

## Study of the Process of Electrochemical Breakdown of Zirconium Fuel Rod Claddings

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### ABSTRACT

The results of experiments on electrochemical dissolution of zirconium and zirconium alloy (fuel rod cladding) in nitric acid solutions are presented. Tables are given for the rate of dissolution as a function of nitric acid concentration, temperature and electrolyte composition. The peak dissolution rate of specimens is shown to be observed in dilute nitric acid at elevated temperatures. The rate of dissolution rises with temperature, reaching ~40-70 mg/cm<sup>2</sup>·h at 90°C. The current yield at this point is 0.6-0.7 g/A·h. Also presented are the results of analysis of the surface oxide film on specimens and of residues formed during dissolution.

### INTRODUCTION

One of the waste types formed during reprocessing of irradiated nuclear power plant fuel is fuel element claddings, which in the conventional chop-leach process remain in the apparatus after dissolution of the fuel. The most commonly-used method of isolating spent fuel claddings is to encapsulate them in concrete and inter them in metal containers.

In view of the high cost of the cladding material (zirconium), there have been a number of proposals for this material to be recovered and re-used. However, the residual contamination of the claddings following the dissolution of the fuel and the chemical stability of the zirconium militate against any proposal for a recycling process that might be economically justifiable. Use of reagents such as hydrofluoric acid is not really feasible on a commercial scale because of the problems in finding materials from which to build the dissolver unit and in dealing with the resulting wastes. There is, however, information to be found in the literature on the synthesis of mineral-like materials based on zirconium.[1-4] The idea of using zirconium, which is contained in irradiated fuel itself in quite large quantities (4-5 kg/t in fuel with a burn-up of 40-50 MW·day/kg uranium), to synthesise compounds that would be suited to long-term storage or underground disposal is conceptually attractive. The aim of this work was to investigate the process of electrochemical dissolution (breakdown) of fuel rod claddings in nitric acid solutions. A successful outcome to this task would enable zirconium separated from claddings to be utilised at the stage of encapsulation of high-level waste through immobilisation in a matrix based on zirconium dioxide, which features a high level of chemical stability. In this case the need to cleanse the zirconium of

radionuclides would be eliminated. It should be emphasised that if this solution were to be adopted, the need for a unit to encapsulate the material in concrete and the disposal of this encapsulated waste would also disappear.

## RESULTS OF EXPERIMENTS AND DISCUSSION

The apparatus used to study the process of electrochemical dissolution of zirconium was comprised of the following units: electric power source, thermostat, electrochemical cells with magnetic mixer and monitoring and measuring instruments. The surface area of the zirconium specimens (anodes) was  $4 \text{ cm}^2$ , and the solution volume was 40 mL. Prior to each experiment, the specimens underwent identical preparation (polishing and oxidation in a  $\text{K}_2\text{Cr}_2\text{O}_7$  solution). In the first phase of the study, flat zirconium electrodes were used. At low voltages (5-25 V), the breakdown process was found not to occur. The reason for this negative result was the presence of a thick oxide film on the surface of the specimens, which at low potential values prevented sufficient current from being passed. The analysis results revealed that when the specimens were passivated, the oxide film thickness on flat electrodes is from  $200 \pm 10$  to  $800 \pm 200$  nm). When the voltage was raised to 180 V in the nitric acid solutions (1-8 mol/L), the rate of breakdown (K) became significant, and absolute values reached a magnitude of  $70 \text{ mg/cm}^2 \cdot \text{h}$ . The results obtained are shown in Table I.

At room temperature, the acid concentration has little influence on the rate of the process. However, at elevated temperature the process slows down as the acid concentration is increased, the reason for which may be the formation of thicker oxide films on the zirconium surface. Results of parallel experiments, with and without mixing of the solution are also shown in Table I. There is a noticeable wide scatter of data obtained, for which there are several explanations. First, despite preliminary oxidation, it proved impossible to ensure identical initial conditions. A second reason may be variation in solution resistance in the near-surface layer as a result of breakdown of the acid and a variation in the solution volume in the cell as a result of evaporation.

Table I. Results of Electrochemical Dissolution of Metallic Zirconium Specimens in Nitric Acid.

