

PRODUÇÃO TÉCNICO CIENTÍFICA
DO IPEN
DEVOLVER NO BALCÃO DE
EMPRESTIMO

ELECTRODISSOLUTION OF METALLIC URANIUM AND ALUMINUM

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ABSTRACT

The electrodisolution is an important alternative for recovering U and other elements from nuclear fuels and irradiation targets with aluminum cladding. This process eliminates some inconveniences observed in the chemical processes commonly employed, such as high costs, high volume of radioactive waste generated and contamination risks. The objective of this preliminar work is to investigate the necessary parameters to make possible the proposed process. The open circuit potentials and the potentiodynamic polarization curves for metallic aluminum and uranium were determined. NaOH solution from 1 to 4 kolm m³ and temperatures in the range of 303,2 to 348,2K were used. The NaOH concentration rising decreased the aluminum open circuit potential and increased the current density. The uranium open circuit potential also decreased with the NaOH concentration increasing and the anodic polarization curves presented a region of active corrosion followed by passivation. As a first approach, it was verified that between the potentials -1200 and -700mV_{Ag-AgCl} Al dissolved and U was inactive. These results show that the selective electrodisolution of the elements is possible due to the difference in the potentials of anodic dissolution.

Keywords: Electrodisolution, Aluminum, Uranium, Recovery, Nuclear Fuels.

RESUMO

A eletrodissolução para a recuperação de U e outros elementos de combustíveis ou de alvos de irradiação revestidos com Al, utilizados em reatores nucleares, é uma alternativa interessante, pois elimina alguns dos inconvenientes dos processos químicos de dissolução atualmente empregados, como o custo elevado, grande quantidade de rejeitos radioativos e riscos de contaminação. O objetivo deste trabalho é iniciar a investigação dos parâmetros necessários para a viabilização deste processo. Foram determinados, para o Al e U puros, o potencial de circuito aberto e as curvas de polarização potenciodinâmicas. Foram utilizadas soluções de NaOH, em concentrações de 1 a 4 kg m³ e temperaturas de 303,2 a 348,2K. O aumento da concentração diminuiu o potencial de circuito aberto do Al e aumentou a densidade de corrente. O potencial de circuito aberto do U também diminuiu com o aumento da concentração e suas curvas de polarização anódica apresentaram trecho de corrosão ativa seguida de passivação. Como primeira aproximação, verificou-se que em potenciais entre -1200 e -700mV_{Ag-AgCl} o Al se dissolve e o U encontra-se inativo. Estes resultados sugerem que é possível a eletrodissolução seletiva destes materiais.

Palavras-chave: Eletrodissolução, Alumínio, Urânio, Recuperação, Combustíveis Nucleares

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. In spite of presenting, in some cases, high costs, 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.

The Chemical and Environmental Technology Division at IPEN (Energetic and Nuclear Research Institute), is developing studies on fuel elements and irradiation targets dissolution by classic chemical processes. As electrochemical technologies have been used with success in many processes of nuclear industry, the electrodisolution of metallic aluminum and uranium was studied. They are basic material for manufacturing targets, used in radioisotopes production for nuclear medicine, and fuel elements for nuclear reactors.

The electrodisolution is, therefore, a feasible alternative for the selective recovery of nuclear metals and elements.

2. METHODS

Pure aluminum (99,9% purity) and metallic uranium produced at IPEN were employed in this study. The composition of aluminum and uranium, determined by emission spectroscopy, are described in Tables 1 and 2, respectively. The aluminum and uranium test samples were prepared embedding them in a sodium hydroxide resistant acrylic resin, as shown in Fig. 1.

