cm}^2]}$$

The area of the element used in the calculation was decreased for the amount of thorium dissolved in each increment, and the respective rates of dissolution were selected from the experimental data to correspond with the composition of the solution at the midpoint in the dissolving of each increment. The sum of the six incremental dissolution times is the time calculated for Step 3 in the model process: dissolution of 1/3 of the thorium. The calculations were repeated for six additional 50-gram increments; this operation gave the time necessary for Step 4: dissolution of the second 1/3 of the thorium.

The calculated dissolving times were verified by dissolving three elements of thorium in a solution of 10M HNO_3 and 0.05M HF. These experiments duplicated the model process used for the calculation, and the results confirmed the calculated dissolving times (Table III). Table III also includes the calculated times that correspond to two higher concentrations of HF and the results of one experimental test with 0.10M HF.

TABLE III

Comparison of Calculated and Experimental Dissolving Times

Initial Dissolving Solution		Thorium Increment Dissolved	Incremental Dissolving Time		Product Solution	
HNO_3, M	HF, M		Actual, hr	Calc.,[a] hr	$Th(NO_3)_4$, M	HNO_3, M
10	0.05	1st 32.2%	8.0	8.1	1.87	0.95
		2nd 33.0%	11.0	11.4	1.95	0.7
10	0.075	1st 33.3%		6.6		
		2nd 33.3%		9.5		
10	0.10	1st 33.3%	4.0	3.5	1.90	1.10
		2nd 33.3%		5.3		

(a) Time required for dissolving first and second 33.3% increments.

CORROSION TESTS

Corrosion tests of coupons of 309Cb and 304L stainless steels were made simultaneously with the measurement of dissolving rates of canned thorium elements. Some of the steel coupons were tested in contact with both the stainless steel (probably 304L) dissolving vessel and the thorium metal, and other coupons were tested in contact only with the solution. The steel coupons were exposed for two complete cycles of the dissolving process: dissolution of the aluminum can, dissolution of the first 1/3 of the thorium, and dissolution of the second 1/3 of the thorium.

The corrosion tests showed a slight gain in weight of the steel during dissolution of the aluminum can, and nominal rates of corrosion, usually less than 10 mils per year, during dissolution of the thorium. The corrosion behavior was about the same for 309Cb and 304L stainless steels. Welded coupons corroded at about twice the rates of unwelded coupons, but examination showed no obvious localized attack at the welds. Rates of corrosion during dissolving with solutions of 10M HNO_3 - 0.1M HF were about twice as fast as during dissolvings with 10M HNO_3 - 0.05M HF. The data are summarized in Table IV.

TABLE IV

Normal Corrosion of Stainless Steel During Dissolution of Thorium

Dissolution Step	Dissolving Solution	Corrosion Rate, mils/yr	
		309Cb	304L
Cans	4M NaOH	(a)	(a)
1st 1/3 of Thorium	10M HNO_3, 0.1M HF	11	9
	10M HNO_3, 0.05M HF	5	5
2nd 1/3 of Thorium	10M HNO_3, 0.1M HF	2	1.2
	10M HNO_3, 0.05M HF	2	3

(a) Slight gain in weight

Corrosion of the steel is inhibited effectively by complexing of the fluoride with the dissolved thorium. The measured dissolving rates show that the concentration of thorium in the dissolver solution is 0.3M within five minutes after the initiation of dissolving. Within experimental error, no decrease in the rate of corrosion was observed when 0.03M $Th(NO_3)_4$ was included in an initial dissolving solution of 10M HNO_3 and 0.05M HF.

CONTACT CORROSION

In the course of the dissolution tests, deep pits were observed in the bottom of the stainless steel dissolver vessel at areas of contact with the thorium element. Stainless steel 304L and 309Cb coupons placed under the thorium were also attacked; one coupon was attacked at a rate of 5 inches per year (Figure 2).

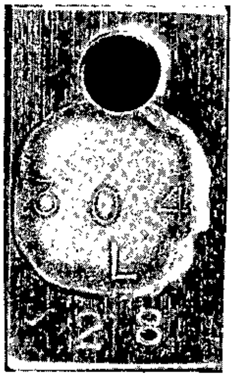

FIGURE 2 - CORROSION OF 304L STAINLESS STEEL IN CONTACT WITH THORIUM

Efforts to correlate the "contact corrosion" with the condition of the steel coupons and the thorium elements were fruitless. Various coupons were hammered, filed, etched with HF, and placed in contact with carefully cleaned thorium metal, but no contact corrosion of the steel occurred when the clean thorium was dissolved. To provide reproducible contacts, steel coupons were bolted to clean thorium metal. None of these measures caused any abnormal corrosion.

