A PROCESS FOR THE DISSOLUTION
OF ALUMINUM-CLAD THORIA FUEL ELEMENTS

J. F. Phillips
H. D. Huber

July 1968

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OF ALUMINUM-CLAD THORIA FUEL ELEMENTS

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A PROCESS FOR THE DISSOLUTION OF ALUMINUM-CLAD THORIA FUEL ELEMENTS

J. F. Phillips and H. D. Huber

INTRODUCTION

Production of ^{233}U requires irradiation of thorium oxide target elements held in aluminum containers. Following suitable cooling periods, the target elements are dissolved in nitric acid-hydrofluoric acid solutions, and the resulting dissolver solution is processed for recovery of ^{233}U .

Prior to dissolving the target elements, the aluminum containers must be removed. These containers may be removed with sodium hydroxide-sodium nitrate as is currently done with aluminum-clad uranium metal. However, when the thoria is present in the element as a loose powder, it settles to the bottom of the dissolver as an almost impervious layer of sludge after the cladding is removed. Draining the alkaline decladding solution through the thoria sludge is difficult and time consuming, but it is necessary to remove the decladding solution prior to dissolving the target element in Thorex reagent.

Alternately, the aluminum cladding may be dissolved with a solvent which also dissolves thoria. Agitation caused by aluminum dissolution would hasten thoria dissolution, and hence alleviate drainage problems by removing thoria fines. Dissolution of aluminum metal in mercury-catalyzed nitric acid is well-known. The mechanism by which mercury(II) ion catalyzes the aluminum dissolution in nitric acid appears to be the reduction of mercury(II) to metallic mercury on the aluminum surface.⁽¹⁾ Amalgamation of the aluminum surface prevents the

formation of aluminum oxide, thus allowing aluminum to dissolve at a rate commensurate with its electromotive potential. This amalgamation process is known as activation.⁽²⁾ The dissolution rate of activated aluminum is as high as 125 mg/cm²/min, while unactivated aluminum dissolves relatively slowly with a reaction rate of 0.5 to 1.0 mg/cm²/min. Schulz and others^(2,3) have indicated that nickel(II) markedly reduces the reaction rate of mercury-catalyzed aluminum in HNO₃.

The purposes of the studies described in this report were to: (1) investigate the factors affecting activation, (2) determine the effect of nickel(II) and other variables on the aluminum dissolution rate in the hope that nickel(II) may be used to moderate the reaction rate of mercury-catalyzed aluminum, (3) investigate the effect of aluminum nitrate and thorium nitrate on the thorium dissolution rate in Thorex reagent, and (4) measure the solubility of thorium nitrate in nitric acid-aluminum nitrate media.

SUMMARY AND CONCLUSIONS

In an effort to develop a process for simultaneous dissolution of thorium and its C-64 aluminum alloy container, the following properties were measured: activation* and dissolution characteristics of C-64 aluminum in mercury-catalyzed nitric acid, nickel(II) nitrate solutions; thorium dissolution rates in nitric acid, hydrogen fluoride, aluminum nitrate, thorium nitrate solution; and the solubility of thorium nitrate in nitric acid-aluminum nitrate.

On the basis of the data obtained, the following co-dissolution process was recommended:

1. Activate and dissolve the containers in 10.0M HNO₃, 0.045M HF, 0.10M Al(NO₃)₃, 0.0120M Hg(NO₃)₂, 0.04M - 0.05M Ni(NO₃)₂.

* Activation is defined and discussed on page 3.

2. When the aluminum is partially dissolved, add additional HNO_3 -HF solution and dissolve the now-exposed thorium to 0.55M - 0.65M $\text{Th}(\text{NO}_3)_4$.

DISCUSSION

ACTIVATION STUDIES OF C-64 ALUMINUM

The purpose of this investigation was to determine the nitric acid and mercury(II) concentrations under which C-64 aluminum would activate.

Criteria for Judging if Aluminum Is Activated

Listed below are some observable characteristics of activated aluminum:

- The aluminum surface becomes rough, irregular, and pitted, and loses its luster.
- An increased dissolution rate, as evidenced by increased gas evolution, is observed.
- A white powder, presumably hydrated aluminum oxide, forms on the surface of the aluminum when it is removed from the test solution.
- Gas evolution, presumably hydrogen, occurs if the aluminum is immersed in warm water immediately after removal from the test solution.

In these studies, aluminum was considered activated when at least two of the criteria were present. In some cases, particularly in the region of seven molar nitric acid and 0.0020 molar mercury(II), the aluminum appeared to activate, but the reaction rate, initially high, immediately fell to almost zero. This indicated that the aluminum, although initially activated, had deactivated. In all other cases, however, the aluminum remained lustrous when it failed to activate, and there was little ambiguity in determining if the aluminum activated.

Experimental Procedure

Extruded C-64 aluminum, obtained from unused containers, was cut into 1.9 x 1.9 cm coupons. The coupons were washed with carbon tetrachloride to remove oil and aluminum turnings and then pretreated by immersion in distilled water maintained at 62 °C for 92 hr, or in distilled water maintained at 60 °C for 17 hr.

In a typical experiment, the washed and pretreated coupon was placed in a stainless steel basket and immersed in 50 ml of test solution at room temperature. The solution was gradually heated to boiling over a period of 20 min and then held there for an additional 15 min. The coupon was then removed from the reaction mixture and washed, first with distilled water and then with acetone, and examined for further signs of activation. All runs were made in triplicate, and failure of one coupon to activate constituted failure of the entire group.

Results

Four series of runs were made with aluminum coupons pretreated in water for 92 hr at 62 °C. In the first series or run, neither nickel nitrate nor hydrogen fluoride was present. In the second series, hydrogen fluoride was absent, and nickel nitrate concentration was 0.025M. In the third series, hydrogen fluoride was absent, and nickel nitrate concentration was 0.0171M. In the fourth series, nickel nitrate concentration was 0.025M, and hydrogen fluoride concentration was 0.0100M. A fifth series of runs was made with aluminum pretreated with water at 60 °C for 17 hr; nickel nitrate concentration was 0.025M, and hydrogen fluoride concentration was 0.0100M.

Data obtained in the five series of experiments are shown graphically in Figures 1 and 2. Figure 1 indicates that C-64 aluminum will not activate at nitric acid concentrations much above 8.5M in the absence of hydrogen fluoride. The region of activation increases slightly with decreasing nickel concentration for reasons as yet unknown. Hydrogen fluoride, at the concentration used, increased the nitric acid concentration at which activation could be achieved to at least 12.5M (see Figure 2). Presumably the fluoride attacks the protective alumina coating and permits activation to occur more readily.

