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ELECTROLYTIC DISSOLUTION OF POWER REACTOR FUELS IN NITRIC ACID

by

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ABSTRACT

The electrolytic oxidation in nitric acid of stainless steel, zirconium, Zircaloy-2, zirconium-uranium alloy, aluminum, and uranium-molybdenum alloy was demonstrated on a laboratory scale. The rate of chemical dissolution of UO_2 in nitric acid was measured. Corrosion of stainless steel by these dissolver solutions was measured and found to be negligible. Electrolytic dissolution was demonstrated to be a practical technique for the first step in processing fuel elements of several types of power reactors.

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ELECTROLYTIC DISSOLUTION OF POWER REACTOR FUELS IN NITRIC ACID

INTRODUCTION

Spent fuel elements from power reactors must be dissolved prior to uranium recovery by solvent extraction. Several processes, such as Darex(1), which uses aqua regia; Zirflex(2), which uses ammonium fluoride - ammonium nitrate; and Sulfex(3), which uses sulfuric acid, have been proposed for the chemical dissolution of the cladding materials. The majority of these claddings, which prevent corrosion of fuel during irradiation, are stainless steel or Zircaloy-2 (Zr - 1.5% Sn). The uranium fuel in most of the elements is in the form of UO_2, although Zr-U alloys, U-Al alloys, and compacts of UO_2 and SS (cermets) comprise an appreciable fraction of the fuels that will require processing.

The Savannah River Laboratory and other sites have been developing techniques(4,5) for the electrolytic dissolution of these elements in nitric acid as the first processing step. This process is attractive in that the electrolyte, nitric acid, is compatible with existing radiochemical separations plants and with demonstrated processes for uranium recovery. Dissolver vessels made of expensive alloys would be necessary to resist chemical corrosion in the alternative processes. In principle, either stainless steel claddings or zirconium claddings can be electrolytically oxidized at the anode of a stainless steel cell. Electrolytic dissolution of elements clad with stainless steel was proposed as early as 1951(4), but was never previously pursued to a development stage because of anticipated engineering difficulties.

Tantalum or columbium were selected as materials of construction for the inert (insoluble) anode basket in which the fuels are suspended during dissolution, because these metals have overvoltages of 180 v and 40 v, respectively(6). This property enables these metals to be used as electrical connectors below the liquid level without dissolving in the electrolyte, provided the applied voltage does not exceed the overvoltage. The high conductivity of nitric acid(7) should permit the operation of an electrolytic cell well below the overvoltage for these metals.

The laboratory work described in this report was undertaken to provide design data for a large-scale electrolytic dissolver.

SUMMARY

The dissolution of stainless steel, zirconium or Zircaloy-2, and aluminum by oxidation at the anode of an electrolytic cell containing nitric acid has been demonstrated on a laboratory scale. The technique of containing the fuels in a tantalum or columbium anode basket, which serves as the electrical connection between the source of power and the fuel, has also been tested, and the high overvoltage of these metals has been verified in a radiation field of 10^7 rep/hr up to a total exposure of 10^9 rep (β,γ). Electrical contact between the anodic fuel and the tantalum or columbium container was maintained by periodically tapping the anode basket with a hammer. In previous work this was done by vibration(4).

Stainless steel anodes dissolve electrolytically in nitric acid at an average rate of 0.6 gram per ampere-hour. At a current density of 1 amp/cm^2 this is equivalent to a penetration rate of 30 mils per hour. At acid concentrations below 2M HNO_3, side reactions reduce the number of grams dissolved per ampere-hour. No anomalous behavior was observed during the dissolution of irradiated stainless steel. Zirconium and Zircaloy-2 anodes disintegrate in nitric acid at an average rate of 1 g/amp-hr. Approximately 15% of the zirconium and tin dissolve; the remainder forms an insoluble ZrO_2 precipitate. The Zr - low U alloys also disintegrate electrolytically in nitric acid; however, the ZrO_2 that is formed contains from 10 to 50% of the total uranium. Aluminum dissolves electrolytically in nitric acid at a rate of 0.37 g/amp-hr. The addition of Hg^{+2} does not enhance this rate. Fuels consisting of graphite impregnated with UC_2 and UO_2 can be disintegrated electrolytically in boiling 10M HNO_3; the sludge contains 0.1% of the total uranium.

A stainless steel dissolver was corroded by nitric acid solutions containing dissolved stainless steel (Fe^{+3}, Cr^{+3}, Ni^{+2}) at a rate of several mils per year at 90°C. At this temperature UO_2 dissolves in solutions containing 5M HNO_3 at a rate in excess of 150 mils/hr.

DISCUSSION

EXPERIMENTAL EQUIPMENT AND PROCEDURES

The results reported herein were obtained primarily with glass equipment in which the maximum current during dissolution was 100 amperes at a maximum potential of 25 volts. Some results from a 500-ampere electrolytic dissolver are also included. In most cases baskets made of tantalum or columbium served as containers which conducted current to the various metals and alloys that were to be dissolved. In some cases, such as the dissolution of the Zr - low U alloys, direct electrical contact between the power supply and metal was used in order to eliminate the variable of contact resistance between the metal and the container. Tantalum or columbium cathodes were used in most of the tests. The glass vessels employed for the tests were equipped with reflux condensers in those cases where the acid was to be returned to the dissolver. No effort was made to scrub the oxides of nitrogen in the condenser, and undoubtedly some acid was lost. Consequently, acid consumption per mole of metal dissolved varied and was higher than that expected on the basis of stoichiometry.

Current utilizations were obtained by measuring the current over a period of time and determining the loss in weight of the anode for that period. In those experiments in which it was desired to measure the gases produced at the cathode and anode a standard H-cell was employed to prevent mixing of the gas from each electrode. The gases were expanded into an evacuated bulb and analyzed by mass spectrometry. Specific descriptions of various techniques and equipment have been previously published(8-15), but some additional details are given in the discussion of results.