Experiment conditions			Current and voltage values		Loss of specimen mass, $\Delta P$ , mg	Mass of residue, $P_r$ , mg	Rate of specimen breakdown, $K$ , $\text{mg/cm}^2 \cdot \text{h}$
Acid concentration, mol/L	T, °C	Mixing	U, V min/max	I, mA			
8.0	$54 \pm 5$	–	178/180	350-70	313	355	19.6
	$51 \pm 2$	+		50-14	2.7	11.4	0.17
3.0	$88 \pm 3$	–	175/180	250-50	613	795	38.3
	$20 \pm 1$	+		70-20	131	64	8.2
	$70 \pm 2$	–	178/180	600-200	498	603	31.2
	$86 \pm 2$	–	175/180	450-200	768	617	48
	$86 \pm 2$	+		250-125	349	666	21.8
1.1	$22 \pm 3$	–	180/180	70-40	118	84	7.4
	$25 \pm 4$	+		50-20	108	68	6.8
	$56 \pm 4$	–	177/180	500-260	680	806	42.5
	$50 \pm 2$	+		200-100	324	317	20.3
	$70 \pm 3$	–	173/180	155-75	792	920	49.5

	91±2	–	173/179	250-75	1047	1280	65.4
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In the next series of experiments, solutions of nitric acid and calcium nitrate were used as electrolytes (Table II). Peak breakdown rates were achieved using 1M calcium nitrate in 1M nitric acid as the electrolyte. When the nitric acid concentration was raised to 8 mol/L, the breakdown rate was significantly lower than in 1M acid, and bore little relation to temperature. The reason for the increase in the zirconium breakdown rate should probably be seen as lying in the formation of calcium zirconate, the properties of which are different from those of zirconium oxide, (the density of zirconium oxide and calcium zirconate is 5.73 g/cm<sup>3</sup> and 4.78 g/cm<sup>3</sup> respectively). The increase in dissolution rate is brought about by a fragmentation of the surface oxide layer; this increases the effective surface and reduces the insulation due to the oxide film. X-ray phase analysis was used to determine the composition of the oxide film formed on the surface of the specimens, following electrochemical dissolution at different acidities. At the same time an analysis was made of the slurry left behind after dissolution of specimens in nitric acid. The results are given in Table III.

Table II. Results of Electrochemical Dissolution of Metallic Zirconium Specimens in Nitric Acid.

Electrolyte composition, mol/L		T, °C	Mixing	Voltage, U min/max	Mass loss, ΔP, mg	Zr concentration, g/L	Current yield, M <sub>i</sub> , g/A·h
[HNO <sub>3</sub> ]	[Ca(NO <sub>3</sub> ) <sub>2</sub> ]						
1.1		56±4	–	177/180	680	0.5	0.65
		50±2	+		324	0.2	0.70
3.1		56±4	–	175/180	892	0.7	0.73
		49±2	+		324	0.3	0.75
8.0		54±5	–	178/180	313	0.3	0.66
		51±2	+		2.7	0.05	0.04
1.0	1.0	50±2	–	140/142	237	0.1	0.35
			+		207	0.1	0.90
8.0	1.0	55±9	–	140/145	468	0.2	0.93
		65±16	+		1390	0.4	0.54
8.0	1.0	88±3	–	140/143	566	0.1	0.88
		88±3	+		407	0.2	0.70

Table III. Results of Analysis of the Composition of the Oxide Film on the Surface of Zirconium Electrodes and Composition of the Slurry Formed on Dissolution.

Acid concentration, mol/L	T, °C	Oxide film composition, %			Slurry composition, %		
		ZrO <sub>2</sub> tetrag.	ZrO <sub>2</sub> monoclin.	Zr met.	ZrO <sub>2</sub> tetrag.	ZrO <sub>2</sub> monoclin.	Zr met.
1	20	15	30	55	90	–	10
3	20				80	–	20
3	90	30	70	–	–	–	–
8	90	30	70	–	80	20	–

When calcium was present in the solution, the X-ray patterns showed lines relating to cubic forms of zirconium dioxide, calcium zirconate and also compounds such as CaO, Ca(OH)<sub>2</sub> and

CaCO<sub>3</sub>. The peak yield of cubic zirconium dioxide was observed in a Ca(NO<sub>3</sub>)<sub>2</sub> solution without nitric acid.

The results obtained are of interest because the formation of the cubic modification of zirconium dioxide under the conditions described is unexpected. We can only assume, with considerable reservations, that the appearance of these forms is linked to the electrochemical process that is occurring at the sample surface. When the acid concentration is raised to 8 mol/L, no zirconate phase is formed, and the results obtained are no different to the data for nitric acid without calcium nitrate.

It should be stressed that in many experiments we were unable to keep the current and voltage parameters constant, and a considerable scatter was seen in the data obtained for parallel experiments. Disruption to the course of the process was caused by the particular features of electrochemical dissolution of zirconium. Strictly speaking, the process we are looking at should be called electrochemical destruction (breakdown), not dissolution.