FIGURE 1. C-64 Aluminum Activation

FIGURE 2. C-64 Aluminum Activation

The data in Figure 2 indicate that prolonged immersion of aluminum in warm distilled water shifts the region in which activation occurs toward slightly lower nitric acid concentrations ($\sim 0.5M$). R. K. Hart⁽⁴⁾ has shown that metallic aluminum oxidized rapidly for two days when immersed in distilled water at 60 °C. However, by the end of the fourth day, the oxidation rate had decreased markedly and the outer layer of corrosion products was loosely adherent. Such loosely adherent films were present on the C-64 aluminum used in these studies. It was concluded that the film thickness will not change significantly after about four days in distilled water at 60 °C, and because the outer layer of the film is fragile, it will not remain intact during handling of fuel elements. Hence, no significant departure was expected from the activation behavior observed in these experiments, due to prolonged storage of fuel elements in water.

DISSOLUTION OF C-64 ALUMINUM IN MERCURY CATALYZED NITRIC ACID

Objectives

This investigation had two objectives. The first was to study the relationship between the dissolution rate of C-64 aluminum and six experimental factors, namely, nitric acid concentration, nickel(II) nitrate concentration, mercury(II) nitrate concentration, hydrogen fluoride concentration, aluminum nitrate concentration, and the ratio of aluminum surface area to solvent volume (A/V ratio).

The second objective was to find a solvent mixture containing the maximum nitric acid concentration at which aluminum will activate and in which aluminum will dissolve at a rate below $30 \text{ mg/cm}^2/\text{min}$, i.e., below 250 mil/hr.

Experimental Design

The region covered by a 3^6 factorial design was chosen for experimentation. The experimental levels of the factors are shown below:

<u>Experimental Factor</u>	<u>Factorial Level, moles/liter</u>		
Nitric Acid	8.0	10.0	12.0
Nickel(II) Nitrate	0.00	0.020	0.040
Mercury(II) Nitrate	0.0040	0.012	0.020
Hydrogen Fluoride	0.010	0.045	0.10
Aluminum Nitrate	0.00	0.35	0.70
A/V Ratio	23.4	32.8	46.2 cm ² /liter

To economize on experimental runs a 1/9 fractional replicate of the 3^6 factorial⁽⁵⁾ was chosen for the experimental design. The 81 experimental points were blocked into nine days of nine experiments each and the order of experimentation within each day randomized. It was thus possible to obtain unbiased comparisons between experimental points, and also to eliminate any day-to-day variation from the experimental error.

Experimental Procedure

Weighed aluminum disks, cut from extruded alloy C-64 aluminum cans, were mounted in Teflon holders. The disks were activated by dipping them in 125 ml of boiling 1.0M HNO_3 -0.00020M $\text{Hg}(\text{NO}_3)_2$ for 1 min and then plunging the now activated disks into the boiling test solution. The holders were designed to expose a known area on one side of the disk.

At the end of the reaction period (usually 1.1 min) the disk was removed from the dissolving solution, dipped into water, then into acetone, and quickly reweighed.

Results

Average Effects and Interactions of Experimental Factors

The 81 experimental points, together with the rate at which aluminum dissolved ($\text{mg}/\text{cm}^2/\text{min}$), are given in Table I. The standard experimental error at the experimental points was estimated as $7.87 \text{ mg}/\text{cm}^2/\text{min}$ by repeating the experimental runs in Blocks (or days) 2, 5, and 8.

Although the design called for equally spaced factorial levels, the levels of hydrogen fluoride and A/V ratio were inadvertently set at 0.045M and $32.8 \text{ cm}^2/\text{liter}$ rather than the specified 0.055M and $34.8 \text{ cm}^2/\text{liter}$. These deviations from the design values were not considered large enough to warrant the more complicated analysis of variance techniques for unequally spaced factorial levels. The analysis of variance, summarized in Table II, was carried out for equally spaced factorial levels. Consequently, the sums of squares for hydrogen fluoride and A/V ratio, and for all interactions involving these factors, are intended only as approximate estimates of the correct sums of squares.

The average effects of the experimental factors upon dissolution are shown in Figure 3. The average effect curve for a given factor was obtained from the 81 experimental points in Table I (omitting the replicated rates in Blocks 2, 5, and 8) by averaging all the observed combinations of levels of the remaining experimental factors. From inspection of the F-ratios in Table II for the main or average effects of the six experimental factors, it is evident that in the order of decreasing magnitude of their average effects, the experimental factors were: aluminum nitrate, nickel(II) nitrate, mercury(II) nitrate, A/V ratio, and hydrogen fluoride. Nitric acid in the range 8 to 12 molar had no significant effect upon the dissolution rate.

TABLE I. Solvent Composition and Observed Dissolution Rate

Solv. No.	HNO ₃ M	Ni(NO ₃) ₂ M	Hg(NO ₃) ₂ M	HF M	Al(NO ₃) ₃ M	$\frac{A}{V}$ cm ² /liter	Observed Rate	Observed Rate on 2nd Run Made on Different Day
1	8	0.00	0.012	0.010	0.70	23.4	57.281	
2	12	0.04	0.020	0.045	0.35	23.4	55.057	
3	10	0.02	0.004	0.100	0.00	23.4	51.360	
4	8	0.04	0.004	0.010	0.00	32.8	30.803	Day 1
5	8	0.02	0.020	0.010	0.35	46.2	66.030	
6	10	0.04	0.012	0.100	0.70	46.2	36.547	
7	12	0.00	0.004	0.045	0.00	46.2	97.086	
8	12	0.02	0.012	0.045	0.70	32.8	45.439	
9	10	0.00	0.020	0.100	0.35	32.8	79.751	
1	12	0.040	0.004	0.010	0.35	46.2	35.218	44.992
2	8	0.040	0.012	0.100	0.00	23.4	77.983	98.832
3	10	0.040	0.020	0.045	0.70	32.8	48.262	41.375
4	12	0.000	0.012	0.010	0.00	32.8	112.170	102.656
5	8	0.020	0.004	0.100	0.35	32.8	67.789	60.176 Day 2
6	12	0.020	0.020	0.010	0.70	23.4	40.529	39.374
7	8	0.000	0.020	0.100	0.70	46.2	40.185	44.348
8	10	0.020	0.012	0.045	0.00	46.2	32.164	21.940
9	10	0.000	0.004	0.045	0.35	23.4	71.308	75.479
1	10	0.02	0.020	0.045	0.70	46.2	40.968	
2	10	0.00	0.012	0.045	0.00	23.4	130.220	
3	8	0.04	0.020	0.100	0.70	23.4	39.674	
4	8	0.00	0.004	0.100	0.35	46.2	69.351	Day 3
5	12	0.04	0.012	0.010	0.00	46.2	13.467	
6	12	0.02	0.004	0.010	0.35	23.4	39.849	
7	8	0.02	0.012	0.100	0.00	32.8	54.023	
8	12	0.00	0.020	0.010	0.70	32.8	38.610	
9	10	0.04	0.004	0.045	0.35	32.8	10.845	
1	10	0.000	0.004	0.010	0.70	46.2	38.387	
2	8	0.040	0.012	0.045	0.35	46.2	50.154	
3	10	0.040	0.020	0.010	0.00	23.4	123.346	
4	12	0.020	0.020	0.100	0.00	46.2	106.214	
5	12	0.000	0.012	0.100	0.35	23.4	78.837	Day 4
6	12	0.040	0.004	0.100	0.70	32.8	64.592	
7	10	0.020	0.012	0.010	0.35	32.8	59.316	
8	8	0.000	0.020	0.045	0.00	32.8	47.413	
9	8	0.020	0.004	0.045	0.70	23.4	47.735	

