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FOR PLUTONIUM AND URANIUM

THE DISSOLUTION OF ZIRCONIUM-CLAD
URANIUM TARGET ELEMENTS

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ABSTRACT

Zirconium-clad uranium elements can be successfully dissolved in nitric acid and fluoride (from HF or HBF_4) to form feed solutions amenable to Purex processing. The clad elements in which the volume ratio of uranium to zirconium is equal to 3 can be easily dissolved to a concentration of 1.35 M $\text{UO}_2(\text{NO}_3)_2$ and 3.5 M HNO_3 . This solution also contains about 3 to 3.5 times as much fluoride as zirconium on a molar basis, but the extractability of uranium with 30 per cent tributyl phosphate in an inert carrier is not appreciably affected, whereas the zirconium is essentially inextractable. At certain concentrations of nitric acid and fluoride in the dissolving solution, a white zirconium precipitate is formed which is difficult to dissolve, but this can be avoided by using proper nitric acid concentrations and fluoride-to-zirconium ratio in the final solution. }-p

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THE DISSOLUTION OF ZIRCONIUM-CLAD URANIUM TARGET ELEMENTS

INTRODUCTION

Zirconium metal exhibits high corrosion resistance at high temperatures toward many coolants which, along with its small neutron capture cross section, makes metallic zirconium an excellent reactor fuel cladding material.

The problem considered herein is concerned with the dissolution of neutron irradiated zirconium-clad uranium plate-type elements to permit chemical separations of plutonium, uranium and fission products by aqueous processes such as the Purex process.

The dissolution of only one type of element has been studied. This element consists of a 60 mil flat uranium plate clad on both sides with zirconium 10 mils thick. The quantitative conclusions of this report apply only to systems having this particular zirconium-uranium ratio; however, the same general results would undoubtedly be obtained with any type element or, for that matter, zirconium-uranium alloy. The results of experiments contained in this report can be used as a guide to predict qualitatively the behavior of any metallic zirconium-uranium system upon treatment with nitric-hydrofluoric acid mixture.

Work has been done at ANL (1, 2) on the dissolution of Mark I SIR assemblies. These assemblies are of the order of 99 per cent zirconium and the dissolving solution is concentrated hydrofluoric acid (~27N). In the work reported here, uranium is the principal material present and the dissolving solutions are hydrofluoric-nitric acid mixtures.

There are three general methods which could be developed for preparing zirconium-clad uranium plate for aqueous processing:

(1) Zirconium is dissolved selectively; the zirconium solution is discharged to waste and the uranium is dissolved in the normal manner. Pure hydrofluoric acid will remove a zirconium plate with small uranium losses.

(2) The clad plates are opened mechanically to expose the uranium and the uranium is selectively dissolved. Pure nitric acid will dissolve uranium but not zirconium.

(3) The zirconium and uranium are dissolved together in an integral dissolution. Hydrofluoric-nitric acid mixtures will effect this dissolution.

The last procedure was thought to be the simplest and most direct, and is the method developed in this report.

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The mechanism of zirconium corrosion resistance is generally believed to involve a zirconium oxide coating which is tightly bound to the metallic surface and is slow to react with most acids. That the corrosion resistance is due to rate phenomena rather than unfavorable equilibria is shown by the fact that the driving force for the reaction is quite large. Values of standard oxidation potentials and standard free energies of reaction are given below for several reactions involving zirconium.

$$\Delta F^0 = -141 \text{ k cal}$$

$$E^0 = 2.49 \text{ v}$$

$$\Delta F^0 = -609 \text{ k cal}$$

Nitric oxide is chosen as the principal reduction product in accordance with experimental evidence.

Hence it can be seen that zirconium metal is quite electropositive. These are standard potentials and free energies which imply unit activities; however, for the purposes of a qualitative discussion, neglecting activity coefficients will not alter the conclusions.

