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ELECTROLYTIC DISINTEGRATION OF
ZIRCALLOY-2 IN NITRIC ACID SOLUTIONS

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OAK RIDGE NATIONAL LABORATORY

operated by

UNION CARBIDE CORPORATION

for the

U.S. ATOMIC ENERGY COMMISSION

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CHEMICAL TECHNOLOGY DIVISION

Chemical Development Section A

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IN NITRIC ACID SOLUTIONS**

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ABSTRACT

Zircaloy-2 is anodically converted to scaly ZrO_2 at 60°C in 8 M HNO_3 . About 0.5 mole of acid is consumed per faraday, and after saturation of the electrolyte with nitrogen oxides about 0.3 mole of gas is evolved per faraday. The nitric acid is reduced to hydrogen, NO , and NO_2 , with hydrogen predominating if the cathode is Zircaloy and NO if the cathode is platinum. Corrosion specimens of HRT metals have been exposed to the electrolysis conditions and given to the Metallurgy Division for evaluation.

From determinations of the decomposition potential of nitric acid it appears that a metal container for the electrolytic process can be protected from stray-current corrosion by holding it at a potential ~ 0.5 volt positive to a platinum cathode operating at a current density of 5 to 10 ma/cm^2 . Practical laboratory experiments tended to confirm this conclusion.

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1.0 INTRODUCTION

To improve the flow pattern in the HRT core vessel, it has been proposed that the diffuser screens in the conical part of the core vessel be removed. It is feasible to saw these screens loose from the vessel, but they cannot be removed without a considerable reduction in size since the opening into the core vessel is only 2 in. in diameter. One method suggested for accomplishing this is electrolytic decomposition in nitric acid solution. While it was known from prior work that this decomposition could be carried out,^{1,2} the work reported here was necessary in order to demonstrate the chemical feasibility of the process, to determine the chemical composition of the off-gas and the anode sludge produced, and to evaluate the possibility of damage to the core vessel as a result of corrosion or of hydrogen embrittlement.

Acknowledgments. The authors wish to express their appreciation to O. K. Tallent who assisted with the laboratory work and to the members of the Analytical Chemistry groups headed by G. R. Wilson, W. R. Laing, and R. L. Sherman for solution, gas, and x-ray analyses, respectively. The corrosion specimens used were prepared under the direction of J. L. English of the ORNL Reactor Experimental Engineering Division. M. L. Picklesimer of the ORNL Metallurgy Division made valuable suggestions concerning valid conditions of exposure for the Zircaloy-2 corrosion specimens and has undertaken to supervise their analysis.

This work was undertaken as a result of discussions with R. Blumberg of REED. Work utilizing the principle of bias potential discussed here was carried out in a scale model of the HRT core by members of the Component Development Section of REED.

2.0 LABORATORY-SCALE DECOMPOSITION EXPERIMENTS

2.1 Experimental

The results of scouting experiments carried out in nitric acid of concentrations varying between 5.3 and 13.2 M at temperatures of 40 to 90°C confirmed the general feasibility of the method. The data (Table 1) indicated that neither acid concentration nor temperature requires close control and that anode current efficiencies of approximately 100% can be obtained over a wide range of conditions. Usually the attack was rather uniform, although some tendency toward increased penetration at the interface was noted, particularly in the more dilute acid. On the basis of these data plus confirmatory experiments by Hannaford and Spiewak,³ 8 M nitric acid at approximately 60°C was chosen as the electrolyte for further investigations.

Table 1. Anodic Decomposition of Zircaloy-2 in Nitric Acid at Different Acid Concentrations and Temperatures

Acid Conc, <u>M</u>	Average Current Density, amp/cm ²	Temperature Range, °C	Maximum ^a Penetration Rate, mm/hr	Anode Current Efficiency, %
5.3	0.35	50-90 (av. =60°C)	0.53	87
5.3	0.35	59-84 (av. =60°C)	0.68	124
5.3	0.33	50-61	0.91	115
7.8	0.26	45	0.89	102
7.8	0.33	60-70	1.0	103
2.6	0.33	53-85 (av. =60)	0.8	96.6
13.2	0.2	35-63	0.2	112
13.2	0.24	43-52	0.2	97.4
6.6 ^b	0.3	40	0.5	97.6

^aNormally at the interface.

