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Chemistry-Separation Processes
for Plutonium and Uranium
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DEJACKETING OF ZIRCALOY CLAD FUEL ELEMENTS WITH AMMONIUM FLUORIDE SOLUTIONS - INTERIM PROGRESS REPORT

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By

J. L. Swanson

Chemical Research
Chemical Research and Development Operation

April 15, 1957

HANFORD ATOMIC PRODUCTS OPERATION
RICHLAND, WASHINGTON

Work performed under Contract No. W-31-109-Eng-52 between the Atomic Energy Commission and General Electric Company

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TABLE OF CONTENTS

Page

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DEJACKETING OF ZIRCALOY CLAD FUEL ELEMENTS WITH AMMONIUM FLUORIDE SOLUTIONS - INTERIM PROGRESS REPORT

I. INTRODUCTION

One of several approaches under consideration for increasing the maximum operable temperature of a production reactor involves the use of zirconium alloy cladding on the fuel elements. Fuel elements clad in zirconium alloys have also been proposed for the Plutonium Recycle Program demonstration reactor. Processing such fuels in the existing Hanford separations plants poses a number of problems, however. These plants were designed to process aluminum-clad fuels by means of techniques employing aqueous nitrate systems, and the stainless steel equipment required for handling nitrate solutions would not be appropriate for the media (e.g., hydrofluoric acid) normally used for dissolving zirconium and its alloys.

With these incentives an experimental program was undertaken with the objective of devising a procedure which would permit selective dissolution of Zircaloy-2* cladding from fuel materials of interest. In the case of many of the fuels under consideration for application at Hanford and elsewhere, the fuel material exposed by such a head-end jacket dissolution step would be readily soluble in nitric acid and subsequent chemical processing could be accomplished via proven technology.

The preliminary studies summarized in this report indicate a high degree of technical feasibility for accomplishing dissolution of Zircaloy-2 cladding in stainless steel equipment by use of aqueous solutions of ammonium fluoride as the dissolving medium. In view of the encouraging nature of the findings to date and the fact that such a means for dissolving Zircaloy-2 jackets would have applicability to the reprocessing of many

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*Zircaloy-2 is a zirconium alloy having the following nominal composition: 1.5 wt per cent tin, 0.15 wt per cent iron, 0.10 wt per cent chromium and 0.05 wt per cent nickel.

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reactor fuels in addition to those contemplated for Hanford use, the preliminary findings are presented in this interim progress report.

Experimental work is still in progress and has as an early objective the establishment of a firm flowsheet which would enable fuels clad in Zircaloy-2 to be processed in existing Hanford separations plants with little or no revision of equipment.

II. SUMMARY

Experimental findings to date provide considerable basis for optimism that chemical decladding procedures employing aqueous ammonium fluoride solutions as the dissolving medium can be applied to removal of Zircaloy-2 jackets from reactor fuels in conventional stainless steel equipment. Results which are of particular interest include the following.

1. The rate of dissolution of Zircaloy-2 in boiling solutions of ammonium fluoride increases essentially linearly with fluoride ion concentration but is affected relatively little by hydrogen ion concentration, being a factor of about four greater at a pH of 5.5 than at a pH of 8.8. Mixtures of potassium and ammonium fluorides at a total concentration of one molar show decreased effectiveness in dissolving Zircaloy-2 when the potassium ion concentration is increased above 0.5 molar. In experiments involving dissolution of Zircaloy-2 in boiling six molar ammonium fluoride, a reaction time of one hour is sufficient for the dissolution of a thickness of thirty mils to a final zirconium concentration of about one molar.

2. The data thus far obtained are consistent with a dissolution mechanism as represented by the following equations:

$$Zr(s) + 6\,F^{-} + 4H_2O \longrightarrow ZrF_6^{=} + 2H_2(g) + 4OH^{-} \qquad (1)$$

$$4NH_4^{+} + 4OH^{-} \rightleftharpoons 4NH_4OH \rightleftharpoons 4NH_3(g) + 4H_2O \qquad (2)$$

As indicated in equation (2), volatilization of ammonia appears desirable since otherwise the pH would increase and the reaction rate decrease as the reaction proceeded.

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3. Although capable of dissolving Zircaloy-2 at a rapid rate, boiling four molar ammonium fluoride corrodes types 304 L or 347 stainless steels at rates of less than 5 x 10^{-4} inches per month. Cycling 304 L and 347 stainless steels from boiling four molar ammonium fluoride to boiling fourteen molar nitric acid does not appear to increase the corrosion rate in either medium.

4. Uranium metal is attacked much less rapidly than Zircaloy-2 by ammonium fluoride solutions. Laboratory experiments indicate that a small amount of uranium dissolves (as uranium IV) in simulated jacket solutions at the boiling point but that the bulk of this dissolved uranium precipitates as a green solid on cooling the solution to room temperature. This solid can be rendered nitric acid soluble and presumably free of fluoride by treatment with hot sodium hydroxide solution and washing with water.

A laboratory experiment testing a tentative dejacketing flowsheet resulted in a total uranium loss of only about 0.1 per cent even under conditions of a substantially higher solution to uranium metal ratio than would be expected in a plant dejacketing operation. Sintered uranium dioxide is attacked even less rapidly than uranium metal by ammonium fluoride solutions.

5. Zirconium concentrations of the order of one molar appear easily attainable by the dissolution of Zircaloy-2 in ammonium fluoride solutions. The solubility of zirconium in these solutions increases as the fluoride to zirconium mole ratio decreases to six.

