

## EVALUATION OF THE ELECTROCHEMICAL BEHAVIOR OF U<sub>2.5</sub>Zr<sub>7.5</sub>Nb AND U<sub>3</sub>Zr<sub>9</sub>Nb URANIUM ALLOYS IN RELATION TO THE pH AND THE SOLUTION AERATION

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### ABSTRACT

The Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) is developing, in cooperation with the Centro Tecnológico da Marinha (CTMSP), the advanced nuclear plate type fuel for the second core of the land-based reactor prototype of the Laboratório de Geração Núcleo-Elétrica (LABGENE). Recent investigations have shown that the fuel made of uranium-based niobium and zirconium alloys reaches the best performance relative to other fuels, e.g. UO<sub>2</sub>. Niobium and Zirconium also increase the corrosion resistance and the mechanical strength of the uranium alloys. By means of electrochemical techniques the corrosion behavior of alloys U<sub>2.5</sub>Zr<sub>7.5</sub>Nb and U<sub>3</sub>Zr<sub>9</sub>Nb, developed at CDTN and heat treated in the temperature range of 200°C to 600°C, was assessed. The effect of the parameters pH and solution aeration was studied as well as the influence of zirconium and niobium alloying elements in the corrosion of uranium. The techniques used were open circuit potential, electrochemical impedance and potentiodynamic anodic polarization at room temperature. The tests were performed in a three-electrode electrochemical cell with Ag/AgCl (3M KCl) as the reference electrode and a platinum plate as the auxiliary electrode. The potentiodynamic polarization curves of uranium and its alloys in acidic solutions showed regions with anodic currents limited by a passive film. The presence of niobium and zirconium contributed for the formation of this film. The impedance data showed the presence of two semicircles in the Bode diagram, indicating the occurrence of two distinct electrochemical processes. The data were fitted to an equivalent circuit model in order to obtain parameters of the electrochemical processes and evaluate the effect of the studied variables.

### 1. INTRODUCTION

The Centro de Desenvolvimento da Tecnologia Nuclear (CDTN) is developing, in cooperation with the Centro Tecnológico da Marinha (CTMSP), the advanced nuclear plate type fuel for the second core of the land-based reactor prototype of the Laboratório de Geração Núcleo-Elétrica (LABGENE) of Brazilian Navy. This reactor, in stage of development, is an advanced concept of pressurized water reactor that uses nuclear metallic fuel instead of the classic fuel of ceramic UO<sub>2</sub> pellets.

Nuclear metallic fuel can contain a density of uranium up to 17.5g/cm<sup>3</sup>, much higher than the density of 10.5g/cm<sup>3</sup> achieved by UO<sub>2</sub>. Higher density of uranium provides greater neutron flux and therefore higher performance in the reactor, even maintaining the fuel enrichment limit of 20% of the isotope U<sup>235</sup> as established by international laws [1,2].

The UZrNb alloy combines high mechanical strength due to niobium with the stability under irradiation achieved by zirconium. These alloying elements also promote an increase in the

corrosion resistance of uranium alloys. However, there is a lack of information in the literature about the alloys studied in this work, what makes it difficult to predict the behavior on the corrosion resistance of the alloys [1-4].

As shown from literature, uranium corrodes in room-temperature air at a rate slightly less than that of cast iron, but with the addition of alloying elements the corrosion behavior greatly improves. Uranium is commonly alloyed with elements stabilizers of  $\gamma$ -phase, such as zirconium, niobium, molybdenum and titanium. Among the factors that affect corrosion of uranium alloys, the main ones are the pH and the solution aeration, content of alloying elements and impurities present in the alloy microstructure [5].

The purpose of this work was to evaluate the corrosion resistance of alloys U2.5Zr7.5Nb and U3Zr9Nb and also uranium metal. The techniques used were open circuit potential, electrochemical impedance and potentiodynamic anodic polarization at room temperature. The effect of the parameters pH, solution aeration and the influence of alloying elements niobium and zirconium on the corrosion of uranium were considered in this work.

## 2. MATERIALS AND METHODS

The samples investigated in this work were cast in an induction furnace at approximately 1500°C, where were obtained ingots in a raw state of fusion for each alloy. From the ingot, samples were cut for each alloy subjected to electrochemical tests: U2.5Zr7.5Nb, U3Zr9Nb and a sample of uranium metal, to compare with the results of the alloys. Each sample had approximately 1cm<sup>2</sup> of surface area, and were prepared identically: embedded in resin, grinded with emery papers 320#, 500#, 600# and 1200# and polishing with diamond paste of 3µm and 1µm.

