THE ZIRFLEX PROCESS

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The Zirflex Process is designed to accomplish selective dissolution of zirconium or zircaloy cladding off reactor fuels. The process involves the dissolution of the cladding material in solutions of ammonium fluoride alone or in mixture with ammonium nitrate. Mixtures of ammonium fluoride and ammonium nitrate are preferred since they result in very little evolution of hydrogen during the dissolution. One of the main advantages to the process is that these solutions attack austenitic stainless steels only slowly, in sharp contrast to the media (e.g., hydrofluoric acid or hydrofluoric-nitric acid mixtures) generally used for dissolving zirconium. In boiling 6 M NH_4F , the rate of penetration of zircaloy-2 is nearly 100 mils/hr, while that of typical austenitic stainless steels is only about 0.5 mils/month.

DISSOLUTION OF ZIRCALOY-2[†]

Rate of Dissolution

Data obtained during dissolution of zircaloy-2 in boiling ammonium fluoride solutions of various concentrations are presented in Figure 1. These data were obtained employing zircaloy-2 coupons having an initial surface area of 15 cm² and initial solution volumes of 100 ml in each case. The final solution volumes and coupon surface areas were generally about 20% lower than the initial values.

It is seen that the rate of dissolution increases regularly with ammonium fluoride concentration up to six molar. The fact that the rate of dissolution in 8 or 10 M NH_4F is less than in 6 M NH_4F is thought to be due to the

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† Zircaloy-2 is a zirconium alloy which has been widely proposed as a cladding material for fuel elements. In addition to zirconium, it contains about 1.5% tin, 0.15% iron, 0.1% chromium, and 0.05% nickel.

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FIGURE 1

DISSOLUTION OF ZIRCALOY-2 IN NH_4F SOLUTIONS

formation of a protective coating of ammonium fluoro-zirconate on the surface of the zircaloy at the higher concentrations of reactant. This hypothesis, which was indicated by the appearance of the zircaloy specimens when they were removed from the solutions, is substantiated by the solubility data given later.

The results of experiments done to determine the effect of zirconium concentration on the rate of dissolution of zircaloy-2 at constant total fluoride concentration are presented in Table I. These rates were measured on short term exposures of zircaloy-2 coupons to boiling solutions of the indicated compositions. The solutions were prepared using appropriate amounts of ammonium hexafluorozirconate ($(\text{NH}_4)_2\text{ZrF}_6$) and ammonium fluoride.

TABLE I

EFFECT OF ZIRCONIUM CONCENTRATION ON RATE OF DISSOLUTION
OF ZIRCALOY-2 BY BOILING NH_4F SOLUTIONS

<u>M F^-</u>	<u>M Zr(IV)</u>	<u>M NH_4^+</u>	<u>Dissolution Rate (mg/min, cm^2)</u>
6.0	0.00	6.0	22
6.0	0.30	4.8	19
6.0	0.60	3.6	10
6.0	0.86	2.5	3.0
6.0	1.00	2.0	0.1

The marked decrease in the rate of dissolution as the fluoride to zirconium mole ratio approaches six is very striking. This is presumed to be due to the formation of highly stable zirconium-fluoride complexes, which effectively reduce the concentration of fluoride ion available for further interaction. It was found that the dissolution rates could be correlated fairly well with a "free" fluoride concentration defined as being equal to the total fluoride concentration minus six times the zirconium concentration. Such a correlation is presented in Figure 2. In addition to the values calculated from the data in Table II, values calculated from the data obtained during dissolutions of zircaloy-2 in 2, 4, and 6 M NH_4F are included in this plot. In these cases, the rates of dissolution employed were those determined during the separate intervals of attack. The "free" fluoride concentrations during the separate intervals were calculated from the initial total fluoride concentration and the average concentration of zirconium present in the solution during the interval. The zirconium concentrations were calculated from the measured weight losses and the initial solution volume.

