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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section B

MODIFIED ZIRFLEX PROCESS FOR DISSOLUTION OF ZIRCONIUM- AND NIOBIUM-BEARING NUCLEAR FUELS IN AQUEOUS FLUORIDE SOLUTIONS: LABORATORY DEVELOPMENT

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ABSTRACT

Modified Zirflex process flowsheets were developed for recovering uranium from the newer power reactor fuel alloys after discharge from the reactor. The STR (1% U-97% Zr-2% Sn) and EBWR Core-1 (93.5% U-5% Zr-1.5% Nb clad in Zircaloy-2) fuels are used as examples of low- and high-uranium fuels, respectively. A dissolvent of 6 M NH_4F yields a solution of zirconium and a precipitate of ammonium uranous fluoride. In one process, ammonium hydroxide is added to produce insoluble hydrous oxides of uranium, zirconium, and niobium. The NH_4F-NH_4OH supernatant is removed by filtration, partially evaporated, and recycled as dissolvent. The uranium and zirconium oxides are dissolved in nitric acid to yield a solvent extraction feed solution of low fluoride content.

In an alternative process nitric acid and aluminum nitrate are added to the ammonium fluoride fuel solution to oxidize U(IV) to soluble U(VI) and prepare a stable solution suitable for solvent extraction. Chromic acid is also added in the case of the STR fuel. In a variation of this flowsheet for the EBWR fuel, only enough 6 M NH_4F is added to dissolve the cladding. Nitric acid and aluminum nitrate are then added to dissolve the core.

Insoluble niobic oxide, which carries about 0.03% of the uranium from the EBWR fuel, is removed by filtration from the solvent extraction feed solutions in the EBWR flowsheets.

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1.0 INTRODUCTION

This report describes flowsheets that were developed for dissolving uranium-alloy fuels containing zirconium and niobium. These new power reactor fuels are resistant to chemical attack in aqueous solutions, and processes are needed to convert them to aqueous solutions suitable for solvent extraction by the Purex[1] or Redox[2] process. The flowsheets presented are based on laboratory experiments and published data and are considered suitable for general application to uranium-alloy fuels. Rates of reaction are sufficiently high for process use, the reagents used are not prohibitively corrosive to stainless steel, and the explosion hazard that exists when high-uranium alloy fuels are dissolved in nitric acid is eliminated by the fluoride. The experiments were carried out with non-irradiated STR (1% U-2% Sn-97% Zr) and EBWR Core 1 (93.5% U-5% Zr-1.5% Nb clad in Zircaloy-2) fuels as examples of low- and high-uranium fuels, respectively.

Dissolution techniques for these newer fuels have not yet reached the level of development achieved with fuels in which aluminum or stainless steel is a major component. A process in which STR fuel is dissolved in hydrofluoric acid[3,4] has the disadvantages of high corrosion rates and large waste volumes and is not well suited to fuels containing more than 1% uranium.

The use of ammonium fluoride solution as a dissolvent has been extensively investigated. Such solutions react readily with zirconium and Zircaloy-2 and many uranium alloys, and they are not very corrosive to stainless steel.[5-9] Core alloy attack by this reagent has been reported.[6,8]

The assistance of P. Thomas, G. R. Wilson, C. Feldman, H. Dunn, and co-workers of the Analytical Chemistry Division is gratefully acknowledged. Dr. K. A. Kraus of the Chemistry Division helped in finding literature values for the equilibrium constants of reactions involving complex fluorides in aqueous solution. A large portion of the laboratory work was done by G. E. Woodall.

2.0 FLOWSHEETS

The flowsheets provide for (1) single-stage dissolution of the fuel in 6 M NH_4F followed by (a) metathesis to oxide with ammonium hydroxide and oxidation-digestion or (b) direct oxidation-digestion, with nitric or chromic acid, of the U(IV) to U(VI); or (2) two-stage dissolution of the fuel to give a solution of hexavalent uranium. When the product contains uncomplexed fluoride, aluminum nitrate is added as a fluoride complexer. Further study of the complicated phase relations in these solutions might permit increasing the aluminum nitrate concentration, which was arbitrarily limited to 0.8 M on the basis of work at Argonne National Laboratory.[3]

Further development is needed before one flowsheet can be recommended over another for any one fuel. A disadvantage of the single-stage dissolution is the solid uranium product, NH_4UF_5, necessitating criticality precautions when processing enriched uranium fuel. The chief advantage of feed preparation by metathesis is the recycle of fluoride, which decreases corrosion in solvent extraction and waste storage vessels and decreases the volume needed by eliminating the need for aluminum nitrate. Volume reduction is of greater advantage with high-uranium fuels, where the only limitation on feed concentration is the solubility of uranyl nitrate. From such solutions uranium is readily extracted with TBP while the zirconium is essentially unextractable, despite the low F/Zr ratio.[10] The chief disadvantage is the necessity of separating a precipitate from a supernatant solution several times. This is more serious with high-zirconium fuels since hydrous zirconium oxide is much more flocculent than uranium oxide. However, hydrous zirconium oxide reportedly[11] can be precipitated in an easily filterable form.

The advantages of the two-step dissolution of high-uranium fuels such as the EBWR fuel are the decreased criticality danger with a soluble product, the faster dissolution rate, and the smaller product volume, which is about 25% of that of the ammonium fluoride dissolution-nitric acid oxidation route because only 25% as much aluminum is added to complex the smaller amount of fluoride. However, this volume is still nearly 5 times that of the metathesis feed preparation route, in which no aluminum is added. The two-step dissolution method has a serious disadvantage in that explosions can occur if the fluoride in the core dissolvent is not maintained at the prescribed flowsheet concentration.[12]

2.1 Dissolution

a. Single-stage

Both low- and high-uranium fuels are dissolved in 6 M NH_4F (Figs. 2.1 and 2.2). The results of several runs under flowsheet conditions are given in Tables 2.1-2.3. The zirconium dissolution product, $(NH_4)_2ZrF_6$,[13] is soluble to the extent of about 1 M between room temperature and the boiling point,[14] while the uranium product, NH_4UF_5, is soluble to about 10^{-4} M[5] and the niobium product, $(NH_4)_2NbF_7$, to 0.011 M (Sect. 3.1) at room temperature. Tin remains undissolved until the feed preparation step. Tin and uranium in STR fuel may be completely dissolved at the same time as the zirconium if 1 M NH_4NO_3 is added to the 6 M NH_4F. Hydrogen evolution is then less, but initial corrosion rates of 309Nb stainless steel, a possible material of construction for the dissolver, are 6-10 mils/month. Corrosion rates of stainless steel in pure ammonium fluoride solutions are about 10-fold lower.[5]

About 2 hr is required for complete dissolution of an STR fuel element. For 240-mil EBWR plates about 25 hr is required, at an average core dissolution rate of 2.5 mg/cm^2·min, and for 280-mil plates, about 28 hr.

b. Two-stage

With a high-uranium fuel the cladding and core may be dissolved stepwise (Fig. 2.3). At first only enough 6 M NH_4F is used to yield a solution with a F/Zr mole ratio of 7.9 after the cladding has dissolved. With this proportion of fluoride, Zircaloy dissolves completely at a rapid rate,[5] and the core is attacked only slightly.

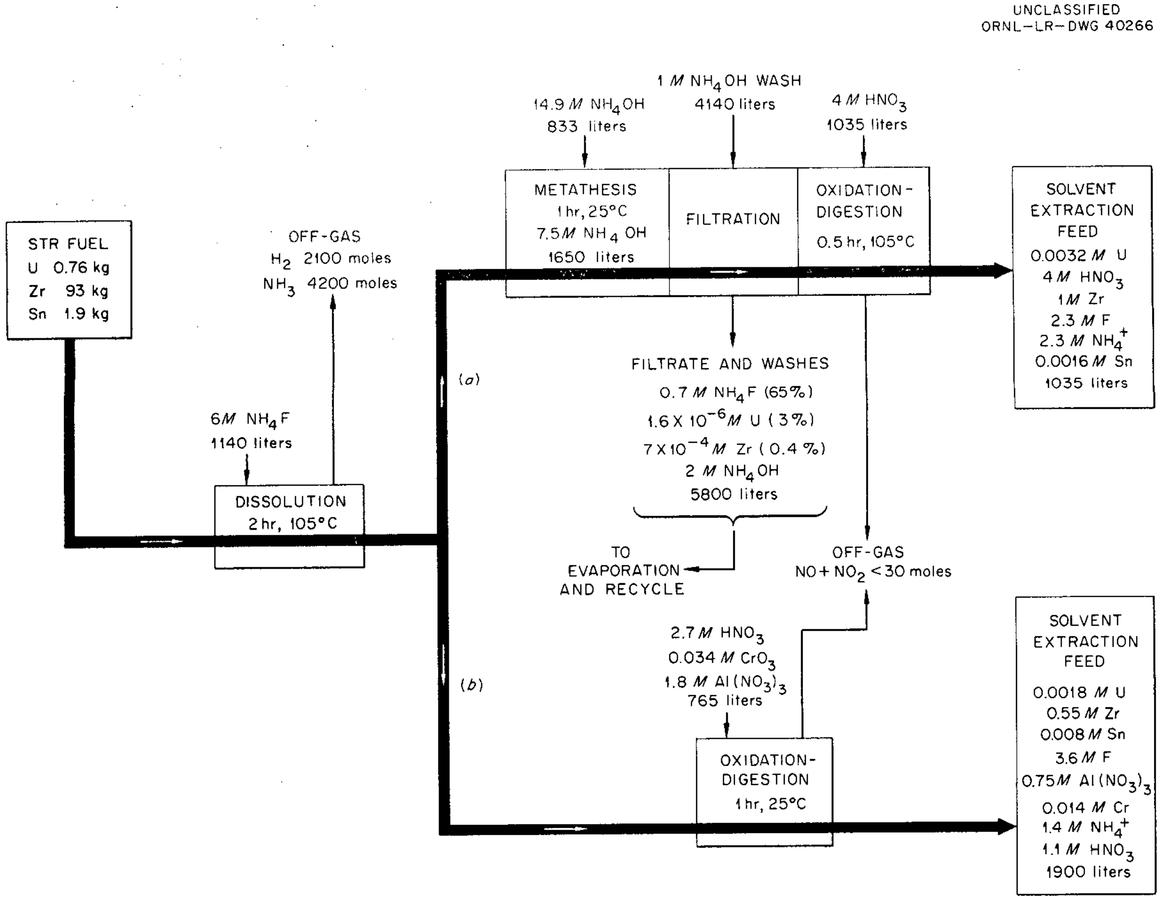

Fig. 2.1. Modified Zirflex process for dissolution of low-uranium (STR) fuel elements in aqueous ammonium fluoride. Solvent extraction feed preparation by (a) metathesis-nitric acid oxidation and (b) chromic acid oxidation.