DISSOLUTION OF STAINLESS STEEL IN NITRIC ACID

Stainless steel anodes were dissolved electrolytically in nitric acid at a rate of 0.58 g/amp-hr. One ampere-hour will theoretically oxidize 0.59 g of Type 304 stainless steel (19% Cr, 9.5% Ni) to Fe^{+3}, Cr^{+6}, and Ni^{+2}. Wide variations of temperature (15 to 113°C) or current density (0.025 to 3.0 amp/cm^2) had no effect on the current utilization. Analyses of the electrolyte during dissolution showed that the iron, chromium, and nickel in the steel were being oxidized to Fe^{+3}, Cr^{+6}, and Ni^{+2}. As the dissolution proceeded the Cr^{+6} was reduced to Cr^{+3} by the oxides of nitrogen that were liberated at the cathode. The time required is dependent upon the rate of dissolution and the solubility of NO and NO_2. Figure 1 is a typical plot of concentration of Cr^{+6} vs. amp-hr in one liter of 4.3M HNO_3. The rate of reduction of Cr^{+6} to Cr^{+3} is apparently independent of Cr^{+6} concentration.

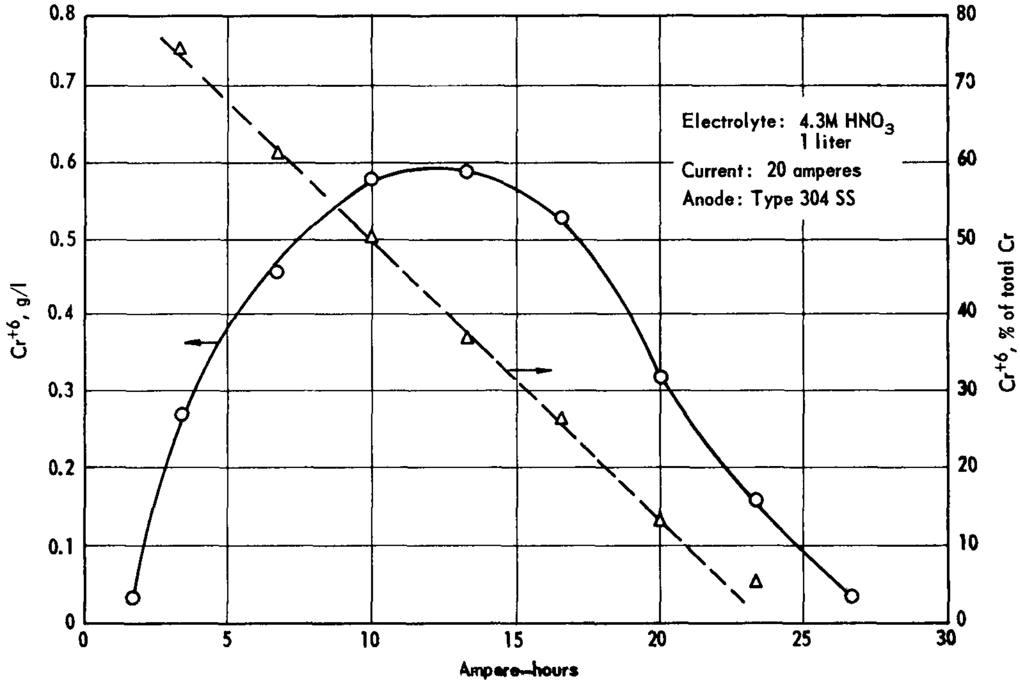

FIG. 1 CONCENTRATION OF CR^{+6} VS. AMPERE-HOURS

In 0.5 to 2M HNO_3, side reactions decrease the current utilization (Figure 2). Measurement and analysis of anode gas from a 1M HNO_3 electrolyte, in which stainless steel dissolves at a rate of 0.4 g/amp-hr, showed that the formation of oxygen accounted for one-third of the decrease in current utilization. Another side reaction is presumed to be the oxidation of nitrite ion. In greater than 2M HNO_3 the current utilization was 0.58 ±0.02 (1σ) g/amp-hr. The presence of dissolved stainless steel (30 g/l) increased the current utilization slightly to 0.625 ±.03 (1σ) g/amp-hr. The presence of 0.5M U in the electrolyte did not change the current utilization. The integrated average dissolution rate of a stainless steel anode in 2M HNO_3 over the concentration range 0 to 30 g/l of dissolved stainless steel was 0.60 g/amp-hr. On an average, 0.06 mole of acid was consumed per gram of stainless steel dissolved.