The line drawn through the data on Figure 2 has a slope near unity, indicating that the rate of dissolution of zircaloy-2 in ammonium fluoride solution is essentially first order with respect to the "free" fluoride concentration as defined here. Values of dissolution rate reported as mg/min, cm^2 on this plot

FIGURE 2

EFFECT OF "FREE" FLUORIDE CONCENTRATION ON THE RATE OF DISSOLUTION OF
ZIRCALOY-2

may be converted to penetration rates in mils/hr by multiplying by the factor 3.7. Reporting dissolution rates as penetration rates is valid for these measurements since the dissolution proceeded evenly and uniformly on all surfaces.

The addition of 1 M NH_4NO_3 to ammonium fluoride solutions having concentrations six molar or less was found to increase the rate of dissolution of zircaloy-2 by about 10%. With 6 M NH_4F + 2 M NH_4NO_3 , however, the rate of dissolution was found to be lower than with 6 M NH_4F alone. The explanation for this lower rate is felt to be the same as that offered for the lower rates observed with 8 and 10 M NH_4F , that is, the formation of a protective coating of ammonium fluorozirconate on the surface of the zircaloy at the higher concentrations of reactants.

Gas Evolution During Dissolution

Mass spectrographic analysis of the gas evolved during the dissolution of zircaloy-2 in ammonium fluoride solution showed the gas to be a mixture of hydrogen and ammonia. The amount of ammonia evolved was determined by measuring the amount of acid neutralized when the gases leaving the dissolver during the reaction were routed through an acid scrubber. The volume of hydrogen evolved was determined by measuring the rate of gas flow downstream from the acid scrubber and graphically integrating a plot of the rate of flow versus time. The perfect gas law was employed to calculate the number of moles of hydrogen evolved.

Results of such experiments employing mixtures of ammonium fluoride and ammonium nitrate as well as solutions of ammonium fluoride alone are presented in Table II. It is apparent that the quantity of hydrogen produced during dissolution is decreased markedly by the addition of ammonium nitrate to the ammonium fluoride solution. In the experiments employing the higher concentrations of ammonium nitrate, the gas leaving the acid trap was found to contain nitrogen in an amount equal to about 25% that of hydrogen. Because of the uncertainties involved in measuring the low gas flow rates in these experiments, the values listed in the table are not corrected to account for the presence of the nitrogen. The approximately forty-fold reduction in the quantity of hydrogen obtained with mixed ammonium fluoride - ammonium nitrate solutions makes the use of this mixture preferred for process application because of the explosive nature of hydrogen-air mixtures.

The data presented in Tables I and II and Figure 2 indicate that the dissolution of zirconium in boiling ammonium fluoride solution proceeds according to equation (1).

With ammonium fluoride - ammonium nitrate mixtures, however, the bulk of the dissolution appears to proceed according to equation (2).

It is desirable to perform dissolutions of zirconium in these solutions under conditions (such as boiling) that result in the removal of the ammonia produced during the reaction. Otherwise, the pH of the solution will increase and the rate of dissolution will decrease.

TABLE II
GAS EVOLUTION DURING THE DISSOLUTION OF ZIRCALOY-2
IN BOILING SOLUTIONS OF NH₄F AND NH₄F-NH₄NO₃

<u>Initial Solution Composition</u>		<u>M Zr(IV) in Final Solution</u>	<u>Moles NH₃ Evolved Per Mole Zr Dissolved</u>	<u>Moles H₂ Evolved Per Mole Zr Dissolved</u>
<u>M NH₄F</u>	<u>M NH₄NO₃</u>			
6.0	0.0	0.96	4.1	
6.0	0.0	0.92	4.0	2.1
6.0	0.0	0.87	4.0	2.2
6.0	0.0	0.86	3.9	
6.0	0.0	0.84		2.0
6.0	0.25	0.84		0.8
6.0	0.33	0.86		0.5
6.0	0.50	0.90		0.07
6.0	0.50	0.84	4.9	
6.0	1.0	0.86	4.9	0.05

Effect of Oxide Film

On exposure of zirconium (or zircaloy) to water or oxygen at high temperature, a passive film of zirconium oxide is formed on the surface of the metal. Thus, the effects of such a film must be considered in the decladding of fuel elements from water-cooled reactors.