The fact that pure zirconium metal does not appreciably dissolve in boiling 8 M HNO_3 (less than 0.1 per cent weight loss in 5 hours) must be attributed to a rate effect. As mentioned previously, this rate effect is generally associated with an oxide coating which is slow to dissolve in acid. It is known that the rate of solution of ignited zirconium dioxide in acid is essentially zero, and even zirconium hydroxide which has been boiled in water is extremely difficult to dissolve. However, the problem is undoubtedly further complicated by the rapid reformation of this surface film; mechanical or chemical removal of an appreciable amount of the surface of metallic zirconium followed by immersion in acid still does not result in dissolution of the remaining metal.

It is necessary, then, to remove and continuously expose fresh metal surface to the action of the acid or oxidizing agent. This immediately suggests the use of agents which form very stable zirconium complexes. The fluoride, oxalate, and sulfate complexes of zirconium are known to be stable in solution and hydrofluoric acid is one of the few agents which will dissolve ignited zirconium dioxide. Further, it has been known for some time that metallic zirconium is dissolved rapidly by dilute (1-2M) hydrofluoric acid. This is consistent with the idea that the zirconium oxide film is being rapidly removed as a stable fluoride complex.

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Although the fluoride complexes are quite stable, as can be seen from the following equilibrium constants, the increase in the driving force is relatively small.

From these values and the values of the standard potentials and free energies previously given, new values may be calculated for the following reactions, for the case of the two-fluoride complex.

$$E^0 = 1.67 \text{ v}$$

$$\Delta F^0 = -155 \text{ k cal}$$

$$E^0 = 2.64 \text{ v}$$

$$\Delta F^0 = -732 \text{ k cal}$$

The first reaction takes place in pure hydrofluoric acid whereas the second takes place in nitric-hydrofluoric acid mixtures where the nitric acid is in considerable excess over the hydrofluoric acid. It may be presumed that as the hydrofluoric acid concentration is raised, the hydrogen evolution reaction will become more important. The changes in potentials are relatively small and again one would conclude that rates are more important than chemical potentials.

Preliminary survey work showed that the only effective reagent which would appreciably affect the rate of dissolution of zirconium in nitric acid was hydrofluoric acid. Dilute solutions of sulfuric acid, oxalic acid or verteric in 8 M HNO_3 did not effect solution of zirconium in nitric acid whereas the dissolution in nitric-hydrofluoric acid mixtures was quite rapid.

It is interesting to note that the mechanisms of dissolution of metallic thorium and metallic zirconium in nitric-hydrofluoric acid mixtures are quite different. Thorium metal, like zirconium metal, does not dissolve at an appreciable rate in nitric acid alone but does dissolve rapidly in nitric-hydrofluoric acid mixtures. However, zirconium metal will dissolve until the ratio of total zirconium concentration in solution to the total hydrofluoric acid concentration is close to unity at which point no further zirconium will dissolve. Thorium metal, on the other hand, will continue to dissolve even at very large (20 to 1) thorium to fluoride ratios, but does not dissolve at an appreciable rate in pure hydrofluoric acid.

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In order that we may further compare zirconium and thorium behavior, equilibrium conditions will be calculated for the two metals when they are dissolved in a particular nitric-hydrofluoric acid solution. The conditions listed in Table I will be assumed:

TABLE I

SOME PROPERTIES OF THORIUM AND ZIRCONIUM IN THE NITRIC ACID-HYDROFLUORIC ACID SYSTEM		
total metal in solution, 0.5 <u>M</u> total nitric acid concentration, 2 <u>M</u> total fluoride concentration, 0.05 <u>M</u> dissolution reaction: $3M + 4 NO_3^- + 16H^+ = 3M^{+4} + 4NO + 8H_2O$ complexing reactions: $M^{+4} + HF = MF^{+3} + H^+, \quad K_1$ $MF^{+3} + HF = MF_2^{+2} + H^+, \quad K_2$		
	Zirconium	Thorium
E^0, v	2.53	2.90
$\Delta F^0, k cal$	-700.	-800.
K_1	6.3×10^5	$4.5 \times 10^4 (4)$
K_2	2.0×10^4	$6.5 \times 10^2 (4)$
Free HF, (M)	4×10^{-7}	5×10^{-6}
$M^{+4}, (M)$	0.45	0.45
$MF^{+3}, (M)$	0.05	0.05
$MF_2^{+2}, (M)$	2×10^{-4}	8×10^{-5}

It can be seen that both the driving force and the free hydrofluoric acid concentration are greater for thorium than for zirconium. However, since potentials for both are quite large and the free hydrofluoric acid is quite small, it would be surprising if the explanation for the difference in the action of hydrofluoric acid on these two metals lies in the differences in potentials and hydrofluoric acid concentrations. The explanation undoubtedly lies in a difference in mechanism of the rate determining steps.

