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AN IMPROVED AQUEOUS PROCESS FOR ZIRCONIUM ALLOY NUCLEAR REACTOR FUELS

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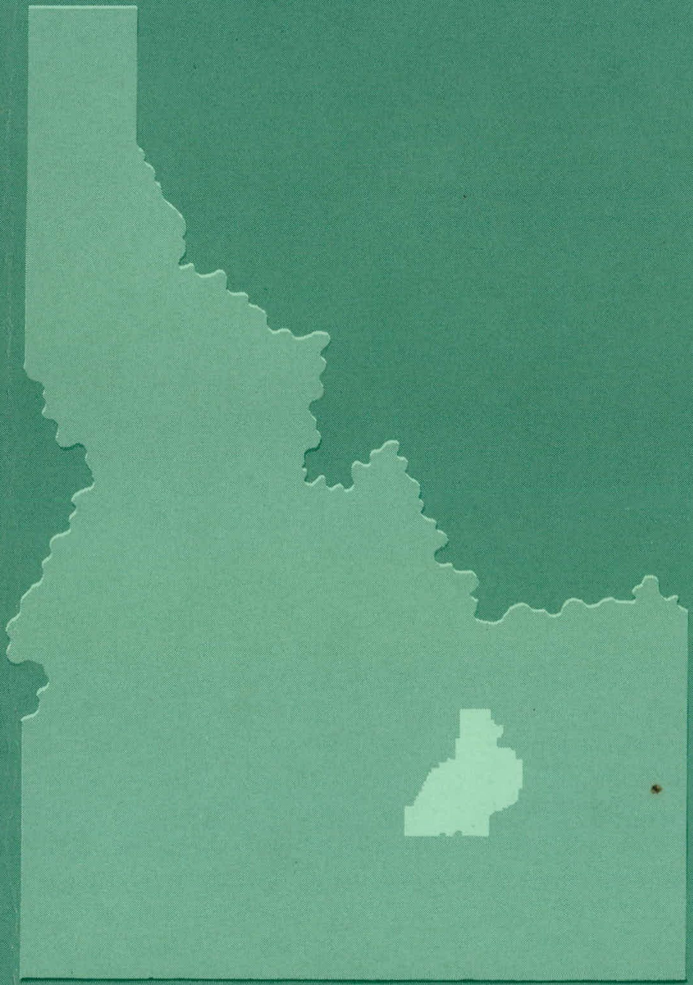
PART II. CONTINUOUS DISSOLUTION WITH 5M HYDROFLUORIC ACID

MASTER

B. J. Newby



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PART II. CONTINUOUS DISSOLUTION WITH 5M HYDROFLUORIC ACID

B. J. Newby

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PART II. CONTINUOUS DISSOLUTION WITH 5M HYDROFLUORIC ACID

B. J. Newby

ABSTRACT

Increased use of uranium-zirconium alloy fuels in propulsion reactors indicates that a high capacity process for the recovery of enriched uranium from such fuels will be needed in the near future. Modification of the existing batch hydrofluoric acid process, to provide continuous dissolution, appears to be the most practicable way to install a high capacity process for uranium-zirconium alloy fuels in the Idaho Chemical Processing Plant. Dissolution in about 5M hydrofluoric acid is preferred because it results in the dissolution of fuels containing higher percentages of uranium and solutions more stable with respect to zirconium and fluoride salts, than do higher concentrations of hydrofluoric acid. All of the zirconium and uranium and one-third of the tin in a 2.5 per cent uranium-Zircaloy-2 fuel can be dissolved continuously and retained in solution with 5M hydrofluoric acid at a dissolution temperature of 60 to 80°C and a dissolver feed-rate to fuel-surface ratio of 0.04 cm/min. The hydrofluoric acid also readily attacks oxidized zirconium alloy. Oxidants are not necessary in the dissolution. The dissolver product contains only a trace of zirconium-fluoride salts, even after standing for several months.

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PART II. CONTINUOUS DISSOLUTION WITH 5M HYDROFLUORIC ACID

B. J. Newby

I. SUMMARY

The increased use of zirconium as an alloying material in nuclear reactor fuels has necessitated the development of a high capacity recovery process for enriched uranium-zirconium alloy fuels. Modifications of the existing Idaho Chemical Processing Plant's hydrofluoric acid batch method to produce continuous dissolution are considered to be the most practicable method for developing a high capacity recovery process with minimum new investment expenditures. The basis of this approach is a detailed evaluation of various fuel reprocessing methods and their possible installation in the ICPP. Dissolution with 5M hydrofluoric acid was selected over higher acid concentrations, because it favors high uranium solubility and produces solutions more stable to precipitation of zirconium salts at the low dissolver feed rates required by engineering design considerations. All of the zirconium and uranium and one-third of the tin in a 2.5 per cent uranium-Zircaloy-2 fuel can be dissolved continuously and retained in solution with 5M hydrofluoric acid at a dissolution temperature of 60 to 80°C and a dissolver feed-rate to fuel-surface ratio of 0.04 cm/min.

