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A KINETIC STUDY OF THE FLUORIDE CATALYZED NITRIC ACID DISSOLUTION OF THORIUM METAL

By

C. A. Goodall, J. L. Hepworth, R. L. Moore and R. A. Watts, Jr.

Chemical Research Sub-Section
Separations Technology Section

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A KINETIC STUDY OF THE FLUORIDE CATALYZED NITRIC ACID DISSOLUTION OF THORIUM METAL

I. INTRODUCTION

Thorium metal, unlike uranium, exhibits a negligible rate of dissolution in boiling nitric acid. Thus the penetration rate of thorium is approximately 1 $mg/hr/cm^2$ versus 1300 $mg/hr/cm^2$ for uranium in 60 per cent nitric acid. Fortunately, the reaction is strongly catalyzed by small concentrations of fluoride, an effect discovered by Schuler, Steahly, and Stoughton,(1) and it is thus possible to prepare a Thorex feed solution by employing fluoride concentrations of the order of 0.1 molar. However, even this concentration of fluoride causes concern because of the increased rate of corrosion of the dissolver and accessory equipment. There is also evidence from ORNL pilot plant runs that a portion of the fluoride is extracted into the tributyl phosphate solvent employed in the Thorex process and may, therefore, cause corrosion in intercycle concentrators or in acid recovery equipment. High concentrations of fluoride are also undesirable if protactinium is to be removed or recovered from the feed by scavenging techniques.(2)

For these reasons it would be very desirable to be able to eliminate the use of fluoride. However, a search for an alternate process not involving fluoride was unsuccessful as most of the reagents tried did not attack the metal. Hydrochloric and phosphoric acid dissolved thorium readily but produced precipitates, presumably the oxide (or oxychloride) and phosphate respectively. Anodic electrolysis also disintegrated thorium but produced a copious precipitate.

A study of the rate of the fluoride catalyzed reaction was accordingly made in the hope that it might be possible to significantly decrease the concentration of fluoride employed without unduly increasing dissolving time cycles. It was also desired for Hanford application to employ a high acid extraction flowsheet analogous to the Purex process and amenable to construction of a dual-purpose separations plant. It was,therefore, of interest to determine what time cycles would result from terminating the dissolving while excess acid was still present rather than digesting to an acid deficient condition, as had been the prior Thorex practice. This report summarizes the results of these investigations.

II. SUMMARY

1. Penetration rate measurements showed that the reaction of thorium metal with boiling nitric acid is strongly catalyzed by fluoride at concentrations up to about 0.1 molar. The rate of reaction also increases with increasing nitric acid concentration, reaching a maximum for nitric acid concentrations in the vicinity of 13 molar.

2. A sample of massive thoria of 97 per cent theoretical density (sintered at 1800 C and 20,000 psi) exhibited penetration rates five to five-hundred fold lower than those of thorium metal. This indicates that dissolution of thoria fuel elements at satisfactory rates may prove difficult unless the specific surface is large. This may influence fuel element design or require fracturing prior to dissolution. The slow dissolution rate also correlates with the reported intractable behavior of the "blue thorium" observed in dissolution of irradiated thorium metal.

3. Dissolved thorium and aluminum were found to markedly inhibit the rate of thorium dissolution. Half molar aluminum nitrate increased the time cycle in a batch dissolving by a factor of about four. It is accordingly recommended, for maximum dissolving rates, that aluminum cans be removed by caustic dissolution or mechanical stripping prior to thorium dissolution.

4. Integral batch dissolvings, simulating plant procedure, were carried out with fluoride catalyst concentrations ranging from 0.005 to 0.075 molar and initial nitric acid concentrations of 8 to 15.7 molar. The fluoride concentration was found to be the more important variable. The time cycles

were also sensitive to the terminal thorium concentration. Thus three to four times longer was required to dissolve to a terminal thorium concentration of two molar as to one molar, and dissolution to a 200 per cent heel (approximately 2.8 molar thorium) increased the time ten fold.

5. A fluoride concentration of about 0.03 molar and an initial acidity of 10 to 13 molar are recommended as representing a satisfactory compromise between the various factors.

6. The integral dissolving data were found to fit an empirical equation:

$$\frac{1}{W_{\infty} - W} = kt + \frac{1}{W_{\infty}}$$

where W is the weight loss in time t and W_{∞} is the weight loss at "infinite" time according to the stoichiometry of the reaction, which corresponded very nearly to:

$$\mathrm{Th} + 6\,\mathrm{HNO_3} \longrightarrow \mathrm{Th(NO_3)_4} + 3\,\mathrm{H_2O} + \mathrm{NO} + \mathrm{NO_2}.$$

The rate constant, k, is proportional to the initial surface area, to the square of the initial acid concentration, and to the first power of the fluoride concentration.

III. EXPERIMENTAL

Two types of experiments were performed. These consisted of the measurement of instantaneous penetration rates and integral dissolvings, the latter simulating an expected plant dissolving procedure. The penetration rates were measured by essentially the same procedure used in earlier studies of uranium dissolution.(3) Wafers 1.3437 inches in diameter and approximately one-eighth of an inch thick (cut from Hanford production slugs) were immersed for periods of two to four minutes in a boiling solution of the desired composition (250 ml contained in a stainless steel beaker). After removal from the dissolving medium they were washed immediately in water

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and then in acetone and the weight loss and final dimensions determined. The specific penetration rate, in terms of weight loss per unit time per unit area ($mg/hr/cm^2$), was calculated from this data. The effects of pitting of the wafer and change in composition of the solution were ignored, and the error from these sources is believed, in general, to have been negligible. A new wafer was used for each measurement. Metal fabricated by both extrusion and rolling was used in the experiments, and no difference was found in the dissolving rate.

The integral dissolvings were carried out in a pot type dissolver equipped with an up-draft condenser. The dissolver consisted of a one-liter stainless steel beaker fitted with a Teflon-gasketed top and heated with a hot plate. The condenser was a water-jacketed thirty-inch length of one-half inch diameter stainless steel tubing. The charge to the dissolver consisted, in most experiments, of a two-inch length (weight approximately 500 grams) of a Hanford slug. The initial specific surface of a two-inch section of slug is 0.022 in.^{2}/gram compared to 0.018 in.^{2}/gram for a complete six-inch slug. The quantity of nitric acid used was based on the empirical equation:

$$Th + 6\ HNO_3 \longrightarrow Th(NO_3)_4 + 3\ H_2O + NO + NO_2$$

and was so computed, in most of the experiments, that a 200 per cent heel of unreacted metal would remain on completion of the reaction, i.e., one-third of the charge was dissolved. The course of the dissolution was followed by analysis for thorium and nitric acid of 0.5 ml samples withdrawn as a function of time. The slug was also periodically removed and weighed as a cross check on the thorium analyses. The dissolutions were all carried out at the boiling point which was approximately 110 C. Due to the extreme vigor and exothermic character of the reaction in the early stages, it was generally necessary to cease external heating during this period to prevent boil-over. Dilution water was added at the end of the dissolving to make up for evaporation and prevent solidification on cooling.

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IV. DATA AND RESULTS

A. Penetration Rate Measurements

The rate of penetration was determined as a function of concentration of fluoride, concentration of nitric acid, and concentration of dissolved thorium. All of the experiments were run at the boiling point of the respective solutions. A few experiments were performed to determine the effect of additives, such as aluminum, and to compare the effectiveness of other fluoride salts such as fluoborate and fluosilicate to hydrofluoric acid. The results follow.

