

## **ELECTROCHEMICAL METHODS FOR REPROCESSING DEFECTIVE FUEL ELEMENTS AND FOR DECONTAMINATING EQUIPMENT**

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### **ABSTRACT**

Reprocessing of fuel elements receives much consideration in nuclear engineering. Chemical and electrochemical methods are used for the purpose. For difficultly soluble materials based on zirconium alloys chemical methods are not suitable.

Chemical reprocessing of defective or irradiated fuel elements requires special methods for their decladding because the dissolution of the clad material in nitric acid is either impossible (stainless steel, Zr alloys) or quite slow (aluminium). Fuel elements are cut in air-tight glove-boxes equipped with a dust collector and a feeder for crushed material.

Chemical treatment is not free from limitations. For this reason we started a study of the feasibility of electrochemical methods for reprocessing defective and irradiated fuel elements.

A simplified electrochemical technology developed makes it possible to recover expensive materials which were earlier wasted or required multi-step treatment. The method and an electrochemical cell are suitable for essentially complete dissolution of any fuel elements, specifically those made of materials which are difficultly soluble by chemical methods.

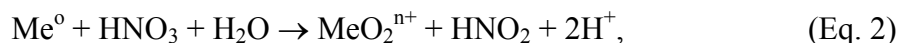
### **ELECTROCHEMICAL REPROCESSING**

The most-used electrochemical method is anodic dissolution of metals to form readily soluble compounds. The anodic dissolution resulting in metal solubilization as hydrated ions or complex ions is the opposite to cathodic dissolution in many respects.

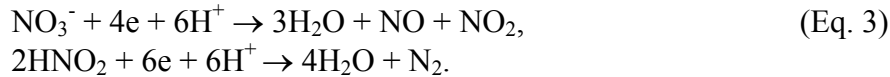
Anodic oxidation or dissolution of fuel element material follows the general scheme:



or



The cathodic reduction of nitric and nitrous acid can be described as:



This sequence of steps is the reverse of the cathodic reduction of metals, i.e. the process starts with destruction of the crystal lattice and ends in the ion formation in solution. The anodic polarization can be attributed to slower rates of such operations as dissolution, transportation, destruction of the solid phase and ionization. The slower processes results in accumulation of solubilized ions near the electrode, with a consequent shift of the potential to the positive side. The anodic process effectiveness depends on the nature of metal to be dissolved, electrolyte compositions and electrochemical parameters.

### **Behavior of Fuel Element Materials during Dissolution**

To specify electrochemical dissolution parameters, the behavior of fuel element materials like stainless steel and zirconium alloys in nitric acid was investigated. During electrochemical dissolution these materials pass into solution either completely to leave small residue (stainless steel) or partially to produce great residue (zirconium alloys). For the most part the uranium content of the residue is low and the residue can be considered as waste. The electrochemical dissolution is characterized on the whole by high extraction of uranium into nitric acid solution, with insignificant uranium losses by residues. The dissolution runs steadily. Its rate depends on the material nature. The process can be controlled by changing the current intensity and density. A current density of 20-100 A/dm<sup>2</sup> and a temperature of 60-80°C are best suited

### **Electrochemical Dissolution of Fuel Elements of U-Al Alloys or Stainless Steel-Containing Materials**

Chemical dissolution by nitric acid is difficult for U-Al alloys and practically impossible for stainless steel. Electrochemical dissolution parameters were studied in a laboratory electrochemical cell using defective fuel elements. The solution temperature range was 60 - 70°C, the free acid concentration was 6-8 mole/l early in the test and 2-3 mole/l at the end of the test.

The test results show that the electrochemical dissolution rate depends on the current density in the range under study (Table I). The dissolution rate increases, as a rule, with increasing current density. The power consumption decreases with higher amount of salts and lower content of free nitric acid in solution.

Table I. Dissolution rate and current efficiency as a function of current density

Material	Anodic current density, A/dm <sup>2</sup>	Dissolution rate, g/dm <sup>2</sup> hr	Current efficiency, %
U-Al alloy	25	8.7	49
	35	10.2	38
	45	11.4	36
	60	15.5	34
	70	15.8	30
Stainless steel	20	18.5	93
	30	22.3	74
	40	22.6	57
	50	26.1	52

As shown by analysis of the gaseous mixture produced within the electrolytic cell, the dissolution of defective fuel elements under optimum conditions produces no more than 1.1 vol.% of hydrogen (Table II).

