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CHEMISTRY - SEPARATION
PROCESSES FOR PLUTONIUM
AND URANIUM

COPY NO. 98

NITRIC ACID DISSOLUTION OF URANIUM-ALUMINUM ALLOY

BY

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TECHNICAL SECTION
ENGINEERING DEPARTMENT

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Chemistry - Separation
Processes for Plutonium
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By

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August 12, 1952

HANFORD WORKS
RICHLAND, WASHINGTON

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ABSTRACT

Mercury-catalyzed HNO_3 dissolution of uranium-aluminum alloys was studied in an attempt to find the optimum conditions to effect dissolution in minimum time. It was found that, for any given concentration of $\text{Al}(\text{NO}_3)_3$ in the solution, there exists a corresponding concentration of HNO_3 for which the dissolving rate is a maximum. Curves are presented showing the variation of dissolving rate with HNO_3 concentration at given $\text{Al}(\text{NO}_3)_3$ concentrations. Calculations based on performing the dissolving in a manner such that maximum dissolving rate conditions always exist indicate a minimum dissolving time of about seven hours for U-Al cylinders 1 3/8 inches in diameter and eight inches in length when the final solution so produced is 1.5 M in $\text{Al}(\text{NO}_3)_3$.

Experiments with a continuous column-type dissolver showed that, while chemically feasible, practical application of the process would require solution of many problems such as excessive foaming, apparent preferential dissolution of aluminum, continuous feed of alloy elements to the column and plugging at the bottom of the column by small pieces of undissolved metal.

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NITRIC ACID DISSOLUTION OF URANIUM-ALUMINUM ALLOY

I. INTRODUCTION

Several pile applications now involve the use of enriched uranium in the form of uranium-aluminum (U-Al) alloy fuel elements. To recover the uranium from these fuel elements by present separation processes it is necessary that the alloy be dissolved. Since the uranium in these alloys is enriched in U^{235} , criticality considerations require that the dissolution be performed on relatively small batches. Also, the practice, common in dissolving natural uranium fuels, of leaving a heel of undissolved metal in each batch in order to decrease dissolving time, is undesirable because of the possibility of preferential dissolving of the aluminum and consequent accumulation of U^{235} in the heel. It is apparent that rapid dissolution of the fuel elements is desirable to minimize the number of dissolvers required to attain a given production rate.

Dissolution of U-Al alloys in nitric acid with Hg(II) as a catalyst has been shown to produce feeds satisfactory for solvent extraction recovery of the uranium⁽¹⁾. However, dissolving times are relatively long. The studies reported here were made in an effort to establish the optimum conditions for Hg(II)-catalyzed nitric acid dissolution of U-Al alloy fuel elements to obtain a minimum dissolving time. Some effort was expended in a study of a continuous dissolver of a column type with fuel elements and nitric acid entering at the top and uranium-aluminum nitrate solution leaving the bottom.

II. SUMMARY

All of these studies were made with U-Al alloy containing 92.5 per cent aluminum (generally 2S) and 7.5 per cent natural uranium. The alloy had been prepared in the form of cylinders 1 3/8 inches in diameter. Results obtained confirmed expectations that the alloy would behave, during dissolution, much like aluminum alone in that the dissolving rate was markedly

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increased by increasing the temperature and by the presence of Hg(II) as a catalyst. It was found that there exists, for any given concentration of aluminum nitrate in the solution, a corresponding concentration of nitric acid for which the dissolving rate is a maximum. When the concentration of Hg(II) was 0.002 M, the optimum nitric acid concentrations corresponding to aluminum nitrate concentrations of 0.0, 0.5, 1.0, and 1.5 M were 4.3, 3.3, 2.3, and 1.3 M respectively. Calculations based on performing the dissolving in a manner such that maximum dissolving rate conditions always existed indicated a minimum dissolving time of about seven hours for a U-Al alloy fuel element 1 3/8 inches in diameter and eight inches long when the final solution so produced was 1.5 M in $\text{Al}(\text{NO}_3)_3$.

Laboratory scale experiments on a column-type continuous dissolver for Hg(II)-catalyzed nitric acid dissolution of U-Al alloy fuel elements (7.5% U-92.5% Al; 1 3/8 inches diameter by 8 inches long) indicate that a column five inches in diameter containing six feet of continuous liquid phase would be required to dissolve alloy equivalent to 3.5 kilograms of uranium per day. Practical application of the process would require solution of many problems such as excess foaming, apparent preferential dissolution of aluminum, continuous feed of fuel elements to the column, and plugging at the bottom of the column by small pieces of undissolved metal.