In experiments with 3 weight per cent uranium fuels, a composition considerably in excess of that to be dealt with in process, difficulty was experienced with the buildup of uranium-containing solids in the dissolver under certain operating conditions. This effect was essentially eliminated by operation at 60°C instead of 90°C and by recirculation of the dissolvent, or other solution motion which would tend to prevent plating of the suspended uranium tetrafluoride on the walls of the dissolver. Both of these are indicated as optimum operating conditions for the standard flowsheet to allow safety factors against uranium precipitation.

The addition of oxidants to dissolver feed slightly increased the percentage of uranium that could be dissolved from zirconium fuels and decreased slightly uranium losses to dissolver residues and interior surfaces.

Hydrofluoric acid readily attacked oxidized zirconium alloy.

II. INTRODUCTION

The increased use of zirconium-uranium alloy reactor fuels containing up to 2.2 per cent uranium required that a high capacity process for the recovery of enriched uranium be developed. Currently, the most successful method for processing zirconium-uranium alloy fuel containing 1.5 per cent uranium or less involves batch dissolution with hydrofluoric acid at the Idaho Chemical Processing Plant (ICPP). Since a high capacity solvent extraction system (which can be used in combination with a hydrofluoric acid dissolution method) is also available at the ICPP, a logical method for increasing the processing capacity for zirconium-uranium type fuel is to adapt the present batch hydrofluoric acid process to continuous dissolution(1). Homogeneous batch dissolution of zirconium alloy fuels containing up to 3 per cent uranium was accomplished in the laboratory both by adding an oxidant to convert uranium(IV) to the more soluble uranium(VI) and by obtaining a dissolver solution so dilute that the uranium tetrafluoride is soluble(2). The latter approach is preferred over methods utilizing higher hydrofluoric acid concentrations, because it favors higher uranium solubility and produces solutions more stable to precipitation of zirconium salts at low dissolver feed rates(3). All the work described in this report was performed using a dissolvent feed-rate to fuel-surface ratio of 0.04 cm/min. This low dissolver feed rate was suggested by engineering design considerations.

Plates of zirconium-uranium alloy clad in Zircaloy-2 were used for simulated fuel in these experiments. In all but two experiments these were selected to have a uranium content of 3 per cent of the total weight. This uranium concentration, in excess of the design, was used to permit evaluation of the relative effectiveness of the different modes of operation at or above the uranium concentrations intended for the flowsheet. When 3 per cent uranium-Zircaloy-2 fuel is dissolved continuously in $5\underline{M}$ hydrofluoric acid, solids containing uranium are found in varying degrees in the dissolver product, adhering to the walls of the dissolver, and at the bottom of the dissolver because, in general, the uranium content of the fuel exceeded that which could be dissolved and retained in solution. To determine the conditions which gave greatest freedom from uranium precipitation, studies in the bench scale continuous dissolver were made to determine how the concentration of dissolved uranium in the dissolver product could be increased by the presence of oxidants in the dissolver feed or by a change in the method of operating the dissolver.

III. EQUIPMENT AND PROCEDURES

All studies were made in a one-inch-diameter continuous laboratory dissolver constructed of Monel. A detailed description of the equipment and procedures is given in Part I of this series of reports(3). The dissolution section of the dissolver was 16 inches high, and the rate of fuel addition was regulated to maintain within the dissolver undissolved fuel having a surface area of approximately 320 square centimeters at all times, which was generally a depth of 6 inches of fuel. Zircaloy-2 fuel containing from 2.2 to 3 per cent uranium was dissolved continuously, with or without oxidant or oxidant and fluoboric acids in 5M fluoride solution at a dissolvent feed-rate to fuel-surface ratio of 0.04 cm/min (a feed rate of about 11 ml/min). The length of a dissolution run depended upon how quickly dissolution equilibrium was attained. It was assumed that the dissolver was at equilibrium when three consecutive specific gravity measurements of dissolver product, taken at half-hour intervals, were identical within the uncertainty of the measurement. In general, equilibrium was reached within three hours, and the total run time was about 6.5 hours. Elevated temperatures were obtained with heating tape wrapped around the dissolution section. Lower temperatures were maintained by inserting the dissolution section into a constant temperature water bath. For determination of the material balance, uranium adhering to dissolver walls was removed by boiling with 20 per cent sodium hydroxide in the presence of metallic zinc.

During the usual method of dissolver operation, feed solution was pumped into the bottom of the dissolver and dissolver product overflowed from the dissolver 16 inches above the feed inlet (upflow dissolution). This method was modified by appropriate means for downflow and recirculating dissolution. During downflow operations, feed was pumped into the dissolver through a line 23 inches above the bottom and dissolver product solution left the dissolver through a line in the bottom. In recirculating operation, dissolver product was removed from the dissolver at a rate of 300 ml/min by a positive displacement pump, through a line one inch below the dissolver outlet for upflow operation and was pumped back into the bottom of the dissolver. Hydrofluoric acid reagent was pumped into the dissolver through the recirculating line and dissolver product solution left the dissolver through the line that served as the dissolver outlet during upflow dissolution.