Table 1. Aluminum composition determined by emission spectroscopy

<i>Aluminum 1060 (1,0 g)</i>			
Impurity	% weight	Impurity	% weight
Bi	5×10^{-3}	Na	3×10^{-3}
Ca	5×10^{-3}	Ni	1×10^{-3}
Cd	1×10^{-4}	Pb	2×10^{-4}
Cr	1×10^{-3}	Si	1×10^{-2}
Cu	2×10^{-3}	Sn	1×10^{-4}
Fe	5×10^{-2}	Ti	5×10^{-3}
Ga	4×10^{-3}	V	5×10^{-3}
Mg	2×10^{-3}	Zn	4×10^{-3}
Mn	1×10^{-3}		

Table 2. Metallic uranium composition determined by emission spectroscopy

<i>Uranium (1,0 g)</i>			
Impurity	% weight	Impurity	% weight
Al	$1,5 \times 10^{-2}$	Mn	$1,0 \times 10^{-2}$
B	$2,0 \times 10^{-5}$	Mo	$2,0 \times 10^{-4}$
Ba	$1,0 \times 10^{-4}$	Ni	$4,0 \times 10^{-4}$
Bi	$2,0 \times 10^{-4}$	P	$1,0 \times 10^{-2}$
Cd	$1,0 \times 10^{-5}$	Pb	$2,0 \times 10^{-4}$
Co	$1,0 \times 10^{-3}$	Si	$2,6 \times 10^{-2}$
Cr	$1,0 \times 10^{-3}$	Sn	$1,0 \times 10^{-4}$
Cu	$1,0 \times 10^{-3}$	V	$3,0 \times 10^{-4}$
Fe	$1,2 \times 10^{-2}$	Zn	$1,0 \times 10^{-3}$
Mg	$3,0 \times 10^{-3}$		

The electrolyte used was 1 to 4 kmol m⁻³ NaOH solutions, varying the temperature during the experiments from 303.2 to 348.2K. Because of the high temperatures employed, Ag-AgCl auxiliar electrode was used.

The behavior of metallic uranium and aluminum in stationary and de-aerated NaOH solutions was verified by the open circuit potentials and potentiodynamic polarizations.

In all experiments a corrosion cell, specially designed for this study, provided with a jacket to allow temperature control, was used (Fig. 2).

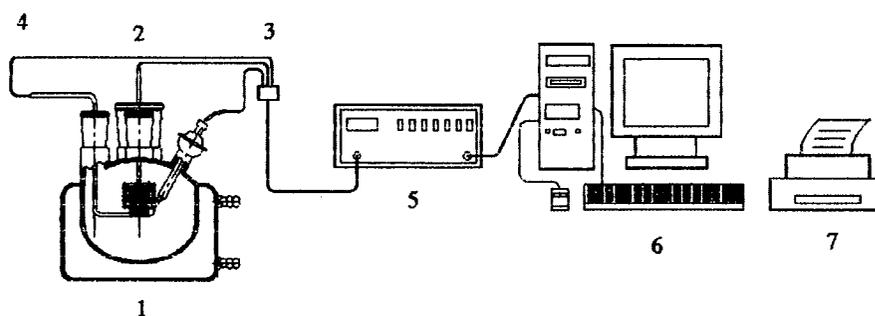


Figure 1- A scheme for electrochemistry experiments: (1) electrochemical cell; (1) working electrode; (3) reference electrode and capillary; (4) counter electrode Pt rod; (5) potentiostat/galvanostat; (6) computer; (7) printer.

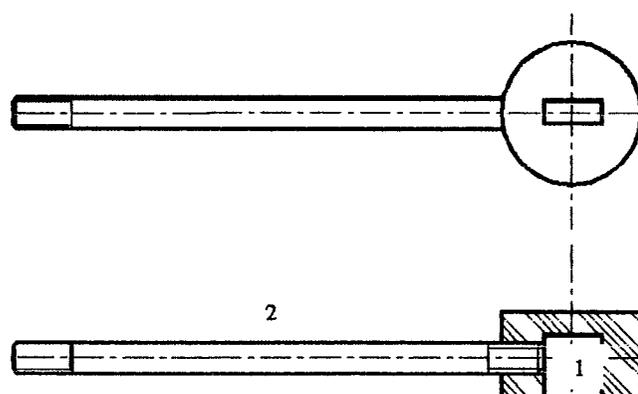


Figure 2- A scheme of a test sample: (1) metallic sample and (2) spindle of stainless steel.