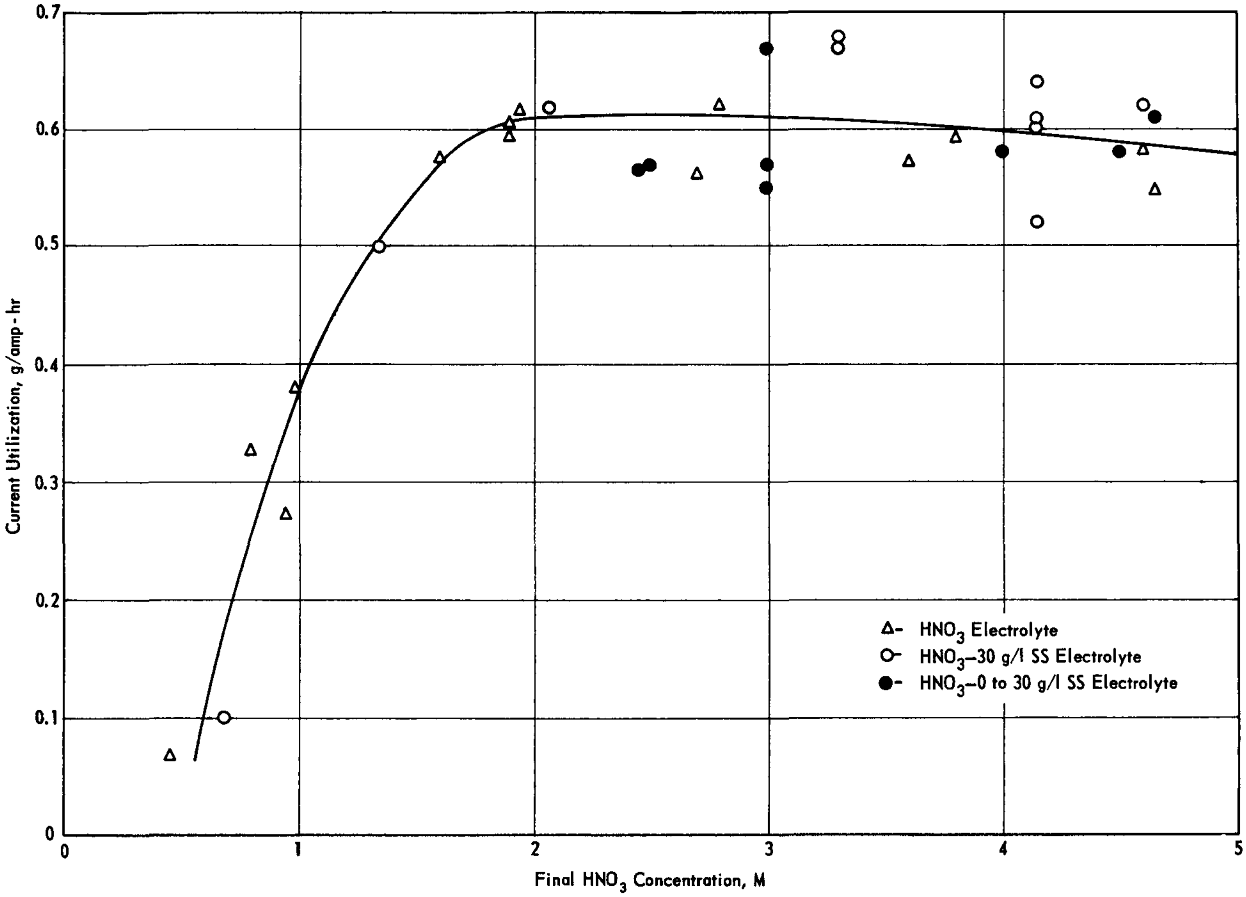

FIG. 2 CURRENT UTILIZATION VS. NITRIC ACID CONCENTRATION FOR STAINLESS STEEL DISSOLUTION

Approximately 2 wt % of the stainless steel anode does not dissolve in the electrolyte. Other workers(4) have indicated that the residue that remains after the electrolytic dissolution of Type 347 stainless steel is CbC. The residue obtained during the dissolution of Type 304 stainless in nitric acid has been identified as undissolved stainless steel by X-ray diffraction and emission spectra. Type 304 stainless is not stabilized with columbium. Occasionally a sludge of iron oxide develops on the surface of the stainless steel anode at the point where it makes contact with the tantalum or columbium anode basket. Arcing between the tantalum anode container and the stainless steel anodes promotes the formation of this oxide, especially if the stainless steel overheats. This arcing, which results from an increase in resistance at the point of contact, has a tendency to pit the tantalum basket and, if very severe, to burn a hole in it. Shaking or vibrating the anode basket at a frequency of the order of ten times per hour creates new points of contact and minimizes the arcing. In the laboratory-scale electrolytic dissolver, in which currents were a maximum of 100 amperes, arcing was not severe and contact between basket and charge was easily maintained. Figure 3 is a plot of voltage vs. time for an electrolytic dissolution in which 99.7% of the stainless steel was dissolved, less 1.5% accumulated as a sludge in the bottom of the vessel.

