MASTER

ELECTROLYTIC OXIDATION OF ZIRCONIUM IN NITRATE SOLUTIONS

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IDAHO CHEMICAL PROCESSING PLANT

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PHILLIPS
PETROLEUM
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Atomic Energy Division

Contract AT(10-1)-205

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U. S. ATOMIC ENERGY COMMISSION

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A B S T R A C T

Zirconium alloys used in the fabrication of nuclear fuel elements can be disintegrated and converted to insoluble oxides by electrolytic treatment in concentrated nitrate solutions. This reaction shows promise as a technique for reprocessing nuclear fuels clad with Zircaloy-2. For a particular applied voltage, nitric acid achieves the highest rate of attack, but the reaction can be carried out at rates of $2 \text{ mg}/(\text{cm}^2)(\text{min})$ or greater in either 7.5M sodium nitrate or 2.3M aluminum nitrate. A reaction rate of $7 \text{ mg}/(\text{cm}^2)(\text{min})$ can be easily attained in either 8M nitric acid or 7.5M sodium nitrate. The rate of reaction is a function of the temperature and the applied voltage. An as-yet unsolved problem is the carry-down of uranium with the insoluble zirconium oxide product.

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I. SUMMARY

Tests were carried out to ascertain optimum conditions for electrolytically oxidizing zirconium alloys used in the fabrication of nuclear fuels. The alloys studied were Zircaloy-2 and PWR fuel alloy. The tests demonstrated that these alloys could be oxidized electrolytically in various concentrated nitrate solutions, but that strong nitric acid gave the highest rate of attack. For example, in 8M nitric acid at 71°C and 13 volts applied potential, the rate for Zircaloy-2 was 6.96 mg/(cm²)(min). When nitric acid was used as the electrolyte, approximately 15 per cent of the zirconium was dissolved, the rest separating out as solid ZrO₂. For PWR fuel oxidized in nitric acid, most of the uranium dissolved, but six to 28 per cent was retained by the ZrO₂ residue.

At a constant acid concentration and temperature, the rate at which Zircaloy-2 is oxidized is nearly a linear function of the applied voltage up to about 10 volts. Data were not obtained for voltages greater than 13, but a rapid increase in voltage to 25 volts or more stopped the reaction. The rate of attack on both Zircaloy-2 and PWR fuel was uniform for all surface areas exposed to solution regardless of whether or not they faced the cathode.

II. INTRODUCTION

Of the several methods currently under study for the dissolution of nuclear fuel elements, only one offers the possibility of handling all present types of alloys with the same dissolvent. Stainless steel alloys⁽¹⁾ and aluminum fuels⁽¹⁾ can be dissolved electrolytically in nitric acid, and zirconium⁽²⁾, when similarly treated, can be oxidized and disintegrated to a sludge of zirconium oxide. Electrolytic treatment in nitric acid of these very dissimilar fuels yields, in each case, pure nitrate solutions for which there exists a vast amount of well established separations technology.

Early electrolytic work with zirconium⁽²⁾ was directed toward removal of Zircaloy-2 screens from a reactor vessel. The design of an electrolytic headend process for zirconium-containing fuel elements required additional study of this reaction, with respect to its stoichiometry and kinetics. In addition, the reactions of uranium in such a system needed further investigation to find means for decreasing its retention in the zirconium oxide sludge, or to discover ways of adequately removing the retained uranium after dissolution. A program was initiated at the Idaho Chemical Processing Plant to find optimum conditions for the electrolytic disintegration of Zircaloy-2 in a nitrate system, and, using these optimum conditions, to decrease to an acceptable level uranium retention in the solid phase by application of unusual techniques, e.g., ultrasonics. A similar program has been undertaken at Savannah River Laboratory^(3,4).

Because of changing overall program commitments at the ICPP, work on the electrolytic zirconium process was terminated before all of the planned studies had been carried out. Consequently, this report deals primarily with optimum conditions for Zircaloy-2 disintegration from a rate standpoint, and presents only a few preliminary tests on uranium-Zircaloy-2 fuel elements.

III. EXPERIMENTAL

A. Test Apparatus

All tests were carried out in the specially designed cell shown in Figure 1. This apparatus was designed to study reaction rates under closely controlled conditions, but was not intended to simulate a process vessel.

The electrolytic cell consisted of a round 750-ml glass container with a tightly fitted Teflon cover. The cover had precision-cut holes through which were inserted a cathode, a zirconium coupon, a thermostat, a cooling coil, a thermometer, a high-speed stirrer, a Luggin capillary probe, and a condenser. The cathode fitted into a machined Teflon mask that was bolted to the cover, permitting only the side of the cathode facing the Zircaloy and below the liquid surface to be exposed. A Luggin

CPP-S-2093

Figure 1
Test Apparatus (Assembled)

probe for measuring single electrode potentials at the cathode was positioned so that its tip was in proximity to the lower end of the cathode surface. The reacting piece of Zircaloy had approximately the same face-to-face surface area as the cathode and was spaced 1/4" away. The back side of the Zircaloy was not masked.