3. RESULTS AND DISCUSSION

Open Circuit Potential in NAOH solutions.

Aluminum. The open circuit potential transients in 1 to 4 kmol m^{-3} NAOH solutions and at temperatures of 303.2 and 348.2K were determined (Fig. 3) The rising of temperature displaced the initial potential, E_{oc_0} , set after aluminium immersion in 1 to 3 kmol m^{-3} NAOH solutions (Fig. 3a-3c) to the positive direction, but at 4 kmol m^{-3} NAOH solution (Fig. 3d) the potential displaced to the negative direction. The increase in NAOH concentration made the E_{oc_0} more positive at 303,2K, but at 348,2K, E_{oc_0} displaced to the negative direction (Fig. 3e and 3f). 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.

Figures 3a to 3f show that open circuit potential rapidly increases the growth rate at the beginning and decreases with the time, reaching the steady state. In 1 and 2 kmol m⁻³ NaOH solutions (Fig. 3a and 3b) the rising in temperature increased the corrosion or stationary potential, E_{corr} ; but at 3 and 4 kmol m⁻³ NaOH solutions, E_{corr} became more negative (Fig. 3c and 3d). The rising of NaOH concentration displaced E_{corr} to the positive direction at 303.2K (Fig 3e), but at 348.2K (Fig.3f), E_{corr} decreased. Because 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.

Uranium. The open circuit potentials of uranium in NaOH solutions at various temperatures are described in Figure 4. After an immersion time of 600s in NaOH solutions, the rising in temperature displaced the uranium initial potential, E_{oc0} , to the negative direction (Fig.4a-4d). The increase of NaOH concentration affected the initial and corrosion potentials, displacing them to the negative direction at 303.2K (Fig.4e); but at 348.2 (Fig 4f), the rising in concentration displaced the initial and final potentials to the positive direction.

Figures 4a to 4f show that open circuit potential slowly increases with time to reach the steady state, indicating the formation of a passivated layer. The formation of a green layer on the metallic uranium surface, probably UO_2 , $UO_3 \cdot 2H_2O$ or U_3O_8 , even all of them, was observed, as predicted in thermodynamic diagrams [3].



These oxides in alkaline and neutral solutions are stable, therefore, the uranium solubility up to 30 % NaOH is negligible [8].

Potentiodynamic Polarization in NaOH solutions

Aluminum. The aluminum anodic polarization was performed in 1 to 4 kmol m⁻³ NaOH solutions at 1 mV s⁻¹, in the range from -2000 to 500 mV_{Ag-AgCl} after immersion time of 600s (Figure 5).

From -2000 to -1500 mV_{Ag-AgCl} (Fig. 5a to 5c), corresponding to the cathodic region, aluminum dissolved and simultaneous water reduction and hydrogen evolution at the aluminum/solution interface, under cathodic control, were observed [1].