1. Effect of Fluoride Concentration - The effect of fluoride concentration on the initial rate of attack of thorium by boiling 60 per cent nitric acid (13 M) is shown in Table I and graphically in Figure 1. It will be noted that the dissolving rate is very nearly linear in fluoride concentration at low concentrations of catalyst. The rate reaches a maximum, however, at about 0.1 molar hydrofluoric acid and decreases slightly at higher concentrations, apparently due to exceeding the solubility product of thorium fluoride. The maximum rate of the catalyzed reaction was found to be approximately ten thousand times the rate in the absence of fluoride (1.3 $mg/hr/cm^2$).

It will also be noted that for fluoride concentrations greater than about 0.002 molar the rate equals or exceeds that of uranium which is 1300 $mg/hr/cm^2$ at this acidity. For this reason it was thought that it might be possible to reduce the concentration of fluoride employed in a plant dissolving, say to a few thousandths molar, without drastically increasing time cycles.

2. Effect of Nitric Acid - The effect of nitric acid concentration, at constant fluoride concentrations of 0.005 and 0.05 molar, are shown in Table II and Figure 2. The dissolution rates of uranium(3) without fluoride catalysis are included for purposes of comparison. It will be noted that these initial rates are greater for thorium than for uranium, both for 0.05 and 0.005 molar fluoride

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TABLE I

EFFECT OF FLUORIDE ON PENETRATION RATE OF THORIUM BY NITRIC ACID

All measurements in boiling 13 M HNO_3.
Temperature approximately 110°C.

M Hydrofluoric Acid	Penetration Rate (mg/hr/cm^2)
0	1.3
0.0001	23
0.0002	83
0.0005	230
0.001	470
0.002	810
0.0025	1710
0.005	3410 3020
0.01	5200
0.05	8910 7060
0.1	10440
0.2	11120
0.5	9130
1.0	6950

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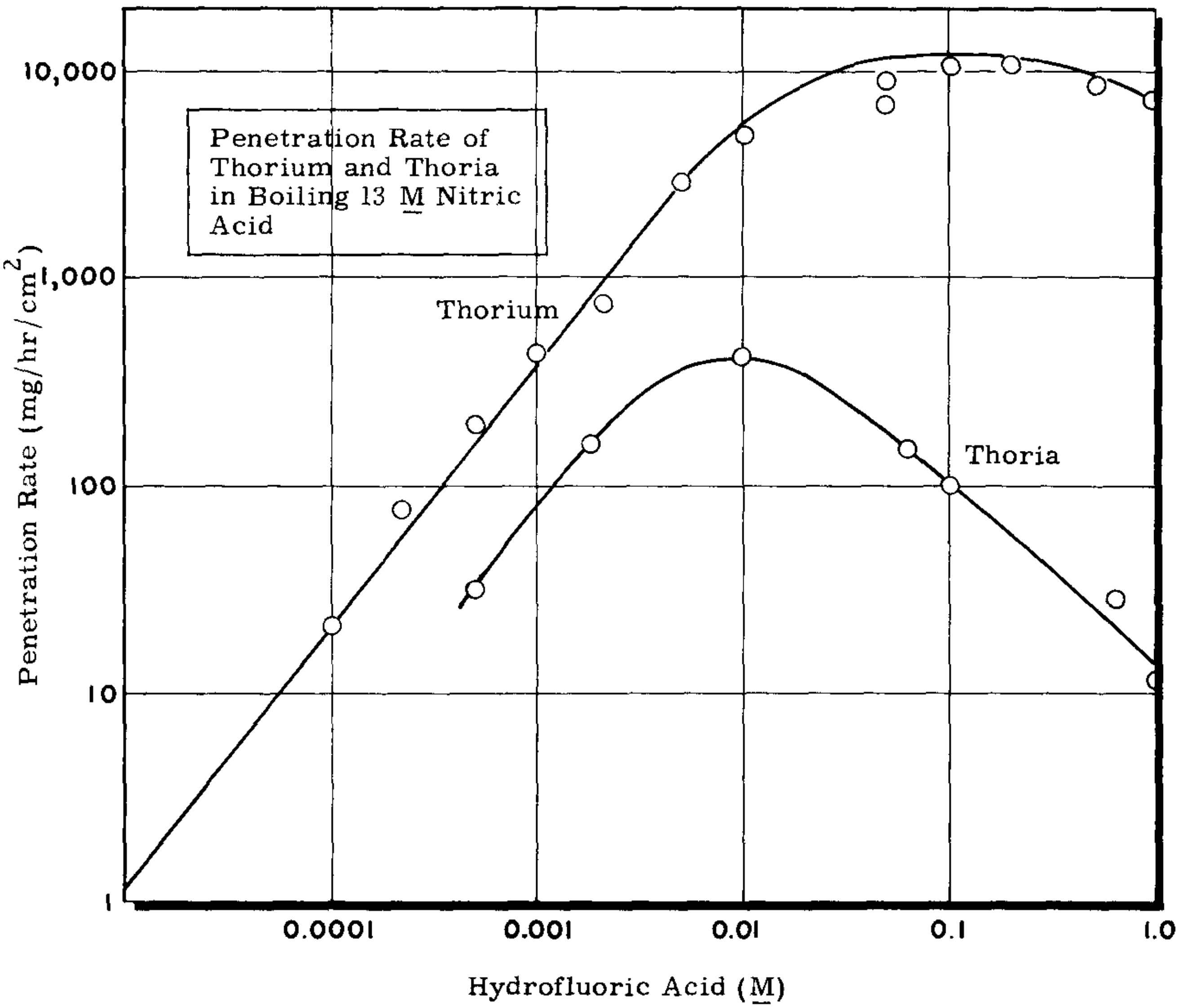

Penetration Rate of Thorium and Thoria in Boiling 13 M Nitric Acid
Thorium
Thoria
Penetration Rate (mg/hr/cm^2)
10,000
1,000
100
10
1
0.0001
0.001
0.01
0.1
1.0
Hydrofluoric Acid (M)

FIGURE 1

[redacted]

TABLE II

EFFECT OF NITRIC ACID ON THE INITIAL PENETRATION RATES OF THORIUM AND URANIUM

Boiling HNO_3 - HF solutions, indicated composition.

Nitric Acid Conc. (M)	Thorium		Uranium
	0.005 M HF mg/hr/cm^2	0.05 M HF mg/hr/cm^2	(No HF) mg/hr/cm^2
2	290	1270	26
4	420	2240	---
5	---	---	150
6	710	3450	---
7.5	---	---	350
8	---	5000	---
10	2410	6740	740
13	3200	8000	1300
15.7	2500	7530	2900

[redacted]

