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MODIFIED ZIRFLEX PROCESS FOR DISSOLUTION OF 1-10% U-Zr ALLOY FUELS IN AQUEOUS NH_4F–NH_4NO_3–H_2O_2: LABORATORY DEVELOPMENT

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UNION CARBIDE CORPORATION
for the
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Chemical Development Section B

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ABSTRACT

A modified Zirflex process was developed in the laboratory for dissolution of 1-10% uranium-zirconium alloy fuels to produce a nitrate solution from which uranium can be recovered by conventional solvent extraction methods. A flowsheet is presented for dissolution of 7% uranium-zirconium alloy in 5.4 $\underline{M}$ NH_4F—0.33 $\underline{M}$ NH_4NO_3. Enough 1 $\underline{M}$ H_2O_2 is added continually during dissolution to yield 0.13 $\underline{M}$ H_2O_2 in the final solution, neglecting the amount reacting. Dissolution is complete in 1 hr. The solvent extraction feed is prepared by adding aluminum nitrate and nitric acid to the dissolver solution to yield a stable solvent extraction feed solution of 0.0075 $\underline{M}$ uranium, 0.25 $\underline{M}$ zirconium, 1 $\underline{M}$ aluminum, 2 $\underline{M}$ fluoride, and 1 $\underline{M}$ HNO_3. The off-gas is approximately 98.5% NH_3, 1% H_2 0.3% O_2, and 0.2% N_2. Conventional stainless steel such as 309SNb, Ni-o-nel, or Hastelloy F appears to be a suitable material of construction with corrosion rates varying from 0.1 to 3.0 mils/month.

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1.0 INTRODUCTION

This report describes laboratory work performed in the development of the Modified Zirflex process for dissolution of uranium-zirconium alloy fuels and the flowsheets based on this work. Complete dissolution of 1-10% uranium-zirconium alloys and feed preparation steps can apparently be carried out in equipment made from conventional construction material such as stainless steel.

A dissolution process is needed for the many uranium-zirconium alloy reactor fuels, such as the PWR seed,[1] which contain 1-10% uranium. The dissolution and uranium recovery process recently operating on a production scale at the Idaho Chemical Processing Plant can handle efficiently only the zirconium alloys containing less than about 1% U.[2,3] Desirable features sought in a new process include rapid dissolution rates, no precipitation (especially of uranium compounds), easily handled off-gas, and low corrosion rates. It is particularly desirable that the process be compatible with existing stainless steel dissolving equipment such as 309SNb. Explosions that occur during dissolution of uranium-zirconium alloys are limited to alloys containing much more uranium (at least 70 wt %)[4] than the 1-10% uranium alloys for which the process is designed.

A flowsheet that represents conditions suitable for fuels containing 1-10% uranium was developed in the laboratory in which 5.4 $\underline{M}$ NH_4F—0.33 $\underline{M}$ NH_4NO_3 is used to dissolve 7% uranium-zirconium alloy. Enough 1 $\underline{M}$ H_2O_2 is added continually during dissolution to yield 0.13 $\underline{M}$ H_2O_2 in the final solution, neglecting the amount reacting. A limitation for uranium-zirconium alloys containing less than 2% uranium was established for the process in that enough fluoride must be used to yield a final mole ratio of fluoride to dissolved zirconium (F/Zr) of at least 6.5. For uranium-zirconium alloys containing more than about 2% uranium, the limitation was established that enough fluoride must be used to yield a minimum final mole ratio of uncomplexed fluoride (i.e., fluoride in excess of the 6 moles complexed by each mole of zirconium) to uranyl ion of approximately 70. When this ratio was allowed to decrease below 70, a surface coat formed and prevented dissolution. This latter limitation restricts the practical application of the process to fuels containing less than about 10% uranium because of the large amount of fluoride needed to dissolve higher-uranium fuels.

The off-gas contains minor amounts of hydrogen and oxygen. Maximum corrosion rates in solution were 2.3, 0.8, and 1.7mils/mo in screening tests with Hastelloy F, 309SNb, and Ni-o-nel, respectively. These rates are 30, 10, and 30%, respectively, of the rates obtained in similar solutions in the absence of hydrogen peroxide.

The Zirflex process using ammonium fluoride solutions as a dissolvent for reactor fuel cladding is being developed at the Hanford Atomic Products Operation.[5] Additional development work has also been performed at ORNL.[6,7] The Zircaloy-2 cladding is dissolved from reactor fuel cores in 6 M NH_4F—1 M NH_4NO_3. Aqueous ammonium fluoride has been used as a dissolvent for uranium-zirconium alloys,[4,8] but uranium is precipitated as NH_4UF_5 during dissolution. Hydrogen peroxide mixed with hydrofluoric acid has been used in the dissolution of non-irradiated uranium-zirconium alloys[9] and a flowsheet for irradiated fuels developed in the laboratory.[10] The HF-H_2O_2 system has the disadvantage of high corrosion rates with most materials of construction.[10]

Further work will be required in developing a solvent extraction flowsheet for the process. The solvent extraction procedures will probably be similar to those in use at the Idaho Chemical Processing Plant. Extensive corrosion tests are underway to check the favorable results obtained in initial screening tests.

The laboratory work was performed by G. E. Woodall and D. M. Helton. Analytical work was performed by G. Wilson and A. D. Horton of the Analytical Chemistry Division. Corrosion tests were planned by W. E. Clark of the Chemical Technology Division and run by E. S. Snavely and co-workers of the Reactor Experimental Engineering Division.

2.0 FLOWSHEET

The flowsheet involves two rapid and simple operations, complete dissolution and feed preparation (Fig. 2.1). The fuel elements are placed in ammonium fluoride—ammonium nitrate solution, which is then heated to the boiling point. Hydrogen peroxide is added continually throughout dissolution to oxidize the insoluble U(IV) product of ammonium fluoride dissolution to the more soluble U(VI). The Zircaloy-2 cladding, as well as the uranium alloy core, dissolves completely and rapidly, tin dissolution being accomplished by hydrogen peroxide addition.