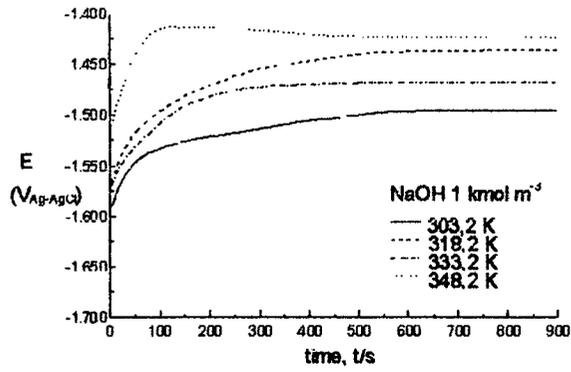


Figure 3a

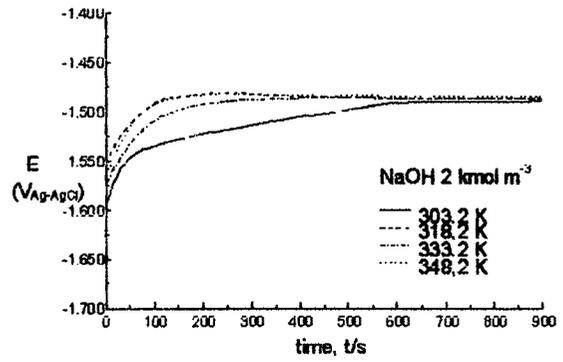


Figure 3b

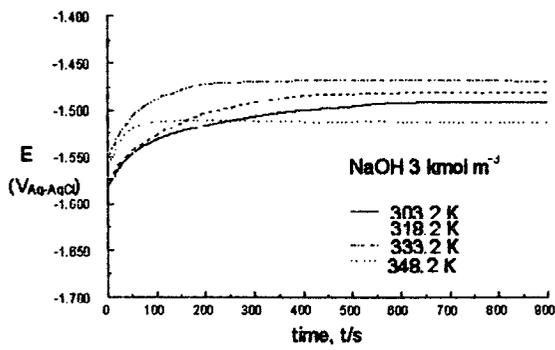


Figure 3c

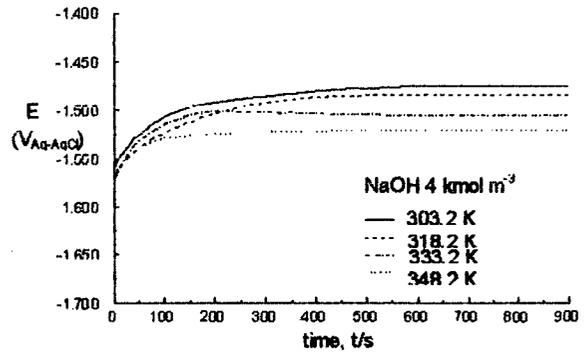


Figure 3d

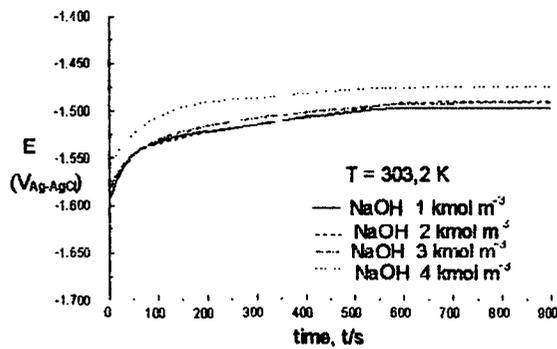


Figure 3e

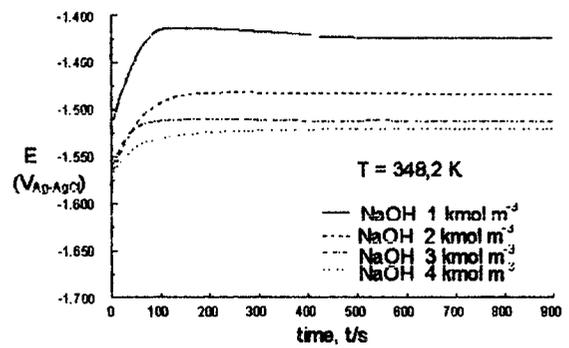


Figure 3f

Figure 3. Open circuit potentials of aluminum in NaOH solution.