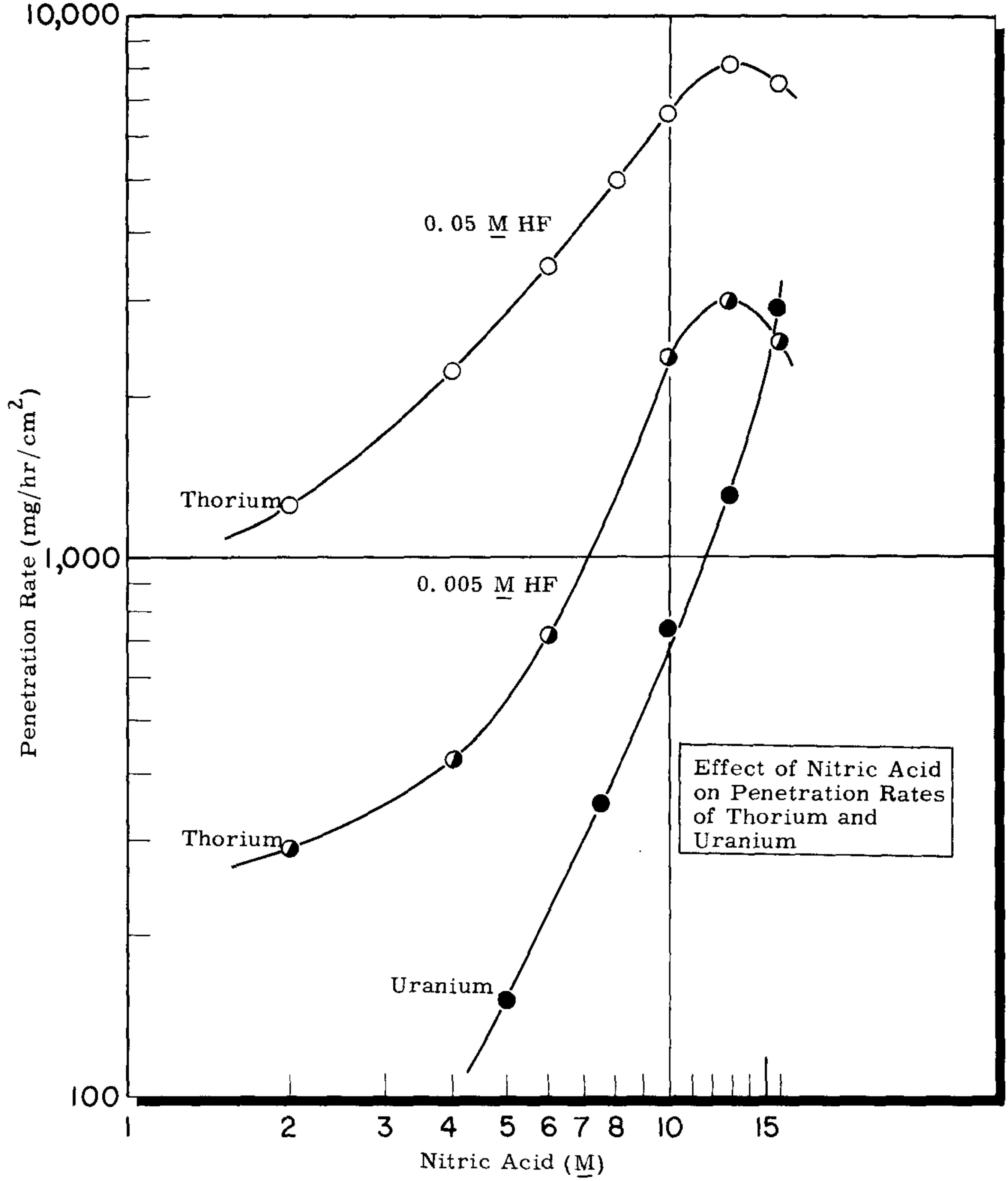

10,000
1,000
100
Penetration Rate (mg/hr/cm^2)
0.05 M HF
Thorium
0.005 M HF
Thorium
Uranium
1
2
3
4
5
6
7
8
10
15
Nitric Acid (M)
Effect of Nitric Acid on Penetration Rates of Thorium and Uranium

FIGURE 2

and at all acidities. It also appears that the dissolution rate of thorium passes through a maximum at about thirteen molar nitric acid.

3. Effect of Dissolved Thorium on Penetration Rate - The pronounced effect of dissolved thorium on the fluoride catalyzed dissolution rate of metallic thorium is shown in Table III. It is seen that dissolved thorium markedly decreases the penetration rate, undoubtedly through complexing of the fluoride. The experiments were not extended to thorium concentrations greater than one molar because of solubility limitations.

4. Effect of Dissolved Aluminum - Several experiments were run to determine the effect of aluminum on thorium penetration rates. The reason for this interest is that co-dissolution of aluminum cans with the thorium slugs would result in aluminum nitrate concentrations of about 0.5 molar, and aluminum ion is known to complex fluoride rather strongly, at least at room temperature and low ionic strengths. Half molar concentrations of aluminum nitrate in 13 $\underline{M}$ HNO_3, 0.05 $\underline{M}$ HF solutions resulted in penetration rates of about 250 mg/hr/cm^2 (mean of four determinations ranging from 91 to 410 mg/hr/cm^2) versus 8000 mg/hr/cm^2 in the absence of aluminum. In another experiment, a penetration rate of 890 mg/hr/cm^2 was observed in a solution of the composition 7 $\underline{M}$ HNO_3, 0.05 $\underline{M}$ HF, 0.5 $\underline{M}$ Th, 0.5 $\underline{M}$ Al. This may be compared with a value of 1390 mg/hr/cm^2 for the same composition, less the aluminum. It thus appears that the reduction of dissolving rate is most dramatic at the start of a dissolving operation. The effect appears to be less marked at lower acidity and in the presence of dissolved thorium which competes with aluminum for the available fluoride.

5. Other Fluoride Compounds - Fluoborate and fluosilicate were suggested as substitutes for hydrofluoric acid on the theory that they might be less corrosive. Fluosilicate was observed to yield a precipitate (presumably silica) in the presence of excess dissolved thorium, and the penetration rates suggested that it was largely hydrolyzed to free fluoride. Fluoboric acid also appeared to be completely hydrolyzed or dissociated in boiling nitric acid solutions. Thus the catalytic effect of 0.01 $\underline{M}$ HBF_4 was found

TABLE III

EFFECT OF DISSOLVED THORIUM ON THORIUM PENETRATION RATES

All solutions 0.05 M HF, indicated Th and HNO_3.
Boiling temperatures (approximately 110 C).

Th (M)	HNO_3 (M)	Rate ($mg/hr/cm^2$)
0	13	8000
0.2	13	5690
0.5	13	4010
0.72	13	2950
1.0	13	1790
0.5	1	110
0.5	4	580
0.5	7	1390
0.5	10	3550
0.5	13	4000
0.5	14.3	4010

[redacted]

to be the same as that of 0.04 M HF for nitric acid concentrations ranging from 2 to 15.7 molar. It was assumed that the corrosion problem would accordingly be the same as with fluoride. No corrosion studies were performed.

6. Dissolution of Thoria - A few measurements were made with thoria. This was done because of interest in the use of thoria slugs in place of thorium metal and also because of reported difficulties in dissolving the oxide impurity present in most thorium metal. This leads to a residue of "blue thorium" in the case of neutron irradiated material. The thoria used was produced at Oak Ridge. It contained about one per cent calcium oxide and had been pressed at 20,000 psi and sintered at 1800 C to 96.9 per cent of the theoretical (crystallographic) density. The results of penetration rate measurements in 13 molar nitric acid are shown in Table IV and are compared with thorium metal in Figure 1. A white coating, believed to be thorium fluoride or calcium fluoride, was observed on the surface of the thoria pieces for hydrofluoric acid concentrations of 0.1 molar or greater.

The reason for the slow dissolution of the thorium oxide impurity and the resultant difficulty in dissolving "blue thorium" is evident from these results. It would also appear that thoria slugs may require fracturing or pulverizing to increase the surface area in order to obtain satisfactory dissolving rates.