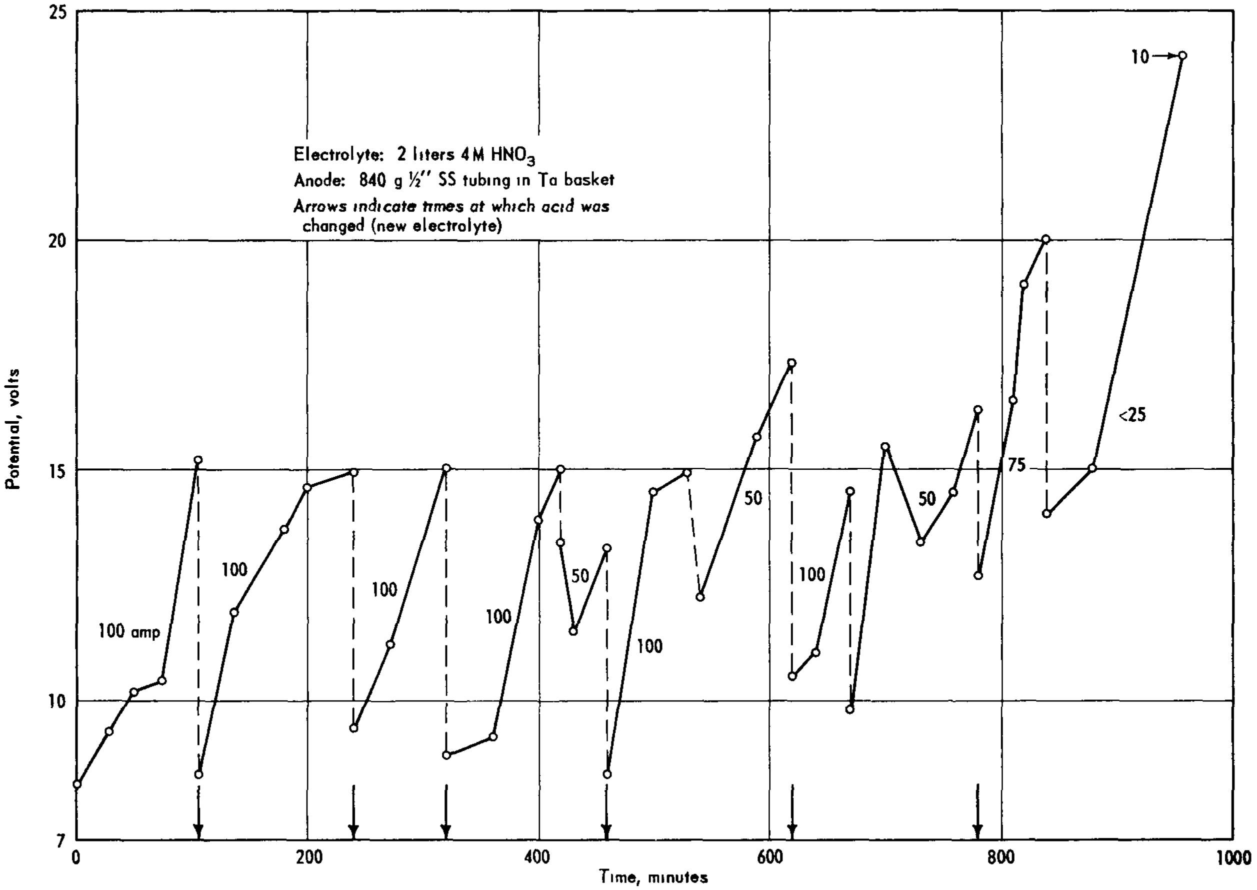

FIG. 3 ELECTROLYTIC DISSOLUTION OF STAINLESS STEEL
Volts vs. Time

Nitric acid solutions of electrolytically dissolved stainless steel are corrosive to stainless steel alloys(14). This chemical attack by the electrolyte must be controlled. McIntosh and Evans(16) concluded that the corrosion of the steel alloy (18 wt % Cr, 13 wt % Ni, Cb stabilized) studied by them was caused by an oxidation-reduction cycle involving chromium and nitric acid. The Cr^{+6} ions were able to oxidize, and so remove, some of the hydrated Cr^{+3} oxide in the protective layer of the alloy. In electrolytic dissolving, the Cr^{+6} produced at the anode is subsequently reduced by the oxides of nitrogen produced at the cathode. At 85 to 90°C, the corrosion rate(17) of Type 304L stainless steel is a few mils per year. Tables I and II summarize these data. The blue solutions are Cr^{+3} and the yellow are Cr^{+6}.

TABLE I

Effect of Temperature on Corrosion of Stainless Steel by Nitric Acid - Stainless Steel Solutions

Solution contained 20 g/l of Type 304L stainless steel electrolytically dissolved in 10M HNO_3. Corrosion rates expressed in mils/yr.

Stainless Steel Specimen	50°C	60°C	85°C	113°C (boiling)
304L	3.5	6.7	11.8	89
304L	3.5	6.8	15.4	91
304L welded	3.1	7.6	13.1	99
304L welded	3.8	9.6	13.4	103
309Cb	3.9	9.6	14.7	124
309Cb	3.9	8.7	15.1	119
309Cb welded	4.2	8.7	15.1	123
309Cb welded	4.0	8.4	15.7	127

TABLE II

Corrosion Rates of Type 304L Coupons During Electrolytic Dissolution of Type 304L Anodes

Initial HNO_3 Conc: 6M
Temperature: 85 to 90°C
Initial Stainless Steel Conc: 0 g/l

	Final Solution			Penetration Rate, mils/yr		
Test Duration, hr	Stainless Steel Conc, g/l	Color	Estimated HNO_3 Conc, M	Coupon No. 1	Coupon No. 2	Coupon No. 3
23	43	Blue	3.0	1.2	1.0	-
24	30	Blue	4.0	1.5	0.1	-
19	34	Blue	3.7	1.7	1.4	-
23	21	Blue	4.5	1.4	1.6	1.2
23	33	Blue	3.7	3.4	3.5	1.3
21	23	Blue	4.4	2.1	2.5	1.8
22	37	Yellow-green	3.4	8.1	8.8	8.3
21	39	Yellow	3.3	13.2	13.2	-

Irradiated stainless steel dissolves electrolytically in nitric acid with no apparent unusual behavior(15). Four fuel rods of the N.S. Savannah type (UO_2 pellets clad in stainless steel), which were irradiated to 1900 MWD/T, were dissolved in pairs in 7.0M HNO_3. The dissolutions were stopped after all the UO_2 and 60% of the stainless steel (including end fittings) had dissolved. The final solution was filtered and diluted about 20% for solvent extraction feed. The composition of this feed solution was 0.6M UNH, 2.75M HNO_3, 30 g SS/liter, 4.2×10^6 Pu α disintegrations/(min)(ml), and 1.7×10^7 γ counts/(min)(ml). Pertinent decontamination factors and the solvent extraction flowsheet have been previously reported(15). No difficulties were encountered either in the electrolytic dissolution of the irradiated stainless steel cladding or in the chemical dissolution of the irradiated UO_2 core. No problems of electrical contact between the elements and the columbium anode basket developed during the two experiments.

A depleted uranium mockup of an element for the Army Package Power Reactor was dissolved electrolytically in 10M HNO_3. This element is a 20-mil plate of stainless steel - UO_2 cermet clad with 5 mils of stainless steel. The core of the element is 26 wt % UO_2. The element was dissolved in a tantalum basket at a current utilization of 0.57 g of SS/amp-hr. Approximately 5.5% of the stainless steel collected as a very finely divided sludge in the bottom of the dissolver vessel. In addition, 1.4% of the element failed to dissolve because of poor electrical contact with the anode basket. These fragments contained 0.2% of the total uranium. Approximately 0.4% of the uranium was found in the finely divided sludge on the bottom of the vessel; half of the uranium in the sludge was recovered by boiling the sludge in 10M HNO_3 for 3 hours. The balance of the uranium, 99.4%, was found in the dissolver solution.

DISSOLUTION OF ZIRCONIUM AND ZIRCALOY-2 IN NITRIC ACID

Zirconium and Zircaloy-2 disintegrate when they are used as the anode of a cell in which the electrolyte is nitric acid. At least two of the competing anode reactions are:

$$(1) \quad Zr + 2H_2O \longrightarrow ZrO_2 + 4H^+ + 4e^-$$

$$(2) \quad Zr + H_2O \longrightarrow ZrO^{++} + 2H^+ + 4e^-$$

The zirconium is oxidized anodically in nitric acid by diffusion of the oxygen ions into the metal lattice(18). The resulting oxide layer is less dense than its base metal, so that it spalls off in the nitric acid and settles rapidly to the bottom of the anode basket. About 15% of the zirconium or Zircaloy-2 dissolves, and the balance precipitates as ZrO_2 by reaction (1) above. The average disintegration rate is 1 g zirconium or Zircaloy-2 per amp-hr in 1 to 10M HNO_3. Six tests were made on reactor-grade zirconium to determine the effect of acid strength and current density on the split between the soluble ZrO^{++} and the insoluble ZrO_2. The results are shown in Table III. The quantity of zirconium put into solution was not affected by changing either the concentration of the acid from 4 to 16M, the current density from 0.13 to 0.41 amp/cm^2, or the temperature from 30 to 100°C. The mass of zirconium dissolved per amp-hr of charge ranged from 0.8 to 1.3 g. No explanation for this wide range in effectiveness is apparent. The behavior of Zircaloy-2 is analogous, with 15% of the tin dissolving and the remainder precipitating. Usually the initiation of the dissolution of zirconium in nitric acid is not instantaneous. The electrolyte is maintained near the boiling point, at which temperature the UO_2 cores dissolve rapidly. At temperatures of 85°C or greater the zirconium disintegration can be initiated easily in 5M HNO_3 and continued, once initiated, in >1M HNO_3. This initiation phenomenon is associated with the rate of formation of the ZrO_2 layer on the metal surface and depends upon the history of the metal. Easier initiation at high nitric acid concentration and high temperature is consistent with more rapid oxide formation under these conditions. No quantitative investigation of the rate of oxide formation and its effect on the induction period was attempted.