The conclusion should be drawn, then, that whereas a practical zirconium dissolution system is available, the explanation of which is qualitatively consistent with the removal of an oxide layer potential barrier by continuous fluoride complexing, the details of the mechanism of the dissolution are not understood.

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EXPERIMENTAL WORK AND DISCUSSION

Metal Dissolution

An aqueous solution suitable as feed to the Purex IA column is the goal of the target element dissolution. In the experimental work zirconium and uranium metals were contacted with dissolving solutions containing nitric acid and fluoride ion in various concentrations and combinations. It was soon found that many of these dissolver solutions, although able to dissolve the metal satisfactorily, resulted in the precipitation of a large amount of a white solid. This occurred whether zirconium was dissolved alone or along with uranium. A large number of dissolutions were carried out to determine the concentrations of the nitric acid and fluoride which would dissolve the metals completely without forming this precipitate.

For the sake of simplicity zirconium metal alone was dissolved in the first series of dissolutions. One gram samples of 5 mil thick zirconium sheet were contacted with a number of dissolver solutions of various concentrations of nitric and fluoboric acids (or HF). The dissolutions were carried out at boiling temperature in a round bottom glass flask with reflux condenser. In each case, the volume of the dissolving solution was so adjusted as to result in a zirconium concentration of 0.41 M. This is the zirconium concentration which would result if a fuel plate element having a uranium-to-zirconium cladding volume ratio of three were to be dissolved to give a uranium concentration of 1.35 M. The results of the individual dissolutions were plotted in the form of a stability curve where the region of concentrations resulting in complete dissolution with clear solutions is distinguished from the region of complete dissolution with the formation of the white precipitate. The coordinates of this "dissolution-stability curve" are the total fluoride to zirconium mole ratio, $\frac{(F)}{(Zr)}$ and the final acidity, $(H^+)_f$ where this $(H^+)_f$ is a calculated value based on the assumed reaction:

The concentrated nitric and fluoboric acids were standardized before use and measured to ± 0.02 ml. In the dissolutions where fluoboric acid (HBF_4) was used, the H^+ contributed by the HBF_4 is also taken into account. The data are given in Table II and in the "Dissolution-Stability" curve of Fig. 1. The "Dissolution-Stability" curve is valid of course, regardless of the assumed reaction.

In the second series of dissolutions uranium and zirconium were dissolved together. The same general relationships were found to hold as in the zirconium dissolutions and the data are expressed in the same type of "Dissolution-Stability" curve. The white precipitate is formed at certain concentrations of nitric acid and fluoride. The final (H^+) for these data has been corrected for the H^+ used by the uranium, for which the dissolution reaction was assumed to be $U + 4 HNO_3 = UO_2(NO_3)_2 + NO + 2H_2O$. It was

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○ □ △ SOLID NOT FORMED
● ■ ▲ SOLID FORMED

FIG. 1 - DISSOLUTION - STABILITY CURVE FOR ZIRCONIUM - CLAD URANIUM TARGET ELEMENTS USING NITRIC ACID AND FLUORIDE.

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found that the position of the "Dissolution-Stability" curve was affected by the final concentration of the dissolved zirconium and uranium. Two series of Zr-U dissolutions were carried out, one where the final concentrations were $\text{Zr} = 0.41 \text{ M}$ and $\text{U} = 1.35 \text{ M}$, and one where the final concentrations were $\text{Zr} = 0.33 \text{ M}$ and $\text{U} = 1.10 \text{ M}$. These data are given in Table III and plotted in Fig. 1. As can be seen from the figure, the two sets of concentrations result in stability curves of the same shape with the lower concentrations resulting in greater dissolution stability. It was also found that if solid UNH was substituted for uranium metal in a dissolution making the suitable correction for the nitric acid usage, the resulting dissolution was the same with respect to stability as if uranium metal had been used. (See Table III). This is in line with the relatively weak fluoride complexing of uranyl ion.