III. EXPERIMENTAL⁽²⁾⁽³⁾

U-Al alloy wafers cut from fuel elements 1 3/8 inches in diameter containing 92.5 per cent aluminum and 7.5 per cent uranium were used in these studies. Dissolving rate measurements were made by immersing the wafers for short time intervals in solutions, usually at the boiling point, containing nitric acid and aluminum nitrate. From weight change and dimensional measurements, dissolving rates were calculated in terms of weight per unit area per unit time. No corrections were made for changes in solution composition due to evaporation and to dissolution of the alloy during the immersion period, or for changes in surface area of

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the wafers due to pitting during dissolution. When more than one rate determination was made on a particular wafer, it was water washed and acetone dried between measurements. Aluminum nitrate determinations on the solutions involved were made by the acidometric method.⁽⁴⁾

A. Rate of U-Al Dissolution as a Function of Temperature

To determine the effect of temperature on the dissolving rate of U-Al alloy in nitric acid, with and without Hg(II) catalyst, wafers of the alloy (1 3/8 inches in diameter and 1/4 inch thick) were immersed in the dissolvents at various temperatures for short periods of time. Weight loss and dimension measurements permitted dissolution rate calculation. The Hg(II)-catalyzed dissolvent contained 4.5 M HNO_3 and 5×10^{-4} M Hg(II) while the non-catalyzed dissolvent was 6.5 M HNO_3 . When Hg(II) was present at temperatures above 50°C, the heat of dissolution raised the solution temperature making exact measurement impossible. Foaming of the solutions was pronounced at the higher temperatures. Results of these experiments are tabulated in Table I and shown graphically in Figure 1. As was expected, dissolution rate increases with increased temperature both with and without the Hg(II) catalyst. The presence of the catalyst increases the rate of dissolution markedly.

B. Effect of HNO_3 and $\text{Al}(\text{NO}_3)_3$ Concentration on the Rate of Hg(II)-Catalyzed Dissolution of U-Al Alloy

A series of experiments was performed to determine the effect of HNO_3 concentration on the rate of Hg(II)-catalyzed nitric acid dissolution of U-Al alloy at different $\text{Al}(\text{NO}_3)_3$ concentrations. Alloy wafers (1/2 inch thick and 1 3/8 inches in diameter) were immersed for short intervals in boiling solutions containing 0.002 M Hg(II) and varying HNO_3 and $\text{Al}(\text{NO}_3)_3$ concentrations. Weight change and dimensional measurements permitted calculation of dissolution rate as mentioned previously. Earlier observations of the dissolution of U-Al alloy in nitric acid containing Hg(II) indicated that ionic mercury is reduced to

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FIGURE 1

DISSOLUTION OF U-AL ALLOY
AS A FUNCTION OF TEMPERATURE

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metallic mercury and deposits on the surface of the undissolved metal. It had also been observed that dissolution rates increase as the mercury deposit forms. In an attempt to avoid the varying dissolving rate which occurs while the deposit is being formed, all of the wafers used in these studies were pre-coated with mercury by immersion for a short time in 6.0 M nitric acid containing 0.002 M $\text{Hg}(\text{NO}_3)_2$.

TABLE I
EFFECT OF TEMPERATURE
ON NITRIC ACID DISSOLUTION OF U-Al ALLOY

<u>Temperature, °C.</u>	<u>Dissolution Rate (mg/hr/cm²)</u>	
	<u>6.5 M HNO_3</u>	<u>4.5 M HNO_3, 5 x 10⁻⁴ M $\text{Hg}(\text{II})$</u>
25-29	0.21	--
45-57	--	47.3
53-67	2.39	59.3
70-77	--	91.1
80-84	--	124.0
86-90	--	204.8
97-100	21.80	--
104	--	344

When a particular wafer was used for more than one rate determination, no additional pre-coat was made between measurements. Because data obtained in these experiments tended to spread badly, in general, several rate determinations were made at any given HNO_3 and $\text{Al}(\text{NO}_3)_3$ concentrations. Results of these experiments are summarized in Table II wherein the rates given are the average for the several determinations made at each HNO_3 and $\text{Al}(\text{NO}_3)_3$ concentration. Spreading of the data may have been due to change in area of the wafers during immersion due to surface pitting, non-uniformity of the mercury pre-coat, gas formation on the U-Al

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TABLE IIRATE OF U-AL ALLOY DISSOLUTION AS A FUNCTION
OF $\text{Al}(\text{NO}_3)_3$ AND HNO_3 CONCENTRATION 2×10^{-3} M $\text{Hg}(\text{NO}_3)_2$ present-in all solutions.