III. EXPERIMENTAL DETAILS AND RESULTS

A. Dissolution of Zircaloy-2 in Ammonium Fluoride Solutions

Dissolution rates were measured by immersing coupons of Zircaloy-2 of known weight and surface area in boiling solutions contained in pyrex Erlenmeyer flasks. A condenser of the "cold finger" type was inserted in the neck of the flask to reduce evaporative loss. The coupons were removed at intervals, rubbed with a damp paper towel to remove the

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loose black coating (presumably arising from the tin in Zircaloy-2), and were then dried and weighed. Dissolution rates reported as mils/hour were computed from the measured weight loss on the assumption that dissolution occurs uniformly on all exposed surfaces. The dissolution rate is thus related to the weight loss by the expression:

$$\text{Dissolution rate (mils/hr)} = 3.7\ (\text{wt loss in mg})/(\text{time in min})(\text{area in cm}^2).$$

The assumption of uniform attack of the Zircaloy coupons is considered appropriate since very little pitting attack was observed. In all cases the dissolution rates were computed on the basis of the original surface area of the coupon. The pH measurements were made at room temperature employing a Beckman Model H-2 meter fitted with glass and calomel electrodes.

For simplicity in visualizing the results, the rate of dissolution of the zirconium as the reaction proceeded was plotted against the concentration of zirconium in the solution. Two methods of presentation of the data are used in this report. In the first, used in Figure 1, the dissolution rate plotted as the ordinate is the average rate of dissolution over the time interval required for the zirconium concentration in the solution to increase from the initial value of zero to the value plotted as the abscissa. In the second method, employed in Figure 2, the dissolution rates and zirconium concentrations are average values computed for the separate intervals of attack. The zirconium concentrations used in these plots were calculated from the measured weight loss and the initial volume of the solution. Since some evaporation occurred in these experiments, the concentration values reported are actually lower than the true values. The error introduced by the use of the zirconium concentration so calculated was unimportant except during the later stages of experiments employing long reaction times. In these latter experiments the final volume was generally about seventy-five per cent of the initial volume.

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1. Effect of Ammonium Ion Concentration

Early experiments indicated that whereas Zircaloy-2 is readily dissolved by solutions of ammonium fluoride, it is attacked only very slowly by solutions of potassium fluoride. In an effort to determine the reason for this, a series of experiments was done with mixtures of ammonium and potassium fluorides at a constant total fluoride concentration of one molar at an initial pH of 6.6 (adjusted by addition of hydrochloric acid). The results of these experiments are presented in Figure 1, the rate of dissolution being plotted against the zirconium concentration. It is seen that extrapolation of the curves to zero zirconium concentration gives roughly the same value in each instance even though the rate of dissolution decreased much more rapidly with increasing zirconium concentration in the solutions containing the higher concentrations of potassium ion. It was also observed that the Zircaloy coupons were covered with a tenacious dark coating after exposure to the solutions containing high concentrations of potassium ion, but not after exposure to the solutions containing high concentrations of ammonium ion.

2. Effect of Fluoride Ion Concentration

To determine the effect of fluoride ion concentration on the rate of dissolution of Zircaloy-2 in ammonium fluoride systems, experiments were done at a constant ammonium ion concentration of two molar and a constant initial pH of 6.8 (adjusted by addition of sodium hydroxide). The fluoride ion concentration was varied at constant ionic strength and ammonium ion concentration by substituting ammonium chloride or ammonium nitrate for ammonium fluoride. Rates of dissolution at zero zirconium concentration were estimated by extrapolation as before. The results of these experiments are presented in Table I. It is seen that, for a given fluoride concentration, a higher rate of dissolution was obtained with mixtures of ammonium fluoride and chloride than with mixtures of ammonium fluoride and nitrate. It should be noted, however, that Zircaloy-2 was not attacked by a boiling ammonium chloride solution in the absence of fluoride