To control the temperature, vigorous stirring was necessary. The stirrer consisted of a 1/4" stainless steel shaft with a two-inch-diameter stainless steel propeller having three 45° blades. The shaft of the stirrer passed through a Teflon bearing in the cover, which positioned it at a 10° angle from perpendicular, and the propeller was located in the area immediately below the cathode mask. A cone drive motor rotated the stirrer at 600 rpm, propelling the liquid downward.

The temperature was controlled by a Merc to Merc Thermoregulator which, in conjunction with a relay and a solenoid valve, allowed water to flow through a stainless steel cooling coil when necessary. The vessel sat on a hot plate that provided auxiliary heat. Though the reaction was exothermic, the heat produced was highly localized, and the hot plate helped to promote temperature uniformity.

B. Power Supply

The power supply was built by the Idaho Chemical Processing Plant instrument shop and was designed to supply 100 amperes of filtered direct current at low voltages.

C. Electrical Measurements

Cathode potentials were measured against a saturated calomel electrode with a pH meter and recorded. Total direct current passed during an experiment was measured with a copper coulometer and average amperages were calculated from this result.

D. Test Coupons and Feed Solutions

Zircaloy-2 and PWR type fuel coupons were oxidized. The Zircaloy-2 coupons were initially approximately 3" x 1/2" x 3/16" with a total area exposed to the solution of 17.8 cm². The area of the Zircaloy-2 coupon that faced the cathode was 5.18 cm². The PWR coupons were initially

3" x 1/2" x 1/16"; the total surface area exposed was 13.8 cm². The zirconium alloy specimens were uniformly attacked on all surfaces exposed to solution regardless of whether or not the surface faced the cathode. Rates of attack were calculated based on the total surface area exposed. The cathode used in all tests was made of Carpenter-20 Cb, and its dimensions were 3" x 1/2" x 1/8". The exposed surface area of the cathode was 5.18 cm², all of which faced the anode.

In most of the tests, the electrolyte used was nitric acid of various concentrations. Solutions of 7.5M sodium nitrate and 2.3M aluminum nitrate were used in a few runs, to demonstrate zirconium disintegration in essentially neutral systems.

E. Procedure

The apparatus was assembled, the coupons weighed, and all the electrical connections made before the start of each test. When the assembly was complete, electrolyte was introduced into the vessel. The Luggin capillary was filled with dissolver solution and the calomel electrode well with 1M KCl. Finally, the dissolver solution was warmed to the control temperature by means of the hot plate used as an auxiliary heat source. Then potential was applied to the cell to start the run; in most cases, tests were carried out for exactly one hour.

At the end of each run, a portion of the solution was filtered and submitted for analysis. The Zircaloy specimen and the Carpenter-20 Cb cathode were cleaned, dried, and weighed. The ZrO₂ residue was also washed, dried, and weighed, and for PWR fuel tests, was totally dissolved in 8M hydrofluoric-1M nitric acid solution and an aliquot submitted for uranium analysis.

A copper coulometer was connected in series with the cell for the duration of each test. From the coulometer weight gain, the current efficiency (based on four electrons per atom of zirconium) and the average amperage were calculated.

IV. RESULTS

A. Effect of Temperature

The electrolytic oxidation of Zircaloy-2 or PWR fuel in nitric acid is notably temperature dependent. The lowest temperature at which any

appreciable reaction takes place is about 45°C. As the temperature increases from 45°C, the rate of reaction increases rapidly until a maximum is reached at about 70°C. Increasing the temperature beyond this point slows down the reaction, and at the boiling point, the rate is only about 65 per cent as great as the maximum.

The reaction of zirconium with nitric acid or even with water is highly exothermic. This heat of reaction plus the high electrical power input necessary to promote the reaction at a desirable rate makes the temperature difficult to control. Since the heat is generated at the surface of the zirconium, with poor stirring there is a large temperature difference between this area and the rest of the solution. In preliminary experiments, with inadequate mixing, this temperature difference was found to be 20°C or more. However, in the experiments reported here, there was sufficient agitation to insure that the temperature differential between areas in the bulk solution did not exceed 3°C.

Table 1 shows the reaction rate of Zircaloy-2 in 8M nitric acid at 13 volts direct current for various temperatures.

Table 1^a

Electrolytic Oxidation of Zircaloy-2 at Various Temperatures

Temp. °C	Final Acid ^b Conc.	Rate	Zirconium Dissolved	Current Utilization	Cathode Half Cell Potential	Cathode Corrosion Rate
	<u>M</u>	mg/(cm ²)(min)	%	%	volts	mils/mo
51	7.92	1.49	17.2	96	0.197	24
61	7.78	5.40	16.6	98	0.106	51
67	7.76	6.68	15.4	104	0.162	46
71	7.70	6.96	15.7	100	0.169	40
81	7.67	5.99	13.9	97	0.169	50
91	7.68	4.75	13.5	95	0.134	30

^a All tests carried out using 13 volts d-c applied potential.