The corrosion behavior of the samples were evaluated by means of three parameters: solution pH, solution aeration and content of alloying elements. The effect of solution pH on the corrosion of alloy U3Zr9Nb was studied in four pH's: 1, 4, 7 and 10. The influence of solution aeration in the corrosion of uranium metal and the content of Zr and Nb on the corrosion of uranium were studied in solution of pH 7.

For the preparation of the solutions the following reagents were used with their respective concentrations: 0.1N H<sub>2</sub>SO<sub>4</sub> for pH 1, 0.05M H<sub>3</sub>BO<sub>3</sub> for pH 4, 0.05M H<sub>3</sub>BO<sub>3</sub> + 0.05M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.10H<sub>2</sub>O for pH 7 and 0.05M NaOH + 0.025M Na<sub>2</sub>B<sub>4</sub>O<sub>7</sub>.10H<sub>2</sub>O for pH 10.

The tests were performed in a three-electrode electrochemical cell, at 25°C, with Ag/AgCl (3M KCl) as the reference electrode and a platinum plate as the auxiliary electrode. Before the immersion of the sample in the solution, it was bubbled with nitrogen gas for 50 minutes to remove dissolved oxygen and thus maintained during the tests, except for the aerated solution, which was bubbled with a mixture of 60% O<sub>2</sub> and 40% N<sub>2</sub>.

The polarization resistance test, performed after measurement of the open circuit potential, was made to check the stability of the potential before the test of electrochemical impedance.

The open circuit potential was measured during 1800s, with data acquisition every 5s. The polarization resistance was performed in a range from -0.02V to 0.02V, at the rate of 0.000167V.s<sup>-1</sup> and with data acquisition every 5s.

The potentiodynamic polarization tests were performed according to ASTM G5-94. A scan rate of  $0.000167\text{V}\cdot\text{s}^{-1}$  was applied. The potential was scanned from  $-0.2\text{V}$  to  $1.5\text{V}$  with relation to open circuit potential and acquisition of data every 5s. The impedance measurements were performed with an amplitude of  $10\text{mV RMS}$  and varying the frequency in a range from  $12\text{kHz}$  to  $5\text{mHz}$ .

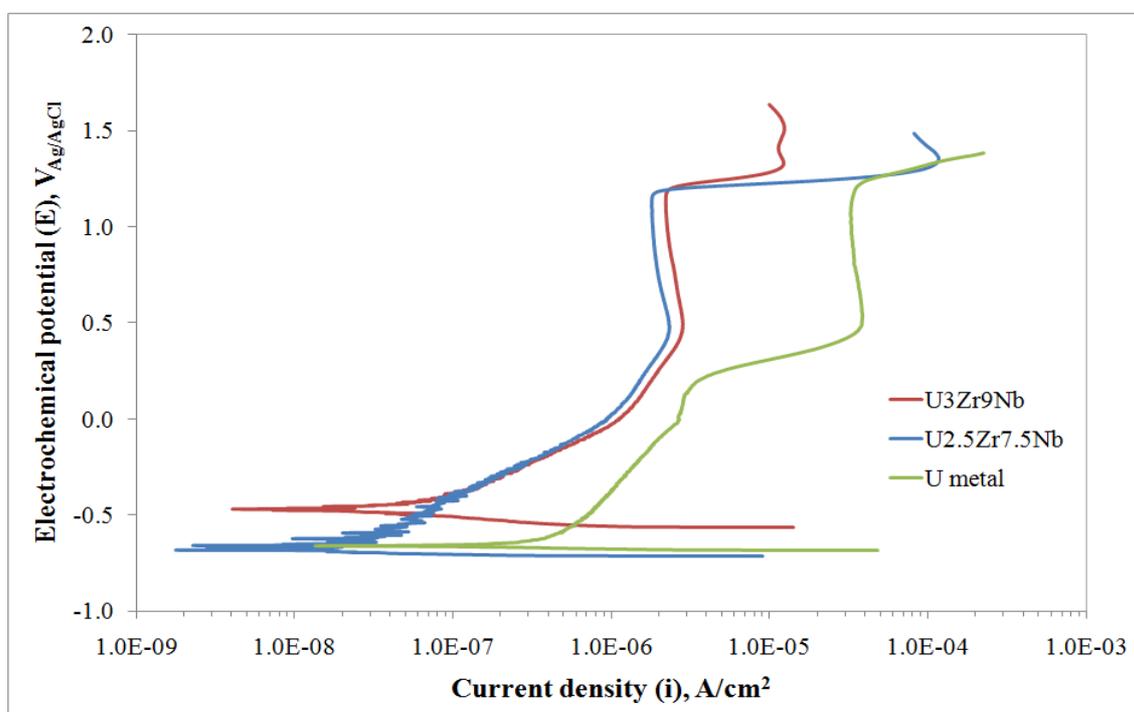
The electrochemical tests were performed using an Autolab potentiostat system, PGSTAT20 with GPES (General Purpose Electrochemical System 4.9) and FRA (Frequency Response Analysis 4.9) softwares. The software ZSimpWin® was used to fit the impedance data.