TABLE I. (contd)

Solv. No.	HNO ₃ M	Ni(NO ₃) ₂ M	Hg(NO ₃) ₂ M	HF M	Al(NO ₃) ₃ M	$\frac{A}{V}$ cm ² /liter	Observed Rate	Observed Rate on 2nd Run Made on Different Day
1	8	0.00	0.020	0.010	0.35	23.4	75.327	70.285
2	12	0.00	0.012	0.045	0.70	46.2	35.126	42.820
3	8	0.04	0.012	0.010	0.70	32.8	52.218	70.243
4	10	0.00	0.004	0.100	0.00	32.8	120.655	120.527 Day 5
5	10	0.02	0.012	0.100	0.70	23.4	51.865	57.181
6	12	0.02	0.020	0.045	0.35	32.8	58.532	55.396
7	10	0.04	0.020	0.100	0.35	46.2	51.833	54.895
8	12	0.04	0.004	0.045	0.00	23.4	17.841	18.317
9	8	0.02	0.004	0.010	0.00	46.2	58.054	83.622
1	10	0.00	0.012	0.010	0.35	46.2	66.742	
2	8	0.00	0.004	0.045	0.70	32.8	56.790	
3	12	0.04	0.012	0.100	0.35	32.8	39.448	
4	12	0.00	0.020	0.100	0.00	23.4	120.811	Day 6
5	8	0.04	0.020	0.045	0.00	46.2	102.270	
6	10	0.02	0.020	0.010	0.00	32.8	122.489	
7	12	0.02	0.004	0.100	0.70	46.2	35.920	
8	10	0.04	0.004	0.010	0.70	23.4	10.094	
9	8	0.02	0.012	0.045	0.35	23.4	83.031	
1	10	0.04	0.012	0.045	0.00	32.8	58.180	
2	12	0.00	0.004	0.010	0.35	32.8	54.761	
3	10	0.00	0.020	0.045	0.70	23.4	51.644	
4	8	0.00	0.012	0.100	0.00	46.2	67.745	Day 7
5	8	0.04	0.004	0.100	0.35	23.4	20.937	
6	10	0.02	0.004	0.045	0.35	46.2	33.350	
7	8	0.02	0.020	0.100	0.70	32.8	57.175	
8	12	0.04	0.020	0.010	0.70	46.2	33.420	
9	12	0.02	0.012	0.010	0.00	23.4	85.734	
1	8	0.00	0.004	0.010	0.00	23.4	124.013	118.9
2	10	0.00	0.012	0.100	0.70	32.8	64.682	46.9
3	12	0.00	0.020	0.045	0.35	46.2	56.472	57.8
4	8	0.02	0.012	0.010	0.70	46.2	39.769	40.9 Day 8
5	12	0.02	0.004	0.045	0.00	32.8	29.291	23.1
6	8	0.04	0.020	0.010	0.35	32.8	80.716	79.9
7	10	0.02	0.020	0.100	0.35	23.4	101.832	69.1
8	12	0.04	0.012	0.045	0.70	23.4	37.929	38.7
9	10	0.04	0.004	0.100	0.00	46.2	26.127	28.3
1	12	0.04	0.020	0.100	0.00	32.8	117.941	
2	12	0.00	0.004	0.100	0.70	23.4	41.016	
3	8	0.04	0.004	0.045	0.70	46.2	28.686	
4	8	0.00	0.012	0.045	0.35	32.8	88.141	Day 9
5	10	0.04	0.012	0.010	0.35	23.4	34.580	
6	12	0.02	0.012	0.100	0.35	46.2	53.591	
7	8	0.02	0.020	0.045	0.00	23.4	85.448	
8	10	0.00	0.020	0.010	0.00	46.2	100.106	
9	10	0.02	0.004	0.010	0.70	32.8	45.252	

TABLE II. Analysis of Variance Table for a 1/9 Fractional Replicate of a 3⁶ Factorial Blocked in Nine Days of Nine Experimental Runs Each

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F-Ratio
Blocks	4036.439	8	504.555	8.16**
Main effects:				
Nitric Acid (A)	397.764	2	173.882	2.81
Nickel(II) (B)	8729.972	2	4364.986	70.55**
Mercury(II) (C)	7003.897	2	3501.949	56.60**
Hydrogen Fluoride (D)	1029.742	2	514.871	8.32**
Aluminum Nitrate (E)	16357.161	2	8178.581	132.19**
A/V Ratio (F)	2473.896	2	1236.948	19.99**
Measurable 2-factor Interactions				
BC	6974.857	4	1743.714	28.18**
BE	3315.139	4	828.785	13.40**
CF	1420.145	4	355.036	5.74**
EF	1584.387	4	396.097	6.40**
AB ²	309.494	2	154.747	2.50
AC ²	854.555	2	427.278	6.91**
AE	509.289	2	254.645	4.12**
AF ²	1179.866	2	589.933	9.54**
BD	305.723	2	152.862	2.47
BF ²	368.591	2	184.296	2.98
CD ²	440.954	2	220.477	3.56**
CE ²	1146.007	2	573.004	9.26**
DE ²	672.259	2	336.130	5.43**
DF	1272.286	2	636.143	10.28**
Nonmeasurable 2-factor Interactions				
AB=DF ²	613.452	2	306.726	4.96*
AC=DE	540.082	2	270.041	4.36*
AD ² =BF	686.987	2	343.494	5.55**
AE=CD	1019.307	2	509.654	8.24**
AF=BD ²	45.064	2	22.532	<1
3-factor Interactions Aliased with 3-factor or Higher Order Interactions and not Confounded with Blocks				
ABC	1018.660	2	509.330	8.23**
BCD	970.356	2	485.178	7.84**
CDF	1504.637	2	752.319	12.16**
BDE	710.428	2	355.214	5.74**
AC ² F	26.844	2	13.422	<1
ABE ²	78.889	2	39.445	<1
DEF	1219.399	2	609.700	9.85**
Estimate of Experimental Error Variance ²		27	61.87	
Estimate of Standard Experimental Error			7.87	

* Probability of so large an F-ratio occurring by chance alone less than 0.05 (1 in 20).