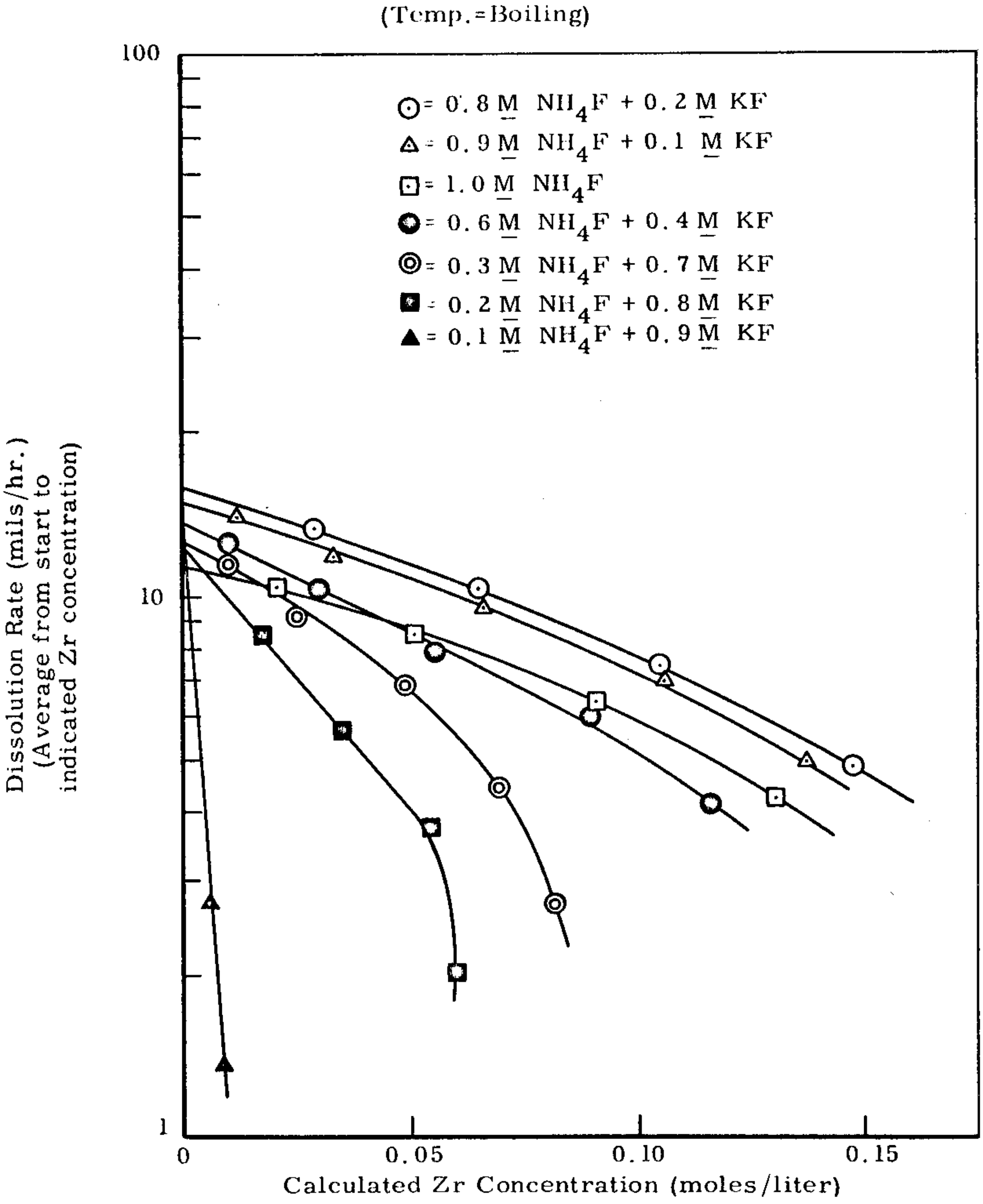

FIGURE 1

RATE OF DISSOLUTION OF ZIRCALOY-2
IN NH$_4$F - KF MIXTURES

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ion. These data indicate that the initial rate of dissolution of Zircaloy-2 is proportional to the fluoride ion concentration raised to a power of about 0.8. Additional work encompassing a wider concentration range will be necessary to ascertain accurately the order of the dissolution reaction in fluoride ion, however.

TABLE I

Effect of Fluoride Ion Concentration on the Rate of Dissolution of Zircaloy-2

(Temperature = Boiling)

$M NH_4^+$	$M F^-$	$M Cl^-$	$M NO_3^-$	Rate of Dissolution at Zero Time* (mils/hr)
2.0	2.0	--	--	27
2.0	1.0	1.0	--	18
2.0	1.0	--	1.0	13
2.0	0.5	1.5	--	11
2.0	0.5	--	1.5	8.0
2.0	0.25	1.75	--	6.0
2.0	0.25	--	1.75	4.6

* Zero zirconium concentration.

3. Effect of pH

The conditions and results of the experiments done to determine the effect of pH on the rate of dissolution of Zircaloy-2 in boiling ammonium fluoride solutions are shown in Table II.

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TABLE II

Effect of pH on the Rate of Dissolution of Zircaloy-2

(Temperature = Boiling)

Solution	Initial pH	At end of first interval MZr	At end of first interval pH	Average rate of dissolution during first interval (mils/hr)
1.0 $\underline{M}NH_4F$+1.0 $\underline{M}NH_4OH$	8.8	0.02	8.0	5.9
1.0 $\underline{M}NH_4F$+1.0 $\underline{M}NH_4NO_3$+0.002 $\underline{M}NaOH$	6.8	0.01	---	13
1.0 $\underline{M}NH_4F$+1.0 $\underline{M}NH_4NO_3$+0.16 $\underline{M}HNO_3$	5.5	0.01	5.9	23

It is seen that, over the range studied, variation of the hydrogen ion concentration has little effect on the rate of dissolution; increasing the concentration of hydrogen ion by a factor of greater than one thousand increased the rate of dissolution by a factor of only four.

4. Effect of Ammonium Fluoride Concentration

In Figure 2 are presented the results of experiments in which the rate of dissolution of Zircaloy-2 was measured at various concentrations of ammonium fluoride. In this figure the average rate of dissolution during the various intervals is plotted against the average zirconium concentration during the interval. It is seen that the rate of dissolution at zero zirconium concentration increases fairly regularly with increased ammonium fluoride concentration up to about six molar. At higher concentrations the shape of the experimental curves make an accurate extrapolation to zero zirconium concentration impossible but it is evident that, into solutions containing moderate amounts of zirconium, the rate of dissolution is greater with six molar ammonium fluoride than with eight molar, which in turn is greater than with ten molar.

In the experiments with ammonium fluoride concentrations of six molar or less, it is seen that the rate of dissolution continually decreases as the concentration of zirconium in the solution increases. In Figure 3,

