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THE DISSOLUTION OF THORIUM METAL AND THORIUM DIOXIDE

IN HNO_3 - HF AND HNO_3 - $(NH_4)_2SiF_6$ MIXTURES

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1

Table of Contents

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ABSTRACT

A satisfactory method has been found for dissolving thorium metal and thorium oxide in 25-12 heat-treated stainless steel vessels without excessive corrosion of the vessels. The dissolution medium consists of strong HNO_3 containing a small amount of fluoride or fluosilicate. The fluoride required has no harmful effects on a subsequent solvent extraction step for a separation of uranium isotopes from the dissolved thorium.

1. Dissolution of Th and ThO_2 in HNO_3
Containing Fluoride or Fluosilicate

In view of the interest in thorium in connection with piles for production of U^{233} (resulting from neutron capture followed by two successive beta emissions), it was desirable to find a convenient method for dissolving metallic thorium and the dioxide, since the antici- pated methods of separation of the U^{233} from thorium involved starting with an aqueous solution of thorium nitrate. Because of the desirability of using stainless steel vessels from an engineering standpoint it was hoped that a medium for the dissolution of the metal could be found which would not excessively corrode stainless steel. Although the basic carbonate, which is soluble in nitric acid, had been used in small scale irradiations, it was not considered satisfactory for large scale bom- bardments because its heat conductivity would not permit sufficiently rapid removal of the tremendous amounts of energy given off by the initial (n, γ) reaction, the two successive beta emissions, and the small amount of U^{233} fission. Satisfactory substances seemed to be the metal itself and a slurry of the dioxide.

According to the literature, the metal was said to be readily soluble in aqua regia, more slowly so in hydrochloric acid, and rendered passive by pure nitric acid. The dioxide was said to be insoluble in

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HCL or HNO_3 and converted to the sulfate by hot concentrated H_2SO_4. The sulfate is only moderately soluble in water.

Since solvent extraction appears to be the most attractive method for separating the U^{233} from the thorium after irradiation of the latter and since the contemplated process involved the extraction of the U^{233} from an aqueous thorium nitrate solution, it was desired that the thorium be converted to the nitrate in the dissolution step or to a compound which could in turn be readily converted to the nitrate. With this goal in mind the experiments now to be described were carried out during the fall of 1944. Nitric acid containing small amounts of fluoride as HF and H_2SiF_6 were tried as the first likely possibilities. It was hoped that with low fluoride concentration the dissolution properties of the solvent would be satisfactory without the danger of excessive corrosion of the vessel or of the precipitation of thorium fluoride.

1.1 <u>Dissolution of the Metal</u>. A 90 gram slab of thorium metal, cut from a larger piece made at Iowa State College under the direction of F. H. Spedding, was obtained for dissolution test experiments. This slab of metal was cut into a number of small slices with which the dissolution tests were carried out. The results of these tests are given in Table 1.

From a comparison of the rates of solution in Experiments No. 3 to No. 7, it is seen that the dissolution rate is approximately proportional to the HF concentration, at constant concentration of HNO_3 and weight of metal. That the HF acts as a catalyst, rather than, for example forming a permanent complex with all the dissolved thorium, is seen from Experiments No. 6 and No. 7 where the final molar ratio of fluoride ion to thorium ion is about 0.03.

Table 1.

DISSOLUTION TIMES FOR Th AND U METALS IN STAINLESS STEEL
VESSELS AT APPROXIMATELY 100°C IN 5 ml OF DISSOLUTION MEDIUM

Expt. No.	Metal	Wt. (g)	Solution for Dissolving Metal	Time for Dissolving
1	Th	0.35	Conc. HNO_3	30% of Metal in 90 min
2	Th	0.70	4 N HNO_3	3% of Metal in 90 min
3	Th	0.51	Conc. HNO_3 +0.1 N HF	Complete in 13 min
4	Th	0.48	Conc. HNO_3 +0.1 N HF	Complete in 17 min
5	Th	0.53	Conc. HNO_3 +0.05 N HF	Complete in 21 min
6	Th	0.48	Conc. HNO_3 +0.012 N HF	Complete in 65 min
7	Th	0.46	Conc. HNO_3 +0.012 N HF	Complete in 72 min
8	Th	0.37	Conc. HNO_3 +0.01 M $(NH_4)_2SiF_6$	Complete in 20 min
9	Th	2.15	Conc. HNO_3 +0.05 N HF	Complete in 90 min
10	Th Fillings	0.38	5 ml 8 N HNO_3 +0.012 N HF	Complete in 6 min
11	U	0.53	Conc. HNO_3	Complete in 30 min

*The temperature of this experiment was about 90°C.
**7 ml of dissolution medium was used in this case.