Table II. Analysis of the gaseous mixture produced within the electrolytic cell during dissolution of defective fuel elements 8 M. HNO<sub>3</sub> ; 80°C (*i<sub>a</sub>*=40A/dm<sup>2</sup>, *i<sub>k</sub>*=5 A/dm<sup>2</sup>)

Test NN	Sampling time, min	Gaseous mixture composition, vol.%			
		Nitrogen oxides	O <sub>2</sub>	N <sub>2</sub>	H <sub>2</sub>
1	154	91.50	0.3	8.0	0.2
	175	89.00	0.8	8.9	0.3
	235	87.90	0.3	11.4	0.4
2	127	90.00	0.7	8.2	1.1
	189	93.40	-	6.6	-
	242	94.50	-	5.5	-

### Electrochemical dissolution of Fuel Elements of Uranium and Zirconium

Chemical reprocessing of zirconium-clad uranium fuel elements calls for their shredding. During shredding and further waste storage zirconium can ignite. For this reason electrochemical option seems to be promising. First the zirconium behavior under anodic polarization in nitric acid was studied because UO<sub>2</sub> fuel easily dissolves in this solution.

Zirconium and zirconium-niobium alloys were found to oxidize under anodic polarization in nitric acid. The oxide film developed on the metal surface cracked, scaled off, fell down and settled to the electrochemical cell bottom as solid zirconium dioxide. The portion of zirconium (≈10%) passed into solution.

Monopolar connection between a specimen and the anodic feeding was used for laboratory tests. The dissolution was tested as a function of the current density and

temperature (Table III). In most cases the dissolution effectiveness and sometimes electrical conductivity decreased with lower temperature and higher current density. Several experiments showed a current efficiency of 100%. In the latter cases electrochemical processes were likely to be accompanied by chemical processes – oxidation and dissolution of claddings being polarized. The current efficiency averaged 0.82 g/A-hr or 95.9%.

Table III. Oxidation and dissolution of Zr-1%Nb claddings under anodic polarization in 8 mole HNO<sub>3</sub>

Temperature, °C	Anodic current density, A/dm <sup>2</sup>	Current efficiency	
		g/a-hr	%
50	20	0,81	94,3
70	20	0,83	98,0
90	20	0,93	(108,8)
50	40	0,95	(111,5)
50	60	0,77	89,3
50	80	0,53	63,2
70	40	0,85	100,0
70	60	0,84	98,6
70	80	0,82	95,9
90	40	0,82	96,7
90	60	0,83	98,1
90	80	0,86	(100,5)

In tests carried out with a pilot electrochemical cell a cladding sample was clamped to the anodic feeding by a grip for electric contact. Experimental conditions and results obtained are reported in Table IV.

Table IV. Oxidation and dissolution of Zr-Nb claddings under anodic polarization in 8 mole HNO<sub>3</sub>

N/N	Parameter	Unit of measure	Value
1.	Current intensity	A	50-70
2.	Voltage	V	7-8
3.	Temperature	°C	78-85
4.	Current density	A/dm <sup>2</sup>	15-18
5.	Current efficiency	%	60
7.	Residue yield	%	90.7
8.	Zr content in solution	g/l	1.34

The amount of residue as zirconium dioxide is 90% of oxidized and dissolved specimen (Table IV). The bulk weight of washed and dried residue is 0.95 g/cm<sup>3</sup>.

Tests of Zr-Nb clads anodically dissolved in nitric acid show that the current density exceeding the maximum permissible one often results in a sharp decrease in electric conductivity, with a consequent marked drop in the current intensity and an increase in voltage.

The pilot electrochemical cell and defective fuel elements were used for specifying dissolution parameters. For the electric contact between a specimen being dissolved and an anodic grip to be stable, the compressive overstress of the grip was needed

Exposure of the residue in heated 6 *M* nitric acid for an hour decreased the uranium content of the residue to 0.10-0.5 wt.%.