It was found that such a film is dissolved only slowly if at all by solutions of ammonium fluoride. The film is penetrated in localized areas, however, thus giving a pitting-type attack of the zirconium as opposed to the very uniform attack observed in the absence of the oxide film. Penetration of the oxide film evidently occurs most readily at sites of surface imperfections, as it was found that surface roughness or sharp discontinuities in the surface (e.g., square edges or sharp corners) results in more rapid attack by ammonium fluoride solution in such areas.

Results of the experiments done in an effort to determine the effect of the amount of the oxide film on the initial rate of attack by 6 M NH₄F are presented in Table III. The zircaloy-2 specimens used in this work were solid cylinders prepared with rounded ends and polished surfaces in an effort to minimize surface imperfections.

TABLE III

EFFECT OF OXIDE THICKNESS ON INITIAL RATE OF ATTACK OF ZIRCALOY-2

Oxidation Treatment			Amount of Oxide Film (mg/dm ²)	Weight Lost (mg)(a)
Medium	Time (hours)	Temp. (°C)		
			0	2500(b)
O ₂	20	440	16	90
H ₂ O	1200	360	35	12
O ₂	240	440	42	4

(a) During 10 minute exposure to boiling 6 M NH₄F.

(b) Assuming 6 M "free" fluoride during entire interval of attack (to give better comparison with other numbers).

It is to be emphasized that the data in Table III should not be taken as meaning that the times required to de-clad fuel elements having the indicated amounts of oxide film will differ by factors as large as do the initial rates of attack. Once the oxide film has been penetrated by the solution, attack proceeds rapidly on the unoxidized zirconium thus exposed. The pit formed at the point of penetration thus continually grows larger, resulting in more unoxidized surface on which the solution can act. The result, illustrated in Figure 3, is an induction period followed by a period of fairly rapid dissolution. As the pits grow they eventually unite and the amount of unoxidized surface available for attack then decreases, giving a slower rate of dissolution.

The data presented in Figure 3 were obtained with a zircaloy-clad, uranium dioxide cylinder having hemispherical ends and a highly polished surface (total surface area 21 cm²). The oxide film on this particular specimen was very passive; only four points of penetration were observed throughout the reaction. It is seen that even with this extremely passive surface, 50% of the cladding was removed in two hours and 70% was removed in three hours. The rate of dissolution of the remaining clad was quite low, however, presumably due to the decrease in area of unoxidized zirconium brought about by the union of the individual pits. Thus, it might be desirable from the standpoint of minimizing time requirements for combined de-cladding and core dissolution to only partially de-clad the fuel element before performing the core dissolution. The residual cladding would then dissolve readily along the unoxidized inner surface on subsequent exposure to ammonium fluoride solution.

Another method of decreasing the time required for the de-cladding of fuel elements having an oxidized surface is to break the oxide film by mechanical abrasion prior to the de-cladding step. A controlled mechanical abrasion step would result in more predictable, as well as more rapid, de-cladding rates with irradiated fuels.

FIGURE 3

DECLADDING OF OXIDIZED FUEL ELEMENT

Dissolution of Tin

In the dissolution of zirconium-tin alloys (such as zircaloy-2) in ammonium fluoride solutions, the tin dissolves only slowly if at all and thus remains as a solid. On subsequent exposure to nitric acid, solid tin compounds are formed. The presence of such tin compounds during the dissolution of fuel element core materials could be undesirable from the standpoint of scavenging of plutonium from the solution. The use of mixed solutions of ammonium fluoride and ammonium nitrate to dissolve zirconium-tin alloys, however, may enable the tin to be dissolved along with the zirconium and discarded with the decladding waste.

The results of experiments done to date along these lines are presented in Table IV. Specimens of zircaloy-2 (about 1.5% tin) were completely dissolved and the amount of solid residue remaining was determined by filtration and weighing. It is seen that the amount of residue obtained decreases with increasing time and terminal "free" fluoride (defined as before) and nitrate concentrations. From the standpoint of tin dissolution, it is therefore desirable to use significantly more nitrate in the dissolution of zirconium-tin alloys than is required to suppress the evolution of hydrogen, and also, to have a high "free" fluoride concentration at the completion of the dissolution.