B. Integral Dissolvings

Because of the complexities of the thorium-HF-HNO_3 system and the inter-related effects of the various variables, it is difficult to estimate the time cycles of a plant dissolving from instantaneous penetration rate measurements. Pot type "integral" dissolvings were accordingly carried out as described under Experimental. In most of these, a 200 per cent heel was arbitrarily employed, all of the nitric acid was added at the beginning, and all of the dilution water at the end of the dissolution. In an actual plant operation, however, the acid would probably be added in several cuts (for

TABLE IV

PENETRATION RATE OF THORIA AS A FUNCTION OF HYDROFLUORIC ACID CONCENTRATION

All solutions boiling 13 M HNO_3, indicated molarity of hydrofluoric acid. Thoria produced by sintering at 1800 C, 20,000 psi. Density 96.9 per cent theoretical.

HF Molarity	Penetration Rate (mg/hr/cm^2)
0.0005	31
0.002	176
0.01	340
0.05	150
0.1	80
0.5	37
1	12

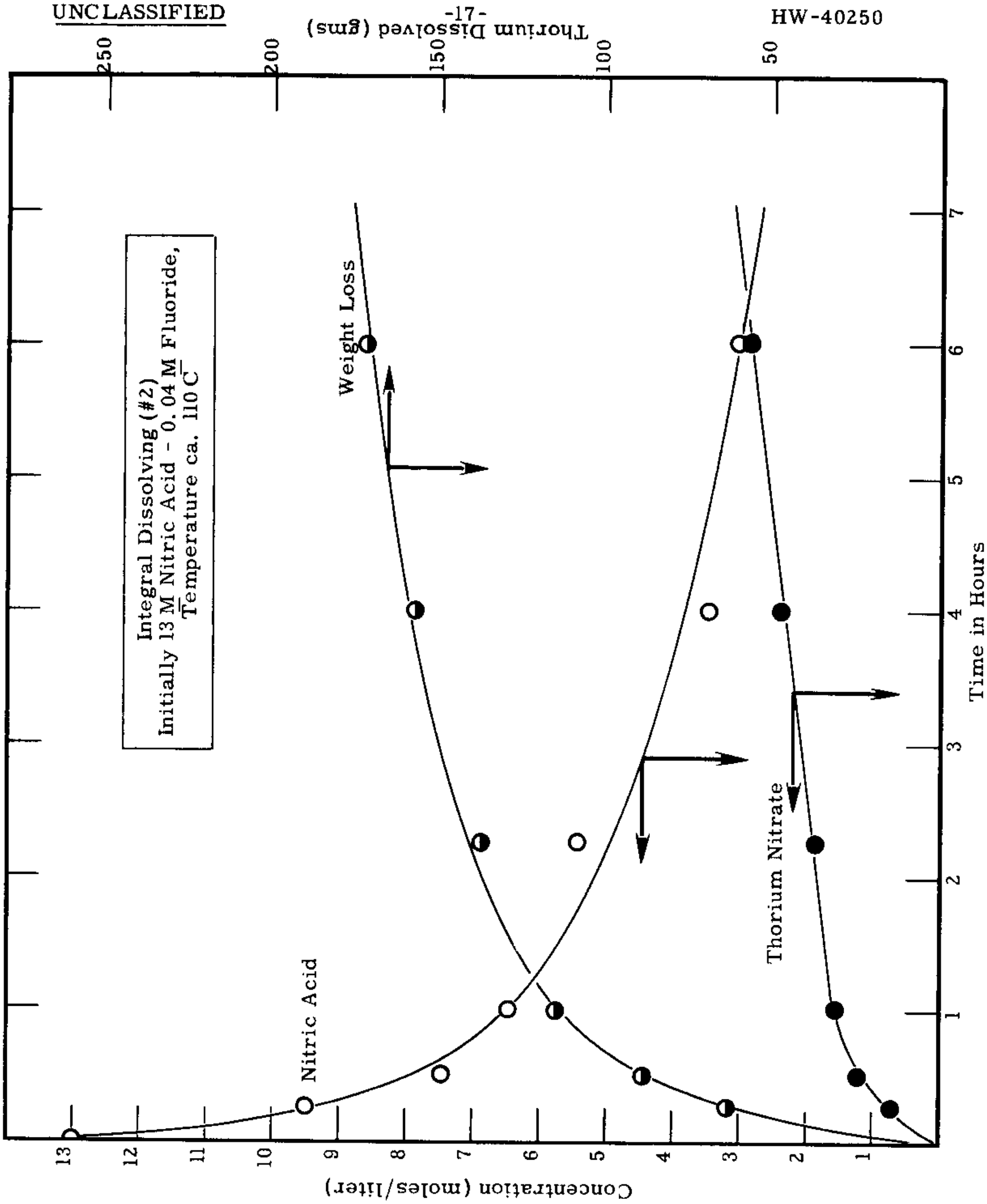
better control during the vigorous first phase of the reaction) and the dilution water prior to termination of the dissolving to prevent solidification in pot or lines should the steam fail. The "equilibrium heel" which would accumulate in a dissolver would also probably have a larger specific surface than in the laboratory dissolvings, where the slugs were used only once, and this would result in somewhat more favorable rates than predicted from the laboratory results. It should also be noted that the boundary conditions may have a marked effect on dissolving rate and time cycles, particularly in view of the adverse effect of dissolved thorium on the fluoride catalysis.

Two series of experiments were carried out. In one the initial nitric acid concentration was held constant at 13 molar and the fluoride concentration was varied from 0.005 to 0.075 molar. In the other series, catalyst concentration was constant at 0.04 molar and the initial nitric acid varied from eight to sixteen molar.

1. Effect of Fluoride Concentration on Dissolution Time - The results of the series of dissolvings with variable fluoride are compiled in Table V, and the data for a representative dissolving is also shown graphically in Figure 3. In all of this series, the initial acidity was 13 molar and a 200 per cent heel of excess metal was present.

It will be noted that the initial rate is very rapid but that it decreases markedly after the solution has become approximately one molar in dissolved thorium. This takes only about one-half hour for the 0.04 M HF case, whereas over six hours are required to reach the cross over point, at which the molar concentrations of dissolved thorium and nitric acid are equal. It should also be noted that the weight loss curve is more accurately indicative of the extent of dissolution than is the thorium molarity since the solution volume decreases with time as a consequence of nitric acid consumption and the loss of some water and acid around the condenser.

FIGURE 3



Integral Dissolving (#2)
Initially 13 M Nitric Acid - 0.04 M Fluoride,
Temperature ca. 110 C

The time intervals required in the above experiments to dissolve to thorium concentrations of one molar, two molar, or to a 200 per cent heel were read from graphs of the data of Table V. It was found that a plot of the logarithm of time versus fluoride concentration resulted in a family of parallel straight lines (Figure 4) for each terminal thorium concentration. Smoothed values read from these curves are given in Table VI. The effects of fluoride concentration and the time penalty for carrying the dissolution to high final thorium concentrations are evident from these numbers.

The number of moles of nitric acid consumed per mole of thorium dissolved was calculated based on all of the nitric acid analyses for each run assuming linear variation of volume with time. The averages are included for the various dissolvings in Tables V, VII, and VIII. The variations in these numbers are believed to reflect the rather large analytical uncertainties in the thorium and nitric acid analyses caused by the difficulty of sampling a boiling solution, by the small samples taken, and by the interference of thorium in the acid analysis. The average obtained for all of the dissolvings, with the exception of the 0.005 molar fluoride case where evaporation losses may have been excessive, was 6.05 ± 0.44 (standard deviation). This corresponds very nearly, perhaps coincidentally, to the relation:

$$Th + 6\ HNO_3 \longrightarrow Th\ (NO_3)_4 + 3\ H_2O + NO + NO_2.$$

It is noted that four moles of nitrate are, of course, required to form the thorium nitrate product. Regeneration of nitric acid from the off-gases, as by use of a down-draft condenser, could accordingly effect a saving of up to about two moles of nitric acid per mole of thorium dissolved.