** Probability of so large an F-ratio occurring by chance alone less than 0.01 (1 in 100).

FIGURE 3. *Aluminum Dissolution Average Effects of Solvent Variables*

In the event the effect of one experimental factor on response (dissolution rate) is dependent on the level of another experimental factor, the two factors are said to interact. Interactions were more prevalent than originally anticipated. A large number of two-factor as well as three-factor interactions appear evident. Consequently, the average effect curves alone cannot summarize the effects of the experimental factors.

These curves should be used only to gain a general idea of the effect of the factors upon dissolution rate.

By far the most significant interaction was the nickel(II) x mercury(II) interaction. Other less significant interactions in decreasing order of magnitude were nickel(II) x aluminum nitrate, aluminum nitrate x A/V ratio, and mercury(II) x A/V ratio. Response curves showing the nickel(II) x mercury(II) interaction are given in Figure 4. The response curve for one factor, i.e., nickel(II), at a specified experimental level of the other factor, mercury(II), was obtained from the 81 experimental points in Table I by averaging the observed combinations of levels of the remaining four experimental factors.

An Activating Solvent Mixture Producing a Dissolution Rate Below 30 mg/cm²/min

A second objective of the experimental program was to find a solvent mixture containing the maximum nitric acid concentration which would activate and dissolve aluminum at a rate below 30 mg/cm²/min. It was known that the thoria dissolution rate decreases with increasing aluminum concentration and passes through a maximum at approximately 0.05M hydrogen fluoride. Since the thoria process equipment is made of stainless steel, the maximum permissible hydrogen fluoride was corrosion-limited, and some aluminum was necessary to retard fluoride-induced corrosion. Therefore, 0.045M hydrogen fluoride and 0.10M aluminum nitrate were thought to be a good compromise.

FIGURE 4. Aluminum Dissolution, Effect of Ni⁺⁺-Hg⁺⁺ Interaction

The response curves, showing the nickel x mercury interaction in Figure 4, indicate that the moderating effect which nickel(II) has upon the dissolution rate decreases as the mercury(II) concentration increases from 0.0004M to 0.20M; and in fact, that nickel(II) increases the dissolution rate in the range of 0.004M to 0.020M nickel when the mercury concentration is 0.02M. Thus, the maximum mercury(II) concentration was limited to about 0.012M.

Figure 2 shows that C-64 aluminum will not activate at 0.012M mercury when the nitric acid concentration exceeds 10.4M. To insure activation, the maximum permissible nitric acid concentration was set at 10.0M. The A/V ratio was set at 46.2 cm²/liter since this most nearly agrees with the expected A/V ratios.

Thus, the solvent composition was fixed at 10.0M nitric acid, 0.045M hydrogen fluoride, and 0.10M aluminum nitrate. Four additional experiments were then carried out using a 2² factorial design in which the nickel(II) and mercury(II) concentrations were varied. The concentrations and observed rates in mg/cm²/min are shown below.

<u>Nickel(II) Concentration</u>	<u>Mercury(II) Concentration</u>	
	0.010M	0.012M
0.05M	12.70 mg/cm ² /min	28.71 mg/cm ² /min
0.06M	4.26 mg/cm ² /min	6.08 mg/cm ² /min

All four solutions produced a dissolution rate below 30 mg/cm²/min, but only solutions at 0.05M nickel(II) activated. In spite of the higher dissolution rate, the solution containing 0.012M mercury(II) and 0.05M nickel was selected as the most promising, since C-64 aluminum would be more likely to activate due to higher mercury(II) concentrations. The estimate of the aluminum dissolution rate for the latter solvent was

later revised downward from 28.71 to 19.74 $\text{mg}/\text{cm}^2/\text{min}$, as a result of additional experimentation which was concerned with the size of the standard experimental error (7.87 $\text{mg}/\text{cm}^2/\text{min}$) in the overall experimental program.

Because of the numerous interactions, interpolation and extrapolation of the average effect and interaction curves for predicting rates is somewhat uncertain. Although additional experimentation was not made at 0.04M nickel(II), both the nickel x mercury interaction curve at 0.012M mercury (Figure 4), and the nickel average effect curve (Figure 3), indicate that a reduction in nickel(II) concentration from 0.05M to 0.04M results in a rate increase of only about 6 $\text{mg}/\text{cm}^2/\text{min}$. Hence, some saving in the cost of nickel reagent might be possible.

The use of the nickel x mercury interaction curve is somewhat justifiable because this is by far the most significant interaction (F ratio = 28.18), but again it is emphasized that the calculated rate differences are only approximate because all other nickel interactions were ignored.

Effect of Metallurgical Differences on Aluminum Dissolution Rate

The sizable standard experimental error (7.87 $\text{mg}/\text{cm}^2/\text{min}$) suggested that differences in the metallurgical properties of the aluminum containers might account for some of this error, since the aluminum disks used in the experimental runs had been taken at random from different aluminum containers. To test this hypothesis, the dissolution rates for nine disks, three taken at random from each of three aluminum containers, were measured in the solvent selected above.

The following results expressed in $\text{mg}/\text{cm}^2/\text{min}$ were obtained:

<u>CONTAINER</u>		
<u>I</u>	<u>II</u>	<u>III</u>
20.76	22.49	21.51
13.96	18.78	22.95
16.27	15.06	24.89

Analysis of variance showed no significant differences in the dissolution rates of disks taken from different containers. Averaging the nine dissolution rates gave a revised estimate of $19.74 \text{ mg}/\text{cm}^2/\text{min}$ for the dissolution rate in the selected solvent mixture.