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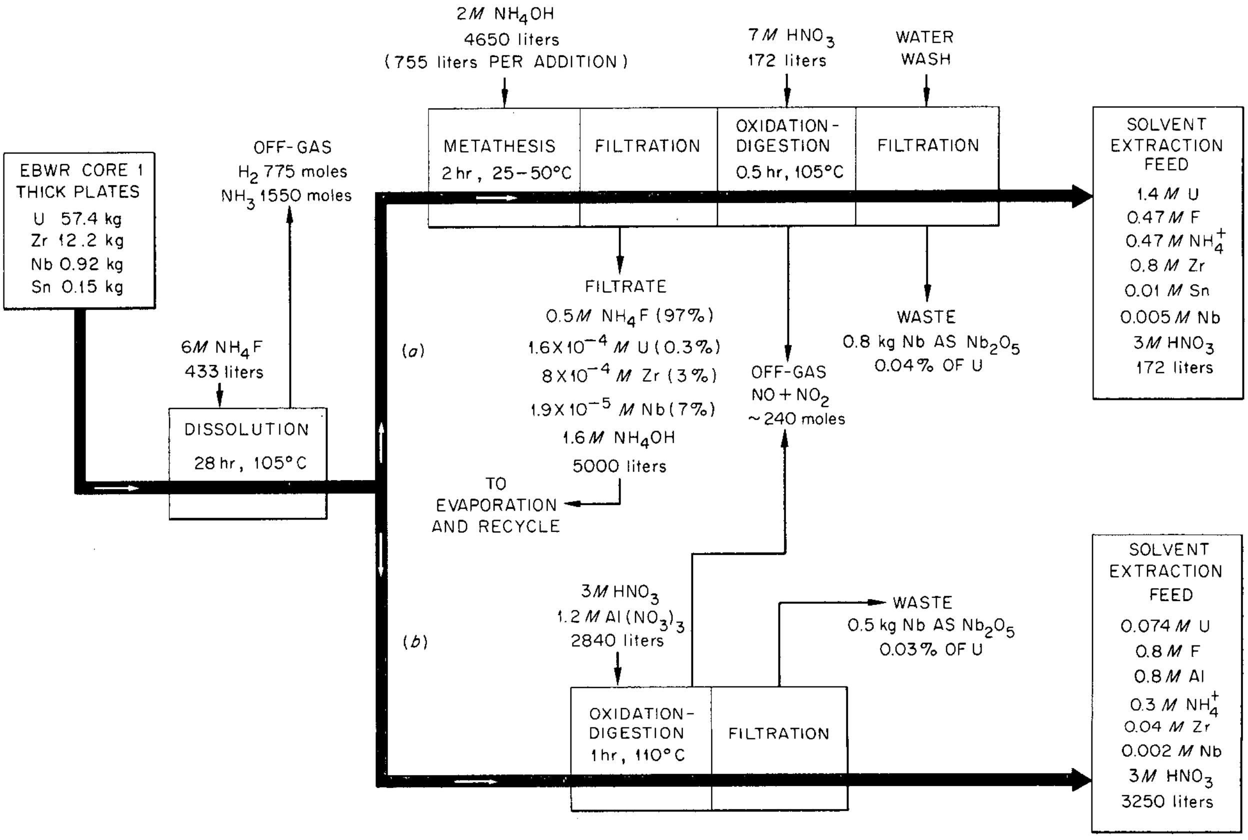

Fig. 2.2. Modified Zirflex process for dissolution of high-uranium (EBWR-Core 1) fuel in aqueous ammonium fluoride. Solvent extraction feed preparation by (a) metathesis and nitric acid oxidation and (b) nitric acid oxidation.

Table 2.1 STR Flowsheet Runs: Dissolution in Refluxing 6 M NH_4F and Metathesis of Dissolution Products with Ammonium Hydroxide

Weight of plate sections: 2.5 g; nonirradiated
Ammonium hydroxide concentrations:
Metathesis: 7.5 M, 300% of the stoichiometric amount
Six washes: 1 M, each containing 50% of stoichiometric amount
Seventh wash: Water

Run	Mole Ratio of F to U+Zr+Sn	Time, hr Dissolution	Time, hr Metathesis	Time, hr Total	% Recycled F	% Recycled U	% Recycled Zr	F/Zr in Solvent Extraction Feed
STRM-1	7	1.5	1.5	3.0	85	2.1	0.2	1.0
STRM-2	7	1.0	1.5	2.5	73	0.9	0.04	1.9
STRM-9	6.5	2.0	1.5	3.5	69	3.9	0.5	1.8
STRM-12	6.5	2.0	1.5	3.5	80	3.9	0.2	1.7
STRM-13	6.5	2.0	1.5	3.5	79	4.4	0.9	1.6
STRM-14	6.5	2.0	1.5	3.5	86	0.9	0.6	1.0

Table 2.2. EBWR-Core 1 Flowsheet Runs: Complete Dissolution in Refluxing Aqueous Ammonium Fluoride Followed by Metathesis with 2.0 M NH_4OH

Run	NH_4F, M	Mole Ratio of F to U+Zr+Nb	Processing Time, hr Dissolution	Processing Time, hr Metathesis	Processing Time, hr Total	% in Waste U	% in Waste Zr	% in Waste Nb	% Recycled F	% Recycled U	% Recycled Zr	% Recycled Nb	F/Zr in Feed
EBM-2	6	12	23	2	25	0.04	0.3	89	98.7	0.3	2.0	5	0.7
EBM-3	12	12	25	2	27	0.06	0.1	85	95.3	0.3	0.6	8	3
EBM-4	6	7	28	2	30	0.01	0.1	-	98.6	0.3	6.5	9	0.5

Table 2.3. EBWR-Core 1 Flowsheet Runs: Complete Dissolution in Refluxing 6 M NH_4F before Addition of HNO_3-$Al(NO_3)_3$

Run	Dissolution Time, hr In 6 M NH_4F	Dissolution Time, hr In $Al(NO_3)_3$-HNO_3	Dissolution Time, hr Total	Solvent Extraction Feed HNO_3, M	Solvent Extraction Feed CrO_3, M	Solvent Extraction Feed Lowest Temperature at Which Stable, °C	% in Waste U	% in Waste Zr	% in Waste Nb	% in Waste Cr	% in Waste Al
EB-74	26	1	27	1.0	0.4	-	0.21	0.5	30	0.007	-
EB-75	25	1	26	5.0	0.0	-30	0.039	1.4	44	0.0	0.09
EB-76	25	1	26	3.0	0.0	-13	0.016	1.1	50	0.0	0.02