^bReaction was initiated in 13.2 M HNO₃ which was then diluted to 6.6 M.

Two electrolytic cells were used in these investigations. The first, a multineck flask, was designed to determine gross amounts and compositions of off-gases and to evaluate corrosion. The second, an H cell, was used for collecting and identifying the separate anode and cathode gases.

The first cell (Fig. 1) was equipped with ground glass fittings to accommodate a cathode fitting, an anode fitting, an off-gas fitting, and a thermometer. The specimen of metal to be destroyed was fastened to a stainless steel rod which could be adjusted vertically through a rubber seal on a snugly fitting glass through-joint. The cathode was a sheet of platinum or Zircaloy-2, in contact with a Zircaloy-2 corrosion specimen and supported on a platinum lead sealed through the glass cathode fitting. The off-gas fitting was connected by Tygon tubing either to a gas buret or to gas-sample-collecting vessels. The off-gas and cathode fittings held hooks from which corrosion specimens could be suspended in the vapor space. These specimens, separated by glass spacers, were suspended between the hooks on a stainless steel wire covered with a woven glass sleeve.

Before operation the cell was approximately half filled with 8 M nitric acid and the vapor space and gas sample vessels were flushed with nitrogen. Temperature was controlled by a water bath at 50-60°C at a point near the edge of the cell, except in one experiment where 30-40°C was maintained. Occasional fluctuations of temperature beyond the intended range occurred. Current was supplied by a d-c power supply at maximum output, about 13 volts

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Fig. 1. Large Cell for Anodic Destruction of Zircaloy-2.

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Fig. 2. H Cell and Electrode Fittings.

for this power supply and cell. Gas evolution rates were determined by collection over mercury of a measured volume for a measured time interval. Gas samples were collected with two vessels in series, the vessel closer to the cell being taken as the sample, the other vessel then being moved in place for collection of the next sample. Ordinarily 1.5 hr was allowed for the cell off-gas to displace the contents of the sample vessel. As the immersed portion of the anode became consumed, the anode was lowered until further lowering brought the stainless steel connections too close to the surface of the electrolyte; then the electrolysis was terminated. Two to four anodes were consumed before the electrolyte was replaced. In most of the experiments the anodes were perforated Zircaloy plate such as that used in the HRT screens. In the last three experiments pieces of 1/4-in. plate were used. The total current passed was measured by means of a copper coulometer.

During electrolysis the current decreased slowly with time and then increased suddenly as the thickened oxide film scaled from the anode. Since interruption of the current caused scaling of the oxide, the power supply was controlled by a timer which turned off the current for 15 sec every 5 min, thus keeping the current at a relatively high value.

The H cell (Fig. 2) accommodated ground glass fittings containing the electrodes. A tube from near the bottom of the cathode side was connected by Tygon tubing to a leveling bulb. The cathode fitting held a platinum foil welded to a platinum wire introduced through a Tygon seal. The anode was Zircaloy rod (3/32 or 1/4 in. dia) introduced through a side arm, and sealed in with high-vacuum sealing wax or rubber tubing. Both fittings held joints to accommodate a 10-ml gas buret or a special gas-sample vessel (Fig. 2). When the smaller Zircaloy-2 rod was used, the anode fitting also held a thermometer. The cell was thermostatted in a 60°C water bath. The cell and attached gas-collectors were filled either with 8 M HNO_3 or with used acid from the large cell.

2.2 Results

2.2.1 Gas Evolution Rate

A number of measurements were made of the rate of gas evolution from the large cell and a few from the separate electrodes of the H cell. Both difficulties in measurement and complications in the actual gas evolution rate led to considerable variation in the rates measured.