TABLE IV

AMOUNT OF SOLID RESIDUE RESULTING FROM THE DISSOLUTION OF ZIRCALOY-2

Initial Solution Composition		Terminal Solution Composition ^(a)		Reaction Time ^(b) (Hours)	Residue %(c)
		"Free" Fluoride	M NO_3^-		
$\text{M NH}_4\text{F}$	$\text{M NH}_4\text{NO}_3$	M	M NO_3^-		
6.0	0.0	0.85	0.0	2	1.4
6.0	0.0	0.85	0.0	4	1.0
6.0	0.5	0.85	0.07	2	1.6
6.0	0.5	0.85	0.07	3	0.19
6.0	0.5	0.85	0.07	4	0.12
6.0	0.75	0.85	0.41	2	0.41
6.0	1.0	0.85	0.57	2	0.07
6.0	0.5	1.2	0.10	2	0.52
6.0	0.5	1.5	0.12	2	0.13

(a) Calculated from equation (2), page 6.

(b) About one hour required for dissolution of zirconium in most cases.

(c) Expressed as percentage of the total amount of zirconium dissolved.

SOLUBILITY OF ZIRCONIUM IN AMMONIUM FLUORIDE SOLUTION

Data obtained on the solubility of zirconium in ammonium fluoride solutions at 100°C are presented in Figure 4. These data were obtained by slowly adding water to stirred mixtures of ammonium fluoride and ammonium hexafluorozirconate. The solubility values were deduced from the known amounts of reagents employed and the volume of the solution at the point when all the solid had dissolved.

These solubility data lend credence to the hypothesis that the presence of a coating of ammonium fluoro-zirconate on the surface of the zircaloy-2 is responsible for the rates of dissolution of zircaloy-2 in 8 M NH_4F and 10 M NH_4F being lower than in 6 M NH_4F . From a comparison of the solubility curve with the lines drawn in Figure 4 to represent the conditions resulting from dissolution, it is seen that with 6 M NH_4F as the dissolving medium, all the zirconium which reacts can remain in solution at the boiling point. With 8 M NH_4F , however, all the reacted zirconium can remain in solution only near the beginning or the end of the reaction. Thus, solid zirconium salt must be present and the formation of a protective coating of this material on the surface of the zircaloy appears reasonable.

The addition of ammonium nitrate to these systems was found to result in a decrease in the solubility of zirconium. In the presence of 1 M NH_4NO_3 , the zirconium solubility curve was found to be essentially identical with the line drawn in Figure 4 to represent the conditions resulting from dissolution in 6 M NH_4F at fluoride to zirconium mole ratios from eight to twenty. This observation supports the conclusion drawn earlier regarding the different rates of dissolution of zircaloy-2 observed in 6 M NH_4F with different ammonium nitrate concentrations; that is, that the lower dissolution rate observed in 6 M $\text{NH}_4\text{F} + 2 \text{ M } \text{NH}_4\text{NO}_3$ is due to the formation of a coating of zirconium salt on the surface of the zircaloy.

Since low rates of dissolution are observed under conditions which result in the formation of insoluble zirconium salts and since the solubility of zirconium decreases as the temperature decreases, it is desirable from the standpoint of rapid and complete dissolution of zirconium to perform such dissolutions at the boiling point.

In Table V are presented the compositions of saturated solutions of zirconium in ammonium fluoride at 22°C. These solutions were prepared by shaking portions of the salt $(\text{NH}_4)_2\text{ZrF}_6$ with solutions of varying composition for a day, a period of time shown by preliminary experiments to be entirely adequate for the attainment of equilibrium. The contactings were carried out in polyethylene bottles partially immersed in a constant temperature bath. Analysis of the solid phase in equilibrium with the solution containing 1.00 M Zr and 6.2 M F showed its composition to correspond quite closely to that of $(\text{NH}_4)_3\text{ZrF}_7$, in agreement with the observation of von Hevesy⁽¹⁾ that the heptafluorozirconate is less soluble than the hexafluorozirconate.