A rough qualitative picture of the effect of metal surface to
weight ratio can be seen by comparing Experiments No. 10 and No. 6
and also No. 5 and No. 9. From Experiments No. 5, No. 8, and No. 11
it is seen that HNO_3 containing a small amount of HF or H_2SiF_6 (In this
case the fluosilicate was added as $(NH_4)_2SiF_6$ will dissolve thorium metal
as rapidly as pure HNO_3 dissolves uranium metal).

1.2 Dissolution of ThO$_2$. A very pure grade of finely divided ThO$_2$ (i.e., particles of the order of 50 microns in diameter) was obtained from the Lindsay Light and Chemical Company of West Chicago for the dissolution experiments with the dioxide. Each experiment involved 0.5 g ThO$_2$ and 10 ml HNO$_3$ in the reaction vessel, heating to 97°C, where HF was used, and to about 80°C where (NH$_4$)$_2$SiF$_6$ was used, then adding the fluorine containing reagent and heating at 100°C until all the oxide had dissolved. The recorded time is the time between the addition of HF or (NH$_4$)$_2$SiF$_6$ and the complete solution of the oxide. The results of these tests are given in Table 2.

Table 2

A. DISSOLUTION OF 0.5 g ThO$_2$ IN 10 ml
HNO$_3$ - HF AT 100°C IN PYREX GLASS VESSELS

HNO$_3$ N	HF N	Time (Minutes) for Complete Solution
8	0.011	11
8	0.0082	13
8	0.0055	15
8	0.0027	Not dissolved in 5 hrs.
16	0.011	3.5
16	0.0055	3.5
16	0.0027	5

B. DISSOLUTION OF 0.5 g ThO_2 IN 10 ml HNO_3 –
$(NH_4)_2SiF_6$ AT 100°C IN PYREX GLASS VESSELS

HNO_3 N	$(NH_4)_2SiF_6$ N	Time (Minutes) for Complete Solution
16	0.010	9
8	0.010	6
16	0.015	9
8	0.0027	9.5

According to the results of Table 2A, at constant but low concentrations of HF thorium dioxide is appreciably more readily dissolved in 16 N HNO_3 than 8 N HNO_3. In order to be sure that this ThO_2 was not readily soluble in pure HNO_3 in order to test the present method of dissolution on a somewhat larger scale, three 10 gram samples of ThO_2 were treated with 28 ml of 16 N HNO_3 (i.e., three times the stoichiometric amount required to convert ThO_2 to the nitrate) as indicated in Table 3 with the results shown there.

The higher temperature is believed to be chiefly responsible for the shorter dissolution time required for sample (a) than for (b), although the difference in pyrex and stainless steel vessels may also have been a contributing factor.

A 0.5 g sample of ThO_2 was heated in an evaporating dish in a Meker burner flame until the evaporating dish had been held at red heat for several minutes. After this treatment, 5 ml of an 8 N HNO_3 – 0.01 N HF mixture failed to dissolve the sample in 30 minutes at 100°C, showing that this heat treatment caused the ThO_2 to be more difficult to dissolve. The HF concentration was raised to 0.02 N, after which the sample dissolved in 30 minutes additional heating at 100°C. A similarly heated 10 g sample of ThO_2 did not dissolve in 22 ml of an 8 N HNO_3 – 0.01 N HF mixture (this quantity of HNO_3 should result in a 1 N HNO_3 solution after complete solution of the oxide) in one hour

Table 3

DISSOLUTION OF 10 g SAMPLES OF ThO_2
IN HNO_3 MEDIA (28 ml OF 16 N IN EACH CASE)

Sample	Conditions	Time for Complete Dissolution
a	HF added to 0.05 N and mixture heated in stainless steel beaker at 105-110°C	20 min
b.	HF added to 0.05 N and mixture heated in pyrex glass vessel at 100°C	50 min
c	No HF or fluosilicate added; mixture heated in pyrex glass vessel at 100°C	1.2% dissolved in 50 hours

at 100°C nor in 30 minutes additional treatment at this temperature after raising the HF concentration to 0.02 N. At this point 5 ml concentrated HNO_3 were added and the vessel kept at 100°C overnight, resulting in complete solution of the oxide.