TABLE III

Electrolytic Dissolution of Zirconium in Nitric Acid

HNO_3, M	Anode Current Density, amp/cm^2	Current Utilization, g/amp-hr	Zr Dissolved, %
4	0.19	0.8	14
10	0.13	0.8	16
10	0.13	1.0	15
10	0.26	1.3	15
10	0.41	1.1	14
16	0.24	1.1	14

The ZrO_2 sludge that was produced by the electrolytic dissolution of Zircaloy-2-clad UO_2 fuels in boiling 10M HNO_3 contained 0.15% of the total uranium. Half of this was recovered by boiling the sludge in 10M HNO_3 for 3 hours. X-ray diffraction analysis of this sludge indicated a highly amorphous solid with weak ZrO_2 lines. No other solid phase could be detected. In the 500-amp dissolver the acid consumption averaged 3 moles per mole of zirconium disintegrated.

Unirradiated Detroit-Edison core elements (U - 10% Mo clad with 4 mils of zirconium) were dissolved electrolytically in 10M HNO_3. Two experiments were performed in which the fuel pins were connected directly to the power source. Direct current was used in one experiment and alternating current in the other. Since a tantalum cathode was used in each run, the imposed AC potential produced a half-wave rectified current through the cell. It was necessary to heat the solutions above 50°C before starting the electrolysis. During dissolution the voltage required to maintain 10 amperes dropped about fivefold, presumably when the cladding disappeared, and remained fairly constant until dissolution of the core was complete. In contrast to UO_2, uranium metal and U-Mo alloy dissolve electrolytically in nitric acid. The sludge was leached for 3 hours in boiling 10M HNO_3 and then dissolved in HF-HNO_3 for analysis. The loss of uranium to the residue was 0.005%. Pertinent data are given in Table IV.

TABLE IV

Electrolytic Dissolution of Detroit-Edison Core Elements

Run Number	PRDC-1	PRDC-2
Power Source	DC	AC
Avg Current Utilization[a], g/amp-hr	2.1	3.3
Distribution of Original Uranium, %		
Dissolver Solution	~100	~100
Leach Solution	0.005	0.008
Precipitate	<0.005	<0.004
Distribution of Original Molybdenum, %		
Dissolver Solution	99	99
Leach Solution	0.8	0.8
Precipitate	0.2	0.2
Distribution of Original Zirconium, %		
Dissolver Solution	13	13
Leach Solution	6	2
Precipitate	81	85

(a) The average of the electrolytic attack on the cladding and the combined electrolytic and chemical attack on the core.

Solutions of Zircaloy-2 that were electrolytically dissolved in 10M HNO_3 did not accelerate the corrosion of stainless steel. Corrosion rates of welded and wrought Type 304L and Type 309 Cb in such solutions containing 8.5 g/l of dissolved zirconium were less than 3 mils/yr. All the corrosion tests were made at the boiling point (113°C). There is no indication that solutions containing nitric acid and dissolved Zircaloy would be corrosive to an electrolytic dissolver made of stainless steel.

DISSOLUTION OF Zr-U ALLOY IN NITRIC ACID

The Zr - low U alloys are the only major type of power reactor fuel element that cannot be dissolved electrolytically in nitric acid without a high loss of uranium to the sludge. During electrolysis the surface of the element is oxidized to ZrO_2, which spalls off and carries with it a variable but high percentage of the uranium. Table V summarizes the data for the disintegration of Zr - 10 wt % U alloy. The percentage of zirconium dissolved is twice that dissolved from pure zirconium, but uranium losses varied from 10 to 50%, even after boiling the sludge in nitric acid. Loss of uranium decreased with increasing acidity, but no correlation with temperature was observed. An attempt was made to effect better dissolution of the uranium by interrupting the electric current to promote descaling of the surface of the alloy and produce a smoother dissolution. The particles of ZrO_2 produced during current interruption are finer than those normally observed; therefore, it was considered possible that the occluded uranium might be more readily leached from these particles. Two schemes for interrupting the current were tried. One was simply to impose an AC potential across the cell. Since the tantalum cathode will not conduct current anodically the cell served as a half-wave rectifier and a 60-cycle interruption was achieved. The second technique interposed a revolving, brush-contacted commutator between the standard DC power supply and the cell. The output was a square wave with a 90% use cycle and a variable (0 to 27 cps) interruption frequency. The results given in Table VI do not demonstrate any clearly defined advantage for operation with current interruption. The lowest losses of uranium to the precipitate (13 and 14%) were observed during operation with AC voltage; however, losses were not consistently low.

TABLE V

Electrolytic Dissolution of Zr - 10 wt % U Alloy in Nitric Acid

Temperature During Electrolysis, °C	HNO_3 Conc, M	$Al(NO_3)_3$ Conc, M	Duration of Leach with Boiling 10M HNO_3, hr	Zr Dissolved During Electrolysis, %	U Loss to ZrO_2 Ppt, %	
					After Electrolysis	After Leaching
20-90	4	0	1.5	30	(a)	52
20-100	10	0	2	33	46	34
70-107	16	0	2	25	37	12
120	16	0	9	40	(a)	31
110	10	0.5	None	22	73	--
85-114	13	0.4	None	24	69	--
14-46	16	0	1.5	35	(a)	19
15-30	16	0	2	22	36	25
14-20	16	0	2	26	41	24
18-46	16	Sat'd	None	23	31	--
16-20	16	Sat'd	2	38	13	11

(a) Residue digested in original dissolver solution immediately after electrolytic dissolution.

