

Management of zirconium rod claddings with the process of electrochemical breakdown

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ABSTRACT

The main objective of the research was the development the electrochemical process of zirconium rod claddings breakdown.

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 $\sim 40\text{-}70 \text{ mg/cm}^2\cdot\text{h}$ at 90°C . The current yield at this point is $0.6\text{-}0.7 \text{ g/A}\cdot\text{h}$. The results of analysis of the surface oxide film on specimens and of residues formed during dissolution are presented also.

INTRODUCTION

One of the wastes varieties resulted from reprocessing of irradiated fuel issued from nuclear-power plant are fuel rods claddings remaining in the apparatus after fuel dissolution.

The actual volumes of wastes will depend very much on the fuel to be treated and on the degree of segregation of hulls from the rest of the hardware. The average volume of unconsolidated hulls and cladding wastes is about 0.3 m^3 per ton of heavy metal but can vary widely (e.g. $0.2\text{-}0.6 \text{ m}^3$ / depending on the type of fuel assembly being sheared. But, again the bulk density of hulls is approximately $1.8\text{-}2.5 \text{ t/m}^3$, and this will depend on the actual waste densities.

The most common technique of used cladding isolation is its cementing and disposal in metallic containers [1].

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.

At the same time there is a lot of information to be found in the literature on the synthesis of mineral-like materials based on zirconium for the purpose of long-lived radio nuclides immobilization and disposal [2-5].

The concept of using crystalline materials to immobilize high-level radioactive wastes (HLW) has been developed by numerous contributors since it was first pro-posed in 1953.

The idea of using zirconium, which is contained in fuel rod claddings and irradiated fuel itself to synthesize compounds that would be suited to long-term storage or final disposal, is conceptually attractive. In this case the need to cleanse the zirconium of radionuclides would be eliminated.

The object of this work was to carry out a study on process of fuel rod claddings electrochemical dissolution in nitric acid solutions.

Reprocessing of used nuclear fuel will be necessary to continue nuclear power into the future. In the authors' opinion an electrochemical dissolution of fuel rods claddings is the most worth-while technique for preparation of zirconium solutions intended for ceramic matrices synthesis.

It should be noted also 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 described in our paper [6]. 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.

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 mg/cm²·h. The results obtained are shown in Table 1.

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 experiments, with and without mixing of the solution are shown in Table 1. There is a noticeable wide scatter of data obtained, for which there are several explanations.

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 [6].

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

Experiment conditions			Current and voltage values		Loss of specimen mass, ΔP , mg	Mass of residue, P_r , mg	Rate of specimen breakdown, K , $\text{mg}/\text{cm}^2 \cdot \text{h}$
Acid concentration, mol/L	T, °C	Mixing	U, V min/max	I, mA			
8.0	54±5	–	178/180	350-70	313	355	19.6
	51±2	+		50-14	2.7	11.4	0.17
	88±3	–	175/180	250-50	613	795	38.3
3.0	20±1	+		70-20	131	64	8.2
	70±2	–	178/180	600-200	498	603	31.2
	86±2	–	175/180	450-200	768	617	48
	86±2	+		250-125	349	666	21.8
1.1	22±3	–	180/180	70-40	118	84	7.4
	25±4	+		50-20	108	68	6.8
	56±4	–	177/180	500-260	680	806	42.5
	70±3	–	173/180	155-75	792	920	49.5
	91±2	–	173/179	250-75	1047	1280	65.4

In the next series of experiments, solutions of nitric acid and calcium nitrate were used as electrolytes (Table 2). Peak breakdown rates were achieved using 1M $\text{Ca}(\text{NO}_3)_2$ 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.

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. When calcium was present in the solution, the X-ray patterns showed lines relating to cubic forms of zirconium dioxide, calcium zirconate and compounds such as CaO , $\text{Ca}(\text{OH})_2$ and CaCO_3 . The peak yield of cubic zirconium dioxide was observed in a $\text{Ca}(\text{NO}_3)_2$ solution without nitric acid. The results are given in Table 3.