In 24 hr the resulting solution was completely clarified. A sieve analysis of the washed and dried residue showed the predominance (82-85%) of fine fractions ~0.5 mm in size. The bulk weight of the residue varied from 0.960 to 1.524 g/cm<sup>3</sup> depending on the dryness.

The electrochemical dissolution produces stable solution with no salt precipitates at salt concentrations below solubility limits.

The test results suggest an adequate direct recovery of uranium of above 95% by electrochemical dissolution. Higher uranium recovery and low-uranium residue if any call for fusion with sodium carbonate and further fuel leaching.

## CONCLUSION

An electrochemical technology for reprocessing defective fuel elements and process waste has been developed that provides cost-effective recovery of valuable components that are commonly lost in the existing practice.

The electrochemical reprocessing technology makes it possible to:

- exclude preliminary shredding defective products;
- reduce the nitric acid consumption;
- use no catalysts that cause troubles during further reprocessing of spent solutions;
- rise the valuable component recovery from 86 to 95%;
- decrease the evolution of effluent gases by 50%;
- set up reprocessing of graphite waste containing valuable products (earlier this waste was stockpiled without any treatment)

## ELECTROCHEMICAL DECONTAMINATION

In addition to reprocessing defective fuel elements, the electrochemical methods are suitable for decontaminating materials used in nuclear engineering.

We have developed an ion exchange electrochemical decontamination of metallic and non-metallic surfaces. It is a combination of bipolar electrochemical process and ion exchange sorption of radionuclides removed from fibrous materials. The technology provides effective and efficient decontamination as well as small volumes of liquid radwaste.

Technical approaches underlying the technology make possible its mechanization and automated control.

An method of ion-exchange electrochemical decontamination for materials of different nature (metallic and non-metallic) has been developed at VNIINM. The method is a combination of a bipolar electrochemical process and ion-exchange sorption of radionuclides on fibrous materials. It is characterized by a high decontamination level, a low liquid radwaste volume and a high productivity.

Technical approaches underlying the process makes possible its mechanization and automated control.

The ion-exchange electrochemical decontamination power was studied by:

- contaminating specimens;
- identifying optimum conditions for bipolar electrochemical dissolution;
- assessing decontamination of stainless steel and plastic surfaces

### **Samples Preparation**

The specimens were prepared by the following technique.

The stainless steel (12Kh18N10T) surfaces were exposed to ethanol, then to sodium hydroxide (50 g/l) at 95°C for 30 min, to nitric acid (50 g/l) at 95°C for 30 min and to a mixture of nitric acid (50 g/l) and potassium bichromate (5 g/l) for 15 min at 50-60°C.

A ring-limited area of the surface was contaminated dropwise with 0.5 ml of an  $\alpha$ -emitter and allowed to stay for dryness at 20°C. Then the specimens were blotted with paper and kept in air for 15-20 min.

### **Identifying Optimum Conditions for Bipolar Electrochemical Dissolution**

**Complicated configurations present difficulties for electrochemical processes. A special counter-electrode design required for each case increases labor input.**

Bipolar treatment is slower than monopolar dissolution because of not all lines of electric force passing through a specimen but economically more favorable for decontaminating small and irregularly-shaped parts.

The bipolar electrochemical decontamination method is responsible for highly effective cleaning both metallic and non-metallic surfaces [1-3].

Based on our decontamination studies of 65x60x1mm stainless steel specimens, optimum bipolar electrochemical conditions were specified (Tables VI; Fig.1.1 and 1.2.).

