

TREATMENT OF IRRADIATED URANIUM SILICIDE FUELS FOR STORAGE PURPOSES

Christina A. L. G. de O. Forbicini¹, Neusa Alonso-Falleiros² and Sérgio Forbicini¹

¹Centro de Química e Meio Ambiente
Instituto de Pesquisas Energéticas e Nucleares/CNEN-SP
Av. Prof. Lineu Prestes, 2242
05508-000 São Paulo, SP
cforbici@ipen.br

²Departamento de Engenharia Metalúrgica e de Materiais
Escola Politécnica – Universidade de São Paulo
Av. Prof. Mello Morais, 2463
05508-900 São Paulo, SP
nalonso@usp.br

ABSTRACT

The reprocessing of irradiated fuels is one of the greatest problems of fuel cycle. A way to minimize this problem is to reduce the volume by removing of 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 and short time dispensed for the dissolution of aluminum. The studies are just in the beginning, but very promising.

1. 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 due to the intrinsic operational conditions like the reduction of chemical reagents used and waste generated. These features overcome the high initial costs, mostly due to the electrode materials.

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 materials used in nuclear industry leads, mostly, to a significant reduction of generated waste, solving the deposition and storage problems.

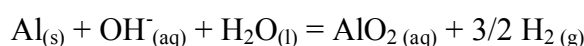
Since the restrictions for the use of enriched uranium were imposed in October 1992 by the U.S. Congress, low enrichment uranium silicide/Al has been used as fuel for Research Reactors and as target for the ⁹⁹Mo production. By this fact, the study had as an initial

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, and heating, all necessary for chemical dissolution. As electrochemical technologies have been used with success in many processes of nuclear industry, the electro dissolution of metallic aluminum, without dissolving uranium silicide, was studied. The electro dissolution is, therefore, a feasible alternative for the selective recovery of nuclear materials.

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]. So, it is very important to reduce this period of storage to avoid subsequent problems, as leaking of radioactivity..

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, even the matrix aluminum, making possible its dissolution. The aluminum dissolves electrochemically according to the reaction[3]:



The hydrogen evolution in this electrochemical process can be controlled by the applied potential, what makes the operation more safe.

2. EXPERIMENTAL

2.1. Equipments, materials and reagents

The following materials and reagents were used in the experiments:

- NaOH p.a., Merck
- Distilled and deionised water
- $\text{U}_3\text{Si}_2\text{-Al/Al}$ cladding plates, from the Department of Metallurgy, IPEN/CNEN-SP

2.2. Electrochemical methods

The open circuit potential and the potentiodynamic polarization experiments were carried out in a borosilicate cell (Figure 1) connected to an AUTOLAB PGSTAT30 Potentiostat/Galvanostat. An Ag/AgCl reference electrode, a Pt anode-support as working electrode and a Pt plate (2.0 x1.0 x 0.05 cm) as auxiliary electrode were used. These experiments were performed in various concentrations of NaOH solutions (electrolyte), at temperatures of 30, 45, 60 and 75°C.

The electro dissolution of aluminum was carried out in 0.5 and 1.0 mol l⁻¹ NaOH solutions using a source of direct current (Tectrol TCA-50-05-XR). The samples were plates of

uranium silicide fuel, measuring 1 cm^2 , wrapped with a Pt wire (anode support). 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, after filtration, for analyzing uranium content.

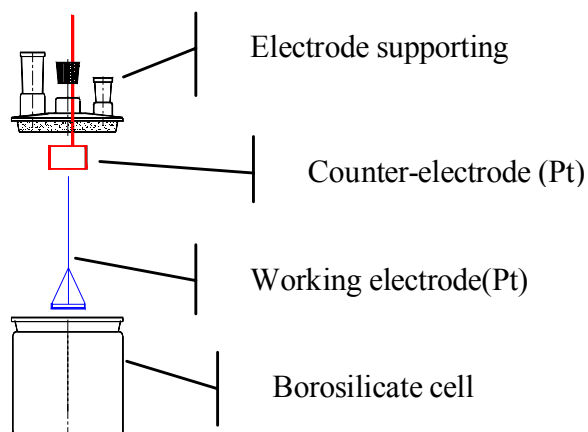


Figure 1. Electrolytic cell used in the experiments.