TABLE VI

Electrolytic Dissolution of Zr-U Alloy in 10M HNO_3

Anode	Impressed Voltage	Temp During Electrolysis, °C	Current Density, amp/cm^2	Current Utilization, g/amp-hr	Duration of Leach With Boiling 10M HNO_3, hr	Zr Dissolved During Electrolysis, %	U Loss to ZrO_2 Ppt, %	
							After Electrolysis	After Leaching
Zr - 5.5% U	DC	46-87	-	1.0	3	15	29	22
Zr - 5.5% U	DC	55-80	0.45	0.86	3	16	47	30
Zr - 5.5% U	AC	50-97	0.40	0.92	3	14	52	14
Zr - 5.5% U	Interrupted DC (20 cps)	57-69	0.40	0.45	3	17	42	28
Zr - 9.4% U	AC	27-41	0.06	0.54	3	37	15	13
Zr - 9.4% U	AC	-	0.22	0.96	-	22	60	-
Zr - 9.4% U	AC	31-61	0.26	1.1	3	17	33	24
Zr - 9.4% U	Interrupted DC (10 cps)	56-80	0.47	0.67	3	17	52	29
Zr - 9.4% U	Interrupted DC (20 cps)	48-83	0.51	0.51	1)8 2)8[a]	29	38 33	33 19
Zr - 9.4% U	Interrupted DC (27 cps)	51-77	0.52	0.71	3	16	56	32
Zr - 16.7% U	Interrupted DC (20 cps)	42-74	0.47	0.50	3	52	36	21

(a) Sludge was ground with mortar and pestle between first and second leaches.

The fact that variations in the current density, acid strength, temperature, and type of voltage had no consistent effect on the high uranium loss to the sludge would support the conclusion that the uranium was being occluded in the ZrO_2 precipitate. In an attempt to influence this occlusion, chemicals such as sodium dichromate, hydrogen peroxide, and hydrofluoric acid (0.03M) were added individually to the nitric acid electrolyte. No benefit from these additions was observed. Only small quantities of uranium were recovered from the sludge when it was boiled in sodium hydroxide, fused in sodium hydroxide, or roasted and then boiled in nitric acid. When the electrolysis was performed in sodium nitrate solutions to study the effect of pH on uranium loss, a hydrated oxide of uranium precipitated in neutral or basic solutions. The addition of sodium carbonate or bicarbonate to the electrolyte decreased the precipitation of the hydrated uranium oxide by the formation of a soluble uranium carbonate complex. In all cases in which the electrolyte contained sodium nitrate, the uranium losses were high (28 to 62%). When potassium iodide was used as the electrolyte, uranium loss to the sludge ranged from 9 to 15%. The solution in the vicinity of the anode was deeply colored by I_3^- ion from the oxidation of iodine at the surface. Iodine reacts with zirconium to form an insoluble zirconium-iodine compound. Other electrolytes tried were sodium carbonate, sodium bicarbonate, sodium hydroxide, phosphoric acid, acidic monosodium phosphate, and oxalic acid. In all of these cases the cell did not conduct sufficient current with the Zr - low U alloy as anode for the disintegration to be measured.

The structures of both the alloy and the ZrO_2 sludge were studied in an attempt to determine the mechanism by which the uranium was held in the sludge. Zr - low U alloy usually consists of two uranium-containing phases: one is the dispersed δ phase, UZr_3-UZr_4, and the other is the ϵ phase, a matrix of zirconium containing dissolved uranium. To test the hypothesis that the uranium in the sludge was originally that in the δ phase, the δ phase was eliminated by heat treatment. Pieces of Zr - low U alloy were heated to 850°C, where δ phase dissolves in the Zr-U matrix, and then were water quenched to retain the uranium in a supersaturated solution. This solution-quenched alloy was immediately dissolved electrolytically. The exceptionally high uranium content of the sludge (Table VII) eliminated the possibility that the δ phase was solely responsible for the loss of uranium to the ZrO_2.

TABLE VII

Electrolytic Dissolution of Heat-Treated Zr - Low U Alloys

Heat Treatment	Alloy	Distribution of Original Uranium, %			Distribution of Original Zirconium, %		
		Electrolyte	Leach	Sludge	Electrolyte	Leach	Sludge
Slow cool (double phase)	Zr - 10 wt % U	48.5	11.1	40.5	28.9	3.1	68.0
Slow cool (double phase)	Zr - 16 wt % U	55.3	9.0	35.7	29.9	5.6	64.7
Solution quench (single phase)	Zr - 10 wt % U	32.3	3.4	64.7	32.2	2.8	64.3
Solution quench (single phase)	Zr - 16 wt % U	39.0	9.2	51.8	37.9	5.1	56.9

The converse possibility, that the ϵ phase alone was responsible for the loss, was investigated by reducing the concentration of uranium in the ϵ phase. Samples of Zr - low U alloy were heated to 500°C (the two-phase region) for one day to speed migration of uranium to the δ phase, and then were cooled slowly to prevent supersaturation of the ϵ phase. The equilibrium solubility of uranium in zirconium is low at room temperature, so that 99.5% of the uranium was precipitated as the δ phase(19). The alloy was electrolytically disintegrated in 10M HNO_3. Although the uranium content of the ZrO_2 sludge was high, it was lower than was found in the single-phase alloy. It can be concluded that the uranium in the sludge comes from both the δ and ϵ phases. A slightly higher percentage of the uranium from the homogeneous phase was retained by the sludge.

The ZrO_2 sludge from the disintegration of Zr - 10 wt % U alloy was analyzed by X-ray diffraction. Heat treatment prior to electrolytic attack did not affect the X-ray diffraction analysis of the ZrO_2. The analyses showed that most of the sludge was an amorphous form of ZrO_2. An X-ray pattern was found that corresponded to a double oxide of zirconium and uranium(20). In some samples a pattern corresponding to zirconium carbide was present; the carbon comes from the graphite crucible in which the alloy was cast. Photomicrographs of the alloy showed zirconium carbide inclusions of 15 to 25 vol %. Ignition in air made the ZrO_2 more crystalline and decomposed the zirconium carbide. The double oxide was not affected.