FIGURE 4
SOLUBILITY OF Zr IN NH₄F SOLUTION AT 100°C

TABLE V
SOLUBILITY OF ZIRCONIUM IN NH₄F AT 22° C

<u>M Zr(IV)</u>	Total Fluoride <u>M</u>	<u>M NH₄⁺</u>	<u>M NO₃⁻</u>	<u>pH</u>	"Free" Fluoride ^(a) <u>M</u>
1.19	7.0	2.22		4.1	0.0
1.00	6.2	2.14		5.3	0.2
0.58	4.4	1.76		5.7	0.9
0.41	3.6	1.70		7.0	1.1
0.37	3.3	1.76		6.0	1.1
0.16	2.5	2.01		6.4	1.6
0.13	2.8	2.14		6.7	2.0
0.037	(4.0)	(4.0)			4.0
0.025	(6.0)	(6.0)			6.0
0.53	3.8	1.88	(0.5)	5.9	0.6
0.23	2.6	2.00	(0.5)	6.1	1.2
0.10	2.3	2.51	(0.5)	6.4	1.7
0.91	5.8	2.85	(1.0)	4.6	0.4
0.89	5.8	2.87	(1.0)	5.0	0.4
0.24	2.2	2.30	(1.0)	5.9	0.7
0.068	2.3	3.16	(1.0)	6.3	1.9

(a) Defined as ((Total M F⁻) - 6 M Zr(IV)).

Values in parentheses deduced from amounts of reagents employed.

It is seen that the solubility of zirconium increases as the "free" fluoride concentration decreases. Thus, when dissolving zirconium in ammonium fluoride solutions, the nearer the reaction is carried to completion (fluoride to zirconium mole ratio of six), the greater the amount of zirconium that will remain in the cooled solution.

BEHAVIOR OF FUEL CORE MATERIALS

Rate of Attack

Ammonium fluoride solutions oxidize uranium metal to uranium (IV), the rate of attack in boiling 6 M NH₄F being about 0.05 g/hr, cm². The addition of 0.5 or 1.0 M NH₄NO₃ to the 6 M NH₄F increases the rate of attack a factor of about two. On exposure of sintered and machined specimens of uranium dioxide to boiling 6 M NH₄F either in the presence or absence of NH₄NO₃, the rate of attack was found to be about the same as that obtained with metallic uranium. The surface area used in the calculation of the rate of attack was that obtained from dimensional measurements.

As would be expected, the rate of attack of uranium-zirconium alloys by ammonium fluoride solutions is higher than the rate of attack of uranium metal. With 95 w/o zirconium alloy, the initial rate of attack in boiling 6 M NH_4F was found to be 2.2 g/hr, cm^2 , which is about 50% greater than that observed with zircaloy-2. The rate remained at values comparable to those obtained with zircaloy-2 throughout the course of the reaction, giving complete dissolution of the zirconium in a short time. With low (5 to 10 w/o) zirconium alloys, the initial rate of attack in boiling 6 M NH_4F was found to be about 1.4 g/hr, cm^2 but the rate of attack decreased greatly as the solution became saturated with uranium (IV) and the alloy piece coated with solid fluoride salt. Thus, on exposure of a 9 w/o zirconium alloy to boiling 6 M NH_4F (initially) for three hours, the extent of attack amounted to only 0.3 g/hr, cm^2 during this time. A similar experiment employing 6 M NH_4F + 1 M NH_4NO_3 gave 0.6 g/hr, cm^2 during the three hour interval.

Exposure of plutonium-aluminum alloy (1.5 w/o Pu) to boiling 6 M NH_4F resulted in a reaction which was initially quite vigorous but whose rate decreased greatly as the alloy became coated with a white solid (presumably aluminum fluoride).

Uranium Loss to Decladding Solution

Since uranium (IV) is only sparingly soluble in zirconium-ammonium fluoride solutions, the loss of uranium to the decladding solution is governed by its solubility in the final solution and, of course, the volume of the solution. The compositions of solutions saturated with respect to uranium (IV) are given in Table VI. In Figure 5, the uranium concentrations are plotted as a function of the "free" fluoride concentration.