DISSOLUTION OF THORIUM OXIDE IN NITRIC ACID, HYDROGEN FLUORIDE, ALUMINUM NITRATE, THORIUM NITRATE SOLUTIONS

Background

The recovery of ^{233}U via solvent extraction requires that the thorium be dissolved, and the solvent commonly used is nitric acid-hydrofluoric acid. Aluminum nitrate is usually added to the solvent to reduce corrosion of the stainless steel dissolvers by complexing the fluoride ion. Initial nitric acid concentrations are in the range of 12M to 13M and terminal concentrations, and are 8M to 9M nitric acid and 1M thorium nitrate.

Thorium oxide dissolves relatively slowly in these reagents. Considerable advantage can be realized by choosing a solvent composition which produces the maximum dissolution rate throughout the dissolution cycle.

An early paper⁽⁶⁾ suggested that the thorium dissolution rate in 13M nitric acid was independent of fluoride ion concentration between 0.010M and 0.50M . Moore, et al.⁽⁷⁾, also reporting on work at 13M nitric acid, argue that the maximum

dissolution rate occurs at 0.010M fluoride. Both groups agree that thorium nitrate decreases the dissolution rate. Another report⁽⁸⁾ indicates that 0.040M fluoride ion and 13M nitric acid produced an adequate dissolution rate. Blanco, et al.⁽⁹⁾ agree that optimum dissolution rates are achieved in this solvent. Japanese workers⁽¹⁰⁾ have also measured the thoria dissolution in the range of 2 to 5 molar nitric acid.

Numerous other reports⁽¹¹⁻¹⁴⁾ relate the dissolution rate of thorium oxide-uranium oxide to solvent composition, mesh size, density, etc.

While there is evidence that aluminum nitrate reduces the thoria dissolution rate,^(11,14) no quantitative data are available at high aluminum ion concentration.

Maximum dissolution rate is not the only basis for judging a thoria dissolution reagent. Maness⁽¹⁵⁾ indicates that the corrosion of 304L stainless steel in nitric acid-hydrofluoric acid is an increasing function of the fluoride ion and nitric acid concentration. Thorium nitrate and aluminum nitrate greatly reduce stainless steel corrosion rates. Hence, thoria dissolution reagents which produce high dissolution rates may also produce high corrosion rates, and for that reason cannot be used in 304L stainless steel equipment.

In view of the paucity of thoria dissolution data at high aluminum ion concentration, and of the somewhat conflicting data in regard to the effect of fluoride ion on dissolution rate, it is desirable to know the relative dissolution rates of thoria in reagents of any likely composition. Such information allows us to accurately compare one proposed reagent with another on the basis of stainless steel corrosion and thoria dissolution rate throughout the entire dissolution cycle.

Experimental Procedure

Six grams of -8/+10 mesh sol-gel thoria were reacted for 2 to 10 min with 25.0 ml of boiling solvent in a Teflon bottle fitted with a water-cooled condenser. The reaction was then quenched with cold water, and undissolved thoria was filtered, washed with water, and dried to constant weight at 150 °C. The amount of dissolved thoria was found by difference. The reaction mixture was agitated at all times with a Teflon-covered magnetic stirring bar.

Because the dissolution rate is markedly dependent on prior treatment, the thoria used in all of these experiments was taken from the same source. The density of the thoria was found to be 9.89 g/cm³ by water displacement. By assuming that the particles are spherical, the thoria particle area (a) and the particle volume (v) are given by:

$$a = 4\pi r^2 \quad (1)$$

$$v = \frac{4}{3}\pi r^3 \quad (2)$$

where (r) is the mean particle radius. The total number of particles (N) is given by:

$$N = \frac{w}{\rho v}$$

where (ρ) and (w) are, respectively, thoria density and sample weight.

Therefore, the total surface (A) is found by:

$$A = Na = \frac{3w}{r\rho} .$$

Experimental Design

The primary objective of this experimentation was to obtain a good polynomial approximation to the functional relationship between the dissolution rate of thorium oxide and the concentrations of the four solvent constituents: nitric acid, thorium

nitrate, aluminum nitrate, and hydrogen fluoride. The region of experimentation was that covered by a 3^4 factorial design. Three equally spaced levels of experimentation was chosen and are shown below:

<u>Experimental Factor</u>	<u>Factorial Level in moles/liter</u>		
Nitric Acid	8.0	10.0	12.0
Thorium Nitrate	0.00	0.50	1.00
Aluminum Nitrate	0.00	0.35	0.70
Hydrogen Fluoride	0.01	0.04	0.07

To economize on the number of experiments, a second order rotatable design,⁽¹⁶⁾ which efficiently estimates the coefficients in a second degree polynomial by the method of least squares, was chosen for the experimental design. This design requires investigating only 25 of the 81 experimental points in the full 3^4 factorial design. Two estimates of the dissolution rate for each of the 25 experimental points were made. Whenever there was considerable variation between these estimates, new solvent mixtures were made and two additional estimates of the dissolution rate were obtained for each new solvent mixture. The dissolution rates obtained for the experimental points in the design, together with the mean dissolution rates, are found in Table A-I of the Appendix. The standard experimental error was approximately 10.3% of the dissolution rate at each of the experimental points.

In order to apply standard statistical techniques, which assume a constant standard experimental error, to the analysis of the experimental design, the statistical analysis was carried out on the common logarithms of the 80 dissolution rates found in Table A-I of the Appendix.

Fitting the polynomial

$$\log_{10} R = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \sum_{j=i}^4 \beta_{ij} X_i X_j$$

(where R is the dissolution rate in $\text{mg}/\text{cm}^2/\text{min}$, and X_1 is moles/liter nitric acid, X_2 is moles/liter thorium nitrate, X_3 is moles/liter aluminum nitrate, and X_4 is moles/liter hydrogen fluoride) to the 80 experimental rates yielded the following least squares estimates of the coefficients:

$$\begin{array}{lll}
 \beta_0 = -1.68235 & \beta_{11} = -5.69767 \cdot 10^{-3} & \beta_{13} = -1.16316 \cdot 10^{-1} \\
 \beta_1 = 2.26643 \cdot 10^{-1} & \beta_{22} = 1.50163 \cdot 10^{-1} & \beta_{14} = -9.45428 \cdot 10^{-1} \\
 \beta_2 = -1.12611 & \beta_{33} = -5.87321 \cdot 10^{-2} & \beta_{23} = -1.71565 \cdot 10^{-1} \\
 \beta_3 = -2.41396 \cdot 10^{-1} & \beta_{44} = -3.23915 \cdot 10^{+2} & \beta_{24} = 1.99954 \\
 \beta_4 = 4.42661 \cdot 10^{+1} & \beta_{12} = 7.51640 \cdot 10^{-2} & \beta_{34} = 1.73178 \cdot 10^{+1}
 \end{array}$$

Predicted rates from the second degree polynomial at experimental points are also given in Table A-I of the Appendix. A comparison with the mean experimental rates of the same table shows reasonably good agreement. Table A-II of the Appendix lists the predicted dissolution rates for the full 3^4 factorial design.