IV. EXPERIMENTAL RESULTS WITHOUT OXIDANTS

Three possible means of achieving higher uranium concentrations in the effluent from continuous dissolution without oxidants are as follows: (1) dissolving at lower temperatures, (2) downflow operation of the dissolver or, (3) use of a recirculating dissolver. Dissolutions with 5M hydrofluoric acid at 60°C produce a higher proportion of the higher hydrate of uranium tetrafluoride, $UF_4 \cdot 2.5H_2O$, than dissolutions at 90°C. At 90°C the lower hydrate, $UF_4 \cdot 3/4H_2O$, predominates. The different hydrates have different densities, solubilities and possibly different adhering tendencies(3). The higher liquid flow rates of a recirculating, rather than an upflow dissolver should give solids less chance to adhere to the dissolver walls and build up in the bottom of the dissolver. Also, uranium solids should be swept out of a dissolver much more easily when the slurry leaves at the bottom rather than overflows from the dissolver at an elevated point.

A. Effect of Method of Operation

Several runs were made at different temperatures using both upflow and downflow dissolution. In addition, one dissolution was made in a recirculating dissolver. The results of this study are summarized in Table 1. The per cent of uranium adhering to the dissolver walls in runs

113 and 114, as shown in Table 1, is biased low because this percentage applied only to the uranium in the dissolution section of the dissolver (part of the dissolver included between feed inlet and product outlet); in other runs, this figure represents uranium on the walls throughout the complete height of the dissolver.

The quantity of uranium solids lost to the dissolver (adhering to sides and on bottom of dissolver) was essentially the same in downflow and upflow dissolution at the same temperature (runs 117 and 118 at 60°C and runs 111, 115, and 128 at about 90°C), indicating that loss of uranium is not dependent on directional flow of dissolvent.

The results of three upflow, three downflow, and one recirculating dissolution, at different measured temperatures, are plotted in Figure 1. This figure includes data from runs 111, 113, 114, 116, 117, 118 and 128. From these data, the operation of a downflow dissolver at 80°C and below, or a recirculating dissolver at 71°C, is indicated as having an advantage over upflow dissolution at the same temperatures for achieving higher concentrations of uranium in solution. Since a high proportion of the uranium present in the fuel was dissolved in downflow and recirculating runs 113, 114, 116, and 117, only a small amount of uranium was present as slurry in the effluents. The difference in apparent uranium solubility, when the manner of operation of the dissolver is changed, is tentatively associated with fluoride-to-zirconium mole ratio. The solubility of uranium tetrafluoride increases sharply as the mole ratio of fluoride to zirconium and the fluoride concentration of the solution decreases(3).

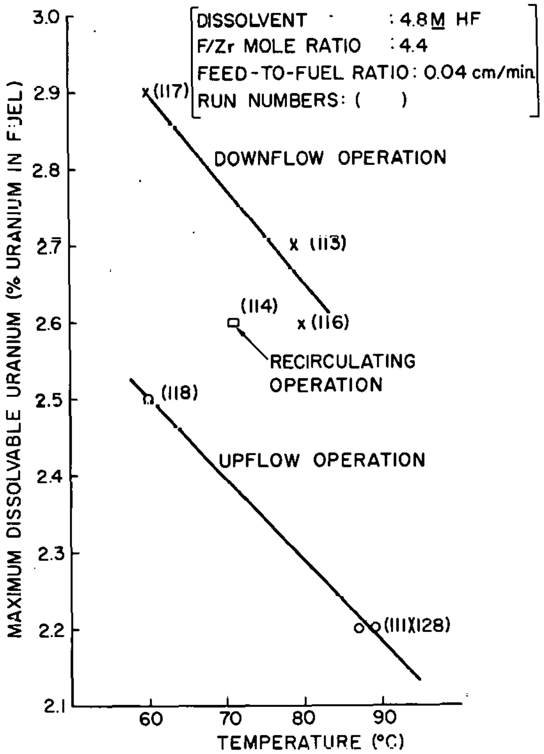

Fig. 1 Influence of temperature and direction of acid flow on dissolution of uranium in Zircaloy-2 uranium fuel.

In downflow operation, dissolution slurries rode higher in the dissolver and undissolved fuel within the dissolver was coated with more zirconium-containing solid than in the other two types of dissolution. In the recirculating operation considerable hydrogen was present in the recirculation loop. The presence of hydrogen in the recirculating loop possibly reduces the effectiveness of an oxidant.

The dissolution temperature for all of the runs was measured with a thermocouple inserted into a thermocouple well that entered the dissolver about two-thirds of the distance up from the bottom of the dissolver section and was bent parallel to the dissolver wall. Using the same amount of applied

Table 1

CONTINUOUS LABORATORY DISSOLUTION OF ZIRCONIUM FUEL WITHOUT OXIDANTS

Conditions: Dissolvent acid feed = 4.8 $\underline{M}$ HF, fuel = 3% uranium-Zircaloy-2, and feed-to-fuel ratio(a) = 0.04 cm/min