The gross gas evolution rates in the large cell (Table 2) varied from about 0.06 to 0.44 mole/faraday. The relatively poor temperature control of the cell together with the relatively large free vapor space above the electrolyte produced volume fluctuations of the same order of magnitude as the gas production rates. During the early part of an electrolysis the picture was further complicated by the high solubility of the oxides of nitrogen produced in the electrolyte. Taking various facts

Table 2. Gross Gas Evolution Measurements

Cathode Material	Expt. No.	Collection			Time, min	Current, amp	Gas Collected, moles/faraday
		Gas, ml	Temp, °C	Pressure, mm			
Platinum	2	40	28	744	11.1	4	0.057
	3	94	27	743	16	2	0.19
	4	98	28	743	7	4.9	0.18
	5	80	28	740	10	3.0	0.17
	6	95	28	738	3.5	4.9	0.35
	7	81	27	737.5	6.33	4.3	0.19
	7	83	27	737.5	5.25	4.0	0.25
	7	88	27	737.5	6.50	2.9	0.30
Platinum	14	78	28	738	4.01	3.6	0.34
	15	80	24	738	5.37	3.3	0.29
	15	75	25	739	3.99	3.1	0.39
	15	76.5	26	738	5.73	2.7	0.31
	15	22	25.5	738	8.62	2.5	0.065
	16	46.2	25	742	4.65	3.3	0.19
	17	59	25	739	2.51	4.0	0.37
Zircaloy-2	9	85	28	739	9.25	3.2	0.18
	9	60.4	27.5	737	19.4	1.3	0.15
	10	77.5	27.5	732	9.01	2.0	0.27
	11	84	27.5	733	6.97	2.7	0.28
	12	85	26	739	7.41	4.0	0.18
	12	88	29	739	3.45	3.6	0.44
	12	75	26.5	738	10.13	2.6	0.18
	13	81	26	737	5.64	2.5	0.36
	13	47	26	737	6.40	1.5	0.31
	13	50	28	738	3.34	2.2	0.43
	13	48	25	739	6.53	2.0	0.23

into account, it appears from the data that the actual gas production rate after the solution was saturated with nitrogen oxides approximated 0.3 mole/faraday. The reactivity of NO_2 toward the mercury in the gas buret made frequent cleaning of the buret necessary, but this could not introduce errors in the measurement to compare with the cell-temperature effects.

Gas evolution from the separate electrodes of the H cell was measured for known times and currents by displacement of electrolyte in gas burets. Analyzed samples of known volume were compared with coulometer measurements. The results (Table 3) indicate that gas evolution at the cathode was roughly 20 times as great as that at the anode. Rates were not constant, and an increase in the evolution rate was always evident during the time required to make a measurement. At the beginning of an electrolysis the cathode rate was zero; the anode rate was of the order of 10^{-3} mole/faraday (the smallest measurement 8×10^{-4}). Both rates increased with time. Displacement of solution from the neighborhood of the cathode, as when filling a sample-collection vessel with electrolyte, led to a sharp drop in gas-evolution rate. Anode-gas samples taken from overnight experiments measured 0.011, 0.0094, and 0.0077 mole/faraday. The cathode-gas rate increased faster, finally exceeding the anode rate and reaching a rate of 0.24 mole/faraday. The cathode gas showed the color of NO_2 . The anode gas was initially colorless but finally assumed the color characteristic of NO_2 .

2.2.2 Off-gas Composition

As with the rate of gas evolution, there was considerable variability in the composition of the gas collected during electrolysis. The most probable reason for this is that principal reduction products are nitrogen dioxide and nitric oxide, which are soluble in the electrolyte. In spite of this fact the data in Table 4 indicate clearly that a much smaller percentage of the cathode gas was hydrogen when platinum instead of Zircaloy-2 was used as the electrode (roughly 0-2% vs 5-12%), and that relatively more NO and N_2 (as opposed to NO_2) was produced at a Zircaloy-2 cathode. Oxygen was found in very few samples, and in most of these cases contamination by air leakage was suspected. Therefore oxygen was either not an electrolysis product or was consumed on evolution by reaction with NO to form NO_2 . The consistent presence of hydrogen in the anode gas indicates the improbability that oxygen was present even as an intermediate.