A number of actual zirconium-clad uranium fuel elements or "sandwiches" were also dissolved. See Experiments 57, 58, 59, 60, and 65 in Table III for these data. The solutions were found to be unstable with respect to the white precipitate formation when the final uranium concentration was 1.35 M . The final zirconium concentration for this uranium concentration was 0.73 M . The solubility of the zirconium-fluoride compound is less than 0.73 M under these conditions.

Purex-Type Distributions

Three of the typical Purex IA feeds prepared by nitric acid and fluoboric acid dissolutions were contacted with an equal volume of 30 per cent TBP- CCl_4 solution to see how the several components in the aqueous solution would distribute. Although, as yet, there is no entirely satisfactory analytical method for zirconium, fluoride, or nitric acid in these solutions, the results, as given, are believed to be of value, especially in the case of the zirconium concentration in the organic phase.

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TABLE II

THE DISSOLUTION OF ZIRCONIUM METAL WITH NITRIC AND FLUOBORIC ACIDS UNDER BOILING REFLUX CONDITIONS								
No.	Zr grams	Conc HNO ₃ (ml)	Conc HBF ₄ (ml)	Total Volume, (ml)	(F)/(Zr)	Calc Final H ⁺ (M)	Time to Dissolve Completely	Formation of Zr Solid
1	1.00	26.7	0.50	27	1.2	~ 10	10 min	No
2	1.00	26.7	0.25	27	0.6	~ 10	0.93 g in 4 hr	No
3	1.00	3.0	0.50	27	1.2	Neutral	Very little dis	Yes
10	1.00	3.1	0.50	27	1.2	Neutral	4 hr	Yes
11	1.00	6.3	0.50	27	1.2	1.6	4 hr	Yes
12	1.00	12.5	0.50	27	1.2	5.8	1 hr	Yes*
13	1.00	18.9	0.50	27	1.2	~ 10	40 min	Yes*
14	1.00	25.2	0.50	27	1.2	~ 11	25 min	No
15	1.00	12.5	0.50	27	1.2	5.8	4 hr	No
16	1.00	12.5	0.50	27	1.2	5.8	6 hr	No
17	1.00	1.2	0.50	27	1.2	~ Neutral	0.36 g in 6 hr	No
18	1.00	15.0	0.20	27	0.5	7.0	0.78 g in 16 hr	No
19	1.00	15.0	1.00	27	2.4	7.4	15 min	No
20	1.00	15.0	2.00	27	4.8	7.6	8 min	No
21	1.00	15.0	4.00	27	9.6	7.8	5 min	No
22	1.00	10.0	0.20	27	0.5	4.1	0.45 g in 6 hr	No
23	1.00	10.0	1.00	27	2.4	4.4	10 min	No
24	1.00	10.0	2.00	27	4.8	4.6	3 min	No
25	1.00	10.0	4.00	27	9.6	5.1	1 min	No
26	1.00	5.0	0.20	27	0.5	1.5	0.40 g in 6 hr	Yes
27	1.00	5.0	1.00	27	2.4	1.5	20 min	Yes*
28	1.00	5.0	2.00	27	4.8	1.7	2 min	No
29	1.00	5.0	4.00	27	9.6	2.2	1 min	No
30	1.00	6.0	0.75	27	1.8	2.0	60 min	Yes
31	1.00	7.7	0.75	27	1.8	3.0	55 min	No
32	1.00	9.4	0.75	27	1.8	4.0	42 min	No
33	1.00	11.0	0.75	27	1.8	5.0	30 min	No
34	1.00	3.4	1.00	27	2.4	0.5	40 min	Yes
35	1.00	4.2	1.00	27	2.4	1.0	25 min	Yes*
36	1.00	14.5	0.50	27	1.2	7.0	2 hr	No
37	1.00	17.8	0.50	27	1.2	9.0	55 min	No
38	1.00	2.5	2.00	27	4.8	0.2	< 1 min	No
39	1.00	3.3	2.00	27	4.8	0.4	< 1 min	No
41	1.00	26.7	none	27	0.0	--	< .01 g in 12 hr	No
55	2.00	6.8	2.00	53	2.4	0.5	---	Yes**
56	2.00	6.8	2.00 (HF)	53	2.4	0.5	---	Yes**