All solutions at boiling point.

<u>ANN, M</u>	<u>HNO_3, M</u>	<u>Dissolving Rate*</u> <u>$\text{mg}/\text{cm}^2/\text{hr}$</u>
0.0	0.0	19
0.0	2.0	1383
0.0	3.0	1882
0.0	3.5	1872
0.0	4.0	1877
0.0	4.5	1990
0.0	5.0	1803
0.0	5.5	1296
0.0	6.0	1283
0.0	7.0	394
0.0	8.0	256
0.0	9.0	310
0.5	2.0	803
0.5	2.5	813
0.5	3.0	906
0.5	3.25	1139
0.5	3.5	1036
0.5	3.75	997
0.5	4.0	874
0.5	5.0	860
1.0	0.5	343
1.0	1.0	486
1.0	1.5	547
1.0	1.75	681
1.0	2.0	532
1.0	2.25	702
1.0	2.5	460
1.0	3.0	342
1.0	4.0	189
1.5	0.0	78
1.5	0.25	202
1.5	0.5	304
1.5	0.75	352
1.5	1.0	491
1.5	1.25	512
1.5	1.5	565
1.5	2.0	256
1.5	2.5	117
1.5	3.0	119
1.5	5.0	33

* Figures given are the average for several determinations

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surface, and change in solution volume during dissolving. These same data are presented graphically in Figures 2 to 5.

It is apparent from Figures 2 to 5 that there appears to be an optimum HNO_3 concentration, for any given $\text{Al}(\text{NO}_3)_3$ concentration, which will produce the most rapid dissolution rate, these HNO_3 concentrations being 4.3, 3.3, 2.3, and 1.3 for $\text{Al}(\text{NO}_3)_3$ concentrations of 0.0, 0.5, 1.0, and 1.5, respectively. These curves are all shown on a single graph in Figure 6 with a line drawn through the points of maximum dissolution rate. Presumably one would achieve maximum dissolution rate for a batch of U-Al alloy fuel elements if the HNO_3 concentration was made to vary as indicated by that curve as the $\text{Al}(\text{NO}_3)_3$ concentration in the solution increased from 0 to 1.5 M.

It is of interest to note that pre-coating the U-Al alloy with mercury as indicated previously leads to an initial dissolving rate in 9-13 M HNO_3 at 0.0 M $\text{Al}(\text{NO}_3)_3$ substantially greater than when the alloy is not pre-coated. As dissolution proceeds, the rate gradually decreases suggesting that, in the presence of high HNO_3 concentrations, the mercury coating is dissolved allowing the uncoated U-Al surface to exhibit the well-known passivity of aluminum to nitric acid. The lower dissolving rates at low HNO_3 and high $\text{Al}(\text{NO}_3)_3$ concentrations is probably related to the approach to saturation with respect to $\text{Al}(\text{NO}_3)_3$.

Figure 7 shows the manner in which the optimum concentration of HNO_3 (to give maximum dissolving rate) varies as $\text{Al}(\text{NO}_3)_3$ concentration varies from 0 to 1.5 M. Figure 8 shows the variation in dissolving rate as $\text{Al}(\text{NO}_3)_3$ concentration increases assuming that the HNO_3 concentration is maintained at the proper concentration to give maximum dissolving rate. Data were obtained from Figure 8 to calculate the minimum time required to dissolve each successive one millimeter layer from a U-Al alloy fuel element 1 3/8 inches in diameter assuming the final concentration of $\text{Al}(\text{NO}_3)_3$ to be 1.5 M. Summation of these times, as shown in

RATE OF URANIUM ALUMINUM ALLOY DISSOLUTION
AS A FUNCTION OF NITRIC ACID CONCENTRATIONS

FIGURE 2

FIGURE 3

FIGURE 4

FIGURE 5

Nitric Acid Concentration, Molarity

FIGURE 6

RATE OF URANIUM-ALUMINUM ALLOY DISSOLUTION
AS A FUNCTION OF NITRIC ACID ALUMINUM NITRATE CONCENTRATION

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FIGURE 7

VARIATION OF HNO_3 CONCENTRATION WITH $\text{Al}(\text{NO}_3)_3$ CONCENTRATION
TO GIVE MAXIMUM DISSOLVING RATE

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FIGURE 8
VARIATION OF MAXIMUM DISSOLVING RATE WITH
CHANGING $\text{Al}(\text{NO}_3)_3$ CONCENTRATION

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Table III, indicates a total dissolving time of about seven hours. Residual HNO_3 concentration would be 1.25 M.