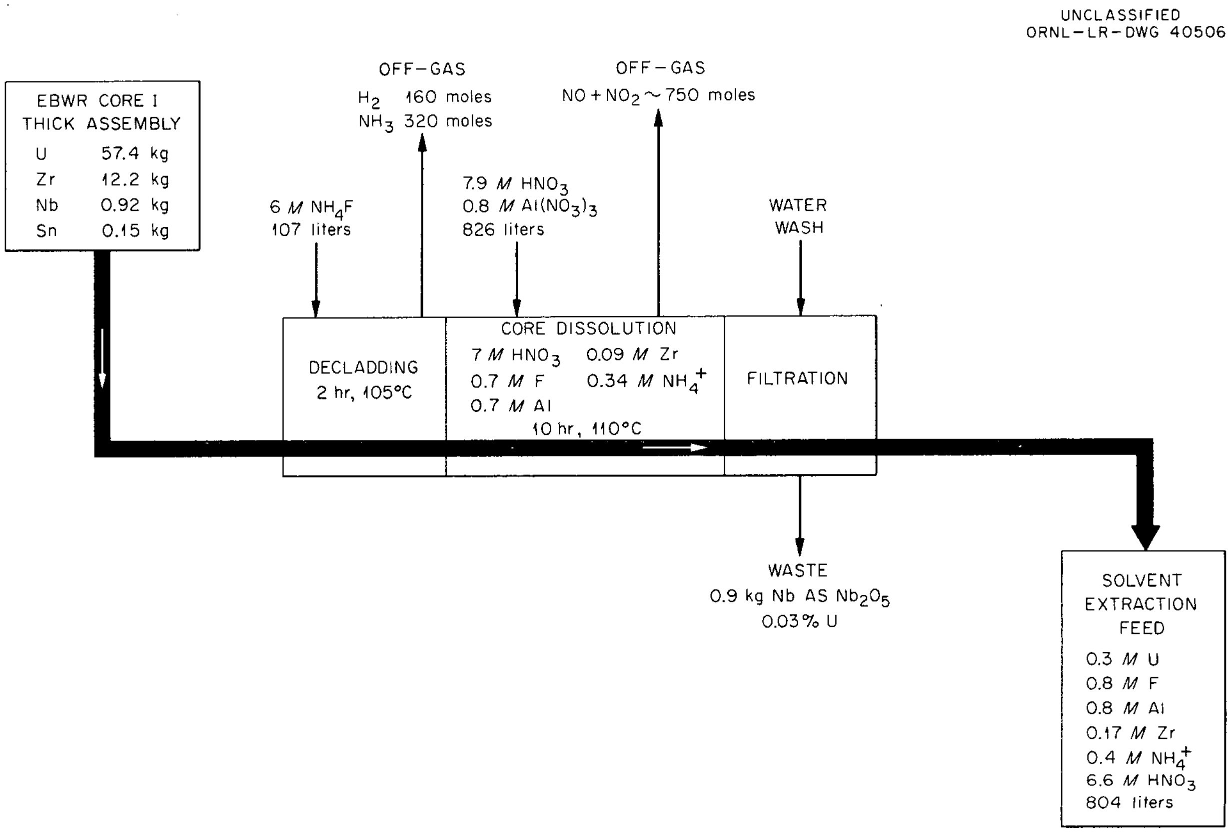

Fig. 2.3. Modified Zirflex process for two-step dissolution of high-uranium (EBWR-Core 1) fuel in aqueous fluoride.

Nitric acid is added to the solution of ammonium fluoride and ammonium fluorozirconate present after decladding to provide a mixed fluoride-nitrate reagent for core dissolution. Tin, present in Zircaloy, does not dissolve during decladding, but dissolves as soon as the nitric acid is added. Because corrosion of stainless steel in the mixed fluoride-nitrate reagent could be excessive[15] during the 10 hr reflux required for core dissolution, aluminum nitrate is added at the same time as the nitric acid in quantities equimolar with the fluoride. The zirconium dissolved during core dissolution decreases the F/Zr mole ratio in solution from 7.9 to 4.7, which is considered high enough to prevent explosions. The niobic oxide precipitate that remains carries about 0.03% of the uranium and is filtered off and discarded.

The results of several runs under flowsheet conditions are given in Table 2.4. Core dissolution rates at lower fluoride or nitrate concentrations were too low (16 hr in 5.3 $\underline{M}$ HNO_3-0.08 $\underline{M}$ HF-0.08 $\underline{M}$ $Al(NO_3)_3$, for example). In one such run (same concentrations) an explosion occurred even though the F/Zr mole ratio was 4.3. At higher fluoride or nitrate concentrations the core dissolved very rapidly. With 11.5 $\underline{M}$ HNO_3-1.1 $\underline{M}$ HF-0.05 $\underline{M}$ $Al(NO_3)_3$, only 2.8 hr was required for complete core dissolution.

2.2 Feed Preparation

a. Metathesis and Oxidation-Digestion

Ammonium hydroxide is added to convert the single-stage dissolution products to hydrous oxides, which are washed and then dissolved in nitric acid to give a solvent extraction feed (Figs. 2.1 and 2.2, routes a, and Tables 2.1 and 2.2).

With STR fuel, 7.5 $\underline{M}$ NH_4OH (300% of the stoichiometric amount) is used, the mixture is agitated 0.5 hr with ammonia gas to increase fluoride removal, and the supernatant is removed by filtration. The precipitates are washed twice with 50% of the stoichiometric amount of 1 $\underline{M}$ NH_4OH required for the metathetical reaction, each wash being removed by filtration after 10 min. The combined filtrate and washes, containing 65% of the fluoride, 3% of the uranium, and 0.4% of the zirconium, is partially evaporated to remove most of the ammonia and excess water and recycled as dissolvent. Fluoride recycle can be increased to 85% or more (Sect. 3.2) by using more washes.

With the EBWR fuel the flowsheet is similar. Six additions of 100% of the stoichiometric amount of 2 $\underline{M}$ NH_4OH needed for metathesis is used to convert the fluoride dissolution products to insoluble oxides. After each addition the mixture is agitated with ammonia gas for 10 min at 25-50°C and the supernatant is then removed by filtration or decantation. The filtrate, containing 97% of the fluoride, 0.3% of the uranium, 3% of the zirconium, and 7% of the niobium, is evaporated and recycled. The number of additions of 2 $\underline{M}$ NH_4OH can be decreased at the expense of less removal of fluoride. The reaction between $(NH_4)_2ZrF_6$ or $(NH_4)_2NbF_7$ and NH_4OH proceeds rapidly to completion at or near room temperature;[16-18] that between NH_4UF_5 and NH_4OH proceeds less rapidly.

Table 2.4 EBWR-Core 1 Flowsheet Runs, Two-stage Dissolution: Decladding in Refluxing 6 M NH_4F before Addition of HNO_3-$Al(NO_3)_3$ for Core Dissolution

Concentration before core dissolution: 0.7 M F, 0.7 M Al, 0.09 M Zr, 0.34 M NH_4^+, 7 M HNO_3, F/Zr = 7.9

Solvent extraction feed concentrations: 0.3 M U, 0.8 M F, 0.8 M Al, 0.17 M Zr, 0.4 M NH_4^+, 6.6 M HNO_3, F/Zr = 4.7

	Processing Time, hr			% in Waste		
Run	Decladding	Core Dissolution	Total	U	Zr	Nb
67	1.2	8.5	9.7	0.02	0.19	100
F-1*	1.2	7.0	8.2	0.05	0.13	85
F-2	1.2	7.0	8.2	0.01	1.7	99
F-3	1.2	8.0	9.2	0.01	1.5	100
F-4	1.5	6.3	7.8	0.02	2.9	88

*Thick plate, 280 mils, including cladding; other runs are with thin plate, 240 mils.

The hydrous oxides are dissolved in nitric acid to give a solvent extraction feed containing 35% of the initial fluoride in the case of the STR fuel and 3% in the case of the EBWR fuel, the F/Zr mole ratios being 2.3 and 0.6, respectively. Since with a F/Zr mole ratio of less than 3 corrosion rates of stainless steel are expected to be low, the addition of aluminum nitrate is probably not necessary. With EBWR fuel, niobic oxide remains and must be filtered off. It carries only 0.04% of the uranium.

The dissolution and metathesis steps together require about 4 and 30 hr, respectively, for the STR and EBWR fuels.

b. Direct Oxidation-Digestion

The U(IV) in the precipitated NH_4UF_5 may be oxidized to the uranyl ion by nitric or chromic acid (Figs. 2.1 and 2.2, routes b, and Table 2.3). The F/Zr mole ratios in the product are 6.5/1 and 20/1 with the STR and EBWR fuels, respectively. Aluminum nitrate is added at the same time as the acid to give, with STR fuel, a final F/Al ratio of 4.8, and with EBWR, 1. If the nitric and chromic acids are mixed with the aluminum nitrate before addition, this mixed solution should be added rapidly to the dissolver solution to decrease the pH rapidly, since aluminum compounds can precipitate at the high pH of the ammonium fluoride dissolver solution. The possibility of precipitation of aluminum compounds can be eliminated by adding the nitric acid before the aluminum nitrate. Chromic acid is recommended for oxidation of the low-uranium fuel products, only 0.014 M chromium being required for the STR fuel. With high-uranium fuels, nitric acid oxidation is recommended to avoid introducing large amounts of chromium. In a single run when 0.4 M chromium was used for oxidation of EBWR fuel products (run EB-74, Table 2.3), the uranium loss was about 10 times as high as when nitric acid alone was used (runs EB-75 and EB-76). With either type of fuel in the absence of chromic acid, the nitric acid concentration must be 3 M or higher since the solution must be boiled to give a satisfactorily rapid oxidation rate and aluminum compounds would be precipitated at lower nitric acid concentrations. With either chromic acid at room temperature or no chromic acid and 3 M HNO_3 at reflux temperature, oxidation is usually complete in 0.5 hr. The 0.8 M fluoride present keeps about half the niobium from the EBWR fuel in solution; the rest remains undissolved, carrying about 0.03% of the uranium. There is no explosion hazard with the EBWR fuel since nitric acid is not added until after the fuel has been completely converted to dissolution products and because a large amount of fluoride is present.

With STR fuel both dissolution and chromic acid oxidation can be performed in 3 hr in a single stainless steel vessel. With EBWR fuel, dissolution and nitric acid oxidation require about 30 hr.

Removal of the ammonium ion from waste solutions by addition of caustic might be necessary before calcining, to prevent ammonium nitrate explosions.