* Slight

** Fluorothene-A carbon beaker used

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TABLE III

THE DISSOLUTION OF ZIRCONIUM & URANIUM METAL WITH NITRIC AND FLUOBORIC ACIDS UNDER BOILING REFLUX CONDITIONS													
No.	Zr g	U g	UNH g	Conc HNO ₃ (ml)	Conc HBF ₄ (ml)	Total Volume	(F)/ (Zr)	Calc Final H ⁺ (M)	Final Zr, (M)	Final U, (M)	Time to Dissolve Completely	Formation of Zr Solid	Remarks
57	3.28	15.62	-	32.3	3.40	48	2.5	2.5	0.73	1.35	1 hr	Yes-Slight	Sandwich
58	3.28	15.62	-	35.3	4.76	48	3.5	3.5	0.73	1.35	Short	Yes-Slight	Sandwich
59	3.28	15.62	-	32.5	6.80	48	5.0	3.5	0.73	1.35	Short	Yes	Sandwich
60	1.00	4.77	-	9.8	1.03	15	2.5	2.5	0.73	1.35	1 hr	Yes	Not Sandwich
42	1.00	8.65	-	12.3	1.45	27	3.5	0.5	0.41	1.35	5 hr	Yes	-
43	1.00	8.65	-	12.0	2.07	27	5.0	0.5	0.41	1.35	5 hr	Yes	-
44	1.00	8.65	-	13.1	1.45	27	3.5	1.0	0.41	1.35	3 hr	Yes	-
45	1.00	8.65	-	12.8	2.07	27	5.0	1.0	0.41	1.35	3 hr	Yes	-
46	1.00	8.65	-	13.9	1.45	27	3.5	1.5	0.41	1.35	1 1/2 hr	Yes	-
47	1.00	8.65	-	13.7	2.07	27	5.0	1.5	0.41	1.35	1 1/2 hr	Yes	-
50	1.00	-	18.1	7.6	1.04	33	2.5	2.4	0.33	1.10	17 min	No	-
51	1.00	-	18.1	6.6	1.45	33	3.5	2.0	0.33	1.10	10 min	No	-
52	1.00	-	18.1	6.3	2.07	33	5.0	2.0	0.33	1.10	5 min	No	-
53	1.00	-	18.1	9.3	1.04	33	2.5	3.2	0.33	1.10	10 min	No	-
54	1.00	-	18.1	3.8	2.07	33	5.0	0.8	0.33	1.10	5 min	Yes	-
61	1.00	-	18.1	5.6	1.66	33	4.0	1.6	0.33	1.10	2-3 min	No	-
62	1.00	-	18.1	8.9	2.07	33	5.0	3.2	0.33	1.10	2-3 min	No	-
63	1.00	-	18.1	9.5	0.42	33	1.0	3.2	0.33	1.10	3 hr	Yes-Slight	-
64	1.00	-	18.1	7.7	0.62	33	1.5	2.4	0.33	1.10	1 hr	No	-
65	3.28	15.62	-	38.7	4.76	65	3.5	3.5	0.54	1.00	Few min	No	Sandwich
40	1.00	8.65	-	15.0	1.04	27	2.5	2.0	0.41	1.35	1 hr	No	-
66	1.00	8.65	-	15.2	2.07	27	5.0	2.0	0.41	1.35	1/2 hr	Yes	-
67	1.00	8.65	-	17.8	0.83	27	2.0	3.5	0.41	1.35	1 hr	Yes-Slight	-
68	1.00	8.65	-	18.5	1.04	27	2.5	4.0	0.41	1.35	1/2 hr	No	-
69	1.00	8.65	-	15.5	2.07	27	5.0	2.5	0.41	1.35	-	Yes	-
70	1.00	8.65	-	15.2	1.04	27	2.5	2.0	0.41	1.35	-	Yes-Slight	-
71	1.00	8.65	-	16.8	1.04	27	2.5	3.0	0.41	1.35	-	Yes-Slight	-
72	1.00	8.65	-	17.6	1.24	27	3.0	3.5	0.41	1.35	-	No	-
73	1.00	8.65	-	21.2	0.60	27	1.5	5.5	0.41	1.35	-	Yes-Slight	-
74	1.00	8.65	-	21.1	0.80	27	2.0	5.5	0.41	1.35	-	Yes-Slight	-
75	1.00	8.65	-	15.6	2.90	27	2.75	7.0	0.41	1.35	-	No	-
76	1.00	8.65	-	16.8	1.24	27	5.0	3.0	0.41	1.35	-	No	-
77	1.00	8.65	-	15.0	0.80	33	2.0	1.5	0.33	1.10	3 hr	Yes	-
78	1.00	8.65	-	22.3	0.60	33	1.5	5.0	0.33	1.10	-	No	-
*48	1.00	0.26	-	3.4	1.66	27	4.0	0.5	0.41	0.00	-	Slight	*