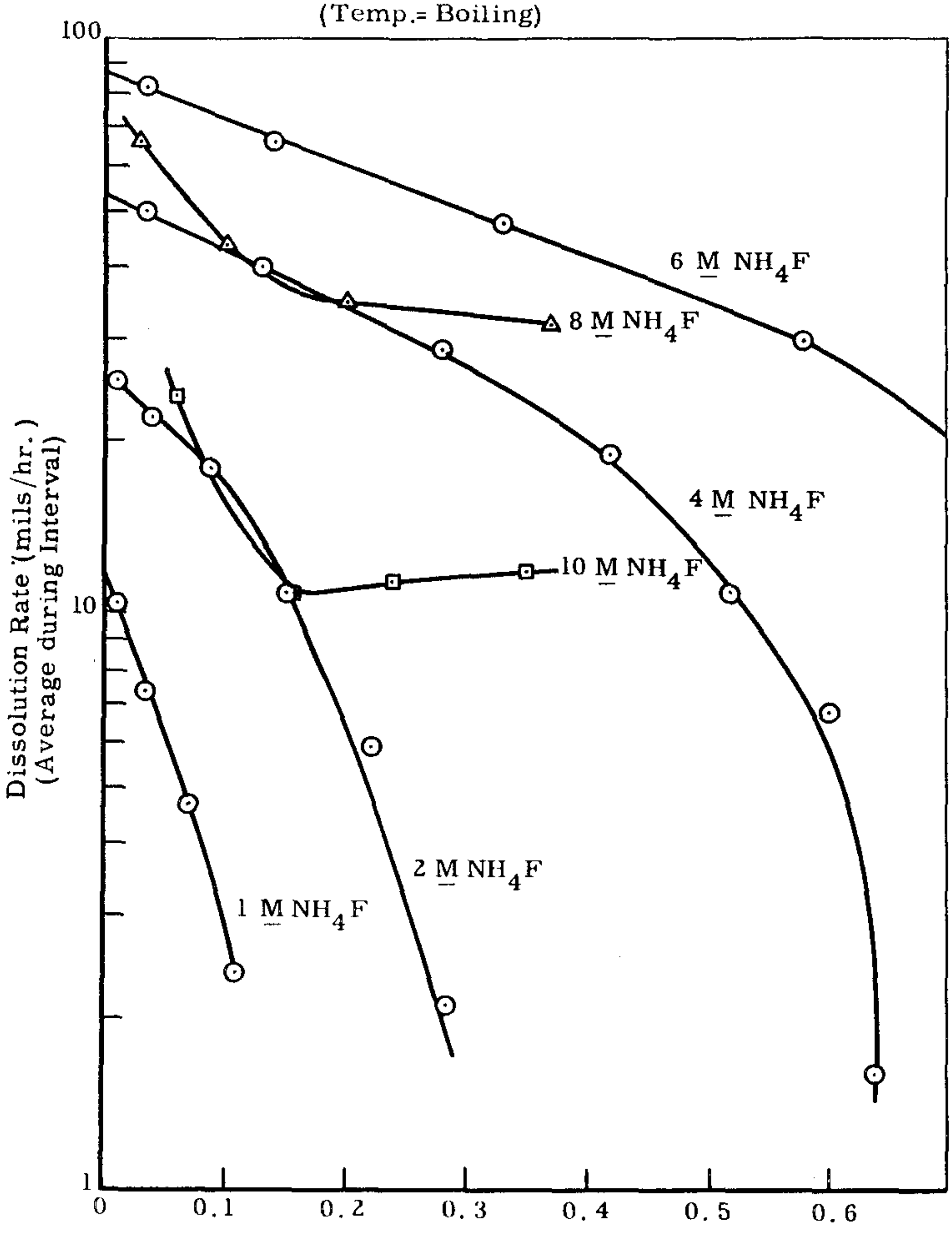

FIGURE 2

RATE OF DISSOLUTION OF ZIRCALOY-2 IN AMMONIUM FLUORIDE SOLUTIONS

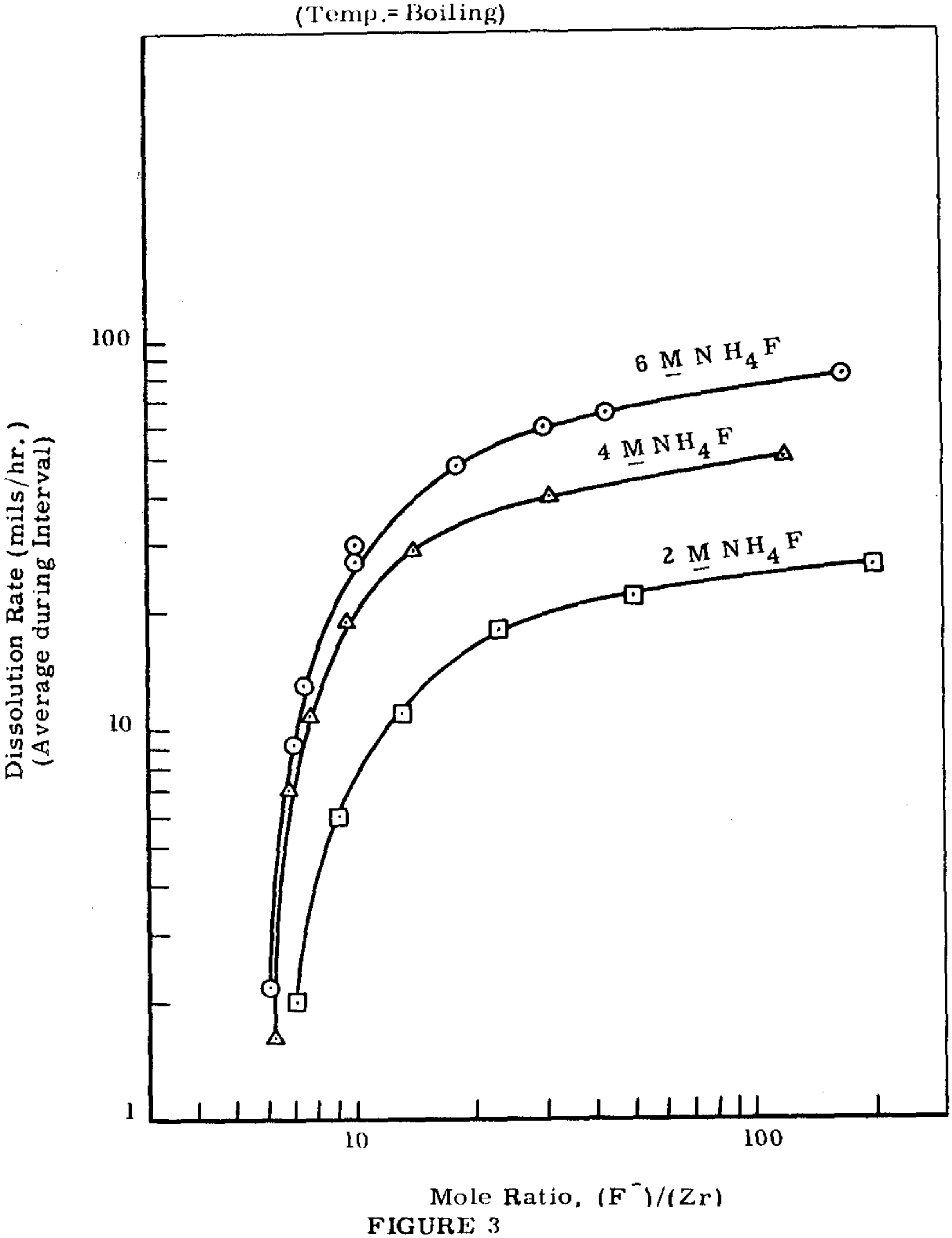

FIGURE 3

DISSOLUTION RATE OF ZIRCALOY-2 AS A FUNCTION OF FLUORIDE TO ZIRCONIUM MOLE RATIO

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the rates of dissolution observed during the various intervals of the experiments employing six, four, and two molar ammonium fluoride solutions are plotted against the mole ratio of fluoride to zirconium in the solution. The mole ratios were computed on the basis of the average zirconium concentration for each interval. It is seen that the rate of dissolution decreases markedly when the mole ratio of fluoride to zirconium in solution approaches six.

In some experiments involving the dissolution of Zircaloy-2 in six molar ammonium fluoride at the boiling point, each time the coupon was removed for weighing the solution was cooled to room temperature and the pH was measured. Results of two such experiments are tabulated in Table III along with the calculated zirconium concentration and the thickness of Zircaloy-2 dissolved off each exposed surface of the coupon (as calculated from the weight loss). The relatively low pH values found at the high zirconium concentrations may be indicative of hydrolysis of the zirconium species. The values of thickness of Zircaloy-2 removed at the end of the various reaction times emphasize the fact that the rate of dissolution of Zircaloy-2 in boiling ammonium fluoride solutions is quite adequate for the removal of a Zircaloy-2 jacket in a short time, giving a reasonably concentrated zirconium solution.

TABLE III

Dissolution of Zircaloy-2 in 6 $\underline{M}$ NH_4F

(Temperature = Boiling)

Vol of Solution (ml)	Time(hr)	MZr*	pH	Thickness removed from each exposed surface* (mils)
100	0	--	7.4	--
	0.25	0.40	7.9	15
	0.75	0.77	6.7	28
	1.50	0.95	6.0	36
	2.50	1.01	5.1	38
150	0	--	7.4	--
	0.25	0.24	7.1	16
	0.58	0.46	7.1	30
	1.25	0.74	6.9	48
	2.00	0.88	5.5	56

*Calculated from weight loss measurements.

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5. Gas Evolution During Dissolution

The quantity of hydrogen evolved during the dissolution of zirconium in ammonium fluoride solutions was estimated by measuring the volume of gas produced by the action of a one molar ammonium fluoride solution on a zirconium turning. The zirconium turning was placed under the ammonium fluoride solution in a gas buret which was then warmed with a heat lamp. Applying the perfect gas law to the increased volume (measured at room temperature) of the gas phase brought about by the reaction it was found that 1.9 moles of gas were produced per mole of zirconium dissolved. Since mass spectrographic analysis showed the gas sample to contain only hydrogen in addition to unexpelled air, it is concluded that two moles of hydrogen are evolved for each mole of zirconium dissolved.

