

2002

ELECTROCHEMICAL SEPARATION OF ALUMINUM FROM IRRADIATED URANIUM SILICIDE FUELS FOR STORAGE PURPOSES

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ABSTRACT

The reprocessing of irradiated fuels is one of the greatest problems of fuel cycle. A way to avoid it is to reduce volume removing the structural materials for storage. In the case of uranium silicide fuels, from Material Testing Reactors (MTR), aluminum can be removed selectively, keeping uranium silicide in its original form. The process consists of the anodic dissolution of aluminum in alkaline media. The potentiostatic control permits its selective dissolution. The advantages of this process are the low alkaline solution concentration e short time dispensed for the dissolution of aluminum. The studies are just in the beginning, but very promising.

I. INTRODUCTION

Nowadays every time one thinks in a new chemical process, may take into account if this process is "ecologically correct". In all branches of chemical industry, this problem has to be considered and solved. Sometimes, the solution is in the improvement of the process.

In this way, electrochemical techniques, when applicable, are more advantageous than other chemical processes. In spite of presenting, in some cases, high initial costs, mostly due to electrode materials, the operational conditions, the reduction of chemical reagents used and wastes generated are very important features.

Because of those advantages, in this study, the use of an electrochemical technique as an alternative for dissolving and recovering nuclear materials was proposed. In this case, the electrodisolution of nuclear materials leads, mostly, to a significative reduction of generated waste, solving the deposition and storage problems.

This study had as an initial purpose to solve the problems related to the ^{99}Mo production that uses uranium silicide as a target, like long dissolution time, too many reagents involved, heating, all necessary for chemical dissolution. As electrochemical technologies have been used with success in many processes of nuclear industry, the electrodisolution of metallic aluminum, without dissolving uranium silicide, was studied.

The electrodisolution is, therefore, a feasible alternative for the selective recovery of nuclear materials.

II. URANIUM SILICIDE FUELS

Uranium silicide/Al has been used as fuel for Research Reactors and as target for the ^{99}Mo production.

Today, most spent fuel assemblies are stored in wet basins and are susceptible to aqueous corrosion. Although water chemistry control can reduce the propensity for degradation, concern is valid for long-term storage [1].

The dissolution of the Al cladding and of the Al powder that is mixed to the uranium silicide, after the irradiation of the fuel, however, presents some peculiarities [2]. The aluminum powder, in the meat of the thermally annealed and irradiated plates, do not dissolve well after the dissolution of the cladding. The silicide particles do not disperse, but remain affixed with matrix aluminum powder in a thin wafer. The annealed plates require approximately double the time of the cold ones.

In this case, the electrochemical process is able to attack all the aluminum present, making possible its dissolution.

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III. EXPERIMENTAL

Materials and reagents. The following materials and reagents were used in the experiments:

- NaOH p.a., Merck
- Distilled and deionised water
- U₃Si₂-Al/Al cladding plates, Department of Metallurgy, IPEN-CNEN/SP

Electrochemical methods. The potentiodynamic polarization experiments were carried out in a borosilicate cell (Figure 1) connected to an EG&G PAR 273 Potentiostat/Galvanostat (Figure 2). An Ag/AgCl reference electrode, a Pt anode-support as working electrode and a Pt foil as auxiliary electrode were used. These experiments were performed in 1.0 mol l⁻¹ NaOH solutions (electrolyte), at room temperature.

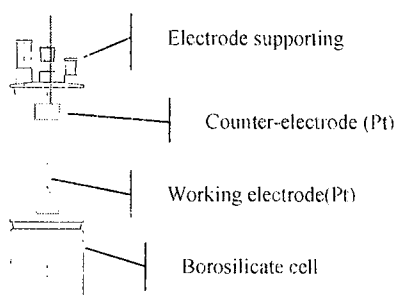


Figure 1. Electrolytic cell used in the experiments.

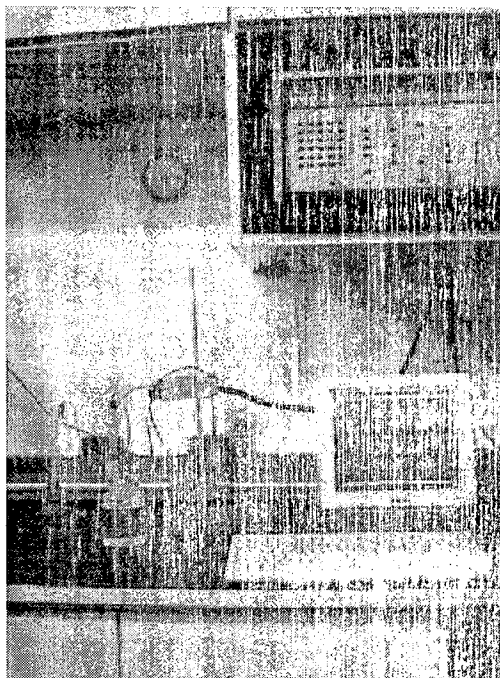


Figure 2. Experimental apparatus for polarization: the electrolytic cell and the potentiostat/galvanostat.

The electrodisolution of aluminum were carried out in 0.5 and 1.0 mol l⁻¹ NaOH solutions using a source of direct current (Tectrol 50-05). The samples were plates of uranium silicide fuel, measuring 1 cm², wrapped with a Pt wire (anode). The solution was not stirred in all experiments.