It was observed that early in the electrolysis the liquid and gas above the anode were colorless, while those above the cathode showed the color of NO_2 . Eventually, as dissolved nitrogen oxides diffused to the anode the NO_2 color reached the anode area, and NO_2 entered the anode gas from the solution.

2.2.3 Stoichiometry of Nongaseous Materials

Measurements of the consumption of Zircaloy-2 and acid are given in Table 5.

Table 3. Separate Electrode Gas Evolution

Sample No. ^a	Vol, ml	Current, amp	Collection Time, sec	Coulometer Gain, g	Gas Collected, moles/faraday	Conditions
C-1	1.5	0.75	7860		0.0010	Beginning of electrolysis of fresh acid
C-2	1.6	0.2-0.8		1.4213	0.0014	After standing overnight after C-1
C-3	10	0.70	223		0.24	Late in electrolysis of used acid
C-4	34	0.60	1.16×10^4		0.018	Immediately after C-3; electrolyte in vicinity of cathode displaced into collection vessel
C-5	10	0.84	191.4		0.235	Late in electrolysis
C-6	10	0.84	213.3		0.211	Immediately after C-5
C-7	10	0.84	171.4		0.262	Immediately after C-6
A-1	1.2	0.75	7860		0.0008	Simultaneously with C-1
A-2	7.5			1.4213	0.0065	Simultaneously with C-2
A-3	3.0		12780	2.9783	0.0013	Beginning of electrolysis with fresh acid
A-4	2.4			0.3934	0.0078	Immediately after A-3
A-5	10.4			3.9975	0.0032	Prolonged electrolysis with used acid; C-3, C-4 collected during this period
A-6	39			3.1153	0.0094	Prolonged electrolysis of used acid
A-7	27			2.9796	0.011	Prolonged electrolysis of fresh acid
A-8	38			6.3124	0.0077	Prolonged electrolysis of fresh acid; C-5, -6, -7 collected during this period

^aC series collected over Pt cathode; A-1 through A-5 over 3/32-in. Zircaloy anode; A-6 through A-8 over 1/4-in. Zircaloy anode.

^bMeasured at approximately 30°C, 740 ml.

Table 4. Gas Sample Analyses

Sample Location	Expt. No.	Concentration, mmoles/liter				
		NO ^a	NO ₂ ^a	H ₂	O ₂	Residual (N ₂)
Large cell, Zircaloy cathode	9	0.6	6.2	7.22		27.28
	9	3.8	7.7	13.83		14.55
	10	2.6	10.7	5.76		13.13
	10	7.6	7.7	9.10		16.27
	11	8.6	8.7	6.00		15.95
	11	7.5	9.0	6.10		18.59
	12	2.3	7.0	4.84	0.56	29.03
	12	1.1	14.6	7.63	0.98	22.54
Large cell, platinum cathode	5	4.7	6.1	0.05	0.05	17.42
	6	22.4	17.9	0.05		1.91
	7	21.7	18.3			6.81
	7	25.3	19.9			1.02
	8	25.9	18.4			1.49
	8	24.6	19.1			4.72
	14	5.9	2.8	1.11	0.05	31.39
	14	8.5	8.1	0.63		24.12
	15	21.3	22.8	2.01		1.55
	15	26.1	17.1	2.35		1.18
	16	13.5	15.0	2.43		1.55
	17	19.8	20.4	1.03		10.58
	17	21.9	16.2	0.96		6.53
	18	11.1	25.5	0.05	0.26	19.88
	19	22.5	22.3	3.27	0.30	1.45
	20	21.9	4.7	6.86	0.32	1.31
H cell cathode compartment	C-4 ^b	31.9-34.8	3.0-11.8	1.17	0.3	1.65
	A-6 ^b	26.8-30.2	3.5-13.8	1.81		2.84
	A-8 ^b	21.1-26.2	5.1-20.4	0.2		2.11
	A-8 ^b	14.4-19.6	5.2-20.7	0.74		8.00
H cell anode compartment	A-6 ^b	27.5-29.7	2.2-8.8	3.77		3.56
	A-7 ^b	3.8-5.5	1.7-6.7	10.15		11.32
	A-8 ^b	16.9-21.5	4.6-18.2	4.53		6.05

^aIn the H cell experiments the gas samples were contaminated with nitric acid solution, obscuring the analyses for nitrogen oxides.