2. <u>Effect of Aluminum on Integral Dissolution</u> - Half molar aluminum nitrate would be present if cans were co-dissolved with the thorium. This concentration was accordingly used in run #7. The results are compiled in

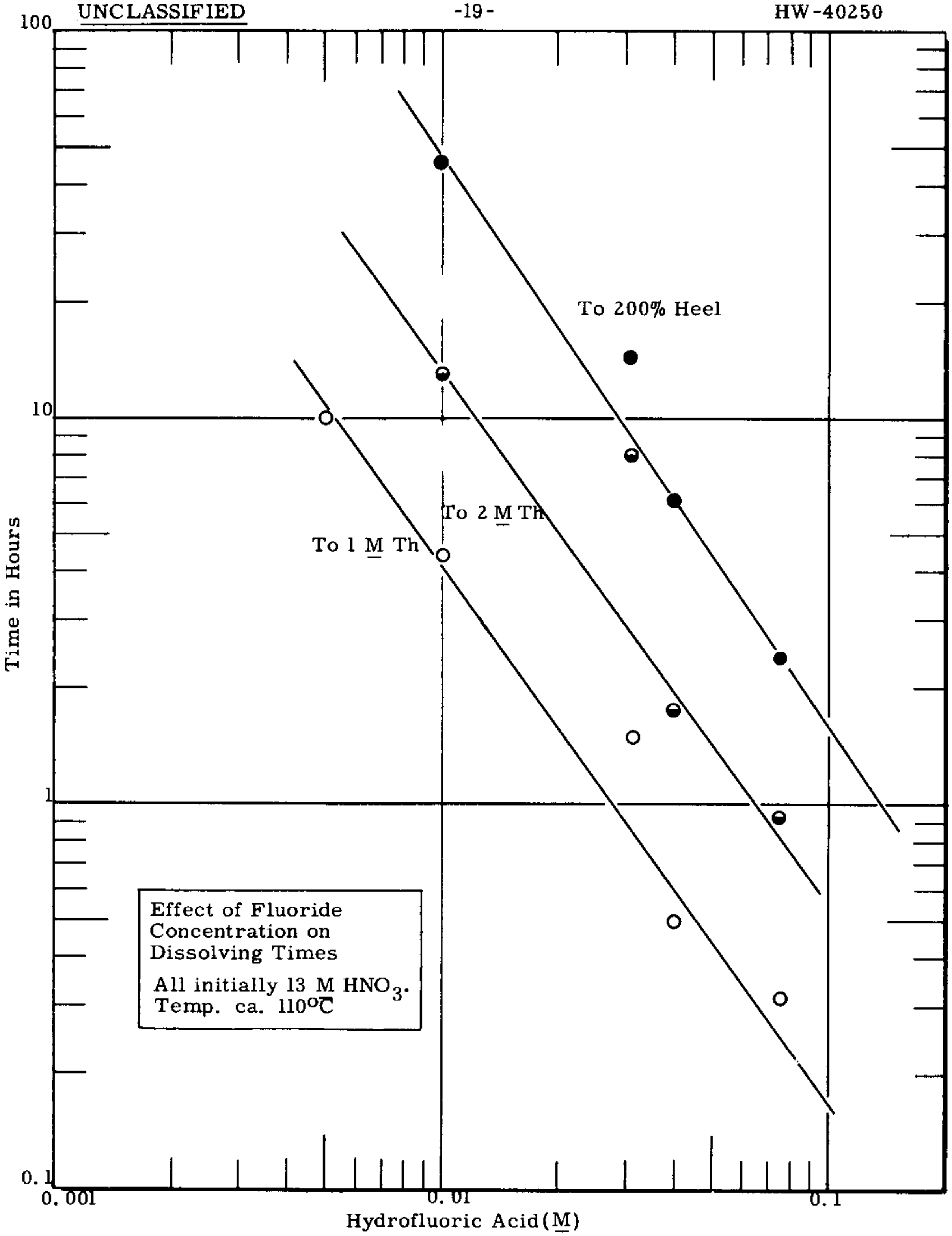

100
10
1
0.1
0.001
0.01
0.1
Time in Hours
Hydrofluoric Acid (M)
To 200% Heel
To 2 M Th
To 1 M Th
Effect of Fluoride Concentration on Dissolving Times
All initially 13 M HNO3.
Temp. ca. 110°C

FIGURE 4

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TABLE V

INTEGRAL DISSOLVINGS - VARYING FLUORIDE CONCENTRATION

All initially 13 M HNO_3, indicated M HF, 200% excess thorium metal. Slugs 1.3437" x 2", initial area 73 cm^2, specific area 0.14 cm^2/gm. Reaction at boiling temperature (approximately 110 C).

No. 1, 0.075 M HF

Charge: 502.5 gms.
Init. Soln. Vol.: 384 ml.
Final Soln. Vol.: 260 ml.

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO_3 (M)
0	0	0	13
1/2	104.4	1.41	6.52
3/4	121.4	1.74	5.44
1	135.5	1.95	5.39
1-1/2	151.8	---	---
2	158.9	---	---
2-1/2	168.7	2.66	2.24

$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 5.86$

No. 2, 0.04 M HF

Charge: 522.3 gms.
Init. Vol.: 400 ml.
Final Vol.: 270 ml.

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO_3 (M)
0	0	0	13
1/4	63.9	0.74	9.47
1/2	89.0	1.22	7.48
1	114.9	1.51	6.50
2-1/4	138.3	1.91	5.45
4	158	2.41	3.49
6	172.7	2.89	3.08

$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 5.72$

No. 3, 0.031 M HF

Charge: 523.5 gms.
Init. Vol.: 398 ml.
Final Vol: 258 ml.

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO_3 (M)
0	0	0	13
1/2	59.1	0.64	7.84
1-1/2	85.0	0.88	7.86
2-1/2	101.5	1.06	5.47
3-1/2	114.6	1.29	5.54
4	120	1.37	5.46
6	136.9	1.66	4.90
8-1/2	152.5	1.98	3.81
11	163.7	---	---
12	167.1	2.72	3.68

$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 6.14$

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TABLE V (Cont.)

No. 4, 0.01 M HF

Charge: 517 gms.
Init. Vol.: 395 ml.
Final Vol.: 190 ml.

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO_3 (M)
0	0	0	13
5	94.5	1.13	7
10	119.2	1.68	6.8
13	128.9	1.89	4.98
18	139.2	2.28	4.79
21	144.2	2.57	4.98
26	147.2	3.15	2.42

$$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 6.54$$

No. 5, 0.01 M HF

Charge: 520 gms.
Init. Vol.: 397 ml.
Final Vol.: 200 ml.

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO_3 (M)
0	0	0	13
1	48.5	---	6.83
2	78.1	0.86	8.66
5-1/2	97.7	1.35	8.15
10	120.2	1.91	6.58
18	137.1	2.95	3.96

$$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 6.44$$

No. 6, 0.005 M HF

Charge: 516 gms
Init. Vol.: 394 ml.
Final Vol.: 240 ml.