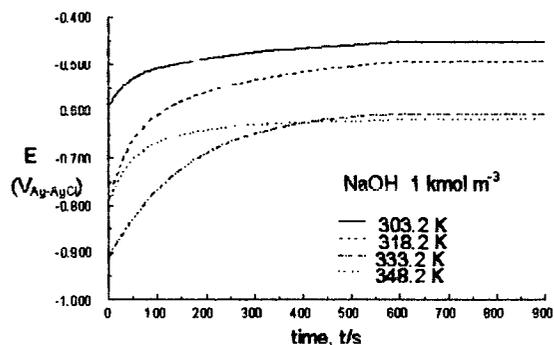


Figure 4a

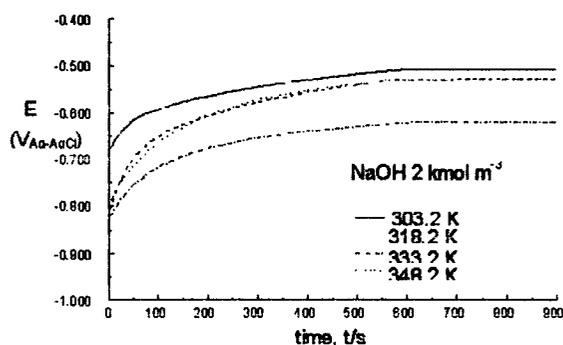


Figure 4b

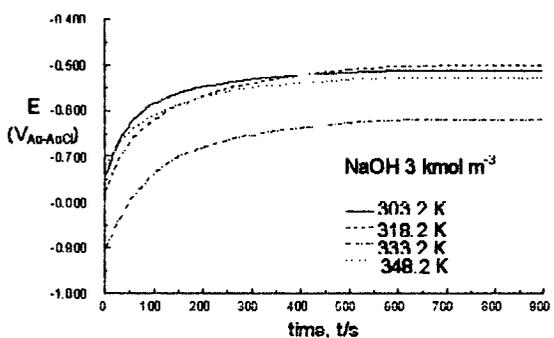


Figure 4c

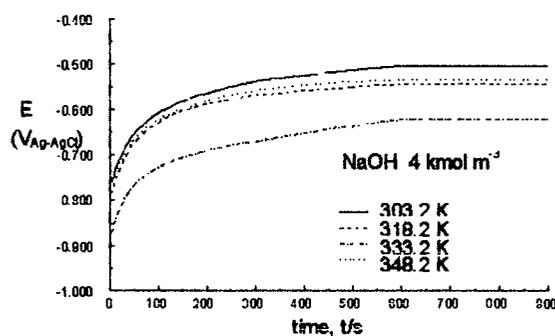


Figure 4d

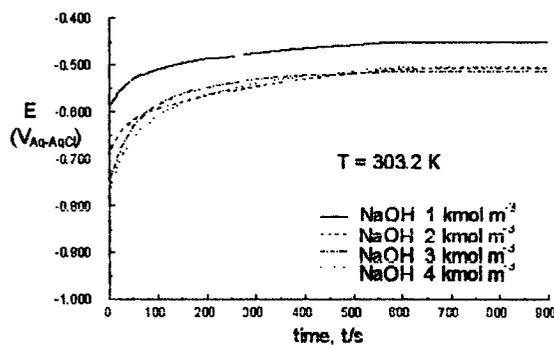


Figure 4e

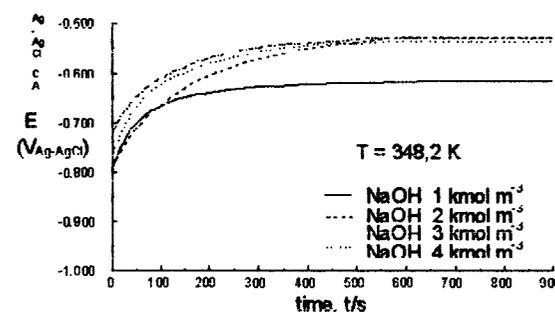


Figure 4f

Figure 4. Open circuit potentials of uranium in NaOH solutions

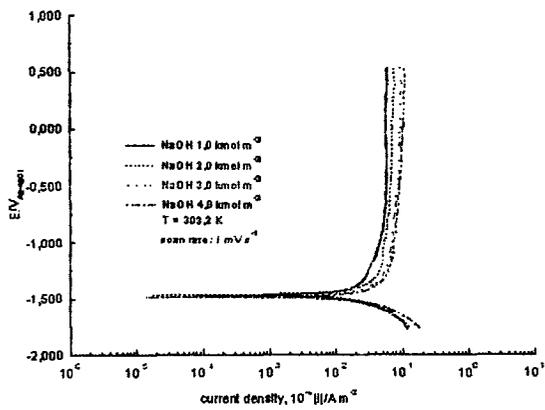


Figure 5a.