The quantity of ammonia produced by the dissolution of zirconium in ammonium fluoride was estimated by passing the gas evolved during a dissolution carried out at the boiling point through a solution of standardized acid to trap out any ammonia. Titration of the excess acid remaining at the end of the experiment showed that 4.0 moles of base were evolved per mole of zirconium dissolved. Thus it is inferred that four moles of ammonia are expelled from the solution for each mole of zirconium dissolved, at least for dissolutions conducted at the boiling point.

B. Attack of Fuel Materials by Ammonium Fluoride Solutions

Having shown that Zircaloy-2 cladding can be removed by dissolution in ammonium fluoride solutions, it was of interest to determine the effect of these solutions on the fuel material. The main points of interest here are the extent of attack of the fuel material, the solubility of the fuel material in the decladding solution and, since it would be desirable to decontaminate and recover the fuel material in existing solvent extraction facilities employing nitrate systems, the fluoride concentration in the solvent extraction feed solution. Preliminary experiments have been carried out with those fuel materials of most immediate interest. The investigation will be extended to other potential fuels at an early date.

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1. Metallic Uranium

Based on the color of the reaction products, metallic uranium is oxidized to uranium (IV) by ammonium fluoride solutions. In addition to the uranium which goes into solution, a fairly adherent coating of reaction products is formed on the metal. The appearance of this coating varies for different conditions of formation. Weight changes observed for uranium metal exposed to boiling ammonium fluoride solutions as presented in Table IV, show that a small fraction of the uranium reacted with the ammonium fluoride solutions. When the hot solutions containing the uranium were allowed to cool, the bulk of the uranium precipitated out leaving a nearly colorless solution. Thus substantially all of the uranium was recovered in solid form (as unreacted metal and precipitated fluoride), only a small portion of which would require chemical treatment to free it from fluoride ion.

TABLE IV

Attack of Uranium Metal* by Boiling Ammonium Fluoride Solutions

System	Time (min)	Change in Weight, Per Cent Weighed with Coating on	 Weighed after Coating was Removed
1 $\underline{M}NH_4F$	100	+ 0.10	- 0.52
4 $\underline{M}NH_4F$	120	- 1.2	- 1.7
5 $\underline{M}NH_4F$	120	- 1.9	- 2.3

*Cylindrical wafers cut from standard Hanford slugs. Weight 80 - 90 grams. Surface area approximately 23 cm^2.