2.3 Chemistry of the Processes

The dissolution reactions in ammonium fluoride solution are:

$$5NH_4F + U \longrightarrow NH_4UF_5 + 4NH_3 + 2H_2 \quad (\text{Ref. } 5) \tag{1}$$

$$6NH_4F + Zr \longrightarrow (NH_4)_2ZrF_6 + 4NH_3 + 2H_2 \quad (\text{Ref. } 5) \tag{2}$$

$$7NH_4F + Nb \longrightarrow (NH_4)_2NbF_7 + 5NH_3 + 2.5H_2 \tag{3}$$

Excess ammonium fluoride can cause precipitation of $(NH_4)_3ZrF_7$, which is less soluble than $(NH_4)_2ZrF_6$.[5,14] If nitrate is present, it is reduced to ammonia and the evolution of hydrogen is decreased[5] by reactions such as

$$6NH_4F + 0.5\ NH_4NO_3 + Zr \longrightarrow (NH_4)_2ZrF_6 + 5NH_3 + 1.5\ H_2O \tag{4}$$

The metathetical reactions between the ammonium fluoride dissolution products and ammonium hydroxide can be written as

$$NH_4UF_5 + 4NH_4OH \longrightarrow U(OH)_4 + 5NH_4F \tag{5}$$

$$(NH_4)_2ZrF_6 + 4NH_4OH \longrightarrow Zr(OH)_4 + 6NH_4F \tag{6}$$

$$(NH_4)_2NbF_7 + 5NH_4OH \longrightarrow Nb(OH)_5 + 7NH_4F \tag{7}$$

The hydrous oxides ultimately lose water and are converted to the more stable oxides. The conversion is apparently slow with the hydrous zirconium oxide since the metathesis product dissolves in nitric acid but zirconium oxide is insoluble in nitric acid. The conversion of hydrous niobium oxide to Nb_2O_5 is also slow.[16] The metathetical reaction between $(NH_4)_2ZrF_6$ or $(NH_4)_3NbF_7$ and ammonium hydroxide proceeds rapidly and goes to completion at or near room temperature.[16-18]

2.4 Other Flowsheet Possibilities

a. Fused Ammonium Bifluoride (Biflex) Process[18]

Anhydrous ammonium bifluoride at 150-220°C reacts rapidly (Sect. 3.3) with all the uranium fuels, including those containing niobium. Many of these fuels are attacked only slowly by aqueous ammonium fluoride. By converting the fuels to complex fluorides with the anhydrous reagent, separating the excess reagent, and/or adding water, a solution is obtained similar in composition to that obtained in aqueous ammonium fluoride dissolution.

b. Nitric-Hydrofluoric Acid

Decladding of EBWR fuel with 9 M HF and leaving the clad solution in the dissolver, followed by nitric acid addition at a controlled rate to dissolve the core, offers the advantages of rapid decladding together with core dissolution control by control of the rate of addition of nitric acid. Concentrated uranium solutions can be obtained without feed adjustment, but the niobic oxide residue must be washed in nitric acid to prevent loss of uranium. In two runs, 0.5 hr was required for decladding in 9 M HF to yield a F/Zr mole ratio of about 6 and an average of 6.6 hr for core dissolution to give 1.5 M uranium and 6 M HNO_3 in the final solution. In both cases about 90% of the niobium was removed in the residue, with 0.04% of the uranium. Since the F/Zr mole ratio of the dissolution product was about 5, aluminum nitrate would have to be added to complex some of the excess fluoride before solvent extraction. At present there does not appear to be a material of construction which is sufficiently resistant to nitric-hydrofluoric acid to be used in a dissolver for this process. Teflon and polyethylene equipment was used in laboratory experiments.

Another flowsheet which was investigated for the EBWR fuel, but which proved impractical because of explosions, involved core dissolution in nitric acid.

3.0 LABORATORY STUDIES

3.1 Dissolution

a. Single-stage

The EBWR Core 1 alloy dissolved at satisfactory initial rates in aqueous ammonium fluoride (Fig. 3.1). At fluoride/dissolved metal mole ratios greater than 50 rates were very rapid when the fluoride concentration was 6-12 M. At ratios below 6 the rate dropped rapidly to about 1 $mg/cm^2 \cdot min$ at the fluoride concentrations studied. When approximately 6 M NH_4F was used, the initial rate was 5 $mg/cm^2 \cdot min$ at fluoride/dissolved metal mole ratios between 50 and 7. The best dissolution rates (about 20 $mg/cm^2 \cdot min$) for Zircaloy-2 (and therefore for STR fuels) are also given with 6 M NH_4F.[5]

The EBWR Core alloy dissolution rate decreased continuously as dissolution proceeded (Fig. 3.2). No apparent increase in rate was achieved by dividing the solution into two batches and removing the first batch and the NH_4UF_5

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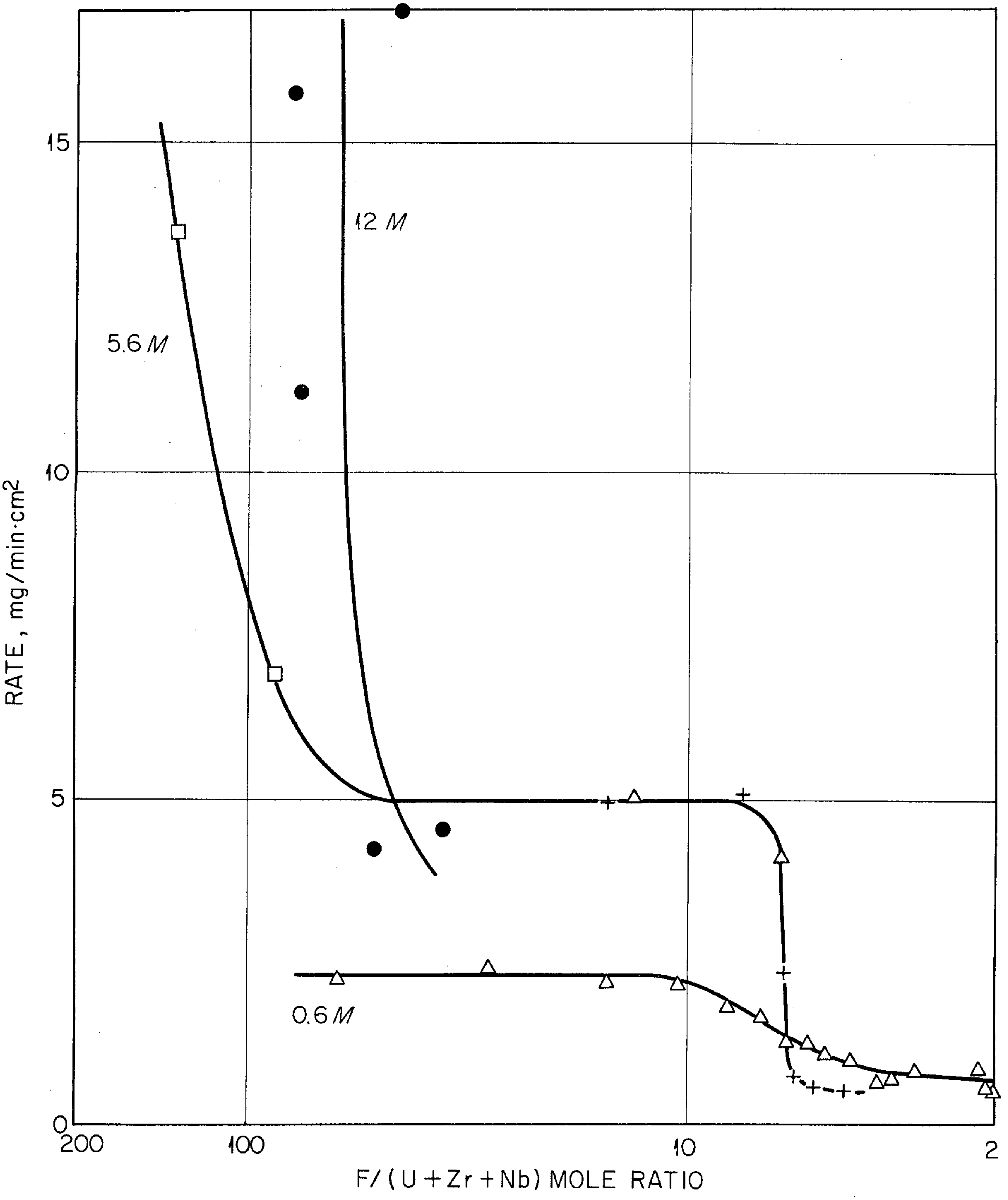


Fig. 3.1. Dissolution rates of the EBWR core 1 alloy in refluxing aqueous ammonium fluoride as a function of F/metal mole ratio.

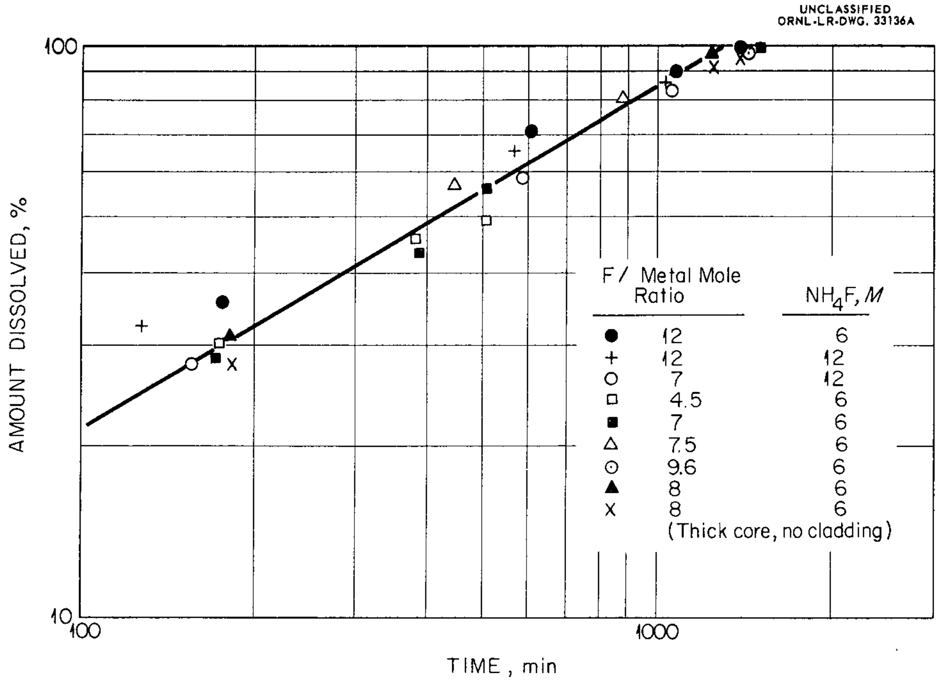


Fig. 3.2. Amount of EBWR core 1 alloy dissolved in refluxing aqueous ammonium fluoride as a function of time and F/metal mole ratio. Sample weights 12-13 g.