A hypothetical zirconium alloy fuel containing 7% uranium and 1.5% tin was selected to represent the 1-10% uranium-zirconium alloy fuel class for which the process was developed. The flowsheet, which is based on a 100-kg fuel charge, shows the approximate volumes needed. Minor modifications in the quantities of reagents used will be necessary to achieve the optimum flowsheet for any particular fuel in this class. For example, if the uranium content of the alloy being dissolved is less than 7%, the final F/Zr ratio can be decreased from 8.0 as shown in Fig. 2.1 to as low as 6.5 (for alloys containing about 2% or less uranium, see Sect. 3.1c). The small amount of tin present in a particular fuel may require addition of slightly more hydrogen peroxide than indicated in the flowsheet (Fig. 2.1 and Table 2.1), since these particular laboratory dissolutions were made with an unclad 7% uranium-zirconium alloy which contained no tin. Numerous runs were made, however,

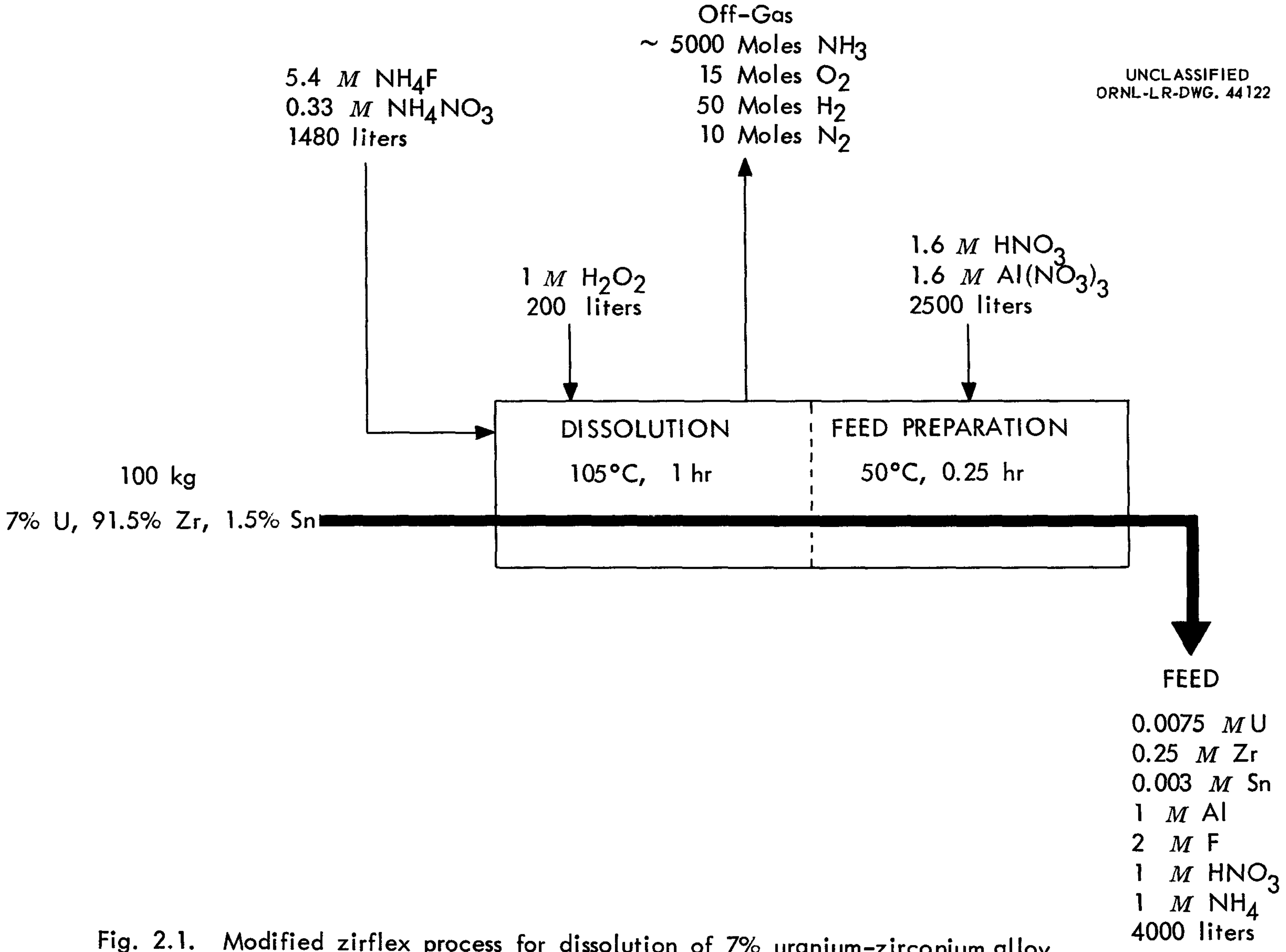

Fig. 2.1. Modified zirflex process for dissolution of 7% uranium-zirconium alloy in NH_4F - H_2O_2.

in which Zircaloy-2 (a zirconium alloy containing about 2% tin) and uranium-zirconium alloys clad in Zircaloy-2 were dissolved completely under conditions closely resembling those of Fig. 2.1. The maximum amount of hydrogen peroxide required to dissolved tin (13 moles in Fig. 2.1) is only a small fraction of that lost through decomposition and side reactions with hydrogen and ammonia (160 moles in Fig. 2.1).

The amount of fluoride (or the F/Zr ratio) used may be decreased if a cleanup dissolution is used or if a small residue from the dissolution step is dissolved during the feed preparation step. The most conservative flowsheet, from the viewpoint of simplicity of operation, safety from criticality incidents (i.e., no precipitation of uranium), and complete dissolution, is presented.

Table 2.1. Modified Zirflex Flowsheet Runs for Complete Dissolution of 7% Uranium-Zirconium Alloy

NH_4F: 5.35-5.43 M
Wt of fuel sections: 1.4-2.0 g (70 mils thick)
Final NH_4NO_3: 0.33 M, neglecting amount reacting

Run	H_2O_2 Used,[a] moles	H_2O_2 Excess over Stoichiometric,[b] %	Final F/Zr	Dissolution Time, min
20	221	640	7.99	40
28	142	375	8.01	40
29	183	510	8.00	58
30	191	535	7.99	54
32	187	525	8.00	75
34	92	210	7.90	31
35	108	260	7.90	39
38	177	490	7.87	60
40	90	200	7.99	60
41	114	280	7.98	52
42	173	480	7.99	74
43	218	630	7.99	66
44	219	630	7.99	65

[a] Minimum amount needed to keep solution yellow, scaled up to 100-kg run.

[b] Based on reaction $NH_4UF_5 + 2NH_4F + H_2O_2 \longrightarrow (NH_4)_3UO_2F_5 + 2HF$, i.e., on 30 moles of H_2O_2 per 100 kg of 7% uranium-zirconium alloy.