In another experiment, an eighty-four gram wafer of uranium metal and a ten gram coupon of Zircaloy-2 were simultaneously exposed to a boiling six molar ammonium fluoride solution of initial volume 100 ml for one hour. The resulting hot solution was found to contain 0.3 per cent of the uranium at a concentration of 2.4 grams/liter. The zirconium concentration in the hot solution was computed from weight loss and volume

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measurements to be one molar. After the solution had cooled and precipitation had occurred, the concentrations found in the solution were 0.73 molar zirconium and 0.08 grams/liter uranium, this amount of uranium being equal to three per cent of that present in the hot solution but only about 0.01 per cent of the total uranium used in the experiment. Thus, 99.99 per cent of the uranium was recovered in solid form and less than one per cent of the uranium would require chemical treatment to free it from fluoride ion. The coated uranium wafer which resulted from this experiment dissolved readily in nitric acid. The solution which resulted from dissolution of 61 per cent of the uranium was two molar in uranium and 0.003 molar in fluoride ion.

2. Uranium Dioxide

Immersion of a twenty-five gram cylinder of sintered uranium dioxide having a surface area of ten cm^2 in 100 ml of boiling six molar ammonium fluoride for 2.5 hours resulted in reaction of from 0.5 to 0.7 per cent of the material, showing that this material is more resistant than metallic uranium to attack by ammonium fluoride solutions. An experiment involving the simultaneous immersion of a twelve gram coupon of Zircaloy-2 and a thirty gram cylinder of sintered uranium dioxide in 150 ml boiling six molar ammonium fluoride for eighty minutes gave a hot solution containing 0.8 molar zirconium (calculated from weight loss and initial volume) and 0.14 grams/liter uranium. Although no attempt was made to determine the amount of fluoride ion associated with the uranium dioxide after the attack by the ammonium fluoride solutions, visual examination did not indicate the presence of any uranium fluoride coating.

C. Test of Method for Recovering Uranium from Ammonium Fluoride Solutions

As was shown in Section III-B-1 (page 17), it might be necessary in some cases to recover the fraction of the uranium which reacts with the ammonium fluoride solutions in order to obtain adequate uranium recovery.

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In order for this uranium to be processed in aqueous nitrate systems in existing facilities it must also be freed from fluoride ion to eliminate the severe corrosion of stainless steels by nitrate-fluoride mixtures. It appeared that the simplest method of freeing the uranium from fluoride ion would be by metathesis of the green precipitate (presumably double salts of uranium(IV) fluoride and ammonium fluoride) to hydrous uranium dioxide and washing the dioxide free of fluoride prior to dissolving it in nitric acid.

An experiment was done to test the uranium recovery and extent of fluoride removal under conditions simulating the processing of Zircaloy clad metallic uranium fuel elements. The experiment consisted of the following steps.

1. Simultaneous attack on metallic uranium (ninety gram wafer) and Zircaloy-2 (twelve gram coupon) in 150 ml boiling six molar ammonium fluoride for one hour. As calculated from weight loss measurements, a thickness of 40 mils was dissolved off each surface of the Zircaloy coupon.
2. Filtration of the hot solution to remove the undissolved tin followed by cooling of the solution to precipitate the bulk of the uranium that had dissolved. In this experiment a large fraction of the zirconium precipitated also, but later information indicates that this could have been avoided by carrying the dissolution to a higher zirconium (and hence lower free fluoride) concentration.
3. Water washing of the precipitated solids to remove zirconium.
4. Conversion of the uranium salt to hydrous uranium dioxide by metathesis with hot five per cent sodium hydroxide solution.
5. Water washing of the hydrous uranium dioxide to remove residual fluoride ion.
6. Dissolution of the hydrous uranium dioxide in nitric acid.
7. Metathesis of the uranium fluoride solid which adhered to the wafer of metallic uranium with hot sodium hydroxide solution. Much less uranium fluoride adhered to the metal in this experiment than in the experiments done in the absence of zirconium.

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8. Water washing of the metathesis product from step 7.
9. Dissolution of the metathesis product and 63 per cent of the metal in nitric acid.

The distribution of uranium throughout the various steps of the experiment is shown in Table V (page 21) along with a partial picture of the distribution of zirconium. It is seen that adequate uranium recovery was achieved even though the loss to the cold jacket solution was a factor of eight higher than was obtained in the preliminary experiment described in Section III-B-1 (page 17). The uranyl nitrate solution prepared by dissolution of the metal and metathesized coat was found to contain only 0.0005 molar fluoride ion. Attempts to analyze for fluoride in the uranyl nitrate solution prepared by dissolution of the metathesized precipitate were unsuccessful due to the presence of an interfering substance (probably zirconium).

To see if plutonium would precipitate out along with the uranium when the hot jacket solution was cooled, a portion of this hot solution was spiked with plutonium nitrate solution to a concentration of 0.002 g/l and then allowed to cool. Analysis of the cold supernatant showed that 85 per cent of the plutonium precipitated as compared to 77 per cent precipitation of the uranium.

D. Solubility of Zirconium in Ammonium Fluoride Solutions

The only solubility data obtained to date are analyses for zirconium in saturated solutions resulting from dissolutions of Zircaloy-2 coupons in boiling six molar ammonium fluoride. These data are shown in Table VI (page 22) and are compared with the concentrations which would have been obtained had all the zirconium which was removed from the Zircaloy-2 coupon remained in solution. The volumes measured at the end of the dissolution experiments were employed in calculating the values shown in the second column of Table VI. The values listed in the third column were computed from the amount of fluoride added to the system and the measured weight loss of the Zircaloy-2 coupon.