Examination of the data in Table III shows, also, that about 95 per cent of the slug weight would dissolve in five hours if the maximum rate curve was followed. Dissolving times of this order could be achieved if a five per cent heel could be left for the succeeding batch.

C. Continuous Dissolution of U-Al Alloy

As an alternative to batch dissolution of uranium-aluminum alloy some consideration was given to a continuous dissolver of the column type. The laboratory column used was two inches in diameter and 18 inches long and was provided with a heating jacket and connections to permit introduction of nitric acid at the top and withdrawal of solution from the bottom. The column was filled with 32 U-Al wafers (7.5 % U 92.5 % Al 1 3/8 inches in diameter by 1/2 inch thick). Solution flow rate through the column was nine liters per hour. In practice, four liters of solution consisting initially of 6 M HNO_3 containing 0.002 M $\text{Hg}(\text{NO}_3)_2$ was passed through the column and the effluent was recycled through the column in successive passes until the effluent was approximately 1.5 M in $\text{Al}(\text{NO}_3)_3$. It was found impossible to maintain an 18 inch depth of liquid in the column since foaming of the solution forced it out the top of the column. The first four passes were made with only six inches of liquid in the column. As the concentration of $\text{Al}(\text{NO}_3)_3$ in the solution increased and the reaction rate decreased it was possible to maintain a greater liquid depth. The last three passes were made with a 12 inch liquid depth. Table IV shows the $\text{Al}(\text{NO}_3)_3$ concentration in the effluent after each pass.

Estimating the two passes at 50°C. to be equivalent to one pass at 80°C. one may conclude from these data that about 4.5 feet of liquid phase would be required to produce an effluent 1.4 M in $\text{Al}(\text{NO}_3)_3$. Since the area exposed to acid attack when wafers are employed as in these experiments is somewhat greater than if full length fuel elements (8 inches) were being

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TABLE III

DISSOLUTION OF ONE U-A1 SLUG FOLLOWING MAXIMUM RATE CURVE

Final ANN Concentration 1.5 M

Penetration mm	Weight Loss, grams	Σ Weight %	Σ ANN, M	Average Area cm ²	Approximate Dissolving Rate mg/hr/cm ²	Time, Min.
1	67.8	11.7	.18	251	1800	9.0
2	63.2	22.5	.34	224	1500	11.3
3	58.6	32.6	.49	208	1250	13.5
4	54.0	41.9	.63	192	1063	15.9
5	49.6	50.4	.76	176	937	18.0
6	45.2	58.2	.87	161	830	20.3
7	41.0	65.2	.98	146	760	22.2
8	36.9	71.6	1.07	131	700	24.1
9	32.8	77.2	1.16	117	660	25.5
10	28.9	82.2	1.23	103	630	26.7
11	25.1	86.5	1.30	89.6	605	27.7
12	21.4	90.2	1.35	76.4	588	28.6
13	17.8	93.3	1.40	63.6	575	29.2
14	14.4	95.7	1.44	51.3	565	29.8
15	11.0	97.6	1.47	39.2	558	30.2
16	7.7	99.0	1.49	27.4	554	30.4
17	4.6	99.7	1.50	16.3	552	30.7
18	1.5	100.0	1.50	5.4	550	30.3
7 hours						423.4

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dissolved one may estimate very roughly that a liquid phase depth of six feet would be required if full length elements were being dissolved.

There was visual evidence suggesting preferential dissolution of aluminum during these experiments. A finely divided dark solid remained undissolved while the solution remained in contact with undissolved alloy but subsequently dissolved when the solution was removed from contact with the alloy. Chemical composition of the dark solid was not determined.

Many other problems such as suppression of foaming, continuous loading of fuel elements to the column, and plugging at the bottom of the column by small pieces of undissolved alloy would need to be solved before continuous dissolution such as tried here could be practical.

TABLE IV

CONTINUOUS DISSOLUTION OF U-Al ALLOY

<u>Pass</u>	<u>Temp. °C.</u>	<u>Liquid Phase Depth, inches</u>	<u>Concen. Al(NO₃)₃ in Effluent, M</u>
1	<u>ca.</u> 50	6	0.07
2	<u>ca.</u> 50	6	0.18
3	<u>ca.</u> 50	6	0.42
4	80	6	0.66
5	80	12	0.84
6	80	12	1.09
7	80	12	1.38

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