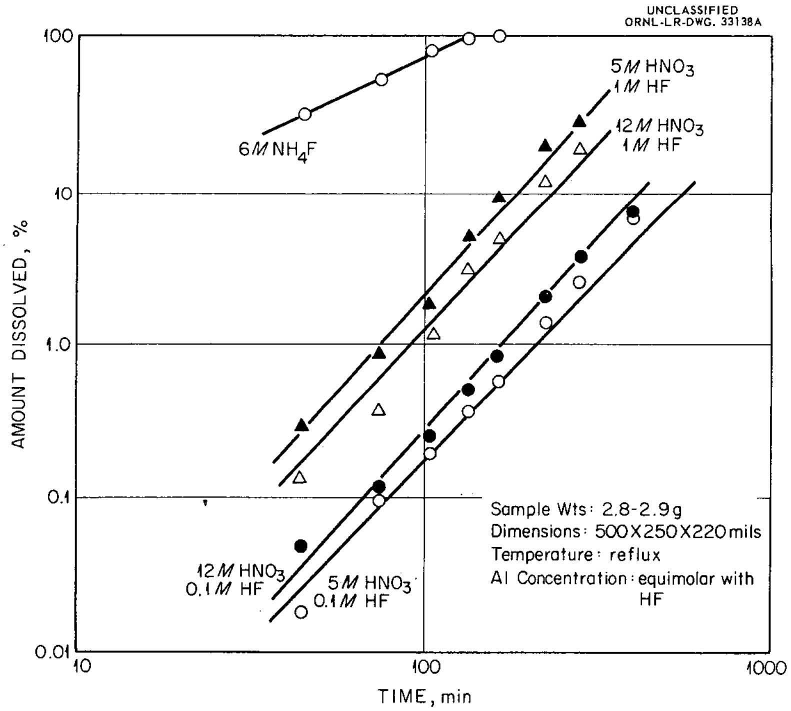


Fig. 3.3. Dissolution of oxide-coated Zircaloy-2 in various fluoride-containing reagents.

precipitate when the dissolution was about 50% complete. The continuous rate decrease is thought to be due to a buildup at the alloy surface of the less-reactive niobium mixed with $(NH_4)_2NbF_7$. Since no data are available on solubility of $(NH_4)_2NbF_7$, some of the salt was prepared for testing. Niobium metal was dissolved in fused ammonium bifluoride at 220°C at a rate of 1.6 $mg/cm^2 \cdot min$. The results of analyses of the product, after thorough washing in water, were:

Theoretical $(NH_4)_2NbF_7$:	NH_4^+, 13.77%	F, 50.77%	Nb, 35.46%
Found:	12.8	55.9	32.0

The solubility of the product in water, determined after standing 6 weeks at room temperature, was 0.011 M. The x-ray pattern showed the niobium product to be crystalline. In an attempt to prepare $(NH_4)_2NbF_7$ by dissolution of niobium turnings in 6 M NH_4F, the dissolution rate, while not measured, was impracticably low.

Single-stage dissolution of the EBWR Core 1 fuel in $HF\text{-}Al(NO_3)_3\text{-}HNO_3$ solution is too slow because of the slow rate of attack on oxide-coated Zircaloy-2 (Fig. 3.3). Experiments were performed in a Teflon dissolver equipped with a heating mantle and a polyethylene condenser. The F/Zr mole ratio was maintained at 4 or higher in all runs. Even in solutions 1 M in HF, which would be very corrosive to stainless steel,[15] complete dissolution of the 20-mil clad would probably require about 10 times as long (i.e. about 20 hr) as would be required in 6 M NH_4F. After the clad has dissolved, the core alloy dissolves rapidly in $HF\text{-}HNO_3$ (Fig. 3.4). At nitric acid concentrations above 8 M, the core alloy dissolves at initial rates in excess of 10 $mg/cm^2 \cdot min$ at fluoride concentrations as low as 0.01 M. These studies were performed at ratios of reagent volume to alloy surface area of only about 4 ml/cm^2 to permit an accelerated buildup of uranium and zirconium in solution and to minimize the rate-decreasing effect of the niobic oxide precipitate. Attempts to find reagents that would delay or prevent niobic oxide precipitation were unsuccessful. Solutions 1 M in uranium were obtained with the final dissolution rate still in excess of 1 $mg/cm^2 \cdot min$ (Fig. 3.5). Under process conditions, a ratio of about 80 ml/cm^2 is expected, and the average dissolution rate is prohibitively low (1 $mg/cm^2 \cdot min$) at about 0.3 M uranium. However, less than a 2-fold decrease in core alloy dissolution rate occurred in the laboratory experiments (4 ml/cm^2) when the uranium concentration increased from 10^{-3} to only 10^{-1} M (Fig. 3.6). The initial rate determinations shown in Fig. 3.4 were all obtained at final uranium concentrations of less than 10^{-1} M.

To simplify the hydrofluoric-nitric acid rate studies with EBWR Core alloy, no zirconium or aluminum was placed in the solutions because of the fluoride-complexing ability of these metals. It was thought that, in single-stage dissolution in $HF\text{-}Al(NO_3)_3\text{-}HNO_3$ solution, the core would dissolve at rates comparable to those of Figs. 3.4-3.6 if the uncomplexed fluoride ion concentration was comparable. The uncomplexed fluoride concentration can be roughly estimated by using the association constants in Table 4.1.

b. Two-stage

The rate data obtained above (Fig. 3.4) in connection with single-stage $HF\text{-}Al(NO_3)_3\text{-}HNO_3$ dissolution of EBWR fuel showed that the initial dissolution

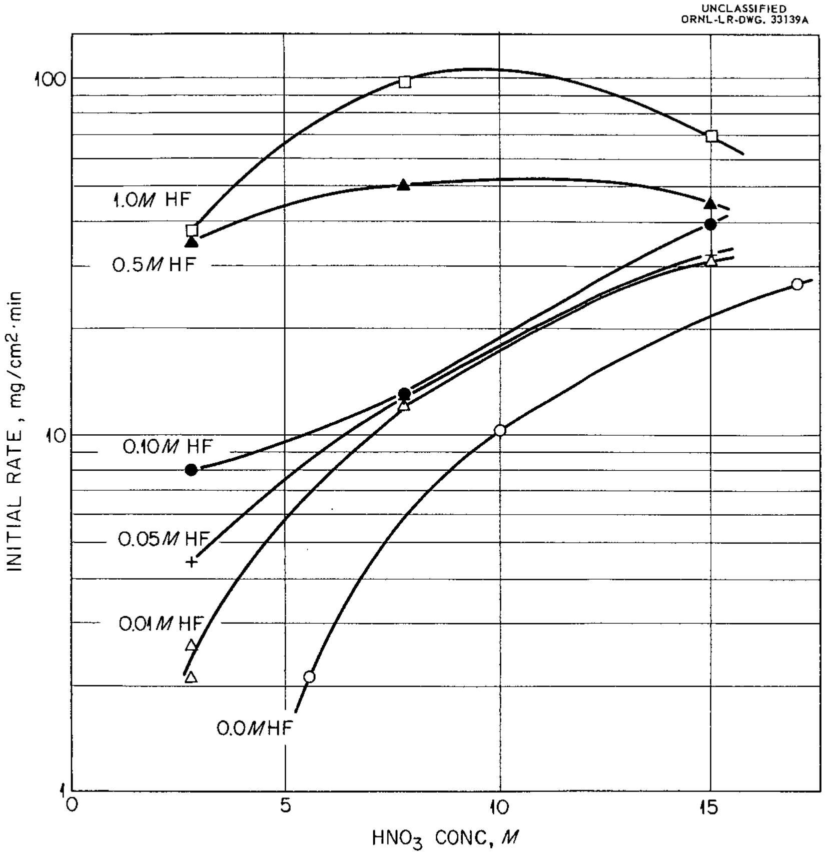


Fig. 3.4. Initial dissolution rates of EBWR core 1 alloy in refluxing nitric-hydrofluoric acid.