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO_3 (M)
0	0	0	13
1/2	13.4	---	---
1	18.7	---	---
3	38.5	---	---
4	46.4	---	---
5	53.6	0.65	---
7	63.7	0.81	---
7-1/2	68	---	9.6
10	73.3	1.0	---
12	78.0	---	---
17	90.0	---	---
19	94.7	1.8	7.92

$$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 7.20$$

[redacted]

TABLE VI

EFFECT OF FLUORIDE CONCENTRATION ON DISSOLVING TIMES

All solutions initially 13 M HNO_3, indicated M HF, 200% metal heel. Temperature approximately 110 C.

M HF	Time (Hours) 1 M Th	2 M Th	200% Heel
0.075	0.33	0.93	2.4
0.04	0.5	2	6
0.031	1.5	8	14
0.01	4.5	13	~46
0.005	10	---	---

TABLE VII

EFFECT OF ALUMINUM ON INTEGRAL DISSOLUTION

Initial solution: 13 M HNO_3, 0.5 M ANN, 0.075 M HF. 200% excess thorium metal. Boiling temperature.

Run No. 7

Initial Vol.: 397 ml.
Final Vol.: 234 ml.

Time (hours)	Wt. Loss (gms.)	M Th	M HNO_3
0	0	0	13
1/2	26.4	0.30	12.2
1-1/2	86.5	1.12	7.83
3	125.3	1.70	4.46
4-1/2	149.3	2.11	3.41
6	163.1	2.21	2.37
7-3/4	169.5	2.05	1.70
8-1/2	172.3	---	---
9	173.9	3.21	1.87

$$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 6.41$$

[redacted]

TABLE VIII

INTEGRAL DISSOLVINGS - VARYING INITIAL NITRIC ACID CONCENTRATION

Procedure and conditions as in Table V except
all solutions 0.04 M HF, indicated M HNO_3

No. 8, 15.7 M HNO_3

Charge: 542.7 gms.
Initial Vol.: 298 ml.
Final Vol.: 22 ml.

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO_3 (M)
0	0	0	15.7
0.17	36.5	0.56	12.3
0.43	79.5	1.29	8.8
1.27	101.0	1.75	6.5
2.7	117.4	2.05	5.2
5.5	135.7	2.56	3.24
13.2	149.0	2.89	1.89

$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 6.43$

No. 9, 15.7 M HNO_3

Charge: 544.8 gms.
Initial Vol.: 343.5 ml.
Final Vol.: 238 ml.

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO_3 (M)
0	0	0	15.7
0.17	42.5	0.60	11.9
0.42	90.0	1.28	8.12
1.08	110.3	1.64	7.16
3.92	151.5	2.51	4.26
6.92	168.3	2.75	2.48
10.6	176.2	3.47	2.12

$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 6.4$

No. 10, 13 M HNO_3

Charge: 541.1 gms.
Initial Vol.: 415 ml.
Final Vol.: 328

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO_3 (M)
0	0	0	13
0.28	73.5	0.83	8.95
0.95	108.1	1.26	7.3
2.02	125.6	1.47	6.4
2.5	140.5	1.69	5.5
6	168.3	2.2	3.45
8	175.1	2.3	2.94

$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 5.49$

[redacted]

[redacted]

TABLE VIII (Cont.)

No. 11, 10.5 M HNO$_3$

Charge: 504.5 gms.
Initial Vol.: 414 ml.
Final Vol.: 325 ml.

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO$_3$ (M)
0	0	0	10.5
0.5	46.4	0.48	7.77
1	57.1	0.62	7.24
4	85.6	0.97	5.74
8	---	1.37	3.49
11.7	126	1.51	3.19
14.9	134.8	1.71	2.3
21.3	145.8	1.91	1.64

$$\frac{\text{Moles HNO}_3}{\text{Mole Th}} = 5.86$$

No. 12, 8 M HNO$_3$

Charge: 345.3 gms.*
Initial Vol.: 428 ml.
Final Vol.: 350 ml.

Time (hrs.)	Wt. Loss (gms.)	Th (M)	HNO$_3$ (M)
0	0	0	8
0.9	42.6	0.44	6.53
1.33	51.8	0.54	5.75
3.12	74.9	0.81	4.32
6	95.8	1.08	3.24
8.5	108.7	1.28	2.73
10.33	114.3	1.38	2.25

$$\frac{\text{Moles HNO}_3}{\text{Mole Th}} = 5.3$$

* 1.3437" diam. x 1.35" slug,
surface area 55 cm^2,
specific area 0.16 cm^2/gm.

[redacted]

Table VII and may be compared with those of dissolution #1 (Table V), to which it was otherwise identical. The times required to dissolve to various thorium concentrations were as follow:

	Time, hrs.		
Thorium Conc.	No Al	0.5 M Al	Ratio
1 M	0.33	1.3	4
2 M	0.93	4	4.3
200% heel	2.4	9	3.8

Thus, the effect of half molar aluminum is to increase all of these times by a factor of about four.

3. Effect of Initial Nitric Acid Concentration - Results of a series of dissolvings with different initial nitric acid concentrations are presented in Table VIII. It is seen from a comparison of the weight losses that the initial dissolving rates are somewhat higher at the higher nitric acid concentration but that the differences are much smaller than in the series in which the concentration of fluoride was varied. It will also be noted that the final thorium concentrations are lower at the lower acidities, partially as a result of the additional water present. Thus dissolved thorium will exert a smaller inhibition on the fluoride catalysis in these solutions, and the dissolution rate does not fall off as quickly as with the solutions of higher initial acidity.

4. Comparison of Thorium and Uranium Integral Dissolving Rates - The results of similar dissolvings with thorium and uranium are shown in Table IX. It will be noted that the initial rate of dissolution is faster in the case of the thorium. Thus the thorium concentration at the end of the first half hour is almost twice that of the uranium; however, approximately the same length of time (100 minutes) is required for both to reach two molar. Since the surface area is smaller in the uranium experiment because of the greater density of uranium, the specific dissolution rate of the uranium is actually somewhat greater than that of thorium at this point.

TABLE IX

COMPARISON OF THORIUM AND URANIUM INTEGRAL DISSOLUTION RATES

Batch Dissolutions: 13 M HNO_3, 100% heel, boiling temperature (ca. 110 C) with up-draft condenser.

No. 13 Uranium

212.6 gm piece, 1.3125" diam. by 0.504" thick, 30.9 cm^2 surface area. Specific area 0.145 cm^2/gm

Initial Volume: 189 ml.
Final Volume: 160 ml.

Time (min)	U (M)	HNO_3 (M)
0	0	13
10	0.24	12.8
15	0.38	12.5
20	0.53	11.5
30	0.78	10.3
60	1.41	7.2
75	1.65	6.6
100	1.95	3.0
120	2.33	1.6
180	2.60	1.04

No. 14 Thorium

0.05 M HF catalyst, 218.4 gm. piece, 1.3437" diam. by 0.844" thick, 41.4 cm^2 surface area. Specific area 0.19 cm^2/gm.

Initial Volume: 206 ml.
Final Volume: 136 ml.

Time (min.)	Wt. Loss (gms.)	Th (M)	HNO_3 (M)
0	0	0	13
30	52.5	1.34	7.49
60	68.7	1.78	5.49
90	78.1	---	---
120	83.9	2.31	3.49
150	87.1	---	---
185	90.5	2.56	2.79
245	96.1	2.76	1.68
300	97.6	2.80	1.44

$$\frac{\text{Moles } HNO_3}{\text{Mole Th}} = 5.7$$

[redacted]

For lower catalyst concentrations than the 0.05 molar hydrofluoric acid used in this experiment, the thorium rate would compare less favorably.