Experimental Results

The average effects of the solvent variables on the dissolution rate are shown in Figure 5. These average effect curves were obtained from predicted values at the 81 points in the full factorial design by averaging all the combinations of levels of the three remaining solvent variables. Significant two-factor interactions were found between hydrogen fluoride and aluminum nitrate, nitric acid and aluminum nitrate, and nitric acid and thorium nitrate. Consequently, the average effect curves alone cannot adequately summarize the effects of the solvent variables, but may be used only to give a general idea of the effect of a solvent constituent upon the dissolution rate.

An alternate representation of the results, which is very useful for estimating dissolution rates, is obtained by drawing contour curves of equal response (dissolution rate) on a graph whose coordinates denote solvent composition. Contour

FIGURE 5. Thorium Oxide Dissolution, Average Effects of Solvent Variables

curves showing combinations of aluminum nitrate and hydrogen fluoride which yield a constant dissolution rate are shown in Figure 6 for (a) 12 molar nitric acid-zero molar thorium nitrate, (b) 10 molar nitric acid-0.5 molar thorium nitrate, and (c) 8.0 molar nitric acid-1.0 molar thorium nitrate. These curves indicate that within the region of experimentation, the hydrogen fluoride concentration, which maximizes the dissolution rate, appears to be an increasing function of the aluminum nitrate concentration. For example, at 12 molar nitric acid and zero molar thorium nitrate, the hydrogen fluoride concentration which maximizes the dissolution rate at 0.10 molar aluminum nitrate is 0.055 molar, whereas, at 0.50 molar aluminum nitrate, it is about 0.065 molar.

FIGURE 6. Thorium Oxide Dissolution Curves, Effect of $\text{Al}(\text{NO}_3)_3$ and HF

Nitric acid x thorium nitrate contour curves are shown in Figure 7 for (a) 0.6 molar aluminum nitrate-0.045 molar hydrogen fluoride, and (b) 0.7 molar aluminum nitrate-0.045 molar hydrogen fluoride. The dotted portions of the curves in Figures 6 and 7 were obtained by extrapolating the polynomial beyond the region of experimentation and thus, should be regarded with some reservation.

FIGURE 7. Thorium Oxide Dissolution Curves,
Effect of HNO_3 and $\text{Th}(\text{NO}_3)_4$

The two-dimensional contour curves were generated from the least squares polynomial:

$$\log_{10} R = \beta_0 + \sum_{i=1}^4 \beta_i X_i + \sum_{i=1}^4 \sum_{j=i}^4 \beta_{ij} X_i X_j$$

Specifying a dissolution rate and values for two of the solvent variables (e.g., X_1 and X_2), yielded a second degree equation in the variables X_3 and X_4 . Substituting values for one of the latter variables (X_3) ranging over the region of experimentation in small increments, and in turn solving the resulting second degree equation in the other variable, X_4 yielded a sufficient number of points to enable a smooth curve to be drawn through them. This curve was taken to represent the desired contour curve.

SOLUBILITY OF THORIUM NITRATE IN NITRIC ACID-ALUMINUM NITRATE

Background

Misciatelli,⁽¹⁷⁾ who first reported work on the thorium nitrate-water system, obtained the temperature-composition curve from the water-rich side of the phase diagram through the eutectic between ice and the first thorium nitrate hydrate, and to the hydrate side at 20 °C. He identified this hydrate as thorium nitrate hexahydrate, $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$. Marshall, et al,⁽¹⁸⁾ substantiated and extended these data to 211 °C and showed that a transition from the hexahydrate to tetrahydrate occurred at 111 °C, and a transition from the tetrahydrate to a lower hydrate occurred at about 151 °C.

On the basis of thorium and water analysis, Templeton⁽¹⁹⁾ indicates that the alleged hexahydrate is, in fact, a hemihydrate, $\text{Th}(\text{NO}_3)_4 \cdot 5.5 \text{H}_2\text{O}$. Other workers⁽²⁰⁾ question the existence of any hydrate higher than five at 25 °C. No solubility measurements of thorium nitrate in nitric acid-aluminum nitrate media have been published so far.

The experiments discussed herein were designed to measure the solubility of thorium nitrate in aluminum nitrate-nitric acid at 25 °C and 50 °C. No effort was made to determine the composition of the solid phase.

Experimental Procedure

A calculated amount of solid aluminum nitrate, nitric acid, and the approximate amount of thorium nitrate required to saturate the solution, were added to a 50 ml flask. The volume was made up to approximately 45 ml with distilled water, and the solution was shaken overnight at constant temperature. Enough thorium nitrate and/or distilled water was then added to bring the volume up to 50 ml while leaving a small amount

of thorium nitrate undissolved. Thorium analysis was made by X-ray fluorescence after the slurries were shaken overnight. Further analyses were made until the thorium concentration no longer increased.

Nitric acid was determined by diluting 0.1947 ml of solution to 10 ml, buffering to pH 4.8 with potassium oxalate, and titrating with sodium hydroxide. Aluminum in aluminum nitrate was determined gravimetrically by converting the nitrate to oxide at 400 °C. Aluminum content found for the aluminum nitrate used was 7.994% as compared to 7.19% in $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Results

Shown in Table III are the results of solubility determinations made at 25 °C and 50 °C. All concentrations are in moles/liter. These results are graphed in Figures 8 and 9. Regions above the curves represent areas where a solid phase is present. No attempt was made to identify this solid phase. By suitable interpolation, the saturated thorium concentration between 0.3 and 0.9M $\text{Al}(\text{NO}_3)_3$ and between 25 °C and 50 °C may be found. Extrapolation to nitric acid concentrations higher than shown on the graphs is dangerous because of the possible presence of an aluminum nitrate solid phase.

DISCUSSION OF PROCEDURES

As previously noted, one method of dissolving irradiated aluminum-clad thoria requires that the aluminum containers be removed with sodium hydroxide-sodium nitrate. Following removal of the caustic decladding solution, the thoria is dissolved in the nitric acid-hydrofluoric acid reagent. Figure 6 indicates that, at 12M nitric acid and 0.00M aluminum nitrate, 0.053M hydrogen fluoride produces the maximum dissolution rate. However, 0.025M hydrogen fluoride-0.10M aluminum nitrate will be used at Hanford to reduce corrosion of stainless

steel equipment. Figure 6 indicates that with this reagent, the initial thoria dissolution rate will be about 5.4 mg/cm²/min. At 0.5M thorium nitrate and 10M nitric acid, the rate will decrease to 2.9 mg/cm²/min, and a further decrease to 1.3 mg/cm²/min may be expected when terminal concentration, i.e., 1.0M thorium nitrate-8.0M nitric acid, is reached.