Run No.	Dissolvent Acid Flow Direction	Dissolution Rate mg/(cm^2)(min)	Dissolution Temperature (°C)	Dissolver Product Analysis Zr (M)	F to Zr Mole Ratio	U g/l	Fuel Uranium Content Dissolvable(b) (% U)	% of U Lost to Solids in Bottom of Dissolver	% of U Adhering to Dissolver Walls	Dissolver Product Stability at 23°C
117	downflow	3.8	60	1.19	4.3	3.3	2.9	0.005	0.08	stable > 2 wks.
118	upflow	3.7	60	1.14	4.6	2.7	2.5	0.1	0.02	sl. unstable after 5 days
114	recirculated	3.7	71	1.19	4.4	2.9	2.6	0.03	0.003	stable > 1 mo.
113	downflow	3.8	79	1.22	4.5	3.1	2.7	0.03	0.001	sl. unstable after 1 mo.
116	downflow	3.7	80	1.17	4.4	2.9	2.6	0.01	0.2	sl. unstable after 2 days
128	upflow	3.7	87	1.26	4.5	2.6	2.2	4.6	0.5	sl. unstable
111	upflow	4.0	90	1.25	4.4	2.6	2.2	4.0	3.0	sl. unstable
115	downflow	3.5	92	1.06	5.4	1.5	1.5	0.5	6	sl. unstable after 8 days

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(a) $\frac{\text{Dissolvent Feed Rate-(cm}^3\text{/min)}}{\text{Fuel Surface Area-(cm}^2\text{)}}$

(b) This calculation (in this Table and in successive Tables and Figures) was experimentally verified by dissolving fuels containing less than 3 per cent uranium. Such dissolutions at 90°C resulted in less uranium being lost to solids held within the dissolver than did similar downflow or upflow dissolutions using 3 per cent uranium fuel.

heat and approximately the same feed rate (runs 111, 113, 114, 116, and 128) the dissolution temperatures measured by the thermocouple for downflow, recirculation, and upflow dissolutions were 80°C, 71°C, and 90°C, respectively. These measured temperatures are influenced by the fact that the dissolution takes place in a different section of the dissolver for upflow and downflow dissolutions; and in the first case, the heated solution is swept away from the thermocouple. Certainly the temperature with recirculation would be expected to be lower because some cooling of the dissolver product occurred in the external loop.

B. Effect of Operating Temperature

The data of Figure 1 indicate that operation of the laboratory continuous dissolver, either upflow or downflow, resulted in a higher concentration of uranium in solution as the dissolution temperature was decreased; the rate of reaction was independent of temperature over the range studied, 60 to 92°C, as shown in Table 1. Where the data were available, the amount of precipitated uranium remaining in the dissolver at the termination of the runs was measured and is plotted against temperature in Figure 2. There was less uranium-containing solid left in the dissolver at the lower temperatures. This difference in solubility of the uranium as a function of temperature is compatible with the fact that a different uranium tetrafluoride species is probably produced at the lower temperature. Hydrolysis of uranium tetrafluoride or colloid formation may also be involved.

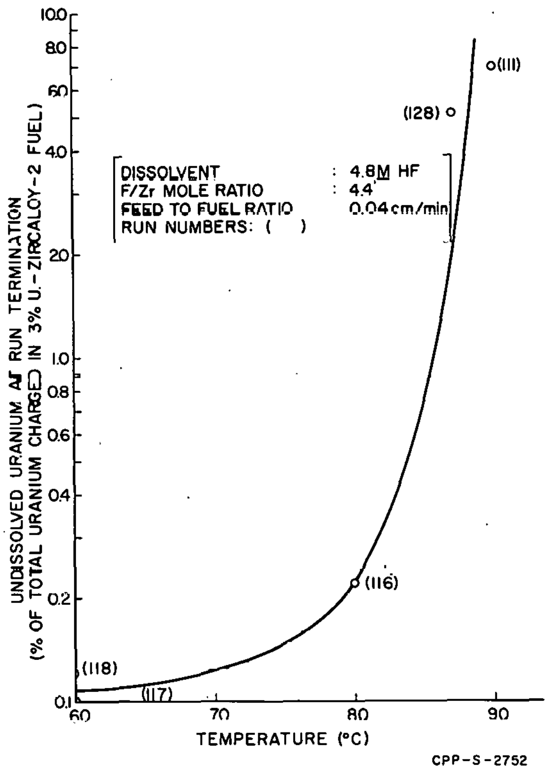

Fig. 2 Effect of dissolution temperature on uranium residue left in the dissolver.

C. Effect of Oxidized Fuel

Since much of the fuel processed at the TCPP is oxidized in reactor environments, the effect of the oxide film on dissolution of the fuel was studied. Three per cent uranium-Zircaloy-2 fuel was oxidized in a muffle furnace for 45 minutes at 1500°F. The batch dissolution characteristics of this oxidized fuel were compared to fuel oxidized in an autoclave(3). Both fuels immersed in boiling 5.0M hydrofluoric acid required an induction period to initiate the dissolution. This induction period was about 2 minutes for fuel oxidized in the autoclave and 6 minutes for fuel oxidized in air. The air-oxidized fuel was used in the laboratory experiments because it probably represented the worse possible condition that would be encountered.

During continuous dissolution

of unoxidized fuel in 5M hydrofluoric acid solutions, no heat is required to initiate the dissolution; the heat of reaction is sufficient to continue the dissolution. To initiate the dissolution of air-oxidized fuel, external heat was necessary, but once the dissolution was started the heat of reaction continued the dissolution. The hydrofluoric acid dissolved the oxide film very slowly, if at all, but seemed to penetrate beneath the film and flake it off. As a result, the quantity of residue remaining in the dissolver was about 3 times as great as when unoxidized fuel was used. Table 2 compares the dissolution of oxidized and unoxidized fuel under the same conditions. The presence of the oxide film depressed the dissolution rate resulting in a corresponding decrease in the zirconium and uranium concentration and an increase in the fluoride-to-zirconium mole ratio in the dissolver product solution. The dependence of uranium solubility on the fluoride and zirconium concentration of a solution will be discussed in a later section.