5. Mathematical Correlation - As pointed out earlier, the thorium dissolution is quite complex and not readily amenable to rigorous mathematical treatment. Thus hydrofluoric acid is relatively weak ($K = 7.2 \times 10^{-4}$ at room temperature)(4) and will therefore be present largely as undissociated HF in the presence of excess nitric acid. Thorium is also known to form a series of very stable fluoride complexes with formation constants:(5) $K_1 = 5 \times 10^4$, $K_2 = 3 \times 10^7$, and $K_3 = 9.4 \times 10^8$ at room temperature and low ionic strengths. The dissolver solutions were also quite concentrated, and the laws of dilute solutions would not be expected to hold, nor are the activity coefficients available.

For these reasons, the data would not be expected to fit any simple idealized reaction rate equation. However, it was found empirically that the weight loss curves could be reproduced by assuming that the reaction behaved as if it were second order in the number of moles of nitric acid present as contrasted to the molar concentration. This is equivalent to

$$\frac{dw}{dt} = k\,(W_\infty - W)^2, \qquad (1)$$

where W_∞ is the total number of grams of thorium which could be dissolved by the acid charged to the dissolver, i.e., weight loss at infinite time, and W is the weight loss at time t. The constant k includes the surface area which varied little in these experiments. It is also a function of the catalyst concentration and of the initial concentration of acid. Integration of equation (1) yields

$$\frac{1}{W_\infty - W} = kt + \frac{1}{W_\infty}, \qquad (2)$$

whence a plot of $1/(W_\infty - W)$ versus time should yield a straight line of slope k. Such a correlation is shown in Figure 5 for the data of Table V.

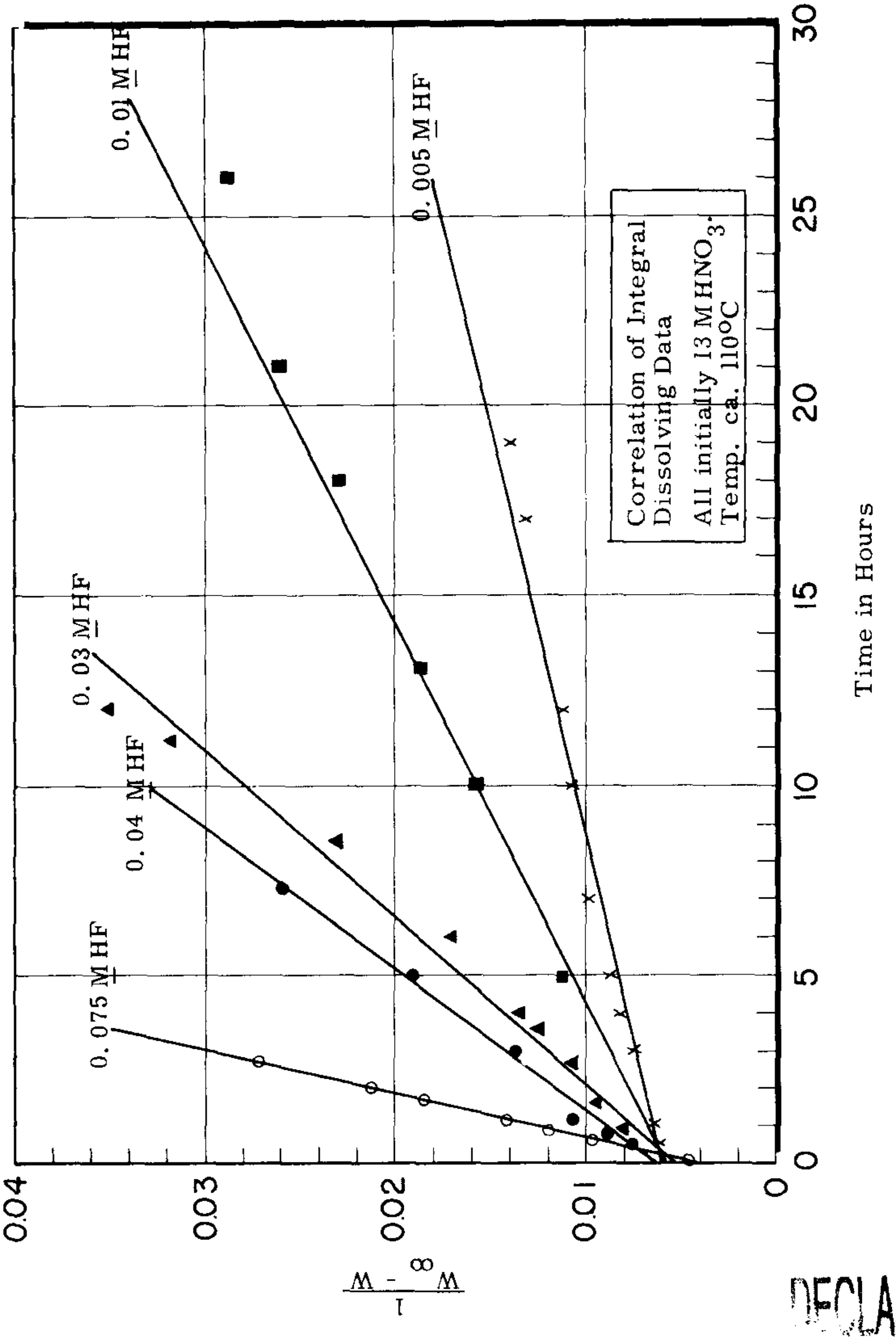

FIGURE 5

[redacted]

The fit obtained is rather sensitive to the value chosen for W_{∞}, i. e., to the value assumed for the number of moles of nitric acid consumed per mole of thorium dissolved, and the points plotted were computed using the experimental values of the moles of nitric acid consumed per mole of uranium (Table V). It should be noted that while the data are correlated very well, these curves cannot be extrapolated to acid deficient conditions. Inferior correlations were obtained when volume concentrations were substituted for weight losses.

The slopes of the lines in Figure 5 were as follow:

$\underline{M}$ HF	k x 10^3
0.075	8.7
0.04	3.31
0.03	2.17
0.01	1.01
0.005	0.46

A logarithmic plot of k versus concentration of fluoride, Figure 6, has a slope of about one, i. e., the rate constant is first order in catalyst concentrations. The point shown at 0.05 $\underline{M}$ is from dissolving #14 and has been adjusted for specific area and amount of acid as described below.