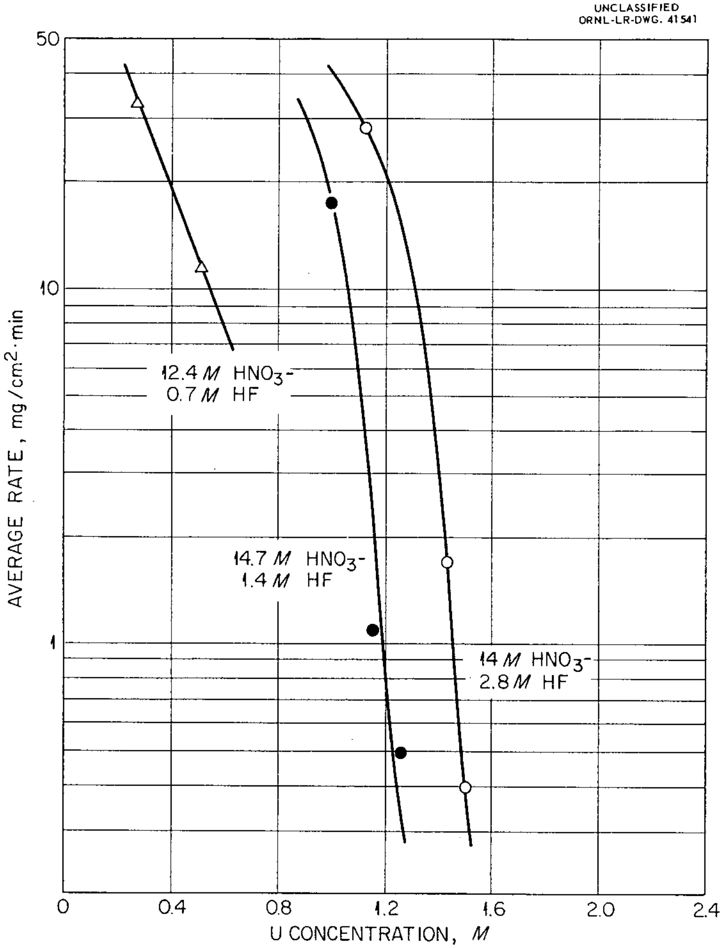


Fig. 3.5. Decrease in the EBWR core 1 alloy dissolution rate with uranium buildup in refluxing nitric-hydrofluoric acid.

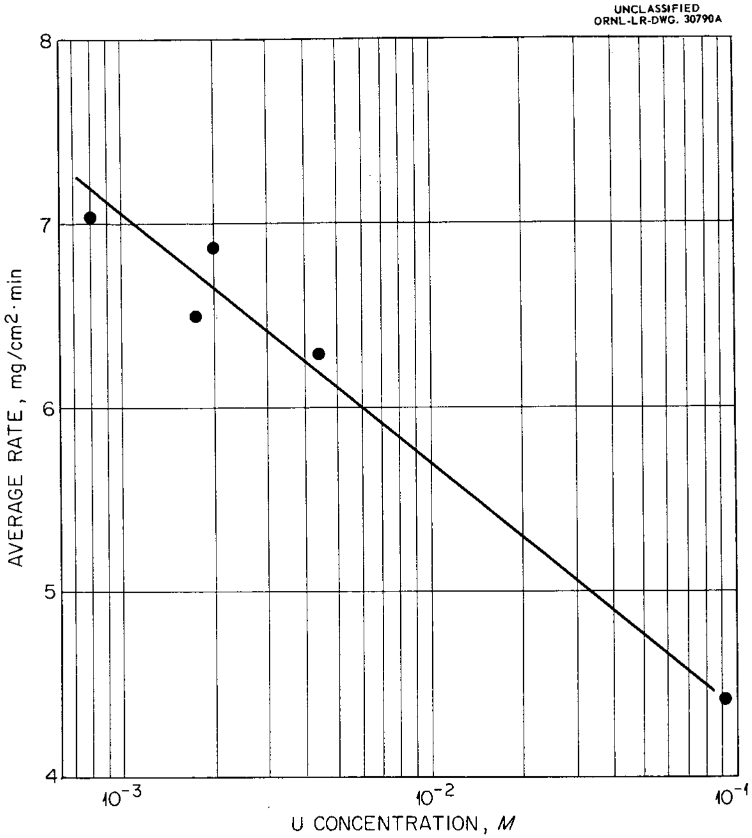


Fig. 3.6. Decrease in the EBWR core 1 alloy average dissolution rate with uranium buildup in refluxing 3 M HNO_3-0.05 M HF.

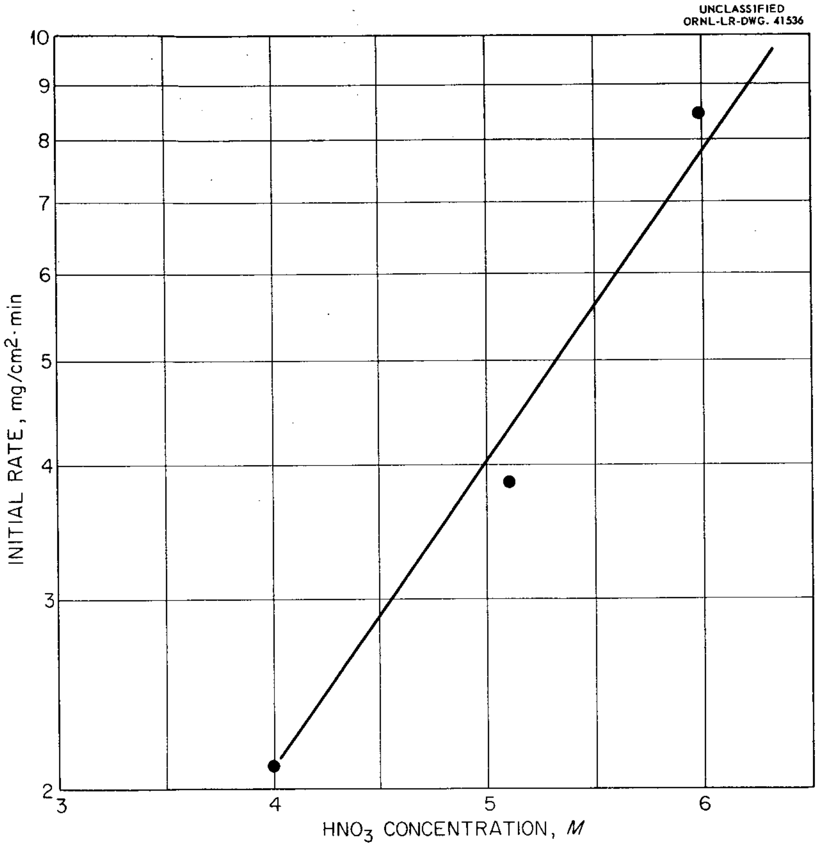


Fig. 3.7. Initial dissolution rate of EBWR core 1 alloy in refluxing 0.4 M NH_4F-0.4 M $Al(NO_3)_3$-HNO_3.

rate of the core alloy (~10 mg/cm^2·min) may be excessive if the uncomplexed fluoride ion concentration greatly exceeds 0.1 M. In selecting a satisfactory nitric acid concentration for core dissolution in the two-stage EBWR process (Fig. 2.3), 0.4 M fluoride was used in rate studies (Fig. 3.7) rather than 0.7 M as shown in the flowsheet, where the presence of 0.09 M zirconium decreases the uncomplexed fluoride concentration to about 0.4 M. It was found that 7 M HNO_3 could be used without producing an initial dissolution rate much in excess of 10 mg/cm^2·min with the solution 0.4 M in $Al(NO_3)_3$. The final selection of aluminum nitrate concentration during core dissolution will depend on the results of corrosion tests now underway. The fluoride concentration cannot be decreased because the amount of 6 M NH_4F used in the flowsheet is the minimum required for rapid decladding. After about two days' standing at 5°C or 3-4 hr at 0°C, slight precipitation occurred in the solvent extraction feed solution of the two-stage EBWR process (Fig. 2.3). The precipitate had the appearance of uranyl nitrate hexahydrate.

3.2 Feed Preparation

a. Metathesis and Oxidation-Digestion

Only a brief report on the reaction between NH_4UF_5 and ammonium hydroxide has been published,[18] and rate studies were made to determine whether the reaction could be carried out in a reasonable time. The results (Fig. 3.8) indicated that the conversion of NH_4UF_5 to hydrous uranium oxide usually approaches completion in a few minutes. No temperature dependence was apparent between 35 and 87°C. For the experiments a weighted quantity of NH_4UF_5 was introduced into a vessel containing a large excess of ammonium hydroxide in a constant-temperature bath. The mixture was stirred rapidly with a magnetic stirrer and a stream of ammonia gas. Samples of the solution were removed periodically by applying vacuum to a Pyrex dip-tube containing a fine Pyrex filter frit at the lower end to remove solids. These samples were analyzed for fluoride, and the quantity of NH_4UF_5 that had reacted was calculated assuming the fluoride to be homogeneously distributed throughout the solution. The amount of NH_4UF_5 in solution may be neglected because of its low solubility. Simple colorimetric fluoride analyses provided only a qualitative indication of the progress of the reaction.

In the flowsheet runs with the high-uranium EBWR fuel (Table 2.2), in order to decrease the time required for the reaction by taking advantage of the rapid initial reaction and also to drive reaction 5 (Sect. 2.3) to completion, repeated additions of fresh 2 M NH_4OH were used. Each addition was removed by filtration after contacting the dissolution products for 10 min. A stream of ammonia was used for agitation. Six applications of the stoichiometric amount of 2 M NH_4OH required for eq. 5 removed more than 95% of the fluoride from the precipitate (Fig. 3.9). Little advantage was gained by decreasing the volume or molarity of the ammonium hydroxide (run EBM-5). An increase in the metathesis rate, as indicated by the color change from green to black, was apparent when the ammonium hydroxide was warmed before use.