Table 2

EFFECT OF FUEL OXIDE FILMS ON THE CONTINUOUS DISSOLUTION OF 3 PER CENT URANIUM-ZIRCALOY-2 FUEL IN 5M HYDROFLUORIC ACID

Conditions: Up-flow dissolver, feed-to-fuel-surface ratio of 0.04 cm/min, and an operating temperatures of ~ 90°C.

Run No.	Oxidized Fuel Used	Dissolution Rate mg/(cm^2)(min)	Dissolver Product Analysis Zr (M)	Dissolver Product Analysis F-to-Zr Mole Ratio	Dissolver Product Analysis U g/l	Maximum Dissolvable Uranium (% Uranium in Fuel)
111	No	4.0	1.25	4.4	2.6	2.2
128	No	3.7	1.26	4.5	2.6	2.2
127	Yes	3.2	1.02	4.9	1.8	1.9

V. EXPERIMENTAL RESULTS WITH OXIDIZING AGENTS PRESENT

Laboratory studies of batch dissolution have shown that the use of low concentrations of oxidizing agents makes possible the homogeneous dissolution of fuels containing up to 3 per cent by weight uranium(2). The increase of uranium solubility by oxidation is recognized as being different in batch and in continuous dissolution, in that in batch dissolution, the oxidation-dissolution of a portion of the uranium tetrafluoride takes place after the dissolution of zirconium is complete, while in continuous dissolution, it appears to be difficult to oxidize uranium in the presence of the high concentration of hydrogen produced from the simultaneous dissolution of zirconium. Oxidation of uranium(IV) to uranium(VI) by chromate or peroxide, based on standard potentials for the reactions involved during dissolution, should not take place until essentially all of the metallic constituents have dissolved. However, it would be possible to oxidize uranium in the presence of hydrogen and dissolving metal if the reaction kinetics do not favor reaction of the oxidant used with hydrogen and dissolving metal. Previous work has indicated that hydrogen peroxide, as the oxidant, survived dissolution of Zircaloy-2 by hydrofluoric acid(3).

Upflow dissolutions having a feed-to-fuel-surface-area ratio of 0.04 cm/min, were made using 4.8M hydrofluoric acid with 0.03, 0.06, 0.15, and 0.5M nitric acid as well as with 0.1M hydrogen peroxide, 0.03M aluminum nitrate, and 0.06M chromic acid to dissolve 3 per cent uranium-Zircaloy-2 fuel. The dissolution temperature of all runs was about 90°C. Approximate corrosion rates were determined on a Monel coupon, located at the point of contact between the feed solution and the fuel. The results of these runs are shown in Table 3 and Figure 3.

A. Nitric Acid as Oxidant

Nitric acid in concentrations up to 0.06M appeared to decrease slightly the uranium adhering to the dissolver walls and the residue in the bottom of the dissolver and to increase slightly the quantity of uranium that could be dissolved from a fuel without increasing Monel corrosion. Greater than 0.06M nitric acid in the feed increased the amount of tin dissolved, which resulted in a corresponding decrease in the amount of solids remaining in the dissolver at the end of a run. Nitric acid in the dissolver feed decreased the fuel dissolution rate, resulting in a corresponding decrease of zirconium concentration and an increase of fluoride-to-zirconium mole ratio in the dissolver product. Excess nitric acid (0.5M) produced a dissolver product solution less favorable for retention of uranium in solution; in addition, the Monel corrosion rate was excessively high. There was less uranium in the dissolver product solution and more uranium lost to the dissolver, than in runs using less or no nitric acid. Figure 3 summarizes the variation of Monel corrosion and uranium behavior as a function of dissolvent nitric acid concentration. The undesirable uranium behavior experienced during the dissolution using 0.5M nitric acid dissolver feed (run 123) was caused by the high fluoride-to-zirconium mole ratio (4.9) of the solutions. Figure 4

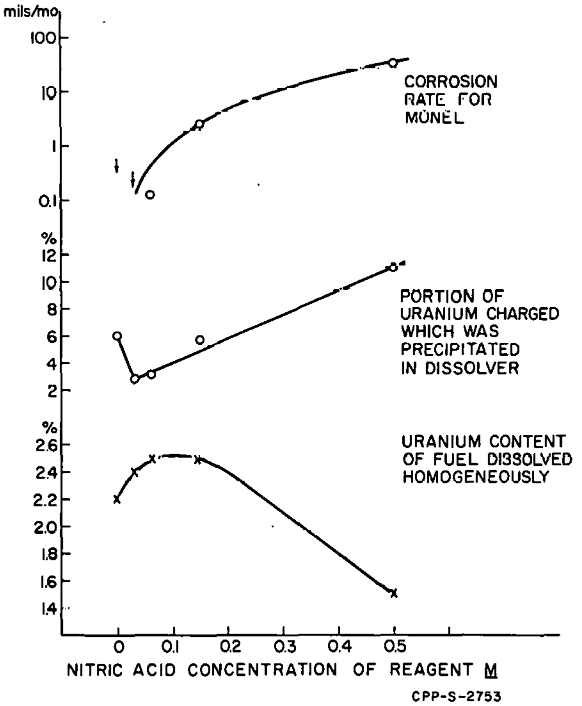

Fig. 3 Effect of nitric acid on uranium behavior and corrosion.