The solutions saturated at the boiling point were prepared by exposing uranium metal or uranium dioxide to attack by solutions having the indicated compositions. The values given in parenthesis were deduced from the known amounts of ammonium fluoride and ammonium hexafluorozirconate used in making up the solutions. Solutions saturated at 22°C were obtained by cooling solutions which had been previously saturated at the boiling point. In some instances the boiling solutions were diluted before cooling to avoid precipitation of zirconium fluoro-zirconate and in other cases a portion of the zirconium was allowed to precipitate along with the uranium.

These data illustrate the desirability of terminating the decladding operation at a low "free" fluoride concentration in order to reduce the loss of uranium to the solution. The reduction in the loss of uranium which can be achieved by cooling the decladding solution before it is discarded is also evident.

Uranium concentrations found in boiling, saturated solutions containing 1 M NH_4NO_3 as well as zirconium and ammonium fluorides were found to be a factor of about three lower than those observed in the absence of the ammonium nitrate (at "free" fluoride concentrations from 0.4 to 2.0 molar). Since uranium (VI) was found to be more soluble than uranium (IV) in ammonium

FIGURE 5

SOLUBILITY OF URANIUM (IV) IN
ZIRCONIUM - AMMONIUM FLUORIDE SOLUTIONS

TABLE VI

SOLUBILITY OF URANIUM (IV) IN ZIRCONIUM-AMMONIUM FLUORIDE SOLUTIONS

Temperature	Total Fluoride <u>M</u>	<u>M</u> Zr(VI)	<u>M</u> NH ₄ ⁺	"Free" Fluoride(a) <u>M</u>	Uranium (g/l)
Boiling	6.0	0.00	5.0	6.0	20
Boiling	3.1	0.00	2.5	3.1	7.5
Boiling	(6.0)	(0.50)	(4.0)	3.0	8.0
Boiling	6.2	0.62	3.0	2.5	5.0
Boiling	(6.0)	(0.70)	(3.2)	1.8	5.0
Boiling	6.4	0.80	3.0	1.6	3.6
Boiling	(6.0)	(0.80)	(2.8)	1.2	1.9
Boiling	6.8	0.96	2.7	1.0	1.6
Boiling	6.0	0.86	(2.6)	0.8	1.5
Boiling	(6.0)	(0.90)	(2.4)	0.6	0.8
Boiling	(6.0)	(0.95)	(2.2)	0.3	0.3
Boiling	(6.0)	(1.00)	(2.0)	0.0	0.07
22°C	6.0	0.00	5.0	6.0	3.0
22°C	3.1	0.00	2.5	3.1	2.0
22°C	3.1	0.31	1.5	1.2	0.65
22°C	3.2	0.31	1.5	1.3	0.60
22°C	(3.4)	(0.48)	(1.4)	0.5	0.22
22°C	3.3	0.54	1.1	0.1	0.04
22°C	2.9	0.20	1.9	1.7	0.32 (b)
22°C	5.1	0.66	(1.6)	1.1	0.19 (b)
22°C	4.3	0.57	1.7	0.9	0.12 (b)
22°C	6.6	1.00	(2.0)	0.6	0.10 (b)
22°C	5.8	0.92	2.1	0.3	0.03 (b)

(a) Defined as ((Total M F⁻) - 6 M Zr(IV)).

(b) Solutions resulting from co-precipitation of uranium and zirconium fluorides.

Values in parentheses deduced from known quantities of reagents employed.

fluoride solutions of about two molar or less concentration, it is inferred from this observation that little if any oxidation to uranium (VI) occurred during the two hour duration of these experiments.

Plutonium Loss to Decladding Solution

Experiments designed to estimate the loss of plutonium from an irradiated uranium fuel element to the decladding solution were performed by exposing uranium-plutonium alloy (in one case irradiated uranium was used) to attack by boiling solutions. The concentrations of uranium and plutonium were determined in the

boiling solutions and also in the solutions after they had cooled to about 25°C. In the cases in which zirconium was present in solution, the hot solution was diluted before cooling to prevent precipitation of zirconium. The results of these experiments are presented in Table VII.