^b Test apparatus initially contained 750 ml of 8M HNO₃.

B. Effects of Voltage

The rate at which Zircaloy-2 is electrolytically oxidized in nitric acid is a function of the applied voltage. Limited data shown in Figure 2 indicate that the rate increases in a linear fashion as the voltage in-

Figure 2

Oxidation Rate for Zircaloy-2 in
8M Nitric Acid as a Function of
Voltage

creases from 0 to about 10 volts; from 10 to 13 volts the reaction rate rises much more rapidly. The rate-voltage relationship has not been determined for potentials greater than 13 volts, but observations indicated that the reaction stops if the cell potential is rapidly increased to 25 volts.

Current fluctuations were observed as the oxide sloughed off in an irregular fashion from the zirconium surface. Some current fluctuation was noted under all test conditions, but preliminary runs showed that if current surges caused a drop in applied voltage, the pulsating effect was greatly magnified. To suppress this effect, later tests were carried out using the highest capacity power supply available.

C. Behavior of PWR Fuel

Table 2 contains the test data for PWR fuel oxidized in nitric acid at various temperatures and acid concentrations. These data indicate that six to 28 per cent of the uranium was retained by the ZrO_2 residue. No special effort was made to remove the retained uranium. The rate of attack on the PWR fuel was about the same as for Zircaloy-2 under comparable conditions.

Table 2^a
Electrolytic Oxidation of PWR Fuel in Nitric Acid

Temp. °C	Acid Conc.		Rate	Constituent Dissolved		Current Utilization	Cathode Half Cell Potential	Cathode Corrosion Rate
	Initial	Final		Zr	U			
	<u>M</u>		mg/(cm ²) (min)	%	%	%	Volts	mils/mo
71	4.0	3.28	4.60	18.1	78	41	0.092	2400
61	8.0	—	6.43	17.2	85	96	-0.034	30
71	8.0	7.70	6.90	17.3	80	100	0.106	none det.
91	8.0	7.54	4.98	15.7	72	96	0.169	34
71	10.0	9.84	5.50	17.4	75	112	0.218	1.3
71	12.0	11.93	4.65	16.6	94	93	0.274	2.7

^a All tests carried out using 13 volts d-c applied potential.

D. Cathode Corrosion

Cathode corrosion rates varied considerably and could not be correlated with the observed half cell potentials. In most cases the corrosion rate was greater than 20 mils per month. This indicates that Carpenter-20 Cb is not a suitable material of construction for a cathode in this system.

E. Oxidation of Zirconium in Neutral Solutions

Zircaloy-2 can be oxidized electrolytically in essentially neutral nitrate solutions. This was demonstrated for 7.5M sodium nitrate and 2.3M aluminum nitrate. These reagents did not produce as rapid a rate of attack as did nitric acid, but they were of interest because certain zirconium-uranium alloys are known to react explosively with nitric acid. Table 3 shows the results of these tests. With sodium nitrate as the electrolyte, neither zirconium nor uranium is appreciably soluble; however, treatment of the residue with 8M nitric acid results in the dissolution of the same relative amounts of these constituents as was observed when the oxidation was carried out in 8M nitric acid.

Table 3
Electrolytic Oxidation of Zirconium in Neutral Nitrates

Alloy	Electrolyte	Temp, °C	Volts	Rate mg/(cm ²)(min)	Current Utilization %	Cathode Corrosion Rate mils/mo
Zr-2	7.5M NaNO ₃	71	13	1.6	96	None detected
Zr-2	7.5M NaNO ₃	91	13	2.8	96	None detected
Zr-2	7.5M NaNO ₃	101	13	3.0	92	None detected
Zr-2	7.5M NaNO ₃	101	15-18	5.2	92	4.2
Zr-2	7.5M NaNO ₃	96	18	7.6	99	None detected
Zr-2	2.3M Al(NO ₃) ₃	101	13	2.3	82	8.9
PWR ^a	7.5M NaNO ₃	96	18	5.5	82	1.4

^a The NaNO₃ solution dissolved only 0.07 per cent of the U and no detectable amount of the Zr. The oxide residue was contacted with 750 ml of boiling 8M HNO₃ which dissolved 83 per cent of the U and 18 per cent of the Zr.

V. CONCLUSIONS

Fuel elements made of zirconium-uranium alloy as well as elements clad with Zircaloy-2 can be electrolytically oxidized in 8M nitric acid at good rates. The reaction can also be carried out in 7.5M sodium nitrate or 2.3M aluminum nitrate. This technique holds promise for processing zirconium clad fuel elements and may also be applicable to processing PWR type fuels. For the latter fuels, the amount of uranium retained by the ZrO₂ must be reduced before the process can be of any practical value.

The possible advantages to be gained by electrolytically processing zirconium fuels make the scheme very attractive. Such a process would greatly reduce liquid waste volumes by removing the bulk constituent from solution as a chemically inert solid. In addition, fluoride corrosion problems encountered in present zirconium processing methods would be eliminated.

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