* To this added 17.5 UNH and boiled, UNH dissolved and a large amount of Zr solid was formed.

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TABLE IV

THE DISTRIBUTION OF THE SEVERAL COMPONENTS BETWEEN "PUREX IA FEEDS" AND 30 PER CENT TBP-CCl ₄					
Number	(F)/(Zr)	H ⁺ _f (M)	U(M)	Zr(M)*	H ⁺ (M)**
50-aqueous	2.5	2.4	0.56	0.40	2.86
50-organic			0.43	<10 ⁻⁵	0.04
51-aqueous	3.5	2.0	0.56	0.40	2.62
51-organic			0.44	<10 ⁻⁵	.06
52-aqueous	5.0	2.0	0.58	0.40	2.85
52-organic			0.44	<10 ⁻⁵	0.04

* Determined spectrophotometrically with alizarin.

** By titration after oxalate complexing of uranium.

These results are very encouraging in several respects. The extractability of uranium and also nitric acid is not markedly affected by the presence of zirconium and fluoride; and secondly, the zirconium is essentially unextractable with 30 per cent TBP in the presence of fluoride. In order to observe further the behavior of uranium in a Purex IA column, a typical feed (experiment number 52) was contacted with 30 per cent TBP-CCl₄. The resulting aqueous phase was contacted four successive times with organic phases. The resulting aqueous phase contained less than 10⁻⁴ M U. This is very similar to extraction conditions where no fluoride and zirconium are present. Plutonium behavior in a Purex IA column containing fluoride and zirconium was estimated by comparing the extractability of Pu⁴⁺ into 0.2M TTA from an ordinary Purex IA feed solution and one containing fluoride and zirconium. The experimental results are presented in Table V.

TABLE V

THE EFFECT ON THE EXTRACTION COEFFICIENT OF Pu ⁴⁺ DUE TO THE PRESENCE OF ZIRCONIUM AND FLUORIDE USING 0.2M TTA AS THE EXTRACTANT					
U(M)	HNO ₃ (M)	(F)/(Zr)	Zr(M)	(Al)/(Zr)	E _a ⁰ (Pu ⁴⁺)
1.1	2.0	3.5	0.33	0.	.0086
1.1	2.0	0.0	0.0	0.	.565
0.85	1.5	3.5	0.25	3.5	.017

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The effect of the fluoride is to reduce the extractability 65-fold. An attempt was made to complex the fluoride with Al^{+3} , thereby reducing the plutonium fluoride complexing. (See solution number 3 in the preceding table.) When the change in hydrogen ion concentration is taken into account, the effect is inappreciable. More work will be done on this phase of the problem.

Properties of Zirconium Precipitate

Some of the zirconium precipitate was isolated. The spectrochemical analysis showed the solid to be a zirconium compound. No uranium was detected. It was not possible to identify the compound by X-ray diffraction because of poor crystal structure of the samples, but it was possible to state that the compound definitely was not ZrO_2 , ZrOF_2 , ZrF_4 , Zr_3N_4 , or ZrC .