The high percentage of niobium recycled (7%; see Fig. 2.2) with the EBWR metathesis filtrates represents only 0.35 mole of niobic oxide per assembly and is probably caused by passage of very fine particles through the filter. New Pyrex filter funnels (medium pore size) were used for each flowsheet metathesis.

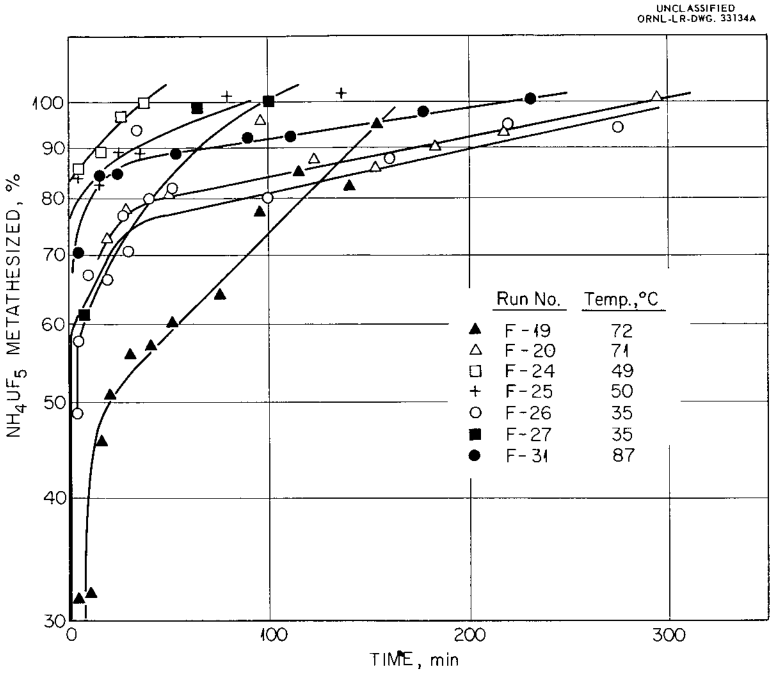
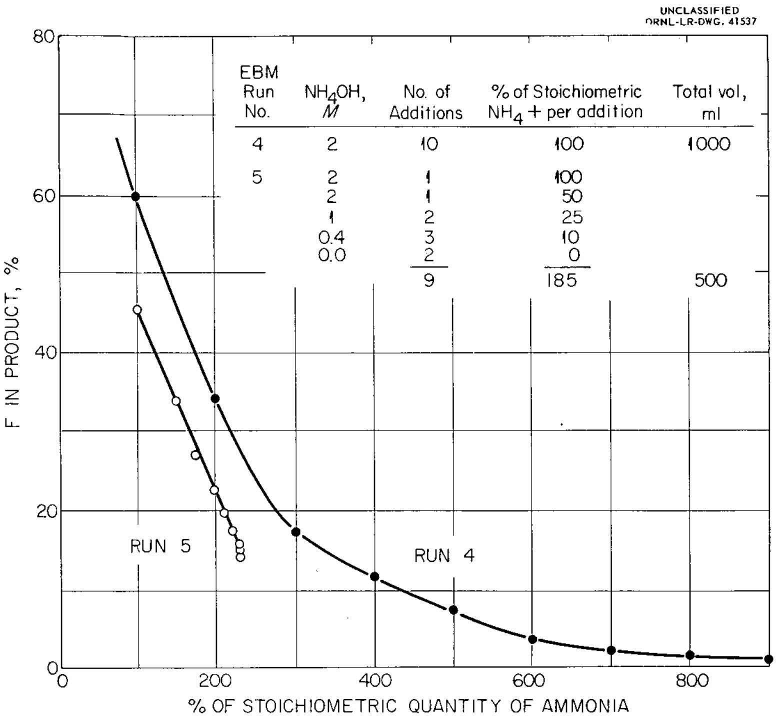


Fig. 3.8. Rate of metathesis of NH_4UF_5 with saturated ammonium hydroxide solutions.



EBM Run No.	NH_4OH, *M*	No. of Additions	% of Stoichiometric NH_4^+ per addition	Total vol, ml
4	2	10	100	1000
5	2	1	100	
	2	1	50	
	1	2	25	
	0.4	3	10	
	0.0	2	0	
		9	185	500

Fig. 3.9. Effect of repeated applications of ammonium hydroxide to drive the reaction $NH_4UF_5 \longrightarrow U(OH)_4 + 5\ NH_4F$.

Separation of the metathesis precipitate from the high-zirconium STR fuel by decantation of the supernatant did not appear feasible because of the slow settling rate of the hydrous zirconium oxide (Fig. 3.10). With high-uranium fuel decantation might be used since the chief product is the dense uranium oxide.

Washing of Hydrous Zirconium Oxide. The hydrous zirconium oxide product of eq. 6, the principal product obtained from the STR fuel, retained a large amount of fluoride, most of which was removed by washing with 100% of the amount of 1 M NH_4OH initially required for the reaction (Fig. 3.11). When the dissolution product was treated with 7.5 M ammonium hydroxide, using 300% of the stoichiometric amount required by eqs. 5 and 6 (Sect. 2.3), and the mixture stirred with ammonia gas for 0.5 hr at room temperature, the oxide precipitate was easier to wash free of fluoride than were precipitates brought down with a smaller excess or with less concentrated ammonium hydroxide. Approximately 40% of the fluoride was found in the filtrate from this step. Washing the oxide precipitate removed part of the remaining fluoride. Neither water nor more concentrated ammonium hydroxide washed the precipitate efficiently. With six washes, 85% of the fluoride was removed and with only two washes (recommended in the flowsheet), 65% was removed. In the flowsheet runs (Table 2.1) each wash contained only 50% of the ammonia initially required for reactions 5 and 6 rather than 100% as in the runs in Fig. 3.3, with no apparent decrease in washing efficiency. The uranium and zirconium "% recycle" figures in Table 2.1, based on six washes, are probably higher than will be obtained if only two washes are used.

Oxide Dissolution and Oxidation. In preliminary experiments with STR fuel, dissolution of the washed hydrous oxides after metathesis gave a stable solution of 1 M zirconium and 4 M HNO_3. Precipitation from this solution occurred only when the temperature was lowered slowly to -22°C. The hydrous oxides dissolve in less concentrated nitric acid, but the oxide solubility in these solutions has not been thoroughly investigated. Experimental work is being continued to determine the optimum concentration for the solvent extraction feed solution. The solubility of zirconyl nitrate in water was found to be about 3 M.

With EBWR fuel, the hydrous oxides after metathesis dissolve readily in nitric acid. Solutions of about 1.4 M uranium have been obtained without precipitation of zirconium compounds. However, no investigations were made of the stability of these solutions under reflux.

b. Direct Oxidation-Digestion

In two flowsheets for the STR- and the EBWR-type fuels (Figs. 2.1 and 2.2), complete dissolution was accomplished in 6 M NH_4F as described in Sect. 2.1. A mixed fluoride-nitrate solvent extraction feed solution was prepared by adding nitric acid to the ammonium fluoride solution after dissolution. Aluminum was also added to partially complex the large amount of fluoride, and, in the STR case, chromic acid was added to oxidize all uranium to U(VI).

Since the STR solvent extraction feed solution differs slightly from that produced by hydrofluoric acid dissolution[4] in that 1.4 M NH_4^+ is present, some preliminary stability tests were made. The following quantities of

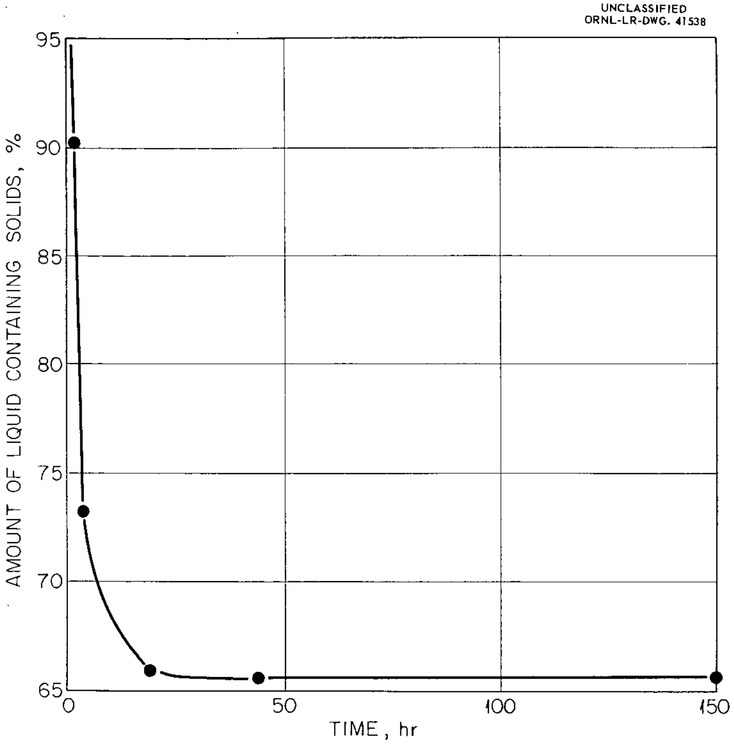


Fig. 3.10. Settling rate of hydrous zirconium oxide (0.5 M) in 3 M NH_4F-4 M NH_4OH solution at 25°C.