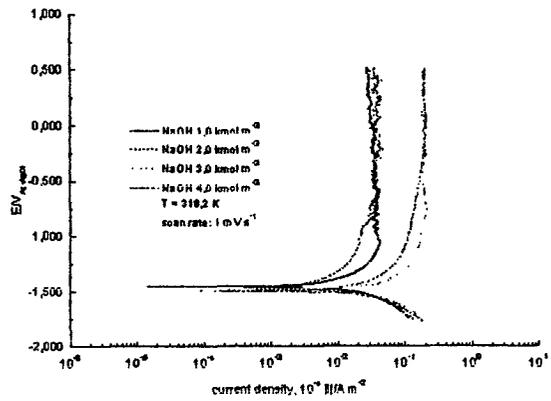


Figure 5b.

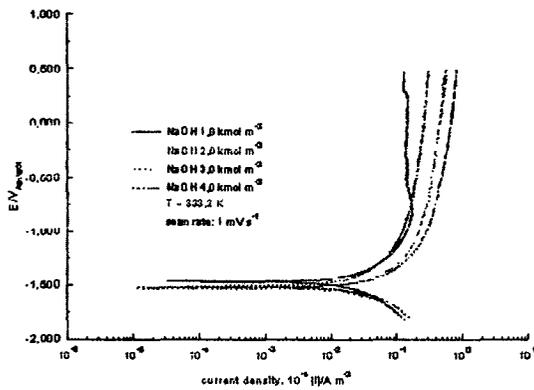


Figure 5c.

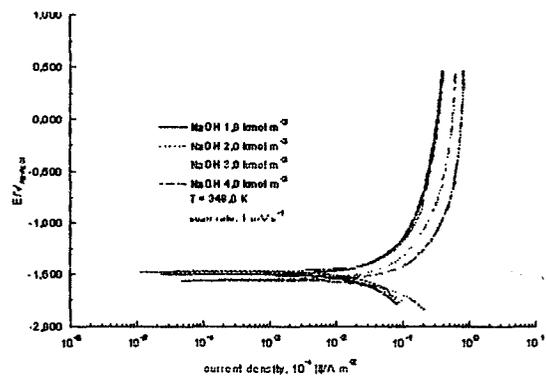


Figure 5d.

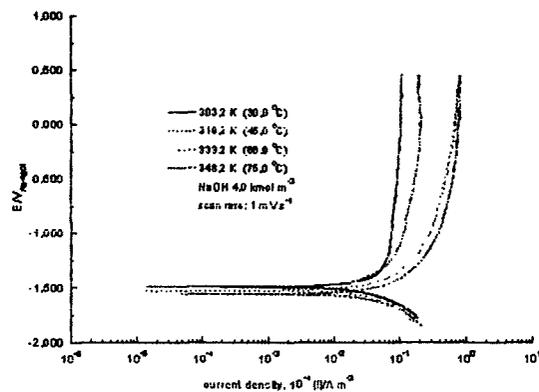


Figure 5e.

Figure 5. Potentiodynamic polarization of aluminum in NaOH solutions.

At the corrosion potential, $E_{\text{corr}} = -1500 \text{ mV}_{\text{Ag-AgCl}}$, aluminum dissolved spontaneously (short-circuited corrosion) without an external work influence, that is, without the imposition of external potential or current.

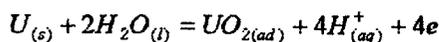
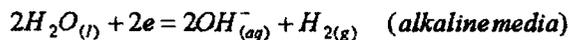
Above $-1500 \text{ mV}_{\text{Ag-AgCl}}$, aluminum was anodically dissolved with hydrogen evolution, both on the auxiliary electrode and on its own surface. The dissolution rate reached its limit at about $-1000 \text{ mV}_{\text{Ag-AgCl}}$. After this it was constant, independent of the applied potential. The rising of NaOH concentrations displaced the corrosion potential to the cathodic or negative direction (Fig 5a to 5d). At 4 kmol m^{-3} NaOH solution, the increasing temperature caused the same effect on the aluminum corrosion potential (Fig. 5e).