Table V. Results of a 5 min bipolar electrochemical treatment of 1Kh18N10T specimens

<b>Solution</b>	<b>Current density, A/dm<sup>2</sup></b>	<b>Voltage, V</b>	<b>Weight loss, g</b>	<b>Specific metal removal, g/dm<sup>2</sup></b>	<b>Current efficiency, %</b>
5.0% HNO <sub>3</sub>	1	8.4	0.0077	0,275	23.3
	5	19.8	0.0145	0,518	8.68
	10	31.8	0.0404	1,443	12.13
	15	40.6	0.0671	2.396	13,42
10.0% HNO <sub>3</sub>	1	5.0	0.0007	0,025	2.12
	5	7.8	0.0380	1.357	22.75
	10	10.9	0.0806	2.879	24.20
	15	13.3	0.1167	4.168	23.34
15.0% HNO <sub>3</sub>	1	3.5	0.0001	0.004	0.30
	5	6.6	0.0294	1.050	17.60
	10	9.4	0.0982	3.507	29.49
	15	10.9	0.1296	4.629	25.92
20.0% HNO <sub>3</sub>	1	2.9	0.0001	0.004	0.30
	5	6.8	0.0327	1.168	19.58
	10	8.5	0.1055	3.768	31.68
	15	10.5	0.1757	6.275	35.14
25.0% HNO <sub>3</sub>	1	2.5	0.0004	0.014	1.21
	5	4.3	0.0004	0.014	0.24
	10	6.9	0.0423	1.511	12.70
	15	7.7	0.1209	4.318	24.18
5.0% NaHCO <sub>3</sub>	1	3.3	0.0003	0.011	0.91
	5	7.1	0.0354	1.264	20.08
	10	8.9	0.1134	4.050	32.98
	15	11.8	0.1622	5.793	33.92
10.0% NaHCO <sub>3</sub>	1	3.7	0.0005	0.018	1.50
	5	5.8	0.0005	0.018	0.31
	10	8.2	0.0391	1.396	12.23
	15	9.4	0.1268	4.529	24.83

Dissolution rate as a function of the current density at anode at various concentrations of nitric acid