TABLE III. *Solubility Determinations*

Thorium Nitrate Solubility in Nitric Acid-Aluminum Nitrate at 25 °C

<u>Nitric Acid, M</u>	<u>Thorium Nitrate, M</u>	<u>Aluminum Nitrate, M</u>
2.77	1.94	0.30
6.4	1.49	0.30
9.83	0.93	0.30
2.6	1.74	0.60
5.03	1.47	0.60
6.40	1.19	0.60
2.70	1.50	0.90
3.10	1.43	0.90
3.60	1.29	0.90
5.76	0.67	0.90

Thorium Nitrate Solubility in Nitric Acid-Aluminum Nitrate at 50 °C

2.2	2.20	0.30
3.05	2.11	0.30
6.0	1.66	0.30
9.6	1.38	0.30
2.2	2.05	0.60
5.3	1.59	0.60
8.0	1.38	0.60
1.41	1.90	0.90
2.3	1.77	0.90
4.50	1.51	0.90
5.62	1.35	0.90

An alternate process consists of dissolving the aluminum containers and thoria in the same solvent. The recommended aluminum activating and dissolving solution is 10.0M nitric acid, 0.045M hydrogen fluoride, 0.10M aluminum nitrate, 0.012M mercury(II) nitrate, and 0.05M nickel nitrate. This solution

produces an initial aluminum dissolution rate of $19.7 \text{ mg/cm}^2/\text{min}$. Average response curves and nickel x mercury interaction curves at 0.012M mercury, indicate that a reduction in nickel(II) concentration from 0.050M to 0.040M would not produce an appreciable increase in aluminum dissolution rate; therefore, some saving in nickel cost might be possible.

Most of the thoria irradiated at Hanford is contained in aluminum cans 8.7 in. long x 1.5 in. O.D. x 0.045 in. thick. Assuming that aluminum dissolves uniformly over the entire can, 32.3 cm^3 or 3.23 moles of aluminum per can must be removed before the thoria is exposed to the dissolver solution. Each can contains about 6 moles of thoria which corresponds to 0.538 moles of aluminum per mole of thoria.

About 3.75 moles of nitric acid are required to dissolve 1 mole of aluminum;⁽²¹⁾ hence, if one liter of dissolver solution per mole of thoria is used, the nitric acid concentration will be 8.0M , and aluminum nitrate concentration will be 0.64M when thoria is first exposed to the dissolver solution.

The aluminum nitrate average response curve (Figure 3) indicates that the aluminum dissolution rate decreases rapidly with increasing aluminum nitrate concentration, and thus, will be quite low when the thoria is first exposed to the dissolver solution. Hence, end caps, can wafers, and some can walls will persist in the dissolver for some time after the thoria has been released.

At the time the thoria is first exposed, the dissolver solution composition is approximately 8.0M nitric acid, 0.045M hydrogen fluoride, and 0.60 to 0.70M aluminum nitrate. Figure 7 indicates that the thoria dissolution rate in this solution is between 2.8 and $3.2 \text{ mg/cm}^2/\text{min}$. Extrapolating to 6.8M nitric acid and 0.3M thorium nitrate, yields a thoria dissolution rate of 1.8 to $2.0 \text{ mg/cm}^2/\text{min}$. There would be

little advantage in dissolving beyond 0.3M thorium nitrate because the increasing thorium nitrate, aluminum nitrate, and decreasing nitric acid concentration will reduce the thoria dissolution rate to a very low value.

However, considerable advantage results when more nitric acid-hydrogen fluoride is added to the dissolver after the aluminum has activated and partially dissolved. The time of addition is not critical.

For example, an additional charge of 0.2 liters of 12.7M* nitric acid-0.045M hydrogen fluoride per mole of thorium oxide produces a solvent composition of 0.53M aluminum nitrate, 0.045M hydrogen fluoride, and 8.8M nitric acid when thoria is first exposed. The thoria dissolution rate in this solvent is at least 3.4 mg/cm²/min (See Figure 7). On dissolving 60% of the thoria charge, the solvent composition is approximately 0.56M aluminum nitrate, 0.5M thorium nitrate and approximately 6.4M nitric acid, and the thoria dissolution rate has decreased to about 1.5 mg/cm²/min (See Figure 7).

At this point much of the fine particles have dissolved, so the dissolver is easily drained in readiness for the next charge of thoria fuel elements. Because these fines are dissolved, little suspended thoria is removed with the dissolver solution, and sparge lines are less likely to become plugged.⁽²²⁾

Figure 8 shows that thorium nitrate will not precipitate from this solution at 25 °C; thus, there is no danger of thorium nitrate precipitating in storage tanks.

The addition of 0.2 liters of nitric acid per mole of thoria is only one of the many possible variations in operating procedure. However, an application of the basic data will help determine the optimum operating procedure in individual situations.

* Although addition of 16M nitric acid is much more amenable toward thoria dissolution, 12.7M nitric acid can be manufactured on site.

FIGURE 8. Thorium Nitrate Solubility in Nitric Acid and Aluminum Nitrate at 25 °C

FIGURE 9. Thorium Nitrate Solubility in Nitric Acid and Aluminum Nitrate at 50 °C

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APPENDIX

THORIUM OXIDE DISSOLUTION DATA

TABLE A-1. Observed and Predicted Thorium Oxide Dissolution Rates at the Experimental Points in a Second Order Rotatable Design