TABLE VII

URANIUM AND PLUTONIUM CONCENTRATIONS IN SIMULATED DECLADDING SOLUTIONS

Pu/U in Alloy ₁ (x 10 ⁴)	In Boiling Solution					In Cooled Solution		
	M F ⁻	M Zr(IV)	g/l U	mg/l Pu	Pu/U (x 10 ⁴)	g/l U	mg/l Pu	Pu/U (x 10 ⁴)
3	6	-	15	4.3	2.9	4.5	1.4	3.1
11	6	-	13	6.6	5.1	2.5	1.7	6.8
11	6	0.7	2.5	0.68	2.7	0.2	0.003	0.15
11	6	0.86	1.4	0.23	1.6	0.3	0.015	0.5

It is seen that in the experiments employing the alloy having a plutonium to uranium ratio of 11 x 10⁻⁴ (which corresponds to 1000 g Pu per ton U), the Pu/U ratio in the solutions was in each case less than the ratio in the alloy. Thus the percentage plutonium loss to the simulated decladding solution was, in each case, less than the percentage uranium loss. This fractionation of uranium and plutonium was more apparent in the solutions containing zirconium, especially on cooling. Plutonium concentrations in solutions prepared by the action of zirconium-ammonium fluoride solutions on plutonium-aluminum alloy did not decrease significantly on cooling, implying that the marked decreases observed on cooling the solutions saturated with uranium (IV) are due to the carrying of plutonium on the uranium (IV)-fluoride salt which precipitates on cooling.

It is of interest to note that roughly equivalent plutonium concentrations were found in the two experiments employing 6 M NH₄F alone, even though the plutonium-uranium ratios in the alloys varied by a factor of almost four. It is possible that this concentration may represent the solubility in 6 M NH₄F of the plutonium species formed by the action of this solution on irradiated uranium fuel elements. If the plutonium loss to the decladding solution proves to be determined by solubility considerations, the relative loss of plutonium will decrease with increased plutonium content in the fuel (i.e., with increased pile exposure for uranium elements).

Feed Preparation

As is apparent from the preceding discussion, portions of the uranium and plutonium in the fuel core material will be present as solid fluorides at the completion of the decladding step. In order to recover this material by solvent extraction from aqueous nitrate media it would be desirable to remove or complex the fluoride so that severe corrosion of stainless steel equipment will

not occur. The decision as to how these solid fluorides should be handled depends in large part on the process which will be used to recover and purify the uranium and plutonium. If the process is such that the complexing of fluoride by aluminum ion gives solutions exhibiting little corrosion of the equipment, the solid fluorides can simply be dissolved in aluminum nitrate or aluminum nitrate - nitric acid solutions. If, however, the process is one in which severe corrosion will occur in the presence of fluoride even with aluminum present, the fluoride must be separated from the uranium and plutonium prior to recovery and purification.

One method for separating uranium and plutonium from fluoride before solvent extraction recovery is to convert the solid uranium and plutonium compounds to hydrous oxides by metathesis with hot alkaline solutions. These solid oxides can then be washed to remove the fluoride from the liquid associated with the solid. The conditions and results of such experiments are given in Table VIII. In these experiments, the metathesis operations were performed by stirring the solution and solid at 100°C for the indicated length of time. The washing steps involved 15 minute contactings at room temperature with 0.5 M KOH as the wash solution. Phase separation was accomplished by centrifugation, with the result that significant amounts of liquid were carried from step to step along with the solid.