Each experiment used 700 ml of the electrolyte and 15 ml sample aliquots were collected at the end of the experiments for analyzing uranium content.

Analytical method. Uranium was analysed by gamma spectrometry, in a ORTEC NaI(Tl) well type scintillator detector, by ²³⁴Th picks.

IV. RESULTS AND DISCUSSION

Open circuit potential [3]. The open circuit potential transients in 1 mol l⁻¹ NaOH solutions are shown in Figure 3. The increase in NaOH concentration made the E_{corr} more positive. Because aluminate ion has amphoteric nature, the increasing temperature may probably favor the solubility of the film [4], promoting alterations on its structure [5], leading to a new porous system and increasing the dissolution rate of the protective film in higher NaOH concentrations.

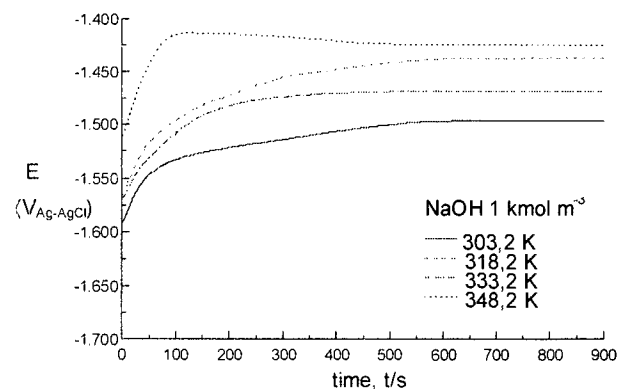


Figure 3: Open circuit potentials of aluminum in 1 mol l⁻¹ NaOH solution at various temperatures [].

Earlier studies [levi] showed that high temperatures decrease the density and viscosity of the electrolyte, the increase of dissolved active species may lead to diffusion and migration of ionic species, resulting in the dissolution of reaction products that has been precipitated in the oxide porous [1,2]. So, more concentrated solutions and higher temperatures increase the dissolution rate of aluminum.. But for the purposes of this work, the reduction of electrolyte concentration and room temperature operation are fundamental for the optimization of the process.

Potentiodynamic polarization experiments. Potentiodynamic polarization curve for aluminum was

obtained in 1 mol l⁻¹ NaOH solutions, at room temperature, and sweep rate of 1 mV s⁻¹. The result is presented in Figure 4.

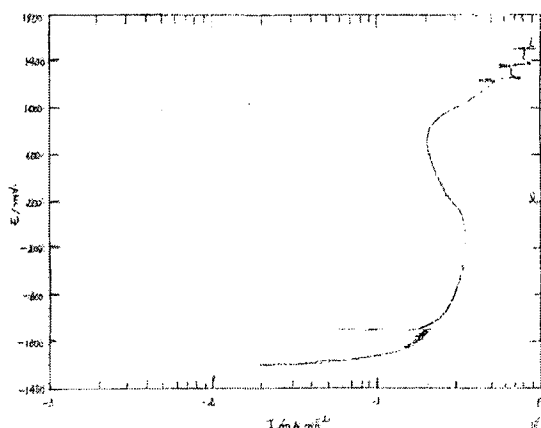


Figure 4. Potentiodynamic polarization curve of aluminum in 1 mol l⁻¹ NaOH solution, sweep rate of 1 mV s⁻¹ and at room temperature

This curve shows the anodic region, with the continuous dissolution of aluminum and oxygen evolution beginning at 1.200 V (Ag/AgCl).

Electrodissolution experiments. Observing the potentiodynamic one can see that Al readily dissolves at all potentials. So, it is possible to dissolve aluminum without dissolve uranium silicide, since the latter remains inert in the range of potentials studied. For the electrodisolution experiments the current applied was varied and the time of complete dissolution of aluminum was determined. Table 1 shows the results.

Table 1. Electrodisolution of uranium silicide fuel plates in NaOH solutions, using a source of direct current.

[NaOH] (mol l ⁻¹)	Sample weight (g)	Sample area (cm ²)	Current (A)	Voltage (V)	Time (h)
1.0	0.5506	8.0	1.2	4.0	3.3
1.0	0.7166	8.0	1.6	4.5	2.5
1.0	0.682	8.0	1.8	5.0	2.2
0.5	0.5987	8.0	1.6	4.5	2.9

An experiment in parallel showed that in 1 mol l⁻¹ NaOH solution one plate of 0.5575g and measuring 1 cm² required more than 8 hours for complete chemical dissolution.

In all experiments aliquots of the final solution was analyzed by gamma spectrometry and no uranium was detected.

V. CONCLUSIONS

The results show that is possible to dissolve aluminum cladding of uranium silicide fuels, using NaOH of lower concentrations, like 0.5 mol l⁻¹, without dissolving uranium silicide. The short time, the low NaOH concentration and the room temperature employed in the experiments are the most important features of the proposed process.

In the next experiments it will be used NaOH at lower concentrations (0.1 and 0.2 mol l⁻¹) and higher currents may be applied. The energy consumption will be analyzed.

Acknowledgement

We thank to Edson Takeshi Osaki for the figures and to Antônio Lívio da Silva Nunes for the laboratory support.

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