2.1 Dissolution and Feed Preparation

A 100-kg assembly of the 7% uranium-zirconium alloy fuel (70 mils thick) is completely dissolved in 1 hr in 1480 liters of refluxing 5.4 $\underline{M}$ NH_4F—0.33 $\underline{M}$ NH_4NO_3. A total of 200 liters of 1 $\underline{M}$ H_2O_2 is added in small amounts throughout dissolution to keep all uranium and tin in solution. Examples of several runs under flowsheet conditions are given in Table 2.1 . A final F/Zr mole ratio of at least 8 must be used to ensure complete dissolution of 7% uranium alloy (Fig. 2.2). The data of Fig. 2.2 were obtained in exploratory runs varying slightly from the flowsheet conditions and represent close to equilibrium conditions. The small amount of undissolved alloy cannot be dissolved by further refluxing or by adding more hydrogen peroxide. The scatter in results is well within the expected experimental and analytical error. A F/Zr ratio of less than 8 can probably be used if a cleanup dissolution is used since, for example, the F/Zr ratio must be increased from 7.6 to 8.0 (a 5% increase in the amount of fluoride used) to dissolve the last 1% of the fuel. It was also found that small undissolved residues (about 0.1%) from the dissolution step went into solution readily upon addition of nitric acid in the feed preparation step. Contacting a small amount of undissolved residue with nitric acid to decrease the amount of fluoride needed in the process is not hazardous because the 1-10% uranium-zirconium alloys do not enter into explosive reactions with nitric acid and, also, the large amount of fluoride prevents explosions.

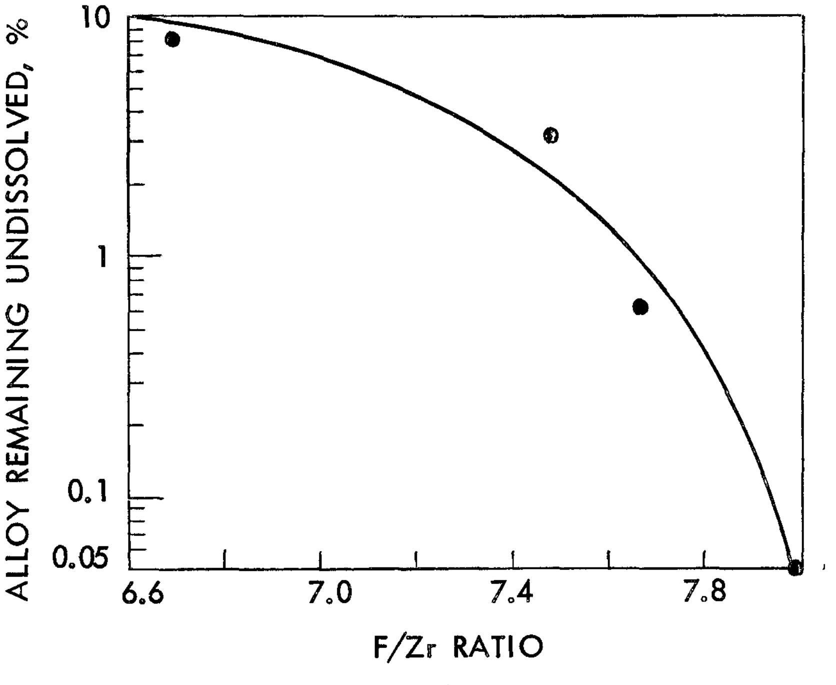

Fig. 2.2 Effect of final F/Zr mole ratio on amount of 7% uranium-zirconium dissolved in refluxing 5.4 M NH_4F—0.33 M NH_4NO_3. Enough 1 M H_2O_2 was added continually during dissolution to yield 0.13 M H_2O_2 in final solution, neglecting amount reacting.

The feed preparation involves addition of nitric acid and aluminum nitrate to provide salting strength and to complex fluoride ions to decrease corrosion of the container. This addition may be made without any previous cooling of the dissolver solution (see Sect. 3.2). The feed solution resembles the present Idaho Chemical Processing Plant[2] feed but differs somewhat because of the requirement of a higher final F/Zr mole ratio (8.0 vs 6.0 in the ICPP feed) after dissolution and because of the higher uranium concentration. This high F/Zr mole ratio requires addition of more aluminum as a fluoride-complexing agent upon acidification, since much of the highly corrosive fluoride is not complexed by zirconium. Thus, if the F/Zr mole ratio should be decreased as suggested above, the feed solution can be decreased in volume. As a guide in preparing the feed solution (corrosion tests have not yet been made), the formula $F = 4Zr + Al$ was used. An aluminum nitrate concentration of 1 $\underline{M}$ was selected as the upper limit because of stability limitations observed in similar feed solutions.[3] The feed solution can probably be concentrated slightly more than shown in the flowsheet, since this solution is stable for several weeks (Sect. 3.2). In processing uranium-zirconium alloys containing less than about 2% uranium, a final F/Zr mole ratio of only 6.5 is needed (Sect. 3.1c). In this case a feed solution almost identical with that of the Idaho Chemical Processing Plant can be produced.

2.2 Off-Gas Composition

The problem of major concern with the off-gas is the amount of oxygen (from peroxide decomposition) and hydrogen evolved because of the explosive potential of these gases in certain mixtures and the difficulty in removing these gases from the off-gas. The hydrogen evolved during dissolution of zirconium alloys in ammonium fluoride solutions can be almost completely oxidized to ammonia and water by adding ammonium nitrate to the ammonium fluoride solution.[5] In this work it was found possible to use the same technique to decrease hydrogen evolution during dissolution of uranium-zirconium alloys. Hydrogen peroxide oxidizes the hydrogen evolved during dissolution in ammonium fluoride solutions to water, but has the disadvantage that much oxygen is liberated by decomposition of the excess peroxide required. In the flowsheet runs enough ammonium nitrate was used to make the dissolver solution 0.33 $\underline{M}$ in NH_4NO_3, neglecting the amount used in reaction. This is 92% of the stoichiometric amount required to satisfy eqs. 3 and 4 (Sect. 2.3), the rest of the oxidation of hydrogen (about 150 moles) being performed by hydrogen peroxide.