TABLE VIII
REMOVAL OF FLUORIDE FROM URANIUM AND PLUTONIUM FLUORIDES
BY METATHESIS AND WASHING

Metathesis Conditions			Cumulative Fluoride DF through Indicated Step					
<u>M KOH</u>		<u>Time^(b)</u> <u>(Hours)</u>	<u>Metathesis</u>		<u>First Wash</u>		<u>Second Wash</u>	
<u>Initial</u>	<u>Final^(a)</u>		<u>Obs.</u>	<u>Calc.</u>	<u>Obs.</u>	<u>Calc.</u>	<u>Obs.</u>	<u>Calc.</u>
2.0	0.8	0.5	16	20	74	500	96	11,000
5.0	2.6	0.5	10	10			95	3,000
5.0	3.3	0.5	19	20	150	200	250	3,000
5.0	3.8	0.5	26	20	550	400		
5.0	3.8	3.0	28	20	350	500	600	9,000
15	14	0.5	20	20	410	400	3,000	7,000
15	14	2.2	33	20	450	400	3,700	7,000

(a) Calculated assuming equation for reaction to be

(b) At 100°C.

The results are presented in terms of decontamination factors (DF), which are equal to the fluoride to uranium ratio in the fluoride salt divided by the fluoride to uranium ratio in the resulting solid plus associated liquid. For purposes of comparison, decontamination factors calculated from the solution and solid volume measurements in each step are included. These calculated values (obtained in each step by dividing the total volume by the volume occupied by the solid and associated liquid) should agree with the observed values if complete conversion of the fluoride salt to hydrous oxide had occurred. It is seen that more conversion is obtained when higher concentrations of base are employed in the metathesis step.

Losses of uranium and plutonium during the metathesis and washing steps were quite low -- about 0.02 percent overall.

SUMMARY

In Figure 6 is presented a flowsheet illustrating the procedure involved in preparing a low-fluoride solvent extraction feed solution from a zircaloy clad fuel element. The case chosen for presentation involves a fuel element having a composition approximating that of the uranium dioxide fuel element proposed for the Plutonium Recycle Test Reactor at Hanford. Values of the amount of plutonium present in the various steps are not included since the experimental evidence indicates that the percentage plutonium losses will be less than the percentage uranium losses.

The conditions given for the decladding step result in a terminal "free" fluoride concentration of one molar. Dissolution to lower "free" fluoride concentration would decrease both the solubility of the uranium in the final solution and the dilution factor required to keep the zirconium in solution on cooling. Thus, the waste loss and waste volume decrease as the terminal "free" fluoride concentration decreases. The time required for the decladding operation, however, increases as the terminal "free" fluoride concentration decreases. The final choice of conditions for the decladding step, then, will probably be based largely on economic considerations. It should also be emphasized that, other things being equal, the waste loss and waste volume increase as the zirconium content of the fuel element increases.

The amount of uranium which will be converted to insoluble fluorides during the decladding operation cannot be clearly determined at this time. From the rate of attack observed with sintered and machined specimens of uranium dioxide in 6 M NH_4F and the ratio of area to mass of the unclad and unirradiated element, it is calculated that 1.5% of the core material will react per hour. During irradiation, however, two changes occur which make an estimate of the amount of conversion when decladding an irradiated element very difficult. The cladding becomes coated with passive zirconium oxide and the uranium dioxide core becomes fractured. The pitting type attack that will then occur in the decladding step tends to give a lower effective area to mass ratio but the result of the fracturing of the core is to give a higher area to mass ratio. For lack of detailed information, a value of 5 to 10% conversion was assumed.

The amounts of metathesis and wash solutions shown in the flowsheet were chosen to give a suitably low fluoride concentration in the feed solution, based on the estimated extent of conversion of uranium and plutonium to solid fluorides. More complete removal of fluoride can be achieved by employing a more concentrated metathesis solution and more extensive washing. As was mentioned previously, if the uranium and plutonium are to be recovered by a process in which the presence of aluminum fluoride complexes is acceptable, simple dissolution of the solid fluorides in aluminum nitrate or nitric acid - aluminum nitrate mixtures could be substituted for the more laborious metathesis and washing procedure.

REFERENCE

- (1) Hevesy, G. v., Christiansen, J. A., and Berglund, V., The Solubility of the Double Fluorides of Zirconium and Hafnium, Z. anorg. allgem. Chem., 144: 69-74, (1925).

FIGURE 6

PREPARATION OF LOW-FLUORIDE FEED SOLUTION FROM ZIRCONIUM CLAD FUEL ELEMENT