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TABLE V

Distribution of Uranium in Operations Simulating Decladding and Feed Preparation

Step	Solution	M Zr(1)	g/l U	g. U	Percent of Total U Lost
1	Hot jacket solution	0.74	2.2	0.33	
2	Cold jacket solution	0.33	0.5	0.073	0.081
3	Water washes of precipitated solid		0.06	0.0088(2)	0.0098
4	Sodium hydroxide metathesis solution		0.01	0.0002(2)	0.0002
5	Water washes of metathesis product		0.04	0.0022(2)	0.0024
6	Nitric acid dissolution of metathesis product		35	0.21(2)	
7	Sodium hydroxide metathesis solution. (from metathesis of coated metal piece)		0.006	0.0006	0.0007
8	Water washes of metathesis product		0.005	0.0003	0.0003
9	Nitric acid dissolution of metathesis product and metal		4 64	55.6	
	Metal heel remaining			33.8	
	Total uranium found			90.0	
	Total uranium added			90.5	
	Total waste loss				0.094

(1) Calculated from weight loss and initial volume of the solution (actual concentration would be higher because of decreased volume at end of experiment).

(2) Calculated values. Only one-third of the precipitated solids was carried through these steps. The amounts of uranium found when working the one-third portion were multiplied by three to give these values.

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It is apparent that the solubility of zirconium in aqueous ammonium fluoride solutions increases rapidly as the mole ratio of fluoride to zirconium decreases, at least over the range covered by the data of Table VI. This observation is in agreement with data reported by von Hevesy and co-workers(1) indicating a decrease in the solubility of zirconium in ammonium fluoride systems as the ammonium fluoride concentration was increased. The salt $(NH_4)_2ZrF_6$ was reported by von Hevesy and co-workers to have a solubility of 1.05 moles per liter in water at 20 C and 2.96 moles per liter at 90 C, and the salt $(NH_4)_3ZrF_7$ was reported to have a solubility of 0.59 moles per liter in water at 20 C.

TABLE VI

Concentration of Zirconium in Solutions Prepared by Dissolving Zircaloy-2 in Boiling 6 $\underline{M}$ NH_4F

Experimental*	Calculated from Weight Loss and Final Solution Volume	Ratio of Total F^- in System to Total Zr Dissolved
0.08 $\underline{M}$Zr	0.52 $\underline{M}$Zr	12.2
0.33	---	8.1
0.58	---	7.5
0.73	0.97	7.2
0.70	0.93	7.1
1.07	1.15	6.8
1.02	1.10	6.5
1.23	1.36	5.8

*Determined after solutions had aged for two to twenty days at room temperature.

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(1) G. v Hevesy, J. A. Christiansen, and V. Berglund, Z. Anorg. allgem. Chem., 144, 69 (1925).

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E. Corrosion of Stainless Steels by Ammonium Fluoride Solutions

The corrosion of stainless steels by ammonium fluoride solutions is presently under study by R. F. Maness, Development and Corrosion Chemistry Operation, Hanford Laboratories Operation. The data obtained to date indicate that conventional stainless steels are satisfactory materials of construction for vessels in which alternate ammonium fluoride and nitric acid dissolutions are to be performed.

In Table VII are presented data obtained by immersing stainless steel coupons in boiling four molar ammonium fluoride.

TABLE VII

Corrosion of Stainless Steels in Boiling 4 $\underline{M}\,NH_4F$

	Corrosion rate (inches per mo. x 10^4)	
Time, hrs	Type 304-L	Type 347
48	6.2	4.2
120	3.7	2.6
168	3.1	3.4
240	3.2	3.5

After the coupons had been immersed in four molar ammonium fluoride solution for 240 hours they were cleaned and placed in boiling fourteen molar nitric acid for 48 hours, showing a corrosion rate of 0.001 inches per month in both cases. The coupons were then returned to boiling four molar ammonium fluoride for 48 hours and were then immersed without cleaning in boiling fourteen molar nitric acid for another 48 hours. The corrosion rate was again found to be 0.001 inches per month for both stainless steels.

IV. DISCUSSION

The data thus far available on the dissolution of Zircaloy-2 in ammonium fluoride solutions are not sufficient to define the mechanism by which zirconium is dissolved in these solutions. However, the observations

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that two moles of hydrogen and four moles of ammonia are evolved per mole of zirconium dissolved and that the rate of dissolution decreases markedly as the mole ratio of fluoride to zirconium approaches six are consistent with the mechanism indicated in the following equations.

$$Zr(s) + 6\ F^- + 4\ H_2O \longrightarrow ZrF_6^= + 2\ H_2(g) + 4\ OH^- \qquad (1)$$

$$4\ NH_4^+ + 4\ OH^- \rightleftharpoons 4\ NH_4OH \rightleftharpoons 4\ NH_3(g) + 4\ H_2O \qquad (2)$$

As indicated in equation (2), volatilization of ammonia appears desirable since otherwise the pH would increase and the reaction rate decrease as the reaction proceeded.

Although no conclusive data are available, the shape of certain dissolution rate curves and visual observation of the Zircaloy-2 coupons indicate the probability of protective films being formed on the Zircaloy-2 coupons in certain of the experiments described in Section III-B, (page 16). It is felt that the reduced attack of solutions containing high concentrations of potassium ion on Zircaloy-2 was due in part at least to the formation of such a protective film. It is also possible that protective films, caused by the reduced solubility of zirconium at higher fluoride to zirconium ratios, were at least partly responsible for the fact that rates of dissolution into eight or ten molar ammonium fluoride containing moderate amounts of zirconium are lower than the rate of dissolution into six molar ammonium fluoride containing the same amount of zirconium.