Off-gas studies were made by collecting the gases over dilute nitric acid from runs made under flowsheet conditions with the exception that various concentrations and methods of adding ammonium nitrate were used. All ammonia and any water-soluble gases were removed by the nitric acid. The remaining gas was analyzed by gas chromatography for oxygen, hydrogen, and nitrogen, the only gases present in measurable quantities. Since the corrosion rates of the stainless steels are known to increase when ammonium nitrate is added to ammonium fluoride solutions,[6,11,12] attempts were made to use the minimum ammonium nitrate concentration that resulted in good conversion of hydrogen to ammonia and water. This was accomplished by adding only part of the ammonium nitrate initially and adding the remainder continually with the hydrogen peroxide throughout the dissolution period. Ammonia was used as a sweep gas before and after dissolution. The amount of ammonia evolved was calculated from eqs. 3 and 4 (see Sect. 2.3), making allowance for the hydrogen that was not converted to ammonia or water.

Under flowsheet conditions (Fig. 2.1) the off-gas contains well below the explosive concentration of hydrogen and oxygen, about 1% and 0.3%, respectively, and 0.2% nitrogen (Fig. 2.3a), the rest being ammonia. Unless future corrosion test results are less favorable than those of Sect. 3.3, all the nitrate should be added to the dissolver solution before dissolution starts to keep the hydrogen and oxygen evolution at a minimum. There apparently is little advantage in increasing the ammonium nitrate concentration above 0.33 M in the dissolver solution since the hydrogen evolution decreased only 60% and the oxygen evolution increased 36% as the ammonium nitrate concentration was increased from 0.3 to 0.5 M (Fig. 2.3b).

About 70% of the hydrogen peroxide probably reacts with hydrogen or ammonia to form water since the off-gas under flowsheet conditions contains only 0.3% oxygen (Fig. 2.3a); this is less than 20% of the oxygen that would be produced from decomposition to water and oxygen of all hydrogen peroxide not required for the oxidation of U(IV) to U(VI) (eq. 6). The quantity of hydrogen peroxide needed in actual processing will vary depending on the rate of its decomposition in solution, which is strongly affected by temperature and certain cations such as iron.[13] Comparison of a run in which no ammonium nitrate or hydrogen peroxide was present during dissolution (the off-gas was 31% H_2) with a run in which enough hydrogen peroxide was used to oxidize all U(IV) to U(VI) (the off-gas was 16% H_2) verifies the reaction in solution of hydrogen peroxide and hydrogen. The nitrogen content of the off-gas from these runs (1.7% and 8%, respectively) indicates that the hydrogen peroxide also oxidizes some ammonia to nitrogen and water.

2.3 Chemistry of the Process

The dissolution reactions of zirconium and uranium in ammonium fluoride solution are

$$6NH_4F + Zr \longrightarrow (NH_4)_2ZrF_6 + 4NH_3 + 2H_2 \qquad \text{(Refs. 5, 14)} \qquad (1)$$

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

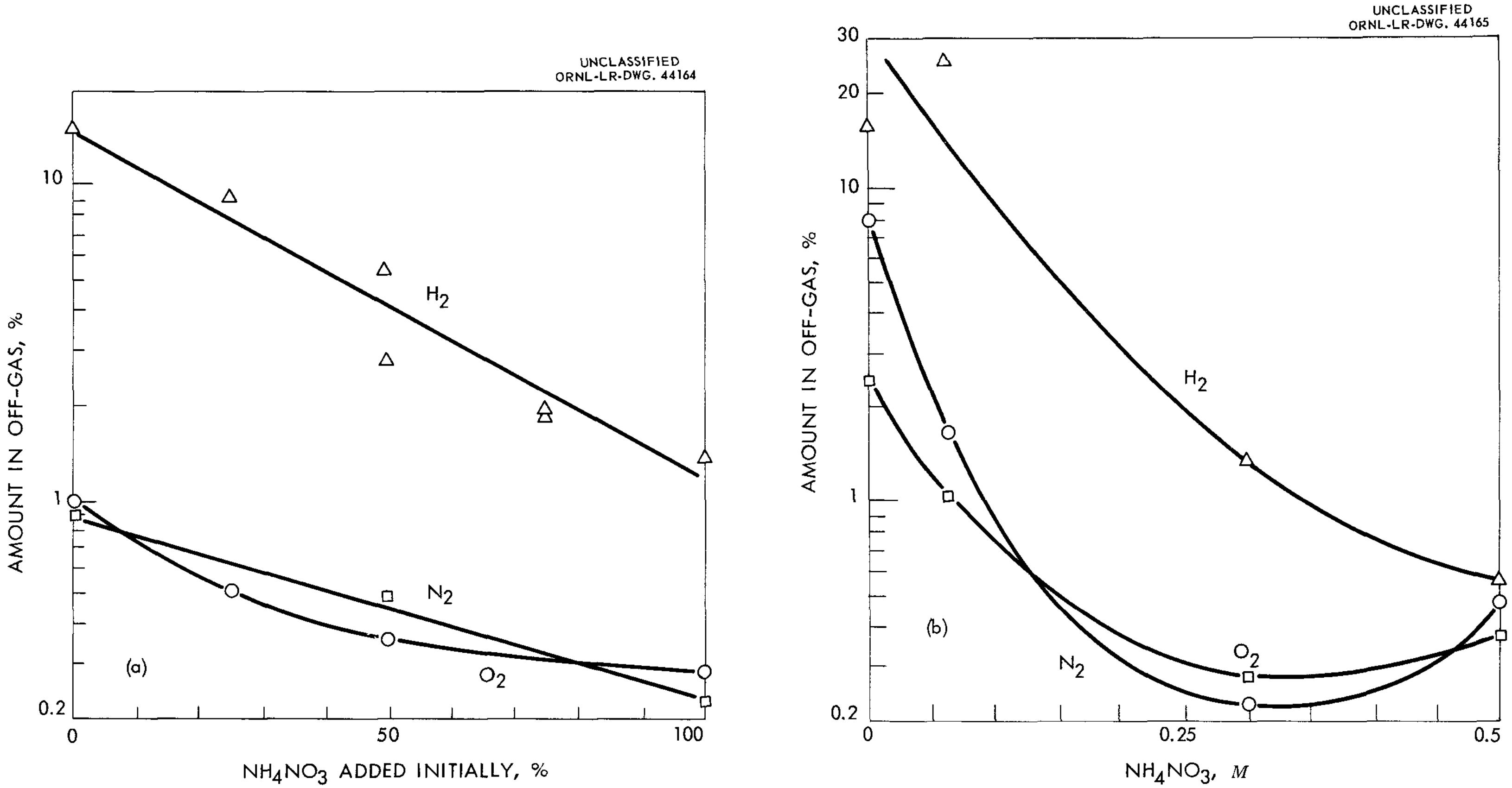

Fig. 2.3. Effect of (a) method of ammonium nitrate addition (final NH_4NO_3 = 0.33 *M*, neglecting amount reacting) and (b) ammonium nitrate concentration (100% added initially) on off-gas composition. Enough 1 *M* H_2O_2 added continually during dissolution to yield 0.13 *M* H_2O_2 in final solution, neglecting amount reacting. In each case the remainder of the off-gas is NH_3.