In the testing of various thorium elements, it was observed that contact corrosion of steel occurred only with elements to which the aluminum cans were bonded by Al-Si dipping processes (Table V). Tests were made with elements with cans bonded by single dip, double dip, and triple dip processes, and by a hot-press process developed by Sylcor. The dipping processes are all similar; the thorium elements are dipped in one or more baths of the bonding alloys and then placed, while the last coating of Al-Si is still molten, in the aluminum can and sealed. This type of canning process produces two or three intermetallic compounds. In the Sylcor hot-press process, the thorium is placed in the can and the element is subjected to a pressure of 20 tons per square inch at 520°C. Intermetallic compounds are formed between the aluminum and the thorium.

TABLE V

Effect of Bonding Alloy on Contact Corrosion

Bonding Process	Tests	Cases of Contact Corrosion
Single dip	7	3
Double dip	12	5
Triple dip	3	1
Sylcor hot-press	42	None

The contact corrosion that occurred when the dip-bonded elements were dissolved was observed only during the second and third dissolving steps (Table VI). It was also observed that the pattern of the contact corrosion was identical with the pattern of the bonding material left on the thorium (Figure 3). A portion of the corrosive bonding material that was flaked from a partially dissolved element was shown by emission spectroscopy to be mainly silicon in the exposed layer and silicon-aluminum intermetallic compound in the layer next to the thorium. No thorium was detected in the flaked material. The observation that the contact corrosion occurs only during the second and third dissolving steps was not explained. The severity of the contact corrosion suggests that it is caused by an electrochemical mechanism.

TABLE VI

Contact Corrosion by Bonded Elements

Thorium Dissolution Step	Total Tests	Observations of Contact Corrosion
First	17	None
Second	9	9
Third	4	4

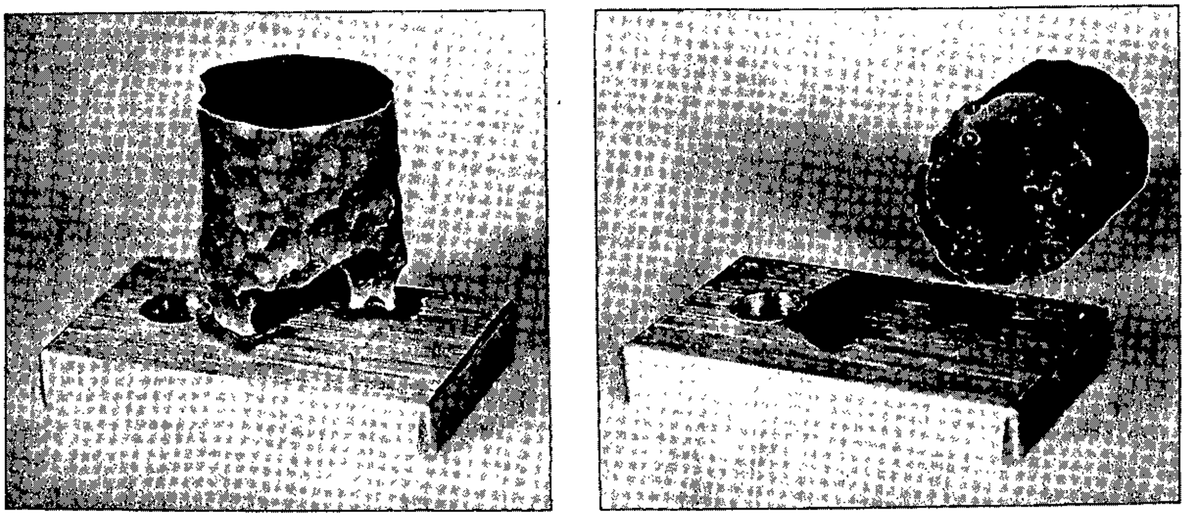

FIGURE 3 - EFFECT OF ADHERENT Al-Si ON CORROSION OF 309Cb STAINLESS STEEL IN CONTACT WITH DISSOLVING THORIUM
(Prior to dissolution the thorium was a smooth-surfaced cylinder, free of adherent Al-Si except for the area at which contact corrosion of the steel coupon occurred)

Changes in the rate of contact corrosion with changes in the composition of the solution were estimated by placing a piece of Al-Si-bonded thorium on a stainless steel coupon and stopping the dissolution at various intervals to measure the loss of weight of the coupon. These data are shown in Figure 4 and Table VII. The decrease in rate of corrosion with increasing concentration of the solution is probably indicative of an effect of the solution on the corrosion, although part of the decrease may be due to a decrease in area of contact.