Similarly, the data thus far available do not enable an accurate prediction of the extent to which fuel materials will be dissolved by ammonium fluoride solutions in a dejacketing operation. Placing an optimistic interpretation on the results obtained to date, it appears that there is a definite possibility that the amounts of either metallic uranium or uranium dioxide fuels which will be dissolved in a dejacketing operation employing ammonium fluoride will be sufficiently small that recovery of

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uranium from the jacket solution may not be necessary. However, it appears probable that a portion of the fuel may be converted to a fluoride salt which adheres to the unreacted fuel, making conversion of this salt to a fluoride-free form necessary in order to minimize fluoride contamination in the final uranyl nitrate feed solution. Results to date indicate that this conversion can be accomplished by treatment with hot sodium hydroxide solution.

Figure 4 shows a schematic flowsheet for an ammonium fluoride dejacketing operation in which fuel materials would be recovered from the jacket solution. The course of plutonium is not shown in this flowsheet, but it has been found to precipitate out along with the uranium and it is presumed that it will follow the uranium through the other steps. Development of a firm flowsheet along the lines indicated in Figure 4 will be a major objective of future experimental work.

A second major objective of future experimental work will be the development of waste treatment methods which will permit the volume of stored zirconium jacket solution to be minimized. If it is assumed that jacket dissolution in ammonium fluoride will result in a solution one molar in zirconium then dissolution of a thirty mil jacket off standard Hanford slugs will result in approximately 1.3 liters of zirconium jacket solution per slug charged. This compares quite favorably with the volume of aluminum jacket solution which is presently produced, which runs about 1.8 liters per slug. There is a possibility of further reducing the volume of zirconium jacket waste by precipitating the zirconium for storage as a solid.

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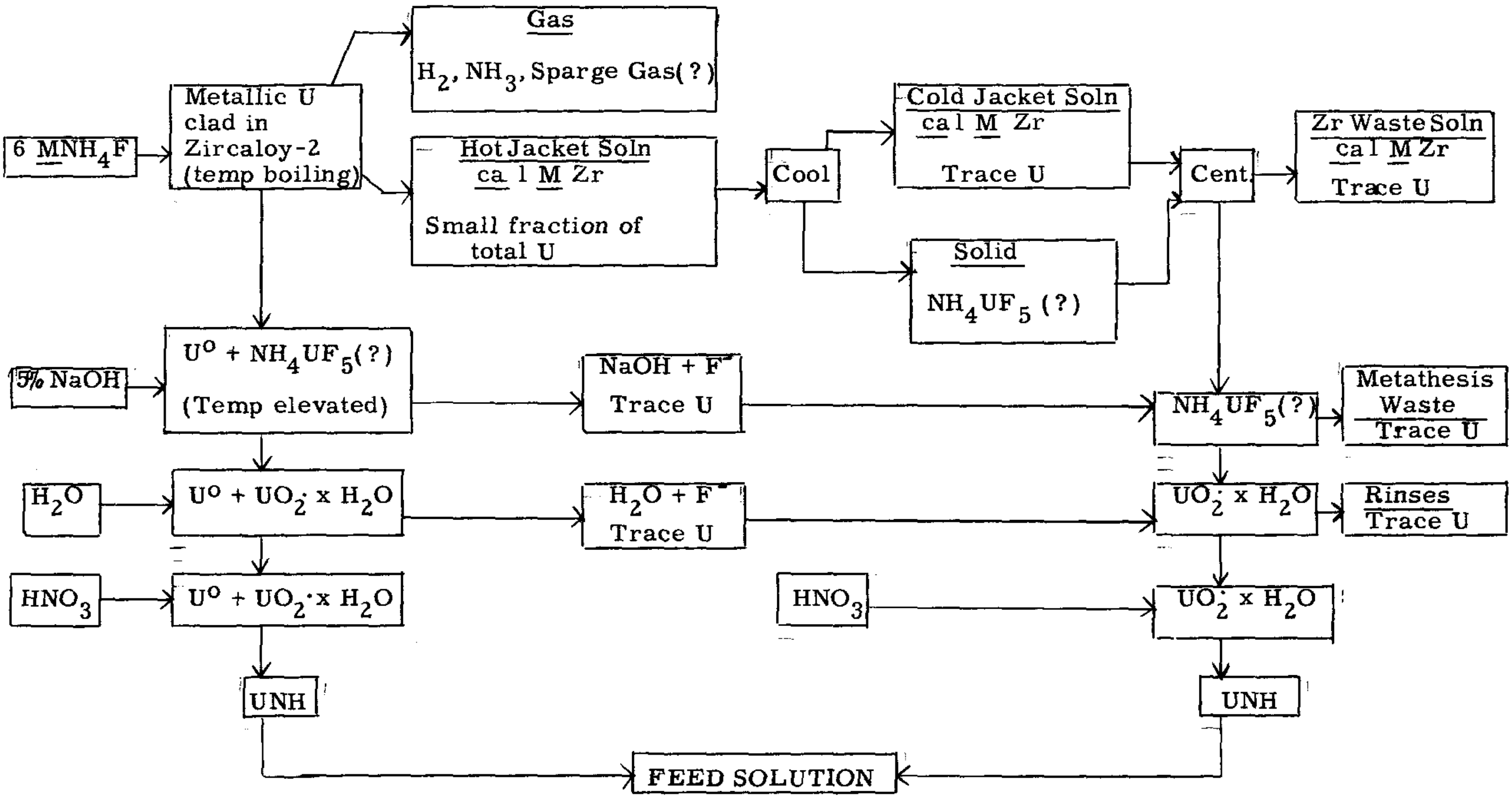

FIGURE 4

Tentative Dejacketing and Feed Preparation Flowsheet

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