The $(NH_4)_2ZrF_6$, ammonium fluorozirconate, is soluble in water to about 1 mole/liter.[5,15] The NH_4UF_5, ammonium uranous fluoride, is an insoluble green solid.[4,5]

When ammonium nitrate is added to the dissolvent, essentially all the hydrogen evolved by reactions 1 and 2 is oxidized to ammonia or water:[5]

$$6NH_4F + 0.5\ NH_4NO_3 + Zr \longrightarrow (NH_4)_2ZrF_6 + 5NH_3 + 1.5\ H_2O \qquad (3)$$

$$5NH_4F + 0.5\ NH_4NO_3 + U \longrightarrow NH_4UF_5 + 5NH_3 + 1.5\ H_2O \qquad (4)$$

and some or all of the ammonium uranous fluoride, depending on the percent uranium in the alloy being processed, is oxidized to more soluble ammonium uranyl fluoride as follows:

$$NH_4UF_5 + 3H_2 + NH_4NO_3 \longrightarrow (NH_4)_3UO_2F_5 + H_2O \qquad (5)$$

Since the nitrate ion cannot oxidize U(IV) to U(VI) fast enough to prevent precipitation of NH_4UF_5, hydrogen peroxide is added to the dissolvent. One mole of hydrogen peroxide is required to oxidize 1 mole of U(IV):

$$NH_4UF_5 + 2NH_4F + H_2O_2 \longrightarrow (NH_4)_3UO_2F_5 + 2HF \qquad (6)$$

In experiments in which zirconium was dissolved in NH_4F-$(NH_4)_3UO_2F_5$ solution, the yellow solution turned green, indicating that U(VI) was being reduced to U(IV). The yellow color returned immediately upon addition of hydrogen peroxide. A reaction such as the following must occur:

$$Zr + (NH_4)_3UO_2F_5 + 6NH_4F \longrightarrow (NH_4)_2ZrF_6 + NH_4UF_5 + 6NH_3 + H_2 + 2H_2O \qquad (7)$$

A similar oxidation-reduction reaction is thought to cause the protective coat formation which prevents dissolution when the solution mole ratio of uncomplexed fluoride to U(VI) drops below 70 (Sect. 3.1c), but in this case the low concentration of uncomplexed fluoride may permit formation of zirconium oxide:

$$Zr + (NH_4)_3UO_2F_5 \longrightarrow ZrO_2 + NH_4UF_5 + 2NH_3 + H_2 \qquad (8)$$

Tetravalent uranium is known to be present in the protective coat because the coat is green. If zirconium oxide is present it must be hydrous and amorphous, since it can be dissolved easily by adding more fluoride and since it does not yield the x-ray pattern of crystalline zirconium oxide.

3.0 LABORATORY STUDIES

3.1 Dissolution Rates at the Boiling Points

a. Effect of Ammonium Fluoride Concentration and F/Zr Mole Ratio. When the ammonium fluoride concentration was decreased to nearly 4 M, dissolution rates were well above 10 mg/cm^2·min with 7% uranium-zirconium alloy until the mole ratio of fluoride to dissolved zirconium decreased to nearly 7 (Fig. 3.1). The rate increased only slightly when the ammonium fluoride concentration was increased to 6.5 M and decreased too rapidly with 3.3 M NH_4F unless enough fluoride was used to give a final F/Zr mole ratio greater than 7. Since it is desirable to dissolve to the lowest final F/Zr mole ratio possible, 4-6 M was chosen as the ammonium fluoride concentration range for the process. When ammonium nitrate was added to 5.4 M NH_4F (the concentration chosen for the flowsheet, Fig. 2.1), the dissolution rates approximately doubled until the F/Zr mole ratio decreased to 7. Ammonium uranous fluoride precipitated continually during dissolution of uranium-zirconium alloys in aqueous ammonium fluoride when no oxidizer was present, but the precipitate apparently had no effect on the dissolution rates.

b. Effect of Uranium Content of the Alloy. The dissolution rates decreased from 10-15 mg/cm^2·min to 5 mg/cm^2·min as the uranium content increased from 7 to 93.5 wt % (Fig. 3.2) in 6 M NH_4F. The 7% uranium-zirconium alloy dissolved at rates about 40% higher than did Zircaloy-2, probably because the tin in Zircaloy-2 (about 2%) impeded the dissolution slightly. The dissolution rates appeared satisfactory for processing zirconium alloys of concern, i.e., those containing 1-10% uranium.

c. Effect of Free F/U(VI) Mole Ratio. Dissolution rates of uranium-zirconium alloys in $NH_4F-H_2O_2$ decreased rapidly when the mole ratio of free fluoride (FF) to U(VI) in solution was decreased much below 100 (Fig. 3.3). These data were obtained by adding between 10^{-4} and 10^{-1} M UO_2F_2 to individual samples of 1, 2, and 6 M NH_4F—0.1 M H_2O_2 and measuring the instantaneous dissolution rate of 7% uranium-zirconium alloy. The rate inhibition phenomenon showed no dependence on the fluoride concentration.

During actual dissolution of uranium-zirconium alloys, the fluoride-complexing action of dissolved zirconium becomes important. For example, when enough 6 M $NH_4F-H_2O_2$ was used to yield a final mole ratio of F/Zr = 9.1 in dissolving 7% uranium-zirconium alloy, the dissolution rate suddenly decreased when the uranium concentration reached about 0.035 M (Fig. 3.4). Here the relations were

$$\underline{M}\ FF = 6 - CF + 2(\underline{M}\ UO_2F_2) = 6 - 6(6/9.1) + 0.07 = 2.11,$$