To test the effect of lowering the temperature on the dissolution of ThO_2 in HNO_3 - $(NH_4)_2SiF_6$ mixtures, each of three 0.5 gram samples of our stock ThO_2 were treated with 5 ml of the acid mixtures at different temperatures: 100°, 76°, and 50°C. The results are presented in Table 4.

The results of Table 4 showed that if it were necessary for reasons such as excessive corrosion, the dissolution of thorium dioxide could be carried out at a feasible rate at temperatures as low as around 75°C.

Table 4

DISSOLUTION OF 0.5 SAMPLES OF
ThO_2 IN 8 N HNO_3 - $(NH_4)_2SiF_6$ MIXTURES

T (^{o}C)	$(NH_4)_2SiF_6$	Time for Complete Dissolution
100	0.003	11 min
76	0.003	22 min
50	0.006	Between 2 and 16 hours

1.3 Larger Scale Dissolution of the Metal. The conditions chosen
for dissolving thorium metal involved concentrated nitric acid con-
taining 0.05 M HF and heating near the boiling point (see Section 2
for corrosion results). Several larger scale dissolution experiments
have been conducted in the Clinton Laboratories Technical Division by
F. L. Steahly, J. O. Blomeke, D. C. Overholt, and R. N. Leuze [1].
They found that thorium metal wafers 1.1 inches in diameter and
1/2 inch thick (85 to 90 grams each) were essentially completely dis-
solved in a five per cent excess of 40-60 per cent HNO_3 containing
0.05 M HF in 23 to 30 hours; actually a small amount of black thorium
oxide remained undissolved, but this oxide should not be present in
future metal production at Iowa State College, according to
F. H. Spedding. With a 15 per cent excess acid, 16 hours were required.

Since the rate of dissolution decreases as both the HNO_3 concen-
tration and the metal surface area decrease, and since it is desirable
to end up with a low concentration of HNO_3 (rather than having to
neutralize), it was considered more expedient to keep an excess of
metal in the dissolver and digest to a rather low concentration of free
acid.

Sufficient 60 per cent HNO_3 - 0.05 M HF solution was added to dissolve 86 grams of a 175 gram piece of metal and the mixture heated to boiling. It was found that 47, 74 and 86 grams of metal had dissolved after 1/2, 1-1/2, and 3-1/2 hours digestion, respectively, showing a considerable decrease in required time with excess metal present. It was found that some of the HNO_3 goes to NO_2 as well as NO, so that the metal dissolved per mole of HNO_3 consumed must be empirically determined.

2. Corrosion of Stainless Steel by HNO_3 - HF and HNO_3 - $(NH_4)_2SiF_6$ Mixtures at High Temperatures

After finding a suitable medium for dissolving thorium metal and thorium dioxide, it was necessary to determine the corrosion rate of this medium on materials from which dissolver vessels could be made. It was expected that heat-treated 25-12 stainless steel would be best of the more common structural materials, with substances like columbium, tantalum, and platinum more corrosive resistant though perhaps prohibitively costly for large scale work.

A number of small scale corrosion tests were carried out in the Technical Division at Clinton Laboratories under the general supervision of M. D. Peterson [2, 3, 4]. Some of the results of these experiments are given in Table 5.

The figures given in Tables 5 and 6 are the maximum values obtained for each set of conditions and were obtained from weight losses of the samples over 21 to 72 hour test periods. There was no evidence that pitting would be an important factor.