2.3. Analytical method

Uranium was analyzed by gamma spectrometry, in a ORTEC NaI(Tl) well type scintillator detector, by ^{234}Th peaks.

3. RESULTS AND DISCUSSION

3.1. Open circuit potential [3]

The open circuit potential transients in 1 mol L^{-1} NaOH solutions, at various temperatures, are shown in Figure 2. The increase in NaOH concentration made the corrosion potential 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.

Earlier studies [3] 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.

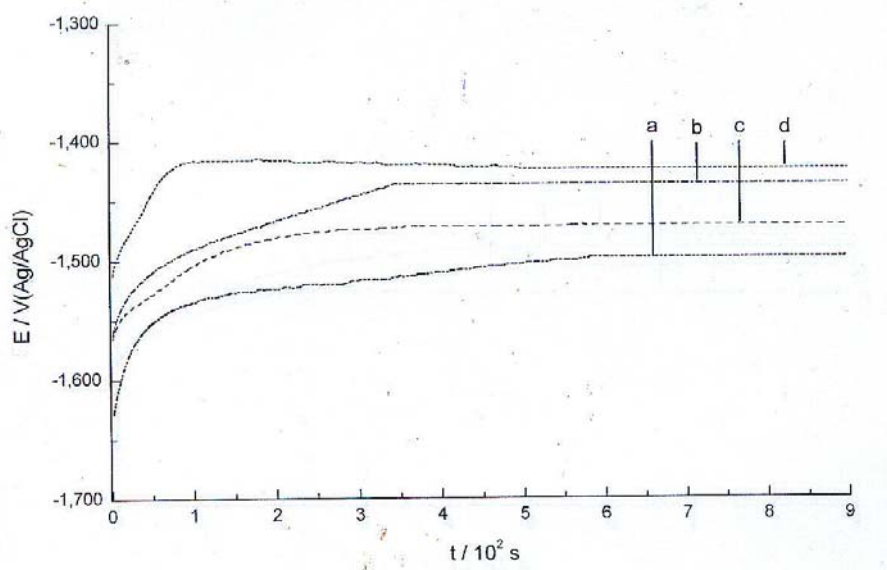


Figure 2: Open circuit potentials of aluminum in 1 mol l⁻¹ NaOH solution at various temperatures; (a) 30°C; (b) 45°C; (c) 60°C; (d) 75°C [3].

3.2. Potentiodynamic polarization experiments

Potentiodynamic polarization curves for aluminum were obtained in NaOH solutions, 1, 2, 3 and 4 mol L⁻¹, at 30°C and sweep rate of 1 mV s⁻¹. The result is presented in Figure 3.

Those curves show that above -1.5 V(Ag/AgCl), at the anodic region, hydrogen evolution occurs, because the applied potentials are still more negatives than the potential of water reduction. From -0.8 V (Ag/AgCl) the current densities are practically independent of the applied potential, and the process is under polarization by concentration control.

3.3. Electrodisolution 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.

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, proving the efficiency of electrochemical process.