^bSample is identified by its measurement number from Table 2 or the similar number of a simultaneously collected sample.

Table 5. Cell Reaction Stoichiometry

Operating Time, hr	Average Current, amp	Faradays	Zirconium	Zircaloy-2	Apparent	Acid		Acid		Acid	
			Equivalent to Electricity, g	Anode Weight Loss, g	Current Efficiency, %	Charged to Cell ml	<u>M</u>	Removed from Cell ml	<u>M</u>	Consumed moles/ moles faraday	
Zircaloy-2 Cathode											
0.4	3	0.047					8.25				
5.87	2.6	0.501	12.80	13.10	102	1080	8.40				
5.62	2.7	0.564	12.87	13.15	102						
4.88	2.9	0.54	11.87	12.11	102			1025	8.03	0.9	0.6
7.65	2.7	0.769	17.54	18.19	104	860	8.40				
6.70	1.8	0.452	10.30	10.44	101			821	8.19	0.5	0.4
Platinum Cathode											
1.3	4	0.20									
5.5	2.6	0.536	12.2	12.31	101						
7.33	3.8	1.04	23.7	22.58	95.5 ^a			820	7.60		
6.0	1.1	0.251	5.71	5.90	103	940	8.25				
3.87	2.9	0.424	9.68	12.01	124 ^b						
5.08	3.3	0.622	14.18	14.56	102						
4.75	3.6	0.630	14.37	14.68	102			850	7.95	1.0	0.5
3.43	3.2	0.416	9.49	10.20	106	1040	8.12				
5.33	3.0	0.620	14.16	14.325	101						
4.88	2.6	0.481	10.99	11.665	106						
7.30	2.97	0.810	18.43	18.88	102.5			940	7.40	1.5	0.65
6.95	7.6	1.97	44.8	46.42	103.6 ^b	970	8.10				
6.98	6.2	1.61	36.6	38.25	104.5 ^b						
9.14	4.9	1.68	38.3	39.66	103.6 ^b			750	6.83	2.73	0.52
4.97 ^c	0.67	0.126	2.86	2.832	102.5		6.83				
4.28 ^c	0.66	0.106	2.41	2.393	99.3		6.83				

^aConsiderable attack occurred on the stainless steel anode support.

^bPieces of anode metal were later found to have fallen into the sludge.

^cH-Cell experiments with 3/32-in. Zircaloy rod anode. Other experiments listed used either Zircaloy-2 screen or 1/4-in. plate as anodes.

On each change of electrolyte in the large cell, the volume and molarity of fresh and spent acid were determined. The acid consumption was generally about 0.5 mole/faraday, although the accuracy of volume measurement did not permit better than a one-figure estimate in the decrease in total quantity of acid. In one series of electrolyses the change was great enough for a better estimate: for 5.26 faradays of electricity, the electrolyte changed from 970 ml of 8.10 M HNO_3 to 750 ml of 6.83 M, a consumption of 0.52 mole of acid and 1.4 moles of water per faraday. These losses may be high because of incomplete draining of electrolyte from the cell, and they do not reflect purely electrolytic consumption since there was some loss by evaporation.

Assuming 4 faradays required to remove 1 gram-atom of zirconium, the weight losses of most Zircaloy anodes corresponded to 1.01 to 1.03 equivalents per faraday. The alloying constituents (principally the 1.5% tin) should add only 0.5% to the weight loss, so there is a real loss in weight above that attributable to electrolytic destruction. Occasional losses have been still greater, but these have been followed by discovery of pieces of metal in the bottom of the cell, resulting from cutting through the anode.