DISSOLUTION OF ALUMINUM IN NITRIC ACID

Aluminum dissolves electrolytically in nitric acid at a rate of 0.37 g/amp-hr. The dissolution rate of the anode was not changed by variation in current density from 0.03 to 1.0 amp/cm^2, in solution temperature from 25 to 108°C, in aluminum concentration from 0 to 1M, or in nitric acid concentration from 1.5 to 6M. The observed rate is slightly higher than one would expect (0.34 g/amp-hr) if the only method of oxidation of aluminum to Al^{+3} were electrolytic. The increase is presumed to be caused by chemical attack on the anodic aluminum. Aluminum cathodes, as well as samples that are electrically "floating" in the solution, dissolve at a much slower rate that is proportional to the surface area exposed to the electrolyte. These pieces of aluminum undergo chemical attack only.

A mercury catalyst is used in the chemical dissolution of aluminum in a nitric acid system. Since the quantity of catalyst required for irradiated aluminum is high, the combination of electrolytic and chemical dissolution was investigated. The dissolution rate of an aluminum anode remained constant at 0.37 g/amp-hr when the Hg^{+2} concentration was varied from 1.6×10^{-4} to 1.0×10^{-3}M in 1.5 to 6M HNO_3. The aluminum cathode dissolved at about twice the rate of a piece of aluminum suspended in the solution, probably because of a higher concentration of Hg^{+2} ions at the cathode than at the surface of the control piece. No measurements were made on irradiated aluminum and none of the samples were pretreated with mercury.

When 60-cps alternating current was applied to two aluminum electrodes, they both behaved anodically, and both electrodes dissolved at a rate of 0.37 g/amp-hr. Apparently the frequent current reversals did not permit Hg^{+2} to penetrate the oxide coating.

Aluminum-clad Al - 16 wt % U alloy was dissolved electrolytically in both 4 and 10M HNO_3 without the addition of mercury catalyst. At a current density of 0.40 amp/cm^2, the current utilizations were 0.48 and 0.45 g of cladding plus alloy per amp-hr, respectively. There was no undissolved residue.

DISINTEGRATION OF GRAPHITE-URANIUM FUEL IN NITRIC ACID

An unirradiated fuel element consisting of graphite - 14 wt % U was disintegrated electrolytically in boiling 10M HNO_3. Similar work has been previously reported(21). The graphite sludge was leached for 3 hours in boiling 10M HNO_3. The remaining sludge was found to contain 0.1% of the total uranium. The current utilization was 0.75 g/amp-hr at a density of 0.63 amp/cm^2. The dissolver solution contained 99.8% of the uranium; the leach solution, 0.1%; and the sludge, 0.1%.

The graphite-uranium fuel specimens used in this study were prepared by mixing UO_2 with graphite flour and a liquid resin binder, and graphitizing the mixture at 2400°C. At this temperature the uranium is converted to UC_2; however, the UC_2 reacts rapidly with moisture and most of the uranium in the fuel was probably present as the oxide. No analysis was made to confirm this.

CHEMICAL DISSOLUTION OF UO_2 IN NITRIC ACID

The chemical dissolution rate of sintered UO_2 pellets was determined at 90°C and at the boiling point as a function of nitric acid concentration, both with and without dissolved stainless steel present. As stated previously, corrosion of an electrolytic dissolver made of stainless steel can be decreased to an acceptable rate by operating the dissolver at 85 to 90°C. Decreasing the temperature from the boiling point to 85°C would have little effect on the electrolytic dissolution rate of stainless steel, Zircaloy, or aluminum claddings, but the rate of chemical dissolution of the UO_2 thus exposed would be expected to decrease.

The pellets that were used for these tests were 3/8 inch in diameter and 3/8 inch high, and had been compacted to 92% of theoretical density before sintering. Since the instantaneous penetration rates increased as the pellets disintegrated, a mean rate was calculated from the original pellet radius and the time required for total dissolution of the pellet. These mean penetration rates for three concentrations of nitric acid at 90°C are given in Figure 4. Rates are also shown for similar solutions that contain about 12 g/l of electrolytically dissolved stainless steel. The increase in rates shown is in accordance with the report that Fe^{+3} increases the dissolution rate of sintered UO_2 in boiling nitric acid(22). No explanation is apparent for the fact that the rate at 90°C is faster than that at the boiling point in 4M HNO_3. The width of the points (X-coordinate) indicates the range of acid concentration during the dissolution except for those solutions containing dissolved stainless steel. The acid-to-UO_2 mole ratio was maintained high in order that the acid concentration would not change appreciably and affect the mean penetration rate.