The amount of zirconium solid which was precipitated during unstable dissolutions was found to depend, in a general way, upon the $\frac{(\text{F})}{(\text{Zr})}$ and $(\text{H}^+)_f$, the lower these numbers the more solid precipitated. Several examples are given in Table VI.

TABLE VI

THE EFFECT OF THE F/Zr RATIO AND $(\text{H}^+)_f$ ON ZIRCONIUM COMPOUND PRECIPITATION				
Exp.	$(\text{F})/(\text{Zr})$	$(\text{H}^+)_f$	Total Zr, (grams)	Zr Compound Precipitated, (grams)
5	1.2	0.7	0.50	0.71
9	0.6	2.0	0.91	0.13
12	1.2	5.8	1.00	0.07
13	1.2	2.0	1.00	0.04

It should be noted that the amount of zirconium in solution for the above experiments is not known.

The solid was found to be quite insoluble in a number of reagents, either hot or cold, including excess nitric and hydrofluoric acids. It was found to be soluble in cold concentrated sulfuric acid to the extent of 2 g/l, but was fairly soluble in hot 50 per cent to 100 per cent sulfuric acid.

A rough quantitative analysis showed the compound to contain fluoride. However, no conclusions were drawn as to the fluoride-to-zirconium ratio.

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Some of the solid was dissolved in hot 50 per cent H_2SO_4 and a quantitative test for nitrate ion carried out using diphenylsulfonic acid. The nitrate concentration was found to be about one-tenth of that expected if the unknown were to have a nitrate-to-zirconium ratio of one. The nitrate-diphenylbenzidine color was also used to determine the nitrate concentration. Four standard nitrate solutions were prepared and the color compared to that of the unknown. The nitrate concentration was estimated to be one-one hundredth of that expected for a nitrate-to-zirconium ratio of one. The diphenylsulfonic acid analysis is believed to be the more reliable test. The small amount of nitrate found probably arises from mechanical occlusion, since the compound was precipitated in a high nitric acid medium. The conclusion was that the compound did not contain nitrate.

In order to establish a zirconium content for the solid, some solid was dried over $\text{Mg}(\text{ClO}_4)_2$ under vacuum at room temperature. The solid lost weight at almost a constant rate for eight days. The solid did not come to constant weight at 110°C . It would appear that the solid is a hydrate.

From the above work it was concluded that the solid was probably of the form: $\text{ZrF}_x(\text{OH})_y \cdot n\text{NH}_2\text{O}$. No more work on the solid was carried out.

Off-Gas Analysis

The composition of the gases given off during the dissolution of zirconium-clad uranium plate elements was investigated. At the time this work was done no simple method of gas analysis applicable to our case was known. Therefore, a method of gas analysis was developed which utilizes a series of absorbers as in the Burrell-type apparatus. This method is the subject of another report and will not be described here in any detail.

A representative gas sample for analysis was prepared by dissolving some zirconium-clad uranium plates in a nitric-fluoboric acid mixture in such a manner as to simulate actual continual plant operation dissolving. The dissolution was carried out in a round bottomed flask with a reflux condenser, the whole system, including the gas sample bottle, being air tight. The system, whose volume was 350 ml, was well purged with 1500 ml of dissolution off-gas to ensure complete removal of all air. The zirconium-clad uranium plate elements dissolved weighed 13.7 grams and had the following dimensions: $2 \times 0.5 \times 0.075$ in. In order to reduce the variation in composition with time during the dissolution, the plate elements were cut into many small pieces and these were slowly fed into the dissolver along with fresh amounts of acid solution. The elements and acid were contained in side arms connected to the dissolver through standard taper joints so they could be added without opening the system to the atmosphere. In this way the ratio of uranium-to-zirconium was held constant in the dissolver. The chemical data on the dissolution for producing a gas sample follows:

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Zr, grams	6.55
U, grams	31.2
16M-HNO ₃ , ml	64.5
27.6M HBF ₄ , ml	6.8
Total Volume, ml	100.0
(F)/(Zr)	2.5
H ⁺ _f , M	2.5

After the purging of the system to remove all traces of air, about 500 ml of gas were taken over a 25 per cent sodium chloride solution. Three analyses were carried out. The results are given in Table VII.