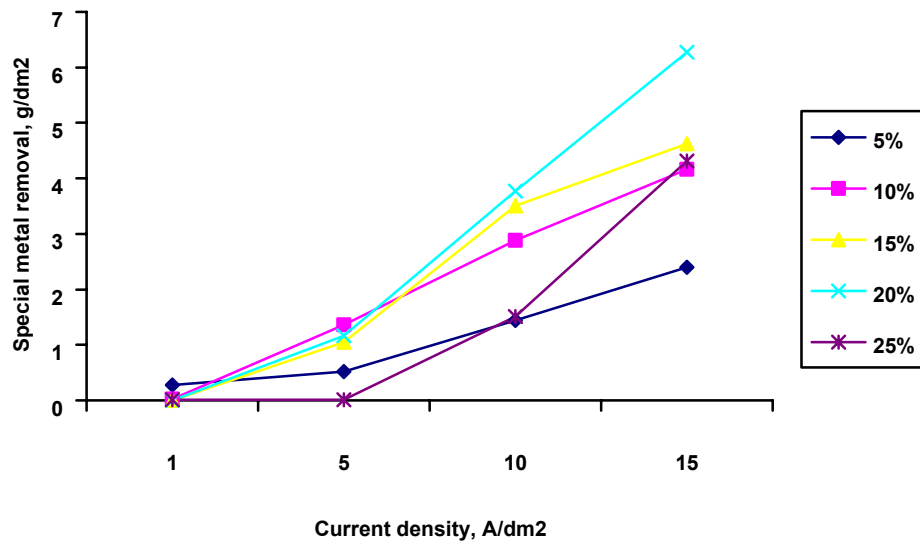


Fig. 1.1

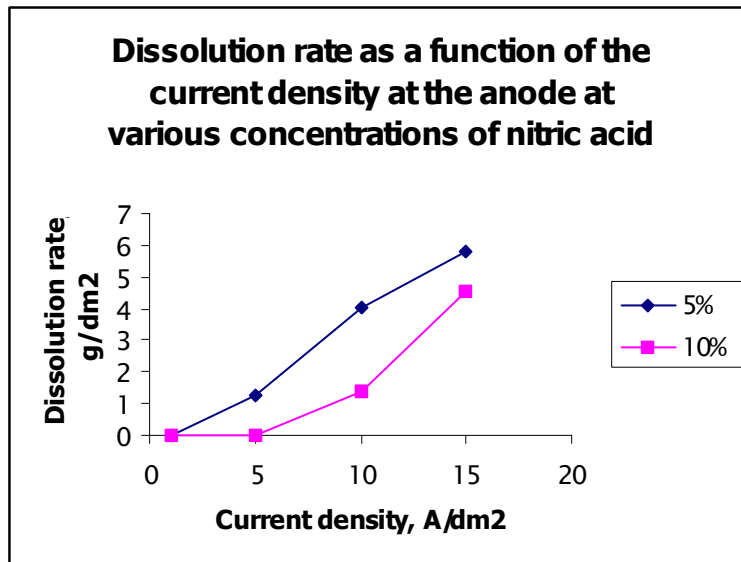


Fig. 1.2

Fig. 1. Decontamination Studies



**Results of electrochemical decontamination**

Decontamination was tested using stainless steel and plastic specimens which were industrially contaminated with aqueous nitric acid solutions containing  $U^{235}$  and  $U^{238}$  after long operation or artificially contaminated in a laboratory by solutions containing  $Pu^{239}$ . Experimental results are given in Tables VI and VII.

Table VI. Results of ion-exchange decontamination of plastic surfaces  
(15 A/dm<sup>2</sup>; 5-6 V; 5 min)

Electrolyte	Contamination with U-235, Bq/cm <sup>2</sup>		Decontamination factor
	initial	Final	
20.0% HNO <sub>3</sub>	300	1.0	300
	380	1.0	380
	320	2.0	160
	290	1.0	290
	380	1.0	380
10.0% Na <sub>2</sub> CO <sub>3</sub>	200	1.0	200
	180	1.0	180
	360	1.0	360
	220	2.0	110
	280	1.0	280

Table VII. Results of ion-exchange decontamination of stainless steel surfaces  
(15 A/dm<sup>2</sup>; 20% HNO<sub>3</sub> ;5-6 V; 5 min)

Contamination with Pu-239, Bq/cm <sup>2</sup>		Decontamination factor
initial	final	
65.0	0.1	650
59.0	0.1	590
57.0	0.1	570
36.8	0.1	368
23.6	0.1	236

As shown by Tables VI and VII, electrochemical treatment using an electrode-tool results in effective removal of radioactive contaminants from stainless steel and plastic surfaces. Moreover, the removal rate depends on sorption rate by ion-exchange sorbent. The combination of the two mechanisms enables for the surface to be adequately cleaned during one cycle of bipolar electrochemical decontamination.

The results of our studies evidence :

- an adequate cleaning of stainless steel and plastic surfaces of radioactive contaminants by the electrochemical ion-exchange method;
- marked reduction of the liquid radwaste volume;
- no secondary contamination of the surface being cleaned due to the radioactivity sorption by ion-exchange material;
- effective decontamination of non-conductive and intricately-shaped industrially-contaminated parts with the bipolar electrochemical method using an electrode –tool(fig.2);

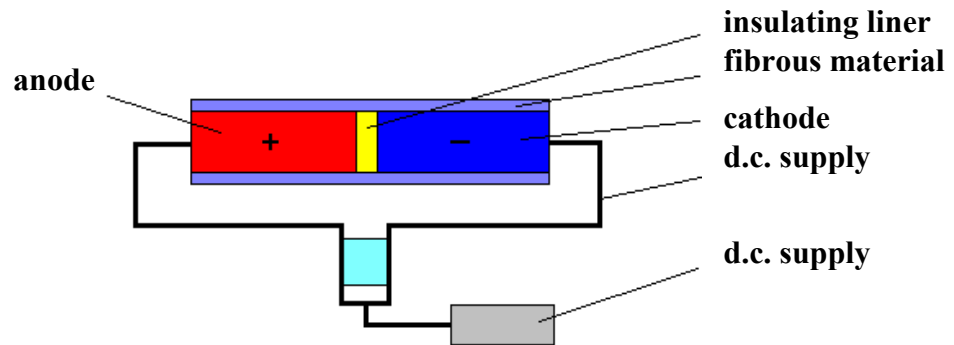


Fig. 2. Effective decontamination of non-conductive and intricately-shaped industrially-contaminated parts with the bipolar electrochemical method using an electrode –tool.