and

$$FF/U(VI) = 2.11/0.035 = 60$$

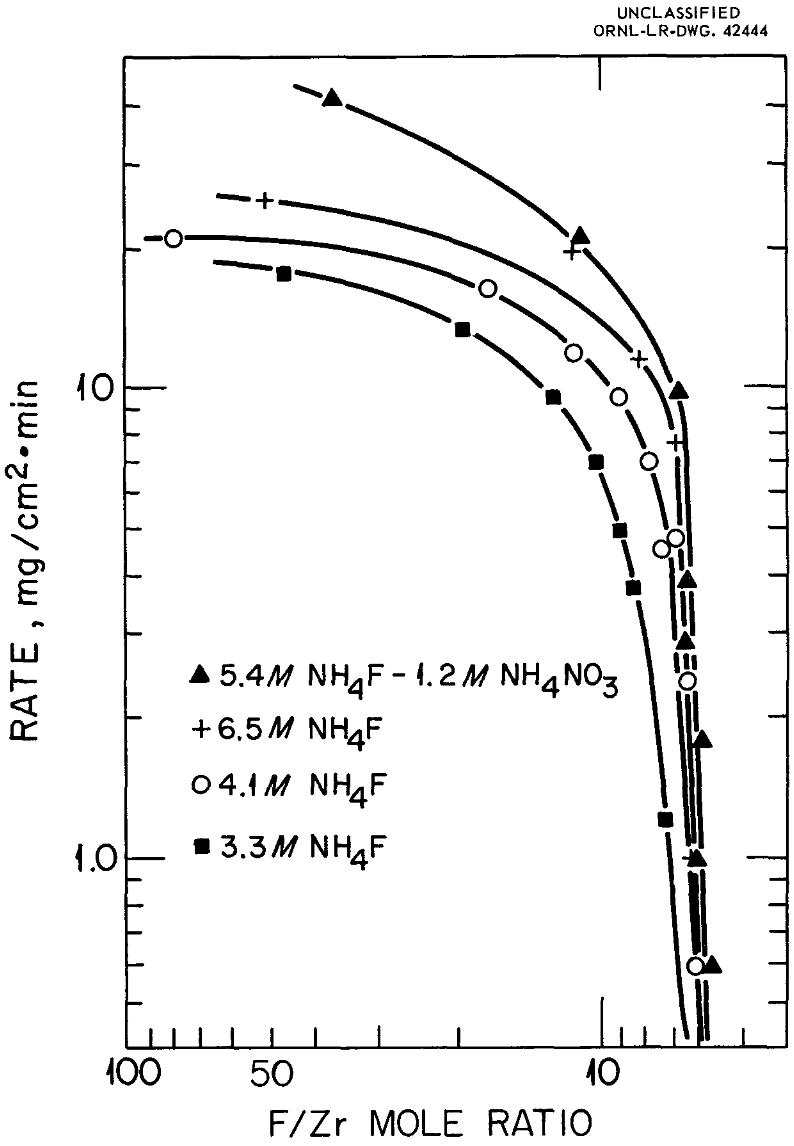

Fig. 3.1. Dissolution of 7% uranium-zirconium alloy in ammonium fluoride solutions.

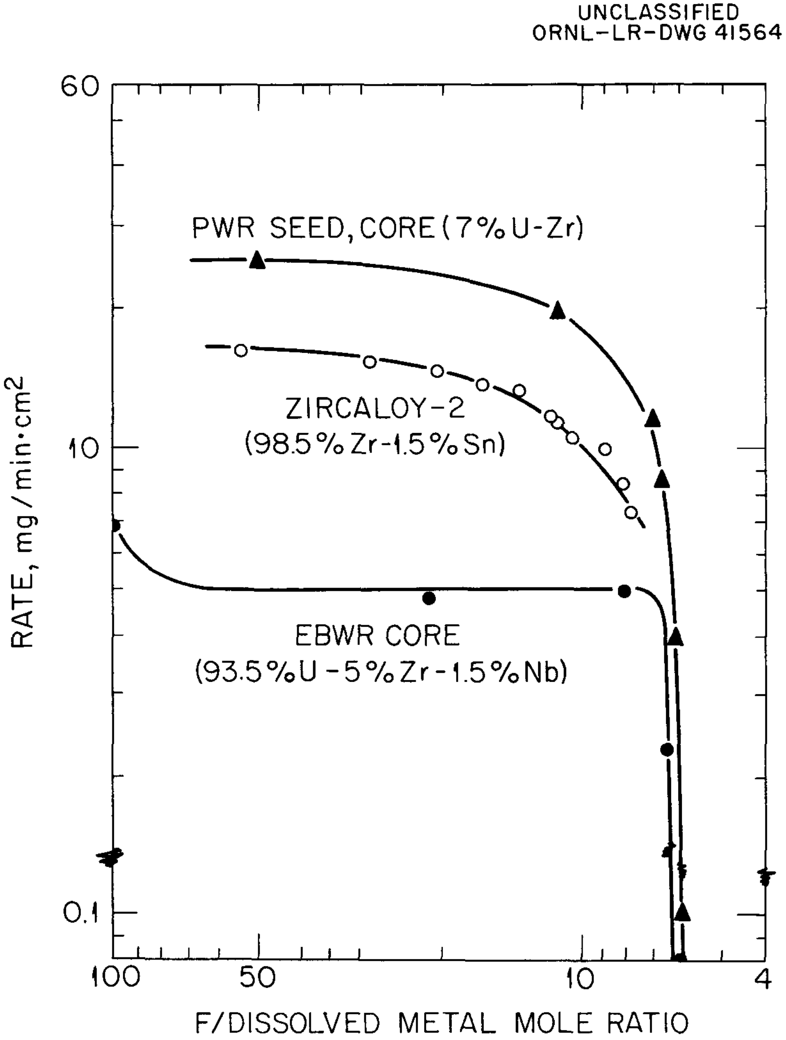

Fig. 3.2. Dissolution of zirconium alloys in 6 *M* NH_4F.