TABLE VII

COMPOSITION OF OFF-GAS IN THE DISSOLUTION OF Zr-U TARGET ELEMENTS				
Gas	Analysis, Volume Per Cent			
	I	II	III	Average
NO	71.2	71.4	69.4	70.7
NO ₂	1.6	1.6	1.7	1.6
N ₂ O	10.0	10.0	10.0	10.0
CO ₂	0.4	0.3	0.3	0.3
CO	0.0	0.0	0.0	0.0
O ₂	0.2	0.1	0.3	0.2
H ₂	0.0	0.0	0.0	0.0
N ₂ *	16.6	16.6	18.3	17.2

* By difference

A qualitative test for ammonium ion in the dissolver solution was negative. Aside from the few extraneous gases, the dissolution off-gas composition was 70.7 per cent NO, 17.2 per cent N₂, 10.0 per cent N₂O, and 1.6 per cent NO₂. No H₂ was detected.

Corrosion

Once satisfactory dissolving media have been found, a new problem is created in finding a suitable container for the dissolvent. A number of materials were examined with respect to their suitability as construction material for a dissolver vessel where refluxing nitric-hydrofluoric acids will be the dissolver solution. Work done elsewhere (5) on the corrosion of likely stainless steels indicated that "Durimet 20" or 309 Cb might be satisfactory at reflux temperatures. However, more data are still needed before a choice could be made.

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It was found that the presence of either gold or platinum metal often caused the dissolving zirconium to ignite with a bright flash and explosion. Small amounts of dissolved gold or platinum salt did not cause an explosion to occur. In all the dissolutions previously carried out on metallic zirconium and uranium no explosions had been observed. The cause of these ignitions is not known but one explanation might be the catalytic decomposition of a nitrogen oxide by metallic platinum or gold to form an active oxidant.

The corrosion rate of a nitric acid-fluoboric acid dissolver solution was compared to a nitric acid-hydrofluoric acid solution by measuring the corrosion penetration upon pyrex glass samples under reflux conditions. A 4M HNO_3 - 4 M HF solution caused a penetration of 35 mils in 6 hours while a 4M HNO_3 - 1M HBF_4 solution gave a penetration of 30 mils in 71 hours. The HF solution was fourteen times more corrosive to pyrex glass than the HBF_4 solution. The two solutions were identical in their ability to dissolve zirconium and uranium, both with regards to rates of dissolution and stability of the final solution.

If no stainless steel can be found which is satisfactory as a construction material, fluorothene A could probably be used.

CONCLUSION

It is possible to dissolve zirconium-clad uranium plate elements in nitric-hydrofluoric acid mixtures to form a stable aqueous solution which would be amenable to Purex-type processing.

No explosions have resulted from the nitric acid-hydrofluoric acid dissolution of plate elements or a combination of zirconium and uranium metals. No zirconium-uranium alloy has been dissolved by this method.

A greater understanding of plutonium and fission product behavior in the Purex process in the presence of the required fluoride concentration will be required. The conditions under which zirconium-uranium alloys will dissolve to form a stable feed solution will also have to be investigated.

BIBLIOGRAPHY

1. ANL-4872, Argonne National Laboratory, Summary Report, April, May, June, 1952, Chemical Engineering Division.
2. ANL-4922, Argonne National Laboratory, Summary Report, July, August, and September, 1952, Chemical Engineering Division.
3. Connick, R. E., and W. H. McVey, J. Am. Chem. Soc., 71, 3188 (1949).
4. Dodgen, H. W., and G. K. Rollefson, J. Am. Chem. Soc., 71, 2600 (1949).
5. LRL-78, California Research & Development Company, The Dissolution of Zirconium and Corrosion of Stainless Steel in Sulfuric Acid and Nitric-Hydrofluoric Acid Mixtures, R. H. J. Gercke and D. Lewis.

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