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.

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 _i , g/A·h
[HNO ₃]	[Ca(NO ₃) ₂]						
1.1		56±4	–	177/180	680	0.5	0.65
		50±2	+		324	0.2	0.70
		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
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 while Dissolution [6].

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

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.

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. 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 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. The results of the experiments are shown in Tables 4.

Table IV. Results of Experiments with Electrochemical Dissolution of Fuel Rod Claddings Using Direct Current [6].

Experiment conditions (VVER fuel rod cladding specimens).			Voltage variations		K, mg/cm ² ·h	M _i , g/A·h
Electrolyte composition	T, °C	Mixing	U _{init} , V	U _{end} , V		
Direct current – 100 mA. PWR fuel rod claddings						
Ca(NO ₃) ₂ – 1.0M HNO ₃ – 1.0M	26±1	–	135	14	5.2	0.13
	26±1	+	150	150	13.0	0.31
	90±2	+	5	405	33.3	0.79
	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						
	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 ₃) ₂ – 1.0M	25±2	–	140	130	10.1	0.23
	84±2	–	136	118	29.7	0.68
	88±1	+	140	108	27.3	0.63

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/cm²·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.

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.

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.

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.

An increase in the current yield magnitude may be attained by the addition of fluoride ions to the solution. 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.

CONCLUSION

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 spent fuel to be utilized at the stage of encapsulation of high-level waste through immobilization in a matrix based on zirconium, which features a high level of chemical stability.

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 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 $\sim 40\text{-}70 \text{ mg/cm}^2\cdot\text{h}$ at 90°C . The current yield under these conditions is $0.6\text{-}0.7 \text{ g/A}\cdot\text{h}$. The highest sample dissolution rate was observed in solutions of dilute nitric acid in presence of calcium nitrate at higher temperatures.

The next stage of investigation will be development innovative technology for ceramic matrices synthesis with using of zirconium solutions arising from electrochemical dissolution of zirconium claddings

The investigations conducted at the Radium Institute have demonstrated the basic possibility of immobilization of the actinide fraction of HLW in ceramics based on the zirconium dioxide or zircon. The stability of these compounds in various geochemical environments over billions of years is the best evidence in favor of promising developments of zirconium based crystalline matrices.

REFERENCES

1. Options Treatment and Conditioning of Radioactive Organic Liquids. Management of Cladding Hulls and Fuel Hardware. International Atomic Energy Agency. IAEA-TECDOC-258, Vienna (1985).
2. Anderson E.B., Burakov B.E., Vasil'ev V.G., Lobach B.K., Lyubtsev R.I., Starchenko V.A., Strel'nikov V.A., Titov S.L. The Technology of New Management in the Project of the Russian Nuclear Fuel Reprocessing Plant. Spectrum '94, Proceedings, August 14-18, 1994, Atlanta, Georgia, USA, v. 3, pp. 1969-1975.
3. Kuramoto K., Makino Y., Yanagi T. et al. Development of Zirconic and Alumina Based Ceramic Waste Forms for High Concentrated TRU Elements. Proc. of Int. Conf. "Global '95", Sept. 11-14 1995, Versailles, France, v. 1, pp. 1838-1845.
4. Burakov B. E., Anderson E. B., Rovsha S. I. et al. Synthesis of Zircon for Immobilization of Actinides. Materials Research Society Symposium / Proceedings Scientific Basis for Nuclear Waste Management XIX, 1996, v. 412, p. 33-39.
5. Burakov B.E., Anderson E.B. Crystalline Ceramics Development for the Immobilization of Actinide Waste in Russia / Proc. Intern. Conf. Radioactive Waste Management and Environmental Remediation – ASME 2001, Bruges, Belgium.
6. V.A. Davydov, Yu.A. Pokhitonov, P.J.W. Rance. Study of the Process of Electrochemical Breakdown of Zirconium Fuel Rod Claddings WM'06 (Proc. Int. Conf. Tucson, 2006), WM Symposia, Inc., Tucson, AZ (2006) (CD-ROM).