These results show that, at constant fluoride concentration, the corrosion rate decreases when thorium ion is present and as the HNO_3 concentration is decreased and suggest that under actual dissolving conditions a lower corrosion rate may be obtained than those indicated by Table 5. In order to show that this was actually the case, the results in Table 6 were then obtained by M. D. Peterson and Leslie Burris [5]. Further corrosion studies by these two authors showed that

Table 5

CORROSION OF HEAT-TREATED 25-12 STAINLESS STEEL BY HNO_3 – HF
AND HNO_3 – $(NH_4)_2SiF_6$ MIXTURES IN PRESENCE AND ABSENCE OF THORIUM

Solution Composition	Molarity	T (°C)	Corrosion Rates (inches/months)
HNO_3 HF	16.0 0.1	105	0.02
HNO_3 HF $Th(NO_3)_4$	16.0 0.1 0.5	105	0.003
HNO_3 HF	16.0 0.01	105	0.0086
HNO_3 HF $Th(NO_3)_4$	16.0 0.01 .05	105	0.0016
HNO_3 HF $Th(NO_3)_4$	7.9 0.05 1.5	110	0.0001
HNO_3 HF $Th(NO_3)_4$	10.4 0.05 1.9	110	0.0004
HNO_3 HF $Th(NO_3)_4$	13.0 0.05 2.4	110	0.004 (0.00004 for Tantalum)
HNO_3 $(NH_4)_2SiF_6$	16.0 0.003	105	0.008
HNO_3 $(NH_4)_2SiF_6$ $Th(NO_3)_4$	8.0 0.003 0.5	105	0.0015
HNO_3 $(NH_4)_2SiF_6$ $Th(NO_3)_4$	8.0 0.003 0.5	76	0.0002

the solutions resulting from the dissolution of thorium metal (in this particular case, 2.5 M Th(NO_3)$_4$. 1.0 M HNO_3, 0.05 M HF) showed very little corrosion at 40°C on heat-treated and on non-heat-treated 18-8 and non-heat-treated 25-12 stainless steel. The actual figures obtained showed 0.00001 to 0.00002 inches per month for the first 64 hours of contact and considerably less for successive exposures of the same steel samples. Hence non-heat-treated stainless steel may be used for equipment other than the dissolver.

Table 6

CORROSION OF HEAT-TREATED 25-12 STAINLESS STEEL AND OF TANTALUM BY HNO_3 - HF - Th(NO_3)$_4$ MIXTURES DURING THE DISSOLUTION OF THORIUM METAL AT 110°C

Solution		Corroded Material	Exposure Time (hours)	Corrosion Rate (inches/months)
Composition	Concentration			
HNO_3 HF Th(NO_3)$_4$	(60-15)% 0.05M (0.0-3.0)	25-12	29	0.00030
HNO_3 HF Th(NO_3)$_4$	(60-3)% 0.05 (0.0-6.2)M	25-12	21	0.00026
HNO_3 HF Th(NO_3)$_4$	(60-8)% 0.05 (0.0-3.0)M	25-12	26	0.00020
HNO_3 HF Th(NO_3)$_4$	(60-8)% 0.05 (0.0-3.0)M	Tantalum	26	0.00000

3. Effect of Fluoride Ion on the Separation of Uranium from Thorium by Solvent Extraction

While it was not supposed that small amounts of fluoride ion in an aqueous solution of high nitrate concentration would noticeably affect either the extraction of uranyl ion into organic solvents or the efficiency of its separation from large amounts of thorium by solvent extraction, it was nevertheless necessary to verify this supposition. The presence of 0.01 N HF in an aqueous phase 1 M in $Al(NO_3)_3$, 1 M in HNO_3, and 1/4 M in $Th(NO_3)_4$, and containing U^{232} tracer was found to have no effect on the uranium-thorium separation. It was desirable to find out at what concentration of fluoride the separation would be affected and whether the separation could be improved by the holding of the thorium in the aqueous phase at, for example, a fluoride to thorium ratio of unity. (See Section 4 for complexing of Th(IV) by fluoride.)

Batch extraction experiments were carried out on a 3 ml (in each phase) scale in which only the HF concentration was varied. The aqueous phases consisted of 7/8 M $Th(NO_3)_4$, by 5/6 M $Al(NO_3)_3$, and 1 M HNO_3, i.e., 7 M total NO_3^-, with enough U^{233} to act as uranium tracer, enough Th^{234} to act as thorium tracer, and with enough HF present to give HF to Th(IV) ratios of 0, 1, or 2. The high nitrate concentration was picked in order to be working under conditions where a significant fraction of both the thorium and uranium was extracted. These experiments were carried out before the required radio-chemical analytical techniques were perfected, and as a result it can be seen (Table 7) that where the values from duplicate runs were obtained the agreement is not as good as desired, though it was satisfactory for the purpose of these tests. The solvent used was diethyl ether.