Analyses for zirconium in the oxidation product averaged 71.6%, compared with 74.0% for pure ZrO_2 or 73.0% for the oxide of zirconium containing 1.5% tin. The difference probably reflects incomplete drying of the oxide; the presence of metal or hydride would lead to a zirconium content higher than 73%. X-ray diffraction analysis of the residue failed to indicate the presence of any hydride or unattacked metal.

2.2.4 Corrosion

Two sets of four corrosion specimens each were exposed in the large cell during the entire operation of 380 amp-hr or 109 hr, one set in the vapor space and the other submerged in the electrolyte. Each set comprised a coupon each of type 347 stainless steel, titanium, and Zircaloy-2 plus coupons of stainless steel and Zircaloy fastened together with a titanium bolt. These specimens were rinsed, dried, and weighed after 50.6 operating hours and again at the completion of the entire 109 operating hours. Weight changes amounted to 1 mg or less. It is felt that none of these changes are significant. Somewhat greater differences in weight were observed in comparison with the initial weights provided by the Reactor Experimental Engineering Division with the specimens. These differences are no greater than would be expected when using a different balance and weights without calibration corrections. The specimens were turned over to the Metallurgy Division for further study and analysis.

The Zircaloy corrosion specimen in contact with the cathode lost 4 mg (out of 26.468 g) during the entire operation. The Zircaloy cathode lost 0.9 mg (out of 1.35 g) in 31 operating hours, 78 amp-hr. The platinum cathode did not change weight in 78 operating hours, 302 amp-hr.

Preliminary information from the ORNL Metallurgy Division⁴ indicates that the Zircaloy in contact with the working platinum electrode picked up hydrogen while those simply exposed to the solution did not. Results of the completed study have not yet been published.

3.0 DECOMPOSITION VOLTAGE AND POLARIZATION STUDIES

The possibility exists that the HRT core vessel would suffer hydrogen pickup and subsequent embrittlement if it should serve as a conductor of stray currents during the electrolytic decomposition of the core screens. It should be possible to prevent the core wall from acting as such a conductor by holding it at a bias potential relative to some reference electrode in the solution such that the decomposition potential of the electrolyte is not exceeded. This would completely eliminate the possibility of an electrolytic reaction at the core vessel wall.

If it is assumed that H_2 and O_2 are the products of electrolysis of 8 M nitric acid between inert electrodes at $60^\circ C$, the minimum possible value of the decomposition voltage (corresponding to the hypothetical case where $\gamma_{H^+} = 1$) calculated from the Nernst equation is 1.2 volts. This calculation is of no real value in predicting the actual decomposition voltage for the case at hand since the reduction of the nitrate ion may take place at the cathode preferentially to the evolution of hydrogen. It does, however, give a minimum value for the cell potential below which no hydrogen can be liberated at the cathode.

The decomposition voltage of 8 M nitric acid was measured between a platinum anode and both platinum and Zircaloy-2 cathodes by means of current vs voltage measurements. The results at $55-73^\circ C$ for electrodes of approximately 2 cm^2 apparent area are plotted in Fig. 3 for high and low current density ranges. No conventional reference electrode appears suitable for use in this solution, but a small platinum electrode polarized cathodically at a current density of 5-10 ma/cm² appears to be a satisfactory substitute. If the core wall can be closely held at about +0.5 volt with respect to such a reference electrode, it follows from the data plotted in Fig. 3 that no appreciable amount of electrolytic reaction of any type can take place at the core wall and that the evolution of hydrogen is completely out of the question.

It will be noted that when a platinum cathode is used the decomposition voltage is rather well-defined and has a value between 0.8 and 0.9 volt. This low value indicates that nitric acid reduction takes place preferentially to hydrogen evolution. With a Zircaloy-2 cathode the decomposition voltage is rather ill-defined, but the minimum value appears to be at least 1.8 volts. The lack of a sharply defined decomposition voltage in this case plus the fact that visible gassing occurs first on platinum cathodes at about 2.5 volts indicates that on a Zircaloy cathode the principal reaction is the evolution of hydrogen but that some reduction of nitric acid probably occurs at voltages below that at which hydrogen is

(a) High Current Range

(b) Low Current Range

Fig. 3. Polarization of Platinum and Zircaloy-2 Cathodes vs Platinum Anodes in 8 M Nitric Acid.