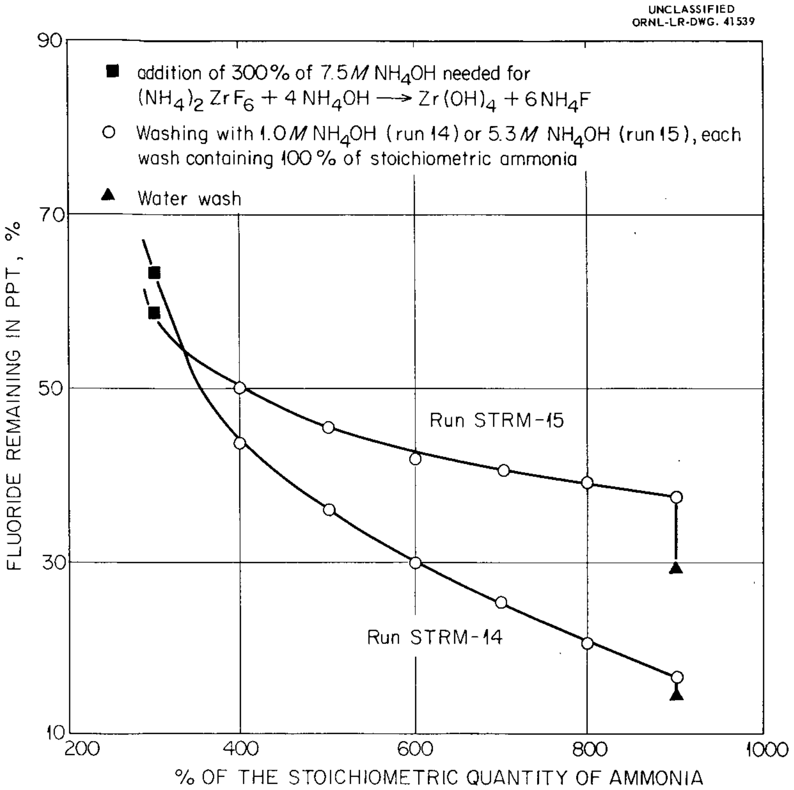


Fig. 3.11. Effect of ammonia concentration on the removal of fluoride from hydrous zirconium oxide.

materials were added to separate samples of the feed solution before precipitation occurred at 25°C: 17 moles of NH_4NO_3, 0.11 mole of hydrofluoric acid (36 M), 3.6 moles of $Al(NO_3)_3 \cdot 9H_2O$, per liter of feed solution. A sample of the solvent extraction feed solution was decreased in volume 47% by vacuum evaporation at 25-30°C during a period of 8 days before precipitation started. In another sample, precipitation started after a 10% volume reduction over three weeks. Several samples of the feed solution formed light precipitates upon standing for 10 weeks at room temperature. The temperature of the feed solutions can be lowered to -22°C before a reversible precipitation will occur immediately after preparation.

The stability of the EBWR feed solution obtained by adding nitric acid and aluminum nitrate after complete dissolution in 6 M NH_4F (oxidation-digestion step in Fig. 2.2, route b) depends on the nitric acid concentration (Table 2.3). In a solvent extraction feed solution of 5.0 M HNO_3, reversible precipitation occurred when the temperature was lowered to -30°C. At 3.0 M HNO_3, this temperature was -13°C. These solutions remained stable upon standing several weeks at room temperature.

3.3 Fused Ammonium Bifluoride (Biflex)[18] Process

The dissolution rate studies with fused ammonium bifluoride (Table 3.1) were all made in a large Pyrex test tube placed in an oil bath. Approximately 10 times the stoichiometric amount of ammonium bifluoride was used. The ammonium bifluoride was continually replenished as it evaporated. Many metals, alloys, and oxides commonly used in reactor fuels dissolve rapidly at 160-220°C. EBWR fuel dissolves completely in less than 1 hr and STR fuel in a few minutes. Fused ammonium bifluoride also rapidly dissolves the oxide coat that forms on Zircaloy-2 in contact with pressurized water.

In 33-hr tests in pure ammonium bifluoride at 220°C, the corrosion rates of 310 and 347 stainless steel, Monel, and Hastelloy C were 21.5, 15.6, 8.5, and 5.2 mils/month, respectively. Four-hour tests indicated that the corrosion rates are all approximately 10-fold lower at 190°C.

4.0 EXPLOSION HAZARD AND CORROSION PROBLEM WITH URANIUM-RICH ALLOYS

The most desirable way to prepare reactor fuels for solvent extraction is by dissolution in nitric acid when such dissolution is possible since the nitric acid solutions can go directly to solvent extraction after a minimum of feed adjustment.[1,2] Uranium-rich alloys such as the EBWR core will dissolve at satisfactory rates in nitric acid but explosions may occur.[12] The initial rates are lower than in mixed fluoride-nitrate solutions (Fig. 3.4) but the total dissolution times are about the same, 6-10 hr. During nitric acid dissolution, much of niobium remains undissolved on the surface, rather than forming the amorphous niobic oxide precipitate which greatly hinders dissolution in mixed fluoride-nitrate solution. This niobium-rich surface deposit can explode violently. Since corrosion increases with the amount of uncomplexed fluoride, and uncomplexed fluoride is required to prevent formation of explosive surface deposits with alloys such as the EBWR core alloy, the corrosion problem is unavoidable with these alloys in solutions such as mixed fluoride-nitrate solution used in the flowsheet in Fig. 2.3.

Table 3.1. Dissolution Rates in Fused Ammonium Bifluoride

Material	Duration of Test, min	Temp., °C[a]	Dissolution Rate, $mg/cm^2 \cdot min$
U	60	220	19
Th	10	160	9
Be	15	220	100
Zircaloy-2	1	160-220	1000
U-10% Si	1	160-220	1000
Nb	80	220	1.6
Al	15	220	0.2
86% U-10% Nb-4% Zr	15	160-220	9
90% U-10% Al	15	220	4
90% U-10% Mo (PRDC)	15	220	17
1% U-Zr Alloy (STR)	2.5[b]	160-220	250
93.5% U-5% Zr-1.5% Nb (EBWR)	15	220	210
93.5% U-5% Zr-1.5% Nb (EBWR)	21[b]	180	175
93.5% U-5% Zr-1.5% Nb (EBWR)	55[b]	160	99
Sintered UO_2 (PWR Blanket)	15	220	6
Sintered UO_2 (PWR Blanket)	420[b]	220	7.3
3.6% UO_2-96.4% ThO_2 (Consolidated Edison)	15	220	6
3.6% UO_2-96.4% ThO_2 (Consolidated Edison)	300[b]	220	7.5

[a] Reflux temperature = 220°C.

[b] Complete dissolution of a sample of nonirradiated reactor fuel.

Several cations which are strong fluoride-complexing agents in acid solutions (Table 4.1) are commonly found in nitric acid solutions used to reprocess spent fuels. The effect of these cations on the free fluoride concentration during dissolution, and therefore on corrosion rates and on the possibility of explosions, must be considered. Considerable uncertainty will exist in comparisons made on the basis of Table 4.1 because of effects caused by differences in ionic strength and other experimental conditions. Consequently, this table should be used only as a qualitative guide. The constant for the Zr (3,4) reaction in Table 4.1 ($ZrF_3^+ + HF \longrightarrow ZrF_4 + H^+$) was not found in the literature, but it is surely smaller than that of the Zr (2,3) reaction and is thought to be larger than that of the U (0,1) reaction ($UO_2^{++} + HF \longrightarrow UO_2F^+ + H^+$). The latter reaction has not been observed to have any effect on the explosions which occur during dissolution in mixed fluoride-nitrate solutions, while the Zr (3,4) reaction apparently has some effect on these explosions.[12] The constants given in Table 4.1 show that the fluoride is complexed approximately as well in a solution with a F/Zr mole ratio of 3 as in a solution with a F/Al ratio of 1. Thus, no aluminum was added as a complexing agent in the fluoride-recycle flowsheets when the final F/Zr mole ratio was less than 3 (Figs. 2.1 and 2.2, routes a). These constants also indicate that the flowsheet in Fig. 2.3, which calls for a final solution mole ratio of F/Al = 1 and F/Zr = 4.7, is bordering on a hazardously low concentration of uncomplexed fluoride. A decrease in the aluminum concentration in this flowsheet would be highly desirable if the results of corrosion tests now underway show that such a decrease will not cause excessive corrosion. The use of a solution mole ratio of F/Al = 1 has been known to result in an explosion on one occasion.[12] In this one run a small explosion occurred at solution mole ratios of F/Al = 1 and F/Zr = 4.3 during dissolution of the EBWR core alloy in a fluoride-nitrate mixture. The use of very dilute fluoride solution (0.076 M) was thought to be partly responsible for this explosion.

If nonhazardous alloys are dissolved in mixed fluoride-nitrate solutions, it may be desirable to keep the fluoride very well complexed to prevent excessive corrosion. However, even with nonhazardous alloys, considerable uncomplexed fluoride is generally required to obtain practical dissolution rates.[20]

Table 4.1. Comparisons of Complexing Power in Acid Solutions at 25°C Among Some Fluoride-complexing Agents[19]

(Highest Valence States)

Fluoride Association Reaction	log K
Zr(0,1)	5.8
Th(0,1)	4.7
Zr(1,2)	4.3
Al(0,1)	3.1
Zr(2,3)	2.8
Th(1,2)	2.8
Fe(0,1)	2.3
Zr(3,4)	2.2 ± 0.6
Al(1,2)	2.0
U(0,1)	1.6
Th(2,3)	1.5
Fe(1,2)	1.0
Al(2,3)	0.9

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