Experimental Points, Moles/liter				Observed ThO ₂ Dissolution Rates, mg/cm ² /min				Average of Observed Rates, mg/cm ² /min	Predicted Rate, mg/cm ² /min
HNO ₃	Th(NO ₃) ₄	Al(NO ₃) ₃	HF						
8.00	0.000	0.350	0.04	2.989,	3.178			3.084	3.476
8.00	0.500	0.000	0.04	4.213,	3.345			3.779	3.397
8.00	0.500	0.350	0.01	0.1815,	0.2628,	0.3815,	0.4020	0.307	0.316
8.00	0.500	0.350	0.07	3.629,	3.387			3.508	3.717
8.00	0.500	0.700	0.04	1.113,	1.544,	1.436,	1.268	1.340	1.279
8.00	1.000	0.350	0.04	1.700,	1.829			1.765	1.536
10.00	0.000	0.000	0.04	6.475,	7.987,	6.657,	7.704,	7.109	7.736
10.00	0.000	0.350	0.01	0.6928,	0.8617			0.777	0.780
10.00	0.000	0.350	0.07	5.009,	6.650,	7.652,	5.592	6.226	6.158
10.00	0.000	0.700	0.04	2.659,	2.902			2.781	2.299
10.00	0.500	0.000	0.01	2.225,	2.336			2.281	1.550
10.00	0.500	0.000	0.07	8.283,	7.933			8.108	6.085
10.00	0.500	0.700	0.01	0.2012,	0.1470,	0.1936,	0.1575	0.175	0.174
10.00	0.500	0.700	0.07	3.932,	4.092,	3.597,	3.173	3.561	3.637
				4.046,	2.527				
10.00	1.000	0.000	0.04	4.478,	5.859,	3.771,	4.504	4.653	5.549
10.00	1.000	0.350	0.01	0.3538,	0.4081			0.381	0.424
10.00	1.000	0.350	0.07	3.627,	4.373			4.000	4.416
10.00	1.000	0.700	0.04	1.157,	1.439			1.298	1.250
12.00	0.000	0.350	0.04	4.933,	5.278,	5.550		5.254	4.761
12.00	0.500	0.000	0.04	7.865,	7.920			7.893	9.570
12.00	0.500	0.350	0.01	0.7589,	0.6429			0.701	0.794
12.00	0.500	0.350	0.07	4.893,	5.848			5.371	5.542
12.00	0.500	0.700	0.04	1.245,	1.522			1.384	1.702
12.00	1.000	0.350	0.04	6.567,	6.055			6.311	4.204
10.00	0.500	0.350	0.04	3.746,	3.118m	2.831,	2.662	3.125	2.108
				3.492,	2.838	3.003,	3.906		
				3.376,	2.854,	3.298,	2.796		
				2.936,	2.899				

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TABLE A-II. Predicted Thorium Oxide Dissolution Rates at the 81 Experimental Points in a Full 3⁴ Factorial Design

Experimental Points, Moles/liter				Predicted ThO ₂ Dissolution Rate, mg/cm ² /min
HNO ₃	Th(NO ₃) ₄	Al(NO ₃) ₃	HF	
8.00	0.000	0.000	0.010	1.261
8.00	0.000	0.000	0.040	5.200
8.00	0.000	0.000	0.070	5.599
8.00	0.000	0.350	0.010	0.555
8.00	0.000	0.350	0.040	3.476
8.00	0.000	0.350	0.070	5.689
8.00	0.000	0.700	0.010	0.236
8.00	0.000	0.700	0.040	2.248
8.00	0.000	0.700	0.070	5.592
8.00	0.500	0.000	0.010	0.769
8.00	0.500	0.000	0.040	3.397
8.00	0.500	0.000	0.070	3.920
8.00	0.500	0.350	0.010	0.316
8.00	0.500	0.350	0.040	2.119
8.00	0.500	0.350	0.070	3.717
8.00	0.500	0.700	0.010	0.125
8.00	0.500	0.700	0.040	1.279
8.00	0.500	0.700	0.070	3.409
8.00	1.000	0.000	0.010	0.557
8.00	1.000	0.000	0.040	2.638
8.00	1.000	0.000	0.070	3.262
8.00	1.000	0.350	0.010	0.213
8.00	1.000	0.350	0.040	1.536
8.00	1.000	0.350	0.070	2.886
8.00	1.000	0.700	0.010	0.079
8.00	1.000	0.700	0.040	0.865
8.00	1.000	0.700	0.070	2.471
10.00	0.000	0.000	0.010	2.138
10.00	0.000	0.000	0.040	7.736
10.00	0.000	0.000	0.070	7.311
10.00	0.000	0.350	0.010	0.780
10.00	0.000	0.350	0.040	4.287
10.00	0.000	0.350	0.070	6.158
10.00	0.000	0.700	0.010	0.275
10.00	0.000	0.700	0.040	2.299
10.00	0.000	0.700	0.070	5.018
10.00	0.500	0.000	0.010	1.550
10.00	0.500	0.000	0.040	6.009
10.00	0.500	0.000	0.070	6.085
10.00	0.500	0.350	0.010	0.527
10.00	0.500	0.350	0.040	3.108
10.00	0.500	0.350	0.070	4.783

TABLE A-II. (contd)

Experimental Points, Moles/liter				Predicted ThO ₂ Dissolution Rate, mg/cm ² /min
HNO ₃	Th(NO ₃) ₄	Al(NO ₃) ₃	HF	
10.00	0.500	0.700	0.010	0.174
10.00	0.500	0.700	0.040	1.555
10.00	0.500	0.700	0.070	3.637
10.00	1.000	0.000	0.010	1.336
10.00	1.000	0.000	0.040	5.549
10.00	1.000	0.000	0.070	6.020
10.00	1.000	0.350	0.010	0.424
10.00	1.000	0.350	0.04	2.678
10.00	1.000	0.350	0.070	4.416
10.00	1.000	0.700	0.010	0.130
10.00	1.000	0.700	0.040	1.250
10.00	1.000	0.700	0.070	3.134
12.00	0.000	0.000	0.010	3.264
12.00	0.000	0.000	0.040	10.363
12.00	0.000	0.000	0.070	8.594
12.00	0.000	0.350	0.010	0.987
12.00	0.000	0.350	0.040	4.761
12.00	0.000	0.350	0.070	6.001
12.00	0.000	0.700	0.010	0.288
12.00	0.000	0.700	0.040	2.116
12.00	0.000	0.700	0.070	4.055
12.00	0.500	0.000	0.010	2.813
12.00	0.500	0.000	0.040	9.570
12.00	0.500	0.000	0.070	8.504
12.00	0.500	0.350	0.010	0.794
12.00	0.500	0.350	0.040	4.103
12.00	0.500	0.350	0.070	5.542
12.00	0.500	0.700	0.010	0.217
12.00	0.500	0.700	0.040	1.702
12.00	0.500	0.700	0.070	3.494
12.00	1.000	0.000	0.010	2.882
12.00	1.000	0.000	0.040	10.507
12.00	1.000	0.000	0.070	10.004
12.00	1.000	0.350	0.010	0.759
12.00	1.000	0.350	0.040	4.204
12.00	1.000	0.350	0.070	6.084
12.00	1.000	0.700	0.010	0.193
12.00	1.000	0.700	0.040	1.627
12.00	1.000	0.700	0.070	3.580

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