Table 3

EFFECT OF OXIDANTS ON THE CONTINUOUS DISSOLUTION OF 3 PER CENT URANIUM-ZIRCALOY-2 FUEL IN 5M HYDROFLUORIC ACID

Conditions: Upflow dissolver, feed-to-fuel-surface-area ratio of 0.04 cm/min, operating temperature 90°C, and a 6.5 hr. dissolution period

			Dissolver Product Analysis									
Run No.	Oxidant in Dissolver Feed	Dissolution Rate mg/(cm^2)(min)	Zr (M)	F to Zr Mole Ratio	U g/l	Sn g/l	Solid Content g/l	Grams of Solid Remaining in Dissolver	Fuel Uranium Content Dissolvable (%)	% of U Lost to Solids in Bottom of Dissolver	% of U Adhering to Dissolver Walls	Monel Corrosion Rates mils/mo.
111 & 128 Ave.	None	3.8	1.25	4.4	2.6	0.6	-	3.73	2.2	4	2	< 0.5
126	0.03M HNO_3	3.7	1.16	4.6	2.7	0.5	-	3.65	2.4	1.1	1.7	< 0.3
121	0.06M HNO_3	3.5	1.08	4.6	2.6	0.63	0.019	3.64	2.5	1.9	1.2	0.13
125	0.15M HNO_3	3.5	1.09	4.6	2.6	1.21	0.037	2.66	2.5	1.7	4.0	2.5
123	0.5M HNO_3	3.2	1.02	4.9	1.5	1.27	0.17	2.45	1.5	6	5	33
119	0.1M H_2O_2	3.5	1.12	4.6	2.7	0.76	0.02	3.51	2.5	2.2	1.3	-
120	0.06M CrO_3	3.5	1.10	4.7	2.6	0.94	0.008	2.34	2.5	1.6	0.6	6.7
122	0.03M $Al(NO_3)_3$	3.5	1.06	4.7	2.5	0.59	0.015	4.24	2.5	2.1	1.8	1.1

shows that the uranium solubility in such solutions decreases markedly as the fluoride-to-zirconium mole ratio is increased from 4.6 to 4.9.

One dissolution was carried out (under the conditions of Table 3) using 4.8M hydrofluoric acid - 0.06M nitric acid to dissolve an alloy which was 5 per cent uranium, 1 per cent tin, and 94 per cent zirconium. The dissolution rate, fluoride-to-zirconium mole ratio, tin concentration, and zirconium concentration of the dissolver product were about identical to those observed in dissolving 3 per cent uranium-Zircaloy-2 fuel under the same conditions. A dissolver product solution containing 3.3 g of uranium per liter was produced; this probably represents the maximum uranium concentration possible when 5.0M hydrofluoric acid is used as the dissolvent. As was expected, uranium lost to the dissolver (12.6 per cent), dissolver product solution solid content (0.45 g/l), and solids remaining in the dissolver (4.43 g) were greater than for dissolution of 3 per cent uranium fuel.

B. Other Oxidants

Dissolutions under the same conditions as those utilizing nitric acid were made using hydrogen peroxide, chromic acid, and aluminum nitrate as oxidants. As shown in Table 3, these oxidants acted similarly to nitric acid. Neither hydrogen peroxide nor aluminum nitrate appeared to offer any advantages over nitric acid. The aluminum nitrate resulted in a greater quantity of solids remaining in the dissolver, probably due to the depletion of free fluoride. Chromic acid appeared to be more effective than the other oxidants in decreasing uranium lost to the dissolver and increasing the amount of tin dissolved, but the high corrosion rate on Monel prohibits its use.

VI. GENERAL OBSERVATIONS ON URANIUM SOLUBILITY BEHAVIOR

The behavior of uranium in the dissolver product solution from the dissolution of zirconium-uranium alloys in hydrofluoric acid is extremely complex. In the process being designed, the processing of fuels containing 2.2 per cent uranium must be provided for. In the dissolver product solution with 5M hydrofluoric acid, the ratio of uranium to zirconium produces a uranium concentration which, in general, exceeds the measured solubility of the lower hydrate of uranium tetrafluoride(3). This lower hydrate, usually described as $UF_4 \cdot 3/4H_2O$ can have from 0.4 to 2 moles of water per mole of uranium tetrafluoride without changing the psuedo-cubic crystalline structure. A higher, better defined hydrate, $UF_4 \cdot 2.5H_2O$, also exists, and may be present in the process solutions. The relative amounts of the two hydrates present in a given solution depend on the temperature and the solution composition. Higher temperatures and higher fluoride concentrations favor the formation of the lower hydrate. Hydrolysis products of uranium tetrafluoride may also be present. Observations from the solubility studies suggest that the lower hydrate converts very slowly to the higher hydrate even in an environment which greatly favors the latter form. Presumably, uranium tetrafluoride, formed by the dissolution of uranium metal, would be in equilibrium with its environment, and might include several species. Such solutions would exhibit the overall solubility of the several species. In addition to the