Table 7

EFFECT OF HF CONCENTRATION OF THE SEPARA-
TION OF URANIUM FROM THORIUM BY SOLVENT EXTRAC-
TION INTO DIETHYL ETHER FROM 7/8 M Th(NO$_3$)$_4$ -
5/6 M Al(NO$_3$)$_3$ - 1 M HNO$_3$ AQUEOUS SOLUTION

Mole Ratio HF/Th(IV)	Distribution Ratio (Ether/Aqueous)	
	Th	U
0	0.23, 0.28	1.8
1	0.22	1.2, 1.9
2	0.145, 0.15	0.53, 0.81

It appears from Table 7 that up to a ratio of fluoride to Th(IV)
of about unity, HF concentration has little effect on the extraction of
either uranyl or thorium; at a ratio of 2 the extraction efficiencies
of both these metallic ions are decreased.

4. On the Mechanism of the Catalytic Dissolution by Fluoride

Essentially nothing is known about the mechanism of the catalytic
effect of HF or fluosilicate on the dissolution of thorium in nitric
acid. As mentioned earlier (see Table 1), under a given set of con-
ditions the rate of dissolution was approximately proportional to the
first power of the HF concentration.

J. C. Hindman and K. McLane [6] of the Metallurgical Laboratory of
Chicago have evidence for a monofluoride complex of Pu(IV) ion, i.e.,
PuF^{+++}, with a dissociation constant of the order of 10^{-7}. This evi-
dence was obtained from a study of the absorption spectra in solutions
containing fluoride, and these authors believe that complexes involving
more than one fluoride per Pu(IV) also exist. Other work at the

Metallurgical Laboratory [7] showed that on adding fluoride to solutions of U(IV) no precipitate was obtained until after two moles of fluoride per mole U(IV) had been added, indicating the existence of the complex UF_2^{++}.

The authors of the present paper found similarly that no precipitate was obtained until after two moles of fluoride had been added to solutions of Th(IV), again indicating Th(IV)-F$^-$ complexes. Perhaps some sort of thorium-fluoride complex enters into the mechanism of the catalytic dissolution of thorium metal and dioxide.

5. On Other Media for the Dissolution of Th and/or ThO_2

While HNO_3 - HF and HNO_3 - $(NH_4)_2SiF_6$ mixtures were found to be satisfactory dissolution media for thorium metal, it was considered desirable to try other media, both out of scientific curiosity and because another mixture might be satisfactory on a large scale. Both perchloric and phosphoric acids were found to attack metallic thorium very slowly. Adding small amounts of H_2SO_4, $Hg(NO_3)_2$, KI, Na_2SO_4, $Co(NO_3)_3$, or $Fe(NO_3)_3$ to nitric acid did not noticeably increase the rate of solution of the metal in this acid. Nor did the use of metallic platinum vessels (with the thorium metal contacting the platinum) appear to increase the rate over that obtained in pyrex glass vessels.

E. G. Bohlman and R. K. Kennedy [8] have reported an apparent increase in solubility in mineral acids of ThO_2 samples after pre-treatment with strong NaOH solution.

6. Summary

(a) Thorium metal and dioxide have been found to dissolve quite readily in strong HNO_3 containing a small amount of fluoride or fluosilicate.

(b) A recommended set of conditions involves concentrated HNO_3 containing 0.05 M HF and temperatures near the boiling point.

(c) The corrosion rate on 25-12 heat-treated stainless steel under the recommended dissolving conditions is only of the order of 0.0003 inch per month. The corresponding corrosion on tantalum is less than 0.00001 inch per month, i.e., too low for detection.

(d) The low concentrations of fluoride in the solutions resulting after dissolution do not effect a subsequent separation of uranium from the dissolved thorium by solvent extraction.

(e) The mechanism of the catalytic dissolution of Th or ThO_2 by fluoride may involve complexes of thorium with fluoride.

(f) Other media for the dissolution of the metal were tried without success.

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(5) Peterson, M. D. and L. Burris, MonC-97, Table 1, April 16, 1946.

(6) Hindman, J. C. and K. McLane, CN-2689, p. 22, March 3, 1945.

(7) Manning, W. M., private communication.

(8) Bohlmann, E. G. and K. K. Kennedy, private communication.

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