Cathodes: ○ Pt at 55-62°C; ● Pt at 60-72°C
 Δ Zircaloy-2 at 62°C; ▲ Zircaloy-2 at 73°C

evolved. Since the decomposition voltage of an electrolyte is independent of the area of the electrode used in its measurement, the current "wave" obtained with the large Zircaloy cathode must have been due either to a small amount of some impurity in the acid or to a somewhat more reactive state of the electrode surface. The higher value of the residual current in this case is probably due to the higher charging current required to maintain the electrical double layer on the larger surface.

4.0 DISCUSSION

The principal anode reaction under the conditions of these experiments corresponds in stoichiometry to the equation

The direct reaction of zirconium with water (in the presence of hydrogen ion) according to the equation

occurs at the anode as a side reaction, to an average extent of about 2%.

The situation at the cathode is considerably more complex since there are a number of different reactions by which nitric acid can be reduced. Reduction to NH_4^+ is considered not to have occurred since tests for this product in the solution were consistently negative. Hydroxylamine and hydrazine derivatives, as well as N_2O , are considered to be extremely unlikely cathode products. The existence of a consistently high inert fraction in the gas (Table 4) from a Zircaloy cathode indicates the probable production of nitrogen at the cathode. Three cathode reactions therefore appear to have taken place in which nitric acid was reduced to NO_2 , NO , and N_2 , respectively. These reactions will presumably occur according to the equations

The direct evolution of hydrogen must constitute a considerable part of the cathode reaction at a Zircaloy cathode and a much smaller part at a platinum cathode:

The considerable disparity between the values of the decomposition potential of nitric acid between Pt vs Pt and Zircaloy-2 vs Pt electrode systems (Fig. 3) implies that the evolution of hydrogen is the predominant primary reaction at a Zircaloy cathode and that the reduction products of nitric acid in this case are due largely to catalytic reaction with hydrogen on the electrode surface. This mechanism may also be of some importance at

a platinum cathode at current densities sufficiently high to polarize it to a potential sufficient to exceed the discharge potential of hydrogen. The question whether any of the observed products are due to a primary or a secondary electrode reaction is of no importance as far as stoichiometry is concerned. The kinetic study of the electrode mechanism is beyond the scope of this investigation.

The products obtained during any single electrolysis can all be explained by assuming various combinations of the reactions expressed by eqs. 1-6. Since it is practically a certainty that the predominant cathode products will vary with current density and with the nature of the cathode surface as well as with the cathode material, it does not appear either logical or profitable to arrive at an empirical chemical "equation" which will quantitatively explain the data in Tables 4 and 5.

5.0 SUMMARY AND CONCLUSIONS

Zirconium can be converted to ZrO_2 by anodic treatment in nitric acid. The principal anode reaction at $60^\circ C$ can be represented by

The measured current efficiency of the reaction is usually greater than 100%. Since hydrogen is given off at the anode the reaction

is believed to be responsible for the excess attack above 100% current efficiency.

When a platinum cathode is used the cathode gases are almost entirely reduction products of nitric acid; when the cathode is Zircaloy-2 a fairly large percentage (~4-13%) is hydrogen. Corresponding to this difference in products, the decomposition potential of 8 M nitric acid between platinum electrodes was about 0.8 volt; between a platinum anode and a Zircaloy-2 cathode the decomposition potential was less well-defined but was in the range 1.8-2.5 volts.

It should be possible to anodically disintegrate the loosened Zircaloy-2 screens in the HRT core without damage to the Zircaloy-2 core by stray current corrosion or hydrogen pickup. To protect the core against stray-current damage it should be biased about 0.5 volt positive to a small platinum cathode held at a current density of 5-10 ma/cm² per square centimeter. If the core can be held at this potential, no electrolytic reaction will take place at its surface and stray currents will be eliminated.

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