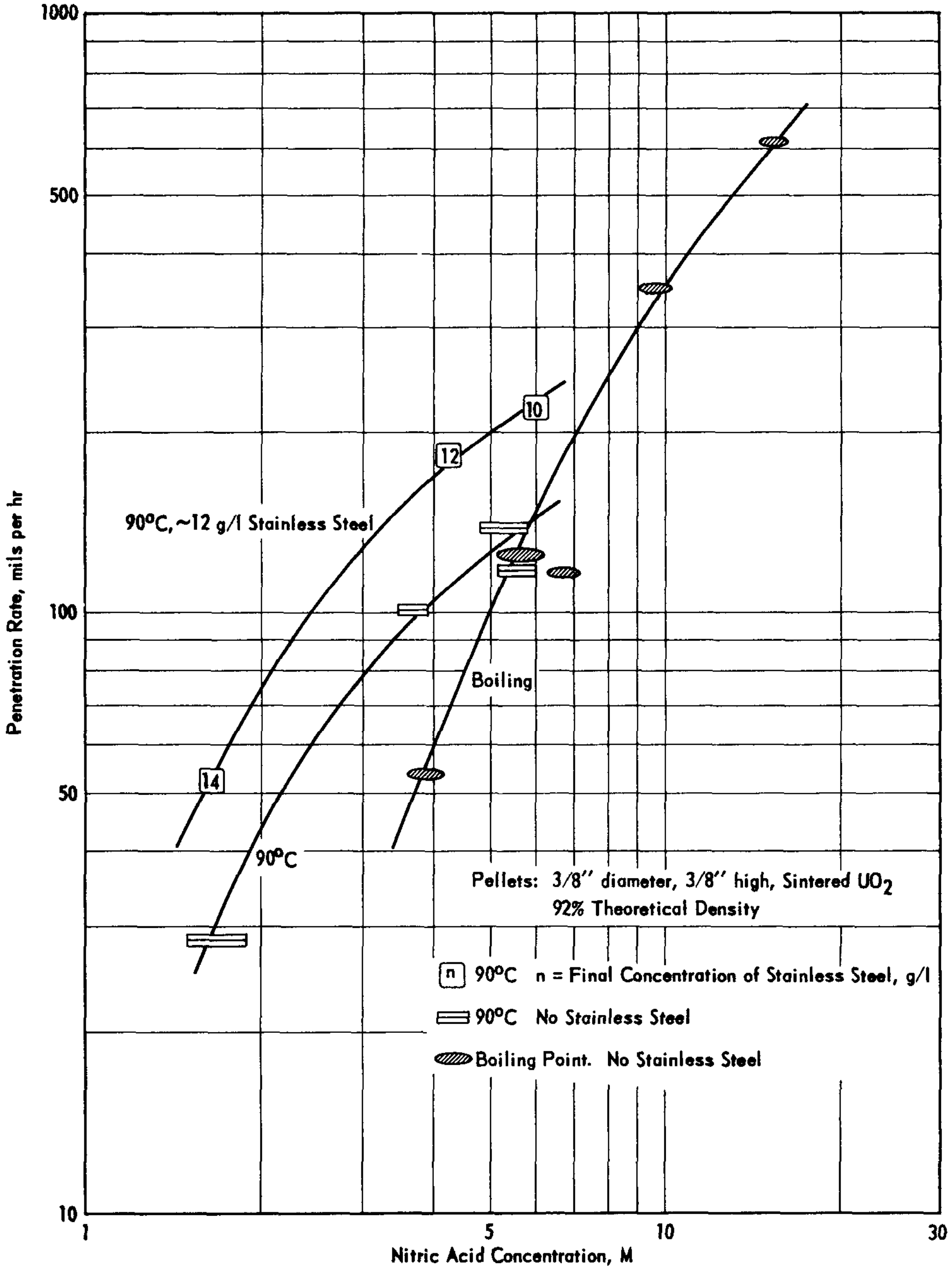

FIG. 4 MEAN PENETRATION RATE OF UO_2 PELLETS IN NITRIC ACID

GASES EVOLVED DURING ELECTROLYTIC DISSOLUTION IN NITRIC ACID

Reduction at the tantalum or columbium cathode of an electrolytic cell containing nitric acid as the electrolyte occurs by five principal processes:

(1) $NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O$

(2) $NO_3^- + 2H^+ + e^- \rightarrow NO_2 + H_2O$

(3) $2NO_3^- + 10H^+ + 8e^- \rightarrow N_2O + 5H_2O$

(4) $2NO_3^- + 12H^+ + 10e^- \rightarrow N_2 + 6H_2O$

(5) $2H^+ + 2e^- \rightarrow H_2$

The solutions were not analyzed for ammonium ion, which is a remotely possible cathodic reduction product. Competition between reactions 1 through 4 for the reduction of nitrate ion is complex, and the quantities of the reduction product measured in the gas phase are a function of temperature and solubility in the electrolyte. The significant point that has been determined is that the formation of hydrogen (reaction 5) accounts for less than 2% of the total cathode gas. A typical composition is of the order of 0.3% H_2 for the period of dissolution. The percentage of hydrogen in the evolved gas may be slightly higher than this in the first stages of dissolution when the electrolyte is being saturated with oxides of nitrogen. Both tantalum and columbium are subject to deterioration by hydrogen embrittlement. The tantalum and columbium cathodes used for the laboratory work have not been so embrittled after over a year of service. This is perhaps the best indication of the minor contribution of hydrogen to the cathode gases. The quantities of gas liberated from a tantalum or columbium cathode in 10M HNO_3 varied from 30 to 150 cc/amp-hr under a variety of conditions. Table VIII summarizes the composition of cathode gases at 50°C in 10M HNO_3.

Table VIII

Cathode Gases Evolved During Electrolysis

Electrolyte: 10M HNO_3

Temperature: 50°C

Cathode	Anode	Nitrogen Oxides and N_2, %	H_2, %
Ta	SS	98.6	1.29
Ta	Zr	99.5	0.51
Ta	Zircaloy-2	99.9	0.03
Cb	Zr	98.9	1.17
Cb	SS	99.6	0.24
Cb	Zircaloy-2	96.7	0.04
Ta	Zr	99.7	0.28
Cb	Al	99.9	0.05
Ta	Al	99.9	0.03
Cb	Zr	98.7	0.02

Only minor quantities of gases, in most cases immeasurably small amounts, are produced at stainless steel, zirconium, or aluminum anodes when these metals are dissolved electrolytically in 2 to 7M HNO_3. These gases are probably not electrolytic in origin but are due to chemical attack on these metals. During the electrolytic dissolution of stainless steel, oxygen will be produced at the anode if the acid is depleted below about 2M. A corresponding decrease in the utilization of current is observed (Figure 2). Measurement and analysis of anode gas from a 1M HNO_3 electrolyte showed that the formation of oxygen accounted for 34% of the decrease in current utilization. Another side reaction is probably the oxidation of nitrite.

ELECTROLYTIC PROPERTIES OF TANTALUM AND COLUMBIUM IN HIGH FIELDS OF RADIATION

As previously discussed, both tantalum and columbium are characterized by abnormally high overvoltages that make them anodically inert during electrolytic dissolution in nitric acid. Thus, these metals are suitable materials of construction for a basket to contain the fuel to be dissolved, unless the high radiation fields anticipated in a plant dissolver significantly decrease this overvoltage. An electrolytic cell with both columbium and tantalum electrodes was suspended in a radiation field of 10^7 rep/hr. The electrodes of this cell were mounted in such a manner that the cell could be connected either with a tantalum anode and columbium cathode, or with a columbium anode and either a tantalum or columbium cathode. The electrolyte was 10M HNO_3. A maximum of 18 v was applied to the cell during the test.

When a potential of 18 v was applied to the cell in the 10^7-rep/hr radiation field, a small diffusion current that decreased from 2 ma to about 0.2 ma was observed during a total exposure of 5×10^7 rep, even though no anodic dissolution or anodic oxygen was observed. The current then remained constant at 0.2 ma for exposure up to 10^9 rep, at which point the test was terminated. A marked increase in current would have resulted if the overvoltages of tantalum or columbium had been decreased to less than 18 v.

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