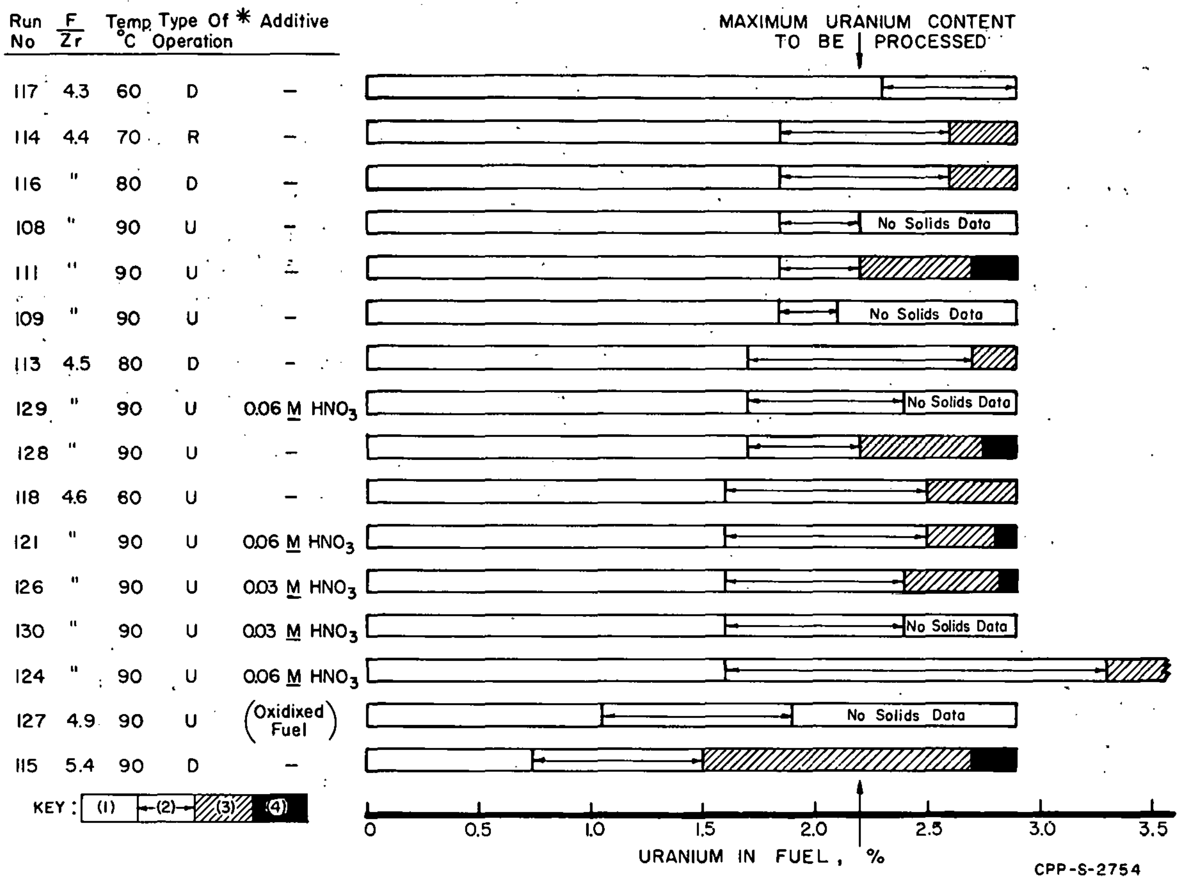

Fig. 4 Uranium behavior during dissolution of uranium-zirconium alloy in $5\underline{M}$ hydrofluoric acid

Area (1) represents the region of solubility of uranium tetrafluoride-three quarter hydrate as determined by solubility measurements made at ANL(4) and ICPP(2). The solubility is essentially independent of temperature between 23° and 95°C.

Area (2) represents additional uranium "solubility" as defined by the uranium concentration of dissolver effluent solution which passes a 10-15 micron filter.

Area (3) represents the uranium which slurries from the operating dissolver but will not pass the 10-15 micron filter.

Area (4) indicates the quantity of uranium found adhering to the walls or in base of the dissolver.

* Downflow, upflow or recirculating operation of the dissolver.

soluble uranium (defined as passing a 10-15 micron filter), there is appreciable uranium which is slurried from the dissolver as particles fine enough to move with the flowing solution, but too large to pass the filter. In some cases, green or discolored uranium tetrafluoride was observed coating the walls of the dissolver, or collected in the base of the dissolver. In Figure 4, the uranium distribution for 16 continuous dissolution runs is shown. The uranium "solubility" in every case exceeded the values predicted from solubility measurements(3). Figure 4 indicates that with 3 per cent uranium fuel, uranium solubility equal to or exceeding that equivalent to the required 2.2 per cent was experienced. One dissolution, run 124, done with a 5 per cent fuel, indicates that the "solubility" of uranium is dependent on the total amount of uranium present, strongly suggesting dependence on several species and possibly on colloid formation. The general trend of increasing uranium solubility with decreasing fluoride-to-zirconium mole ratio is shown in Figure 4 as well as the less significant effects of dissolution temperature and nitric acid, which are discussed elsewhere in greater detail.