The high degree of chemical stability of zirconium is caused by the formation of an oxide film on the surface. Attempts to remove the protective oxide film provide no perceptible benefit, precisely because of the high level of activity of the metal, which gives rise to new oxide layers, and it is consequently quite difficult to evaluate the contribution made by the electrochemical dissolution process itself. A certain amount of information may be obtained if we calculate the rate of dissolution from the loss of mass of the specimen over a unit of time, related to the current magnitude; in other words, if we evaluate the current yield ( $M_i$ ) for different experiment conditions. The current yield values obtained for flat electrodes are given in Table IV.

Table IV. Results of Electrochemical Dissolution of Metallic Zirconium Specimens in Nitric Acid

Electrolyte composition, mol/l		T, °C	Mixing	Voltage, U min/max	Mass loss, P, mg	Zr concentration, g/L	Current yield, $M_i$ , g/A·h
HNO <sub>3</sub>	Ca(NO <sub>3</sub> ) <sub>2</sub>						
1.1		56±4	–	177/180	680	0.5	0.65
		50±2	+		324	0.2	0.70
3.1		56±4	–	175/180	892	0.7	0.73
		49±2	+		324	0.3	0.75
8.0		54±5	–	178/180	313	0.3	0.66
		51±2	+		2.7	0.05	0.04
1.0	1.0	50±2	–	140/142	237	0.1	0.35
		50±2	+		207	0.1	0.90
8.0	1.0	55±9	–	140/145	468	0.2	0.93
		65±16	+		1390	0.4	0.54
8.0	1.0	88±3	–	140/143	566	0.1	0.88
		88±3	+		407	0.2	0.70

It should be emphasised that in this case the current yield magnitude is largely formal, but it does nevertheless enable the required parameters and the productivity of the process to be evaluated. In the light of the results obtained, the mechanism of electrochemical dissolution (breakdown) of zirconium in nitric acid may be presented as follows.

Penetration of the oxide film leads to electrochemical oxidation of the surface with simultaneous formation of a new oxide layer. (The surface oxide layer plays the role of a sort of capacitor, and when it is broken down, there are sharp increases in voltage and current. The dissolution process does not, therefore, take place at low potential values at which the oxide layer cannot be broken down.) Mass loss in the specimen is essentially caused by surface destruction and the formation of quite large fragments of slurry, containing metal particles as well as zirconium hydroxide. When the oxide film has been penetrated, there is partial dissolution of fragments of the specimen surface, and in this case the zirconium concentration is 0.1-0.9 g/L. In neutral electrolytes, breakdown of the specimen is linked to formation of calcium zirconate, as confirmed by the slurry analysis results.

Experiments with specimens of VVER reactor fuel rod claddings and PWR cladding (Zircaloy-4) were performed on the same rig using an equivalent methodology. The specimens used were not subjected to any treatment prior to commencement of the experiment. A stabilising device was included in the electrical circuitry of the rig which enabled a significant smoothing out of the current-voltage relationship. The current magnitude was kept constant (100 mA), and the total charge in any given experiment was 0.2 A·h. In the experiments with alternating current, the same cladding material was used as the second electrode. (In calculating the rate, the loss of mass in the two specimens and their area was correspondingly added). The results of the experiments are shown in Tables V and VI.

Just as in the experiments with flat electrodes, the breakdown rate values obtained had a strong dependence on temperature. With a rise from room temperature to 90°C, the dissolution rate rose by roughly 3 times, reaching values of ~30 mg/cm<sup>2</sup>·h. It is interesting to note that the voltage values in the experiments with tubular electrodes (i.e., sections of fuel pin cladding) were lower than those for the flat specimens. The dissolution rate results obtained for claddings from PWR and from VVER fuel rods differed very little. The only difference was a certain diminution in voltage values for the PWR specimens. This is probably to do with the way the fuel rods are treated during fabrication and unequal thickness of the oxide coating.

In all the experiments with alternating current, the rate of breakdown was lower than with direct current electrolysis using otherwise equivalent conditions (solution composition, temperature). This conclusion is also true for the current yield magnitude. (It should be pointed out that the current and voltage parameters given in Table VI are root mean square (rms) values which were recorded by instruments during the experiment).

Table V. Results of Experiments with Electrochemical Dissolution of Fuel Rod Claddings Using Direct Current.