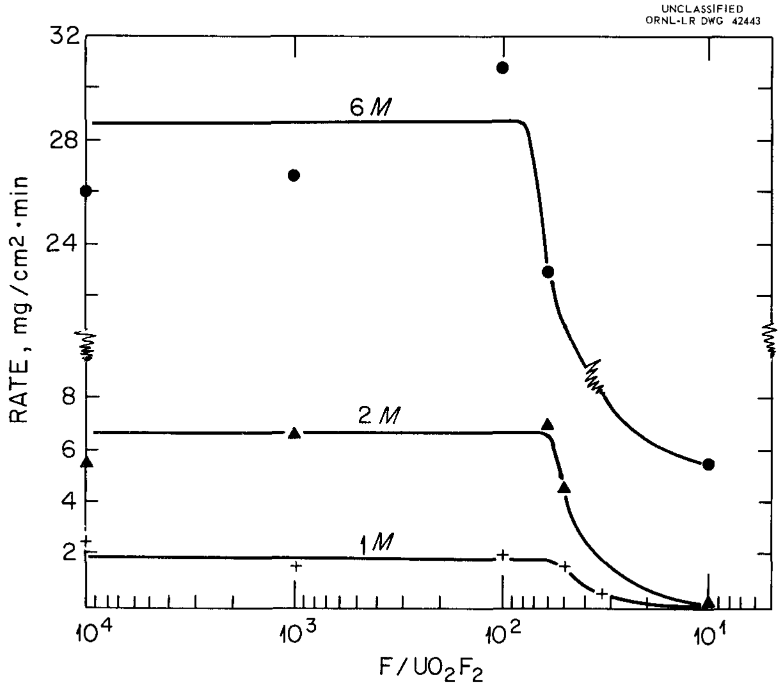

Fig. 3.3 Dependence of 7% uranium-zirconium dissolution rate in refluxing 1 - 6 *M* NH_4F - 0.1 *M* H_2O_2 on the F/UO_2^{++} mole ratio; 3 - 10 min studies.

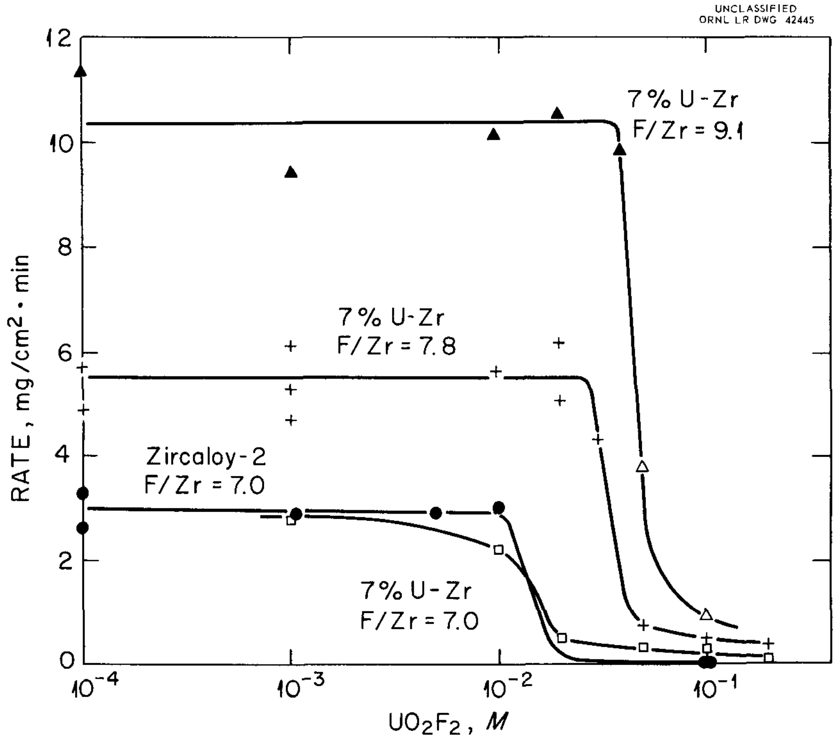

Fig. 3.4. Dissolution rates in 6 *M* F^- - 0.1 *M* H_2O_2 - UO_2F_2; 10 min rate studies, uncomplexed F^- present as NH_4F.

where CF refers to the complexed fluoride and is calculated by assuming that each mole of dissolved zirconium effectively complexes 6 moles of fluoride. Thus, as less fluoride is used (i.e., at lower final F/Zr mole ratios) the amount of U(VI) that can be tolerated decreases. At F/Zr mole ratios of 7.8 and 7.0, only about 0.03 M and 0.01 M U(VI) can be tolerated, respectively, if dissolution is to be complete (Fig. 3.4). Zircaloy-2 behaves similarly to 7% U-Zr alloy, showing that the uranium in the alloy has little effect on the rate decrease.

For complete dissolution of 7% uranium-zirconium alloy in 5.4 M NH_4F, it was necessary to add enough fluoride to yield a final F/Zr mole ratio of ≥ 8 (Fig. 2.2). Here

$$FF = 5.4 - CF = 5.4 - 6\,(5.4/8) = 1.35$$

and

$$FF/U(VI) = 1.35/0.02 = 68$$

The final dissolver solution in Fig. 2.1 contains 0.02 M U(VI). The need for a slightly higher final FF/U(VI) mole ratio during flowsheet runs than predicted from the instantaneous rate data of Figs. 3.3 and 3.4 can be explained by the fact that the protective surface coat has much more time to build up during the flowsheet runs.

It is apparent that the limitation which is important for uranium-zirconium alloys containing less than 2% uranium, the final F/Zr mole ratio, does not govern the process with high uranium-zirconium alloys, where the final FF/U(VI) mole ratio is the limiting parameter. If the limiting minimum values for these parameters are assumed to be F/Zr = 7 and FF/U(VI) = 70, the minimum uranium composition at which the second parameter becomes important can be calculated. This calculation shows 3.6 wt % uranium-zirconium alloy and, if a final F/Zr mole ratio of 6.5 is desired, an alloy being completely dissolved must contain less than 1.8 wt % uranium.

d. Effect of Ammonium Nitrate on Uranium Dissolution. Since 1 M NH_4NO_3 in 6 M NH_4F effectively oxidizes and dissolves the tin from Zircaloy-2,[5] ammonium nitrate could probably also oxidize a small amount of U(IV) to U(VI) during dissolution. The maximum uranium content at which ammonium nitrate can be used to achieve precipitate-free dissolution was not determined. In one run in which a Zircaloy alloy containing about 2% uranium was dissolved in 5.4 M NH_4F—0.3 M NH_4NO_3, a small amount of precipitate, probably NH_4UF_5, was formed. The precipitate dissolved when hydrogen peroxide was added. Initial corrosion tests (Sect. 3.3) indicated the desirability of using hydrogen peroxide as a corrosion inhibitor for the iron alloys, even in cases where the peroxide is not required to oxidize U(IV) to U(VI). The corrosion rates with Monel, however, were increased 6-8 times by the addition of 0.03 M H_2O_2 to 6 M NH_4F—0.3 M NH_4NO_3.

e. Tin and Niobium. Rate studies on tin dissolution in 5 M NH_4F—H_2O_2 at 13°C showing initial rates of nearly 0.2 mg/cm^2·min with 4 M H_2O_2 have been reported previously.[10] These rates were several times higher than the rates in ammonium fluoride—ammonium nitrate solutions, in which all tin from Zircaloy-2 is readily dissolved.[5] In laboratory experiments Zircaloy-2 always dissolved completely in ammonium fluoride—hydrogen peroxide.