Assuming that the aluminum dissolution is controlled by competitive reactions of dissolution and growth of the hydrated oxide film, aimed by the electric field through the oxide or hydroxide [5,6], the passivation of aluminum in NaOH solutions does not occur. The mass transport through the hydrated porous layer [1,6] may be the main factor controlling the process. Because aluminum has a great affinity by oxygen, an oxide film on the surface may be formed. So, even that the anhydrous oxide disappears at suitable negative potential, the aluminum surface would retain the hydrated oxide [7], which would be chemically dissolved at the oxide/solution interface, with simultaneous electrochemical film formation and growth at the aluminum/oxide interface [2,5], aimed by the electric field.

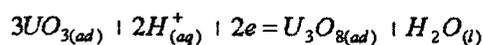
Uranium. The uranium anodic polarization, after immersion time of 600s in stationary and de-aerated NaOH solutions, from 1 to 4 kmol m^{-3} , and temperatures from 303.2 to 348.1K was determined (Fig. 6). A sweep rate of 1 mV s^{-1} at potentials between -1000 and $1500 \text{ mV}_{\text{Ag-AgCl}}$ were used. The curves show a region of immunity, a region of corrosion and a region of passivation.

The uranium potential displaced to the positive direction due to the increase of NaOH concentration, between 303.2 and 333.2K (Fig 6a to 6c). But at 348.2K the increase of alkaline concentration displaced the potential to the negative direction (Fig. 6d).

Below corrosion potential ($-750 \text{ mV}_{\text{Ag-AgCl}}$), that is, at the anodic region, hydrogen evolution and, probably, oxide formation occurred, as suggested by the following equations:



At the active region, between -750 and $0 \text{ mV}_{\text{Ag-AgCl}}$ uranium was actively dissolved. In this interval, the potential provides the oxides formation, which are rapidly dissolved due to the acidity produced at the exposed surface to electrolyte. At 348.2K and 4 kmol m^{-3} NaOH solution, uranium presented a maximum critical current density, $i_{\text{critmax}} = 70 \text{ A m}^{-2}$, at the minimum passivation potential, $E_{p_{\text{min}}} = -100 \text{ mV}_{\text{Ag-AgCl}}$ (Fig. 4e). Because the passivation potential, E_p , was displaced to the negative direction due to the increase in NaOH concentration and temperature, the range of potential corresponding to 100 and $250 \text{ mV}_{\text{Ag-AgCl}}$ should be considered as a transition region from active to passive state. Between 250 and $750 \text{ mV}_{\text{Ag-AgCl}}$ can be observed a break in the passivity caused by the detachment of the green oxide film, U_3O_8 , during the thickening of the protective layer on the uranium surface.