Experiment conditions VVER fuel rod cladding specimens			Voltage variations		K, mg/cm <sup>2</sup> ·h	M <sub>i</sub> , g/A·h
Electrolyte composition	T, °C	Mixing g	U <sub>init</sub> , V	U <sub>end</sub> , V		
Direct current – 100 mA. PWR fuel rod claddings						
Ca(NO <sub>3</sub> ) <sub>2</sub> – 1.0M HNO <sub>3</sub> – 1.0M	26±1	–	135	14	5.2	0.13
	26±1	+	150	150	13.0	0.31
Ca(NO <sub>3</sub> ) <sub>2</sub> – 1.0M	86±2	–	5(60)	5	31.6	0.75
	90±2	+	5	405	33.3	0.79
	28±2	–	145	135	15.7	0.37
	28±2	+	145	145	12.8	0.31
	87±3	–	5.5	5.5	34.6	0.83
	89±2	+	5.5	5.5	29.7	0.71
Direct current – 100 mA. VVER fuel rod claddings						
Ca(NO <sub>3</sub> ) <sub>2</sub> – 1.0M HNO <sub>3</sub> – 1.0M	23±2	–	140	146	13.3	0.31
	22±2	+	136	140	12.9	0.30
	86±2	–	80	82	27.8	0.64
	87±1	+	110(20)	5	33.5	0.77
Ca(NO <sub>3</sub> ) <sub>2</sub> – 1.0M	25±2	–	140	130	10.1	0.23
	25±1	+	150(130)	155	5.7	0.13
	84±2	–	136	118	29.7	0.68
	88±1	+	140	108	27.3	0.63

Table VI. Results of Electrochemical Dissolution Experiments.

Experiment conditions			Voltage variations		K, mg/cm <sup>2</sup> ·h	M <sub>i</sub> , g/A·h
Electrolyte composition	T, °C	Mixing	U <sub>init</sub> , V	U <sub>end</sub> , V		
HNO <sub>3</sub> -0.1M	86±3	-	30	42	8.7	0.40
	87±2	+	70	46	7.9	0.36
HNO <sub>3</sub> -1.0M	22±1	-	105	107	12.3	0.56
	22±1	+	115	125	12.1	0.55
HNO <sub>3</sub> -3.0M	22±1	-	113	115	11.5	0.53
	22±1	+	100	100	11.5	0.53
Ca(NO <sub>3</sub> ) <sub>2</sub> -1.0M HNO <sub>3</sub> -1.0M	22±1	-	84	105	13.1	0.6
	22±1	+	105	110	15.5	0.71

Table VI. Results of Electrochemical Dissolution Experiments (continued)

HNO <sub>3</sub> -0.5M	83±3	-	5,6(59)	7.2	32.9	0.79
NaF-0.1M	84±3	+	5,4(180)	5.2	26.4	0.63

During the experiments with alternating current, instances were recorded where two electrodes (tube specimens of identical size) behaved differently. A clear asymmetry in their mass variation was observed. The specimens also differed in their external appearance. One specimen retained its initial colouring, while the other became covered with a thick white oxide film coat. We were unable to establish any pattern in the asymmetry of properties of specimens in relation to temperature or solution composition.

The sole explanation for the phenomenon identified may be a difference in the state of the specimen surface at the beginning of the experiment. Non-identical conditions for the passage of current through the oxide film probably led to an enhancement of the differences in the structure of the oxide layer on one of the specimens. In this case a current rectification effect may occur, with the dissolution process taking place on one specimen only, while the other is not broken down i.e. minor differences in starting properties are enhanced through a feedback route controlled by the electrical properties of the oxide layer.

These considerations provide further proof of the complexity of the process as a whole and the presence of a number of conditions that are difficult to control and serve, in the final analysis, to bring about a considerable scatter in the results, as was observed throughout the work. An increase in the current yield magnitude may be attained by the addition of fluoride ions to the solution (Table VI). When this is done, finely-disperse residues are seen to form, which could not be separated out from the solution even using a centrifuge. The rate of dissolution was comparable with the levels obtained in calcium nitrate solutions. The specimen mass loss in this case is probably governed by the electrochemical process as such, rather than by the reaction with fluoride ions. (Control experiments without current applied to the specimens showed that the dissolution rate in a 1M HNO<sub>3</sub> – 0.1M NaF solution did not exceed 0.03-0.05 mg/cm<sup>2</sup>·h i.e. 0.1-0.2% of the electrochemical rate shown for 1M HNO<sub>3</sub> – 0.1M NaF in Table VI.)

## CONCLUSION

The mechanism of the electrochemical breakdown process is fairly complex and the results obtained do no more than provide us with an idea of some of the features of the physical/chemical process under consideration. The main obstacle to direct anode dissolution is the formation of thick oxide film layers on the zirconium surface. This makes it necessary to apply quite high potentials (over 100 V) and gives rise to regimen instability (sudden jumps in current, sparking).

The process of electrochemical dissolution (destruction) of zirconium claddings may nevertheless be carried out in nitric acid, preferably in dilute solutions and with calcium nitrates present. The rate of dissolution rises with temperature, reaching ~40-70 mg/cm<sup>2</sup>·h at 90°C. The current yield under these conditions is 0.6-0.7 g/A·h.

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