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

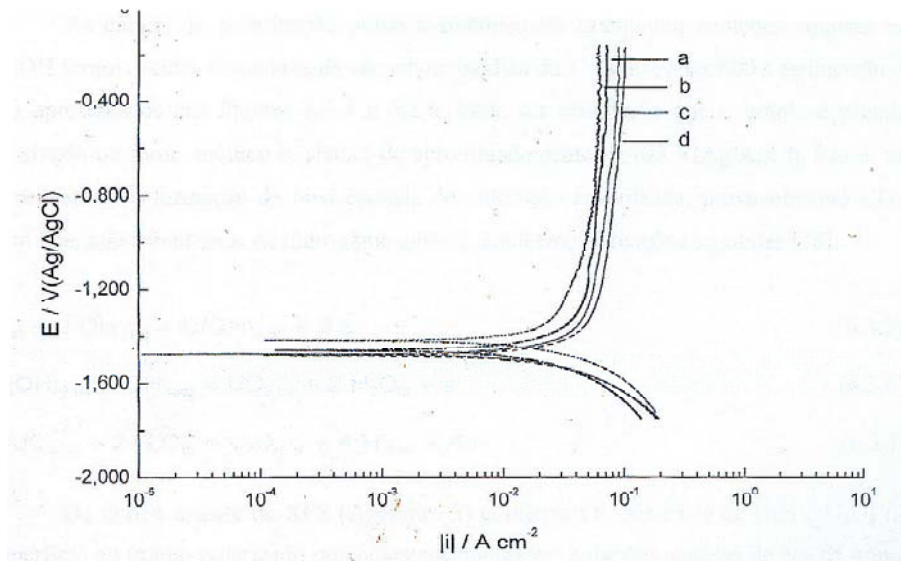


Figure 3. Potentiodynamic polarization curves of aluminum, in NaOH solutions, sweep rate of 1 mV s^{-1} and at 30°C ; (a) 1 mol L^{-1} ; (b) 2 mol L^{-1} ; (c) 3 mol L^{-1} ; (d) 4 mol L^{-1} [3].

4. CONCLUSIONS

The results show that is possible to dissolve aluminum of the cladding and matrix of uranium silicide fuels using NaOH solutions of low concentrations, like 0.5 mol l^{-1} , without dissolving uranium silicide, by electrochemical process. The short time, the low NaOH concentration and the approximately room temperature employed in the experiments are the most important features of the proposed process.

Table 1. Electrodissolution 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	2.0	1.2	4.0	3.3
1.0	0.7166	2.0	1.6	4.5	2.5
1.0	0.682	2.0	1.8	5.0	2.2
0.5	0.5987	2.0	1.6	4.5	2.9
0,5	0,5615	2.0	1.8	5.0	2.5
0,3	0,5432	2.0	1.6	4.5	3.2
0.3	0,5573	2.0	1.8	5.0	3.1
0.2	0.5744	2.0	1.6	4.5	3.5
0.2	0.5638	2.0	1.8	5.0	3.4

In the next experiments it will be studied the electrodisolution at lower concentrations of NaOH (0.1 and 0.2 mol l⁻¹) and the necessary currents to be applied. The energy consumption will be evaluated.

A complete study must be carried out, to evaluate the influence of high temperature and irradiation over the targets, as the important effect of annealing that could influence the electrodisolution of the matrix Al, and the behavior of fission products.

ACKNOWLEDGMENTS

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

REFERENCES

1. H. D. PEACOCK JR, T. M. ADAMS, N. C. IYER, "Development of the melt-dilute treatment technology for aluminum-base DOE spent nuclear fuel", *Proceeding of RERTR '96*, Seoul, Korea, Oct 7-10 (1996).
2. B. A. BUCHHOLZ, G. F. VANDEGRIFT, "Processing of LEU targets for ⁹⁹Mo production – Dissolution of U₃Si₂ targets by alkaline hydrogen peroxide". *Proceeding of RERTR '95*, Paris, France, Sep (1995).
3. L. S. RODRIGUES, "Eletrodissolução de alumínio e urânio metálicos em meio aquoso", Dissertation, Instituto de Pesquisas Energéticas e Nucleares, São Paulo (2001).
4. D. CHU, R. F. SAVINELL, "Experimental Data On Aluminum Dissolution In KOH Electrolytes", *Electrochimica Acta*, v. **36 (10)**, pp. 1631-1638 (1991).
5. Y. S. KIM, S. I. PYUN, S. M. MOON, J. D. KIM, "The effects of applied potential and pH on the electrochemical dissolution of barrier layer in porous anodic oxide film on pure aluminium", *Corrosion Science*, v. **38 (2)**, pp. 329-336 (1996).