It can be concluded that dissolutions carried out at a fluoride-to-zirconium mole ratio of about 4.6 and with either a lower temperature or a few hundreths molar nitric acid present, or both, will yield adequate uranium solubility for a 2.2 per cent fuel, with a margin of safety in the solubility above that equivalent to a 2.2 per cent fuel plus the demonstrated ability to carry additional uranium from the dissolver as a slurry. In process, all species of uranium are converted continuously to highly soluble uranyl ion in the adjustment vessel which immediately follows the dissolver.

VII. CONCLUSIONS

All of the zirconium, a third of the tin, and 70 per cent of the uranium can be dissolved continuously from 3 per cent uranium-Zircaloy-2 fuel with 5M hydrofluoric acid using a feed-rate to fuel-surface ratio of 0.04 cm/min in an upflow dissolver (usual mode of operation) at about 90°C, the approximate temperature maintained by the heat of reaction. Much of the remaining undissolved tin and uranium are slurried out of the dissolver in the dissolver product solution. However, about 7 per cent of the uranium either is lost to solids, that can not be slurried out of the dissolver with the low dissolver feed rate used, or adhered tightly to the dissolver walls. Operation under these conditions would require frequent dissolver "clean-outs" to recover lost uranium and to prevent plugging of the dissolver.

Forcing an upflow dissolver to operate at 60°C results in only about 0.1 per cent loss of uranium to the dissolver using a 3 per cent uranium-Zircaloy-2 fuel. Eighty per cent of the uranium is dissolved and the remaining 19.9 per cent is in the form of a slurry. Cooling could probably be simplified, uranium losses to the dissolver maintained at a low value, and dissolvable uranium kept high by the use of a recirculating dissolver.

It is recommended that a recirculating dissolver be used to continuously dissolve zirconium alloy fuel containing up to 3 weight per cent uranium if a feed-rate to fuel-surface ratio as low as 0.04 cm/min is essential. A properly designed recirculating dissolver should be able to sweep all undissolved residue out of the dissolver by the use of high recirculating rates while maintaining a low feed rate, thus eliminating the danger of the dissolver becoming plugged. A subsequent adjustment step would dissolve solids that have been slurried out of the dissolver. Essentially no uranium adheres to the dissolver walls during this type of an operation. With fuel of 2.2 per cent uranium content, greater latitude is avilable for the selection of dissolver operating conditions.

The short term dissolutions, described in this report, showed some advantage of adding oxidants to dissolver feed. Small amounts of nitric acid, hydrogen peroxide, or aluminum nitrate were not corrosive to Monel, the oxidants decreased slightly the amount of uranium lost to the dissolver walls and dissolver residue, and slightly increased the quantity of uranium that could be dissolved from a fuel.

It is desirable to maintain a fluoride-to-zirconium mole ratio no greater than 4.7 to dissolve and keep in solution a high proportion of the uranium in a zirconium fuel containing 2 to 3 per cent uranium. However, a fluoride-to-zirconium mole ratio less than 4.7 leads to zirconium fluoride instability. At a given dissolver feed rate, there is very little that can be done to increase or decrease the fluoride-to-zirconium mole ratio during dissolution. For example, the addition of 5.0$\underline{M}$ hydrofluoric acid to a continuous dissolver at a feed-rate to fuel-surface ratio of 0.04 cm/min produced dissolver product having a fluoride-to-zirconium mole ratio of 4.3 to 4.6. The addition of oxidant to the feed, in quantities that will not corrode Monel excessively, gives a solution with a ratio of from 4.6 to 4.7. Dissolver products having a fluoride-to-zirconium mole ratio varying from 4.3 to 4.7 generally contain a trace of fine solids almost as soon as they are cooled to room temperature; the quantity of solid doesn't increase after several months of standing, however. Such a small amount of solid could easily be transferred from vessel to vessel and would be dissolved in a subsequent adjustment step.

Hydrofluoric acid attacks zirconium fuels having thick oxidized films after initial heat is applied to start the dissolution reaction. Thus, hydrofluoric acid should readily dissolve fuel oxidized under any reactor environments.

The recommended material balance for the dissolution of 2.2 per cent uranium-Zircaloy-2 fuel in 4.8$\underline{M}$ hydrofluoric acid is shown in Table 4. This is a typical material balance obtained from using an upflow dissolver at 60°C, a downflow dissolver at from 60 to 80°C, or a recirculating dissolver at 70°C.

Table 4

MATERIAL BALANCE FOR THE CONTINUOUS DISSOLUTION OF 2.2% URANIUM-ZIRCALOY-2 FUEL IN $5\underline{M}$ HYDROFLUORIC ACID

		Fuel Charge	Dissolver Feed	Off-Gas	Dissolver Product Solution
Flow Rate,	(l/h)		967		895
U,	g/l	2.2 Kg			2.46
Zr,	$\underline{M}$	96.3 Kg			1.18
Sn,	g/l	1.5 Kg			0.6
H^+,	$\underline{M}$		4.8		0.46
F,	$\underline{M}$		4.8		5.19
Solids,	Kg				1.3 (0.9 Kg of Sn)
H_2				4230 moles	

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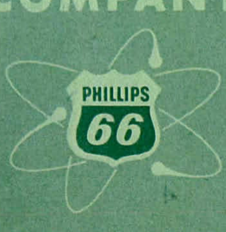

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