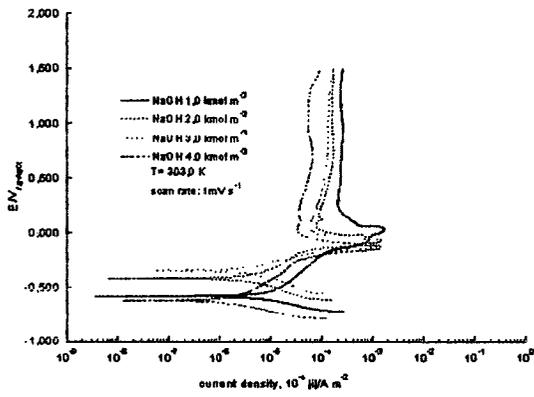


Figure 6a

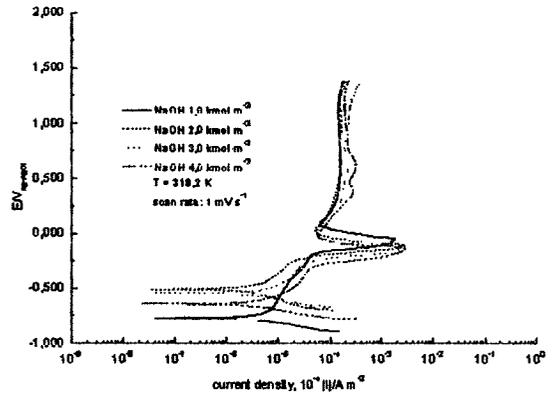


Figure 6b

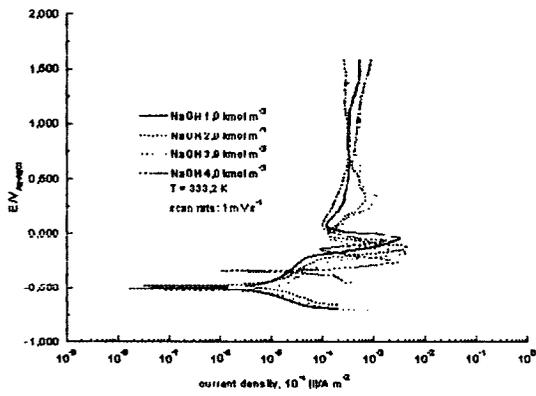


Figure 6c

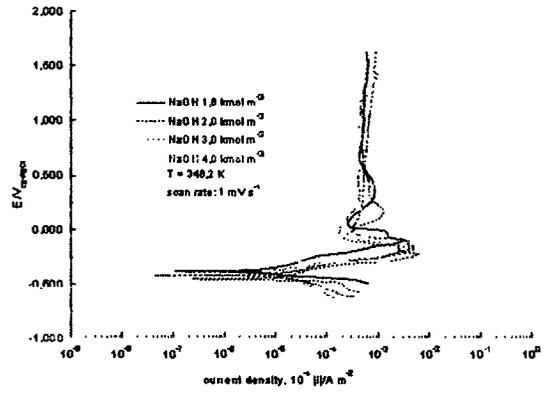


Figure 6d

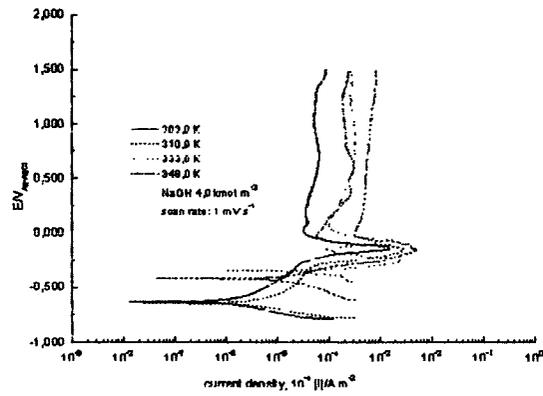


Figure 6e

Figure 6. Potentiodynamic polarization of uranium in NaOH solutions.

Over 750 mV_{Ag-AgCl} uranium was passivated by a green oxide film that became dark brown during the anodic polarization, probably U₃O₈. In fact, the XPS (X-ray Photoelectron Spectroscopy) analysis showed the existence of this oxide on the anodic polarized uranium surface. The maximum current density, $i_{\max}=10\text{A m}^{-2}$, was observed in 4 kmol m⁻³ NaOH solution at 348.2K, suggesting control by diffusion (Fig. 6e).

4. CONCLUSION

As shown in the results, aluminum and uranium have very distinct potentials at the same conditions, that makes possible their separation during electrodisolution using NaOH as the electrolyte.

The open circuit potential and the potentiodynamic polarization in NaOH solution varying from 1 to 4 kmol m⁻³ and temperatures from 303.2 to 348.2K, show that aluminum and uranium have a very opposite conditions for electrodisolution in this media. Between the potentials -1200 and -700mV_{AgAgCl}, aluminum dissolves and uranium does not react.

So, the main objective of this study was reached, and proved that these materials can be selectively dissolved. It is important to the process where aluminum, used as structural material, has to be separated from uranium, and where the time is an important feature in the treatment of nuclear materials, because of the very short half-life of some radioisotopes used in medicine diagnosis.

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