Niobium does not dissolve rapidly in ammonium fluoride solutions. In 30-min tests in refluxing 6 M NH_4F, no measurable dissolution occurred. A dissolution rate of 0.03 mg/cm^2·min was observed in each 30-min study with refluxing 6 M NH_4F—1 M H_2O_2, 6 M NH_4F—5 M H_2O_2 and 6 M NH_4F—0.3 M NH_4NO_3—1 M H_2O_2.

3.2 Stability of the Dissolver and Solvent Extraction Feed Solutions

Care must be taken to avoid precipitation in both the Modified Zirflex dissolver solution and the solvent extraction feed solution. Precipitation of ammonium fluorozirconate has been observed upon cooling of Zirflex dissolver solutions, which resemble closely the dissolver solution of Fig. 2.1.[6,7] In the Idaho Chemical Processing Plant STR process,[2] in which the solvent extraction feed solution resembles that of Fig. 2.1, the aluminum, zirconium, and fluoride concentrations must be maintained within a narrow range to avoid precipitation.[2,3]

The solubility of the zirconium dissolution product, $(NH_4)_2ZrF_6$, is depressed by free fluoride ion.[15] Therefore, during most of the dissolution process, the ammonium fluorozirconate product would precipitate rapidly if the solution temperature should be decreased because much of the free fluoride ion would not have been complexed by zirconium. It was observed that this precipitation may start at temperatures as high as 90°C. This ammonium fluorozirconate precipitate redissolves rapidly at temperatures above 90°C. Therefore the flowsheet (Fig. 2.1) recommends maintaining the dissolver solution at reflux until the feed preparation step.

The solubility of the uranium dissolution product, $(NH_4)_3UO_2F_5$, is also depressed by free fluoride ion[16] and increases greatly with increasing temperature. At the boiling point a small amount of $(NH_4)_3UO_2F_5$ precipitation from a 0.02 M uranium solution (the concentration in the final dissolver solution, Fig. 2.1) was observed when the free fluoride concentration was increased to 6 M. Since the free fluoride concentration in the final dissolver solution is only 1.3 M, the uranium dissolution product will not precipitate from the warm solution. The solubility of $(NH_4)_3UO_2F_5$ at 25°C is only 0.002 M in 6 M NH_4F.[16] The apparently large temperature dependence of the $(NH_4)_3UO_2F_5$ solubility is an additional reason for keeping the dissolver solution hot until nitric acid is added in the feed preparation step. The uranyl ion is very soluble in the acid solution, even at room temperature.[17]

After dissolution of 7% uranium-zirconium alloy is complete, 25% of the fluoride still remains uncomplexed by the dissolved zirconium. This free fluoride depresses the ammonium fluorozirconate solubility sufficiently to cause precipitation in 15 min at 25°C. The final dissolver solution is stable indefinitely at temperatures of 60°C or higher.

The solvent extraction feed solution (Fig. 2.1) is stable for as long as 1 hr under reflux, but heavy precipitation occurs with further refluxing. If the nitric acid concentration is decreased to 0.5 M, precipitation occurs immediately when the boiling point is reached. Solutions at both 0.5 and 1.0 M HNO_3 have been stored for several weeks at 25°C and 1 week at 35°C without precipitation.

3.3 Corrosion Tests

Maximum corrosion rates in solution were 2.3, 0.8, and 1.7 mils/mo in screening tests with Hastelloy F, 309SNb, and Ni-o-nel, respectively (Table 3.1). A hydrogen peroxide concentration of 0.03 M was arbitrarily chosen as the amount present in the dissolver solution at any instant during dissolution so that evaluation of corrosion rates of several prospective construction alloys could be started. This concentration corresponds to 22% of the total amount of peroxide recommended in the flowsheet. The highest corrosion rates are expected in the dissolver solution before any zirconium has been dissolved. To obtain the maximum expected corrosion rates, refluxing 6 M NH_4F—0.3 M NH_3NO_3—0.03 M H_2O_2 was used in the tests. These early screening results must be confirmed by careful, long-term tests. A comparison of the results with those obtained in the absence of hydrogen peroxide indicates that the hydrogen peroxide decreases corrosion, by factors up to 10, of all the materials tested except Monel (Table 3.1). This result with Monel contrasts with the initial corrosion rates observed in refluxing 6 M NH_4F—0.003 M H_2O_2, in which Monel corroded at rates of less than 1 mil/mo in 24-hr tests. A solution of 6 M NH_4F was chosen instead of the 5.4 M NH_4F recommended in the flowsheet so that the results might be compared with corrosion results in the Zirflex process (6 M NH_4F—1 M NH_4NO_3). The corrosion rates in 6 M NH_4F—0.3 M NH_4NO_3 were found to compare closely with those in 6 M NH_4F—1 M NH_4NO_3 and 6 M NH_4F—0.5 M NH_4NO_3.[6,11,12]

Table 3.1. Corrosion Rates in the Modified Zirflex Process, Refluxing 6 M NH_4F-0.3 M NH_4NO_3, with and without 0.03 M H_2O_2

Material	Contact Time,[a] hr	Corrosion Rate, mils/month		
		Vapor	Interface	Solution
Hastelloy F	3	0.07,[b] 0.7[c]	7,[b] 0.7[c]	7.3,[b] 2.3[c]
	6	0.4, 0.4	5.3, 0.8	7.1, 1.7
	9	0.4, 0.4	3.8, 0.7	5.0, 1.4
309SNb	3	1.2, 0.7	9.0, 1.1	8.7, 0.7
	6	0.6, 0.1	6.2, 0.9	6.1, 0.6
	9	0.3, 0.1	4.6, 1.0	4.6, 0.8
Ni-o-nel	3	1.4, gain	9.6, 3.3	6.0, 0.8
	6	0.5, gain	7.5, 2.0	5.9, 1.0
	9	0.2, gain	6.6, 2.1	4.8, 1.7
Monel	3	1.6, g	6.3, 69	9.3, 77
	6	2.4, g	13.0, 73	15.1, 91
	9	1.8, -	10.4, -	12.4, -

[a] Solution changed each 3 hr.

[b] First set of data in each column obtained without 0.03 M H_2O_2 in solution.

[c] Second set of data in each column obtained with 0.03 M H_2O_2 in solution.

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