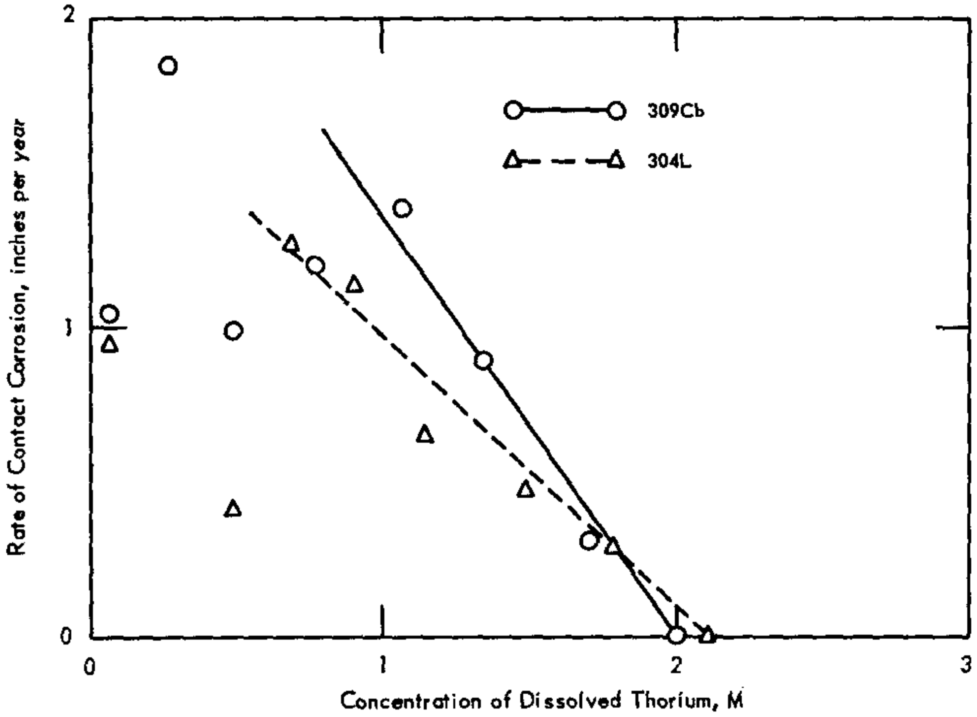

FIGURE 4 - CONTACT CORROSION OF STAINLESS STEEL DURING DISSOLUTION OF THORIUM

The study of contact corrosion established the correlation between Al-Si-bonded Th and contact corrosion, but no method of prevention was found. It was concluded that only hot-press bonding should be used for canning elements that are to be dissolved in solutions of HNO_3-HF in stainless steel equipment.

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TABLE VII

Contact Corrosion Rates During Dissolution of Thorium

Contact Time, min.	Peak Temp., °C	Time at Peak Temp., min.	Thorium in Solution, M	Corrosion of Steel: Wt. Loss, mg	Corrosion of Steel: Rate, inches/year
309Cb Stainless Steel					
8	80	-	0.077	6.1	4.9
8	100	-	.268	10.6	8.6
12	110	-	.494	8.5	4.6
17	110	5	.788	14.3	5.5
21	108	10	1.058	21.7	6.7
37	108	20	1.35	21.8	4.2
57	107	40	1.72	13.6	1.6
100	106	80	1.97	0.7	0.05
304L Stainless Steel					
10	80	-	.1(a)	3.3	4.3
9	100	-	.3(a)	2.6	1.9
12	110	-	.5(a)	10.3	6.0
15	110	5	.891	12.4	5.4
21	108	10	1.16	9.9	3.1
37	107	20	1.47	13.5	2.0
58	107	40	1.81	14.2	1.6
93	107	80	2.12	1.3	0.09

(a) Estimated

BIBLIOGRAPHY

1. Gresky, A. T. et al., Laboratory Development of the Thorex Process. Oak Ridge National Lab., ORNL-1267 (Rev.) December 17, 1952 (Declassified).

2. Fritz, J. J. and Ford, J. J., "Titrimetric Determination of Thorium." Anal. Chem. 25, 1640-2 (1953).

3. Murray, B. B., The Determination of Fluoride in Plutonium Fluorides. E. I. du Pont de Nemours and Co., DP-247, October 1957.