Similar calculations were also made for the data of Table VIII. Since short slug was used for the eight molar case (#12), it was necessary to multiply the experimental slope of 2 x 10^{-3} by a factor before comparing with the other numbers. This is because the slope, k, is proportional to the specific area of the piece and inversely proportional to the scale of the dissolving, i. e., to the number of grams dissolved (W_{∞}) or to the number of moles of nitric acid employed. The resultant values were

[redacted]

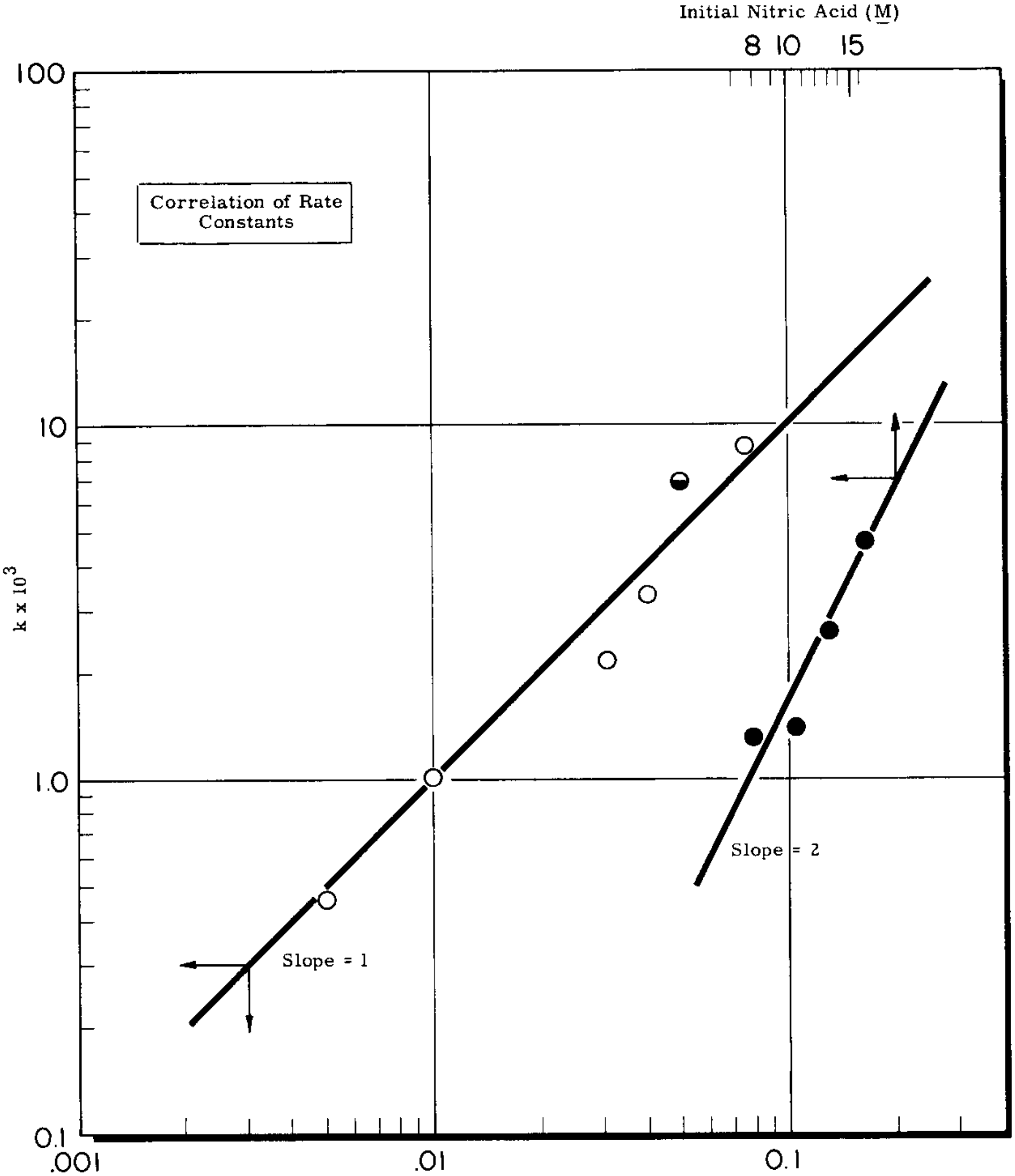
Initial Nitric Acid (M)
8 10 15
100
10
1.0
0.1
k x 10^3
Correlation of Rate Constants
Slope = 1
Slope = 2
.001
.01
0.1
Hydrofluoric Acid (M)

FIGURE 6

$\underline{M}$ HNO_3	$k \times 10^3$
15.7	4.7
13	2.6*
10.5	1.4
8	1.3

*Average of 1.9 for #10 and 3.3 for #2.

These results suggest, as shown in Figure 6, that the slope has a second order dependence on the initial nitric acid concentration.

The k values can thus be represented by an equation

$$k = \frac{KA}{(N_{HNO_3})^2} (HF)(HNO_3)^2 \qquad (3)$$

where (HF) is the molar concentration of fluoride catalyst, (HNO_3) is the <u>initial</u> molar concentration of nitric acid, A is the area of metal exposed to the solution, and N_{HNO_3} is the number of moles of nitric acid charged to the dissolver. The factor $A/N^2_{HNO_3}$ is needed to correct for the effect of specific area and for the fact that gross weight losses, rather than concentrations, were used in equations (1) and (2). The constant K has the approximate value of 2.2×10^{-4} when A is measured in square centimeters. Alternately, equation (3) may be written as

$$k = \frac{K' A (HF)(HNO_3)^2}{W_\infty^2} \qquad (4)$$

in which case K' has the value of about 0.36 if W_∞ is in grams.

It will be noted that the instantaneous penetration rates at different stages of a dissolution can be obtained from (1) and (3) or from (1) and (4) by solving for $\frac{dw}{A\ dt}$. Thus effective penetration rates can be obtained for solution compositions which would be difficult to duplicate synthetically because of room temperature solubility limitations.

V. DISCUSSION

From the above results it is seen that the penetration rate of thorium and the dissolving time cycles may vary greatly depending on the fluoride catalyst concentration, nitric acid concentration, presence of fluoride complexing agents (e. g., aluminum), and the terminal composition. While none of the dissolvings was carried to an acid deficient condition, it is evident from the curves of Figure 3 and the data in Tables V to IX that to do so would take a very long time. It was also seen (Table VI) that the dissolving rate is greatest when the dissolution is terminated at a low thorium concentration. Dissolver capacity could, therefore be maximized by dissolving to a low thorium concentration and then concentrating, and reducing the acidity, by evaporation. It would thus be possible to obtain dissolving times of as little as ten hours with 0. 005 molar fluoride if the dissolution were terminated at a thorium concentration of one molar.

Another way to minimize the concentration of fluoride required, or to increase dissolving rate, is to increase the surface area of metal exposed to the solution. This might be done by use of a packed continuous dissolver of either the trickle or submerged type or by taking advantage of the multiple stage dissolver principle.(6)

For a conventional batch type dissolving, it is recommended that a fluoride concentration of about 0. 03 molar be employed, that the initial nitric acid be equivalent to about 13 molar and that the dissolving be terminated when thorium and acid concentrations are about equal, as this avoids prolonged digestion and yields a suitable feed for subsequent Thorex processing using an acid flowsheet. Fluoride concentrations greater than 0. 03 molar are undesirable because of the detrimental effects in subsequent operations.(2)

Extensive measurements on irradiated thorium were not carried out. However, thirty gram scale dissolvings(2) of thorium irradiated to 1330 to 1650 MWD/AT revealed no abnormal behavior. Dissolving times were essentially identical to those of a control experiment with unirradiated metal. The irradiated metal may, in fact, have dissolved slightly faster. It is, therefore, believed that the data of this report are fully applicable to irradiated material, at least up to the above irradiation levels.

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ABSTRACT

The penetration rates of thorium metal by boiling nitric acid were measured as a function of the concentration of fluoride catalyst and of nitric acid. Dissolved thorium and aluminum were found to inhibit the reaction. Thoria exhibited penetration rates much lower than those of thorium metal. In addition to the specific rate measurements, pot type batch dissolvings were carried out to estimate plant time cycles. An empirical mathematical equation was devised which correlates the results of these batch dissolvings and facilitates application of the data to other types of dissolvers.

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