### 3. RESULTS AND DISCUSSION

#### 3.1. Influence of Alloy Composition

Figure 1 presents the potentiodynamic polarization curves for alloys  $\text{U}_3\text{Zr}_9\text{Nb}$ ,  $\text{U}_2.5\text{Zr}_7.5\text{Nb}$  and the uranium metal. Curves more displaced to the right indicate a higher tendency to corrosion, which occurred with the sample of unalloyed uranium. The alloy  $\text{U}_3\text{Zr}_9\text{Nb}$  corroded less than alloy  $\text{U}_2.5\text{Zr}_7.5\text{Nb}$ , possibly because this alloy has higher concentration of niobium.

Alloy  $\text{U}_3\text{Zr}_9\text{Nb}$  showed the highest corrosion potential, indicating a higher corrosion resistance. The passive currents of alloys  $\text{U}_3\text{Zr}_9\text{Nb}$  and  $\text{U}_2.5\text{Zr}_7.5\text{Nb}$  were low, indicating a high degree of passivation (when the current remains constant with the increasing of the potential). Table 1 presents electrochemical parameters taken from these curves.

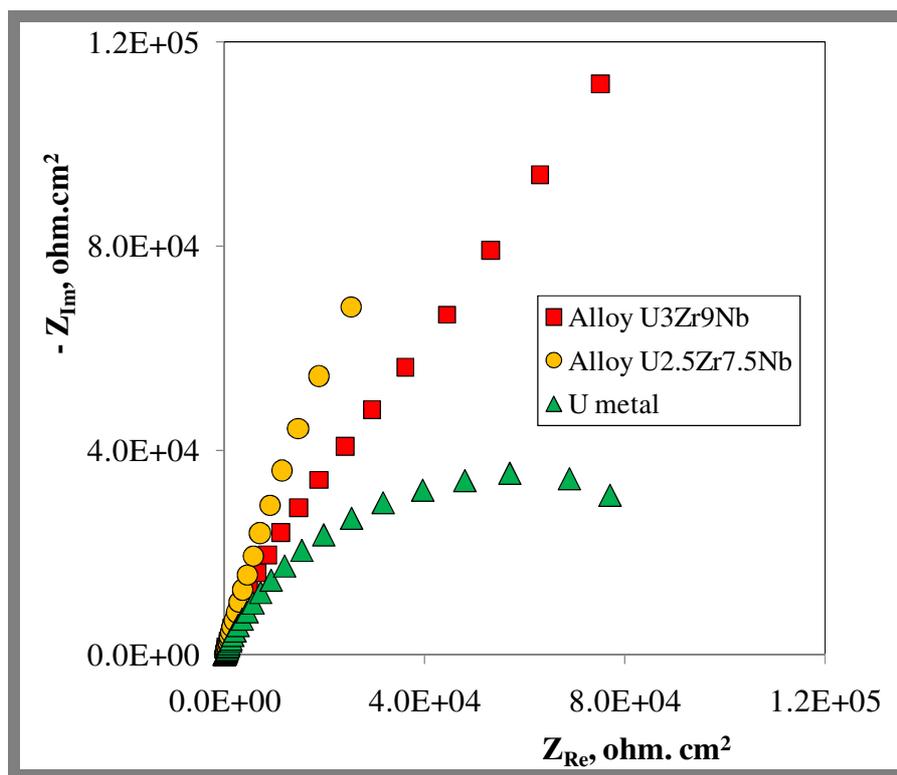


**Figure 1. Polarization curves of alloys  $\text{U}_2.5\text{Zr}_7.5\text{Nb}$ ,  $\text{U}_3\text{Zr}_9\text{Nb}$  and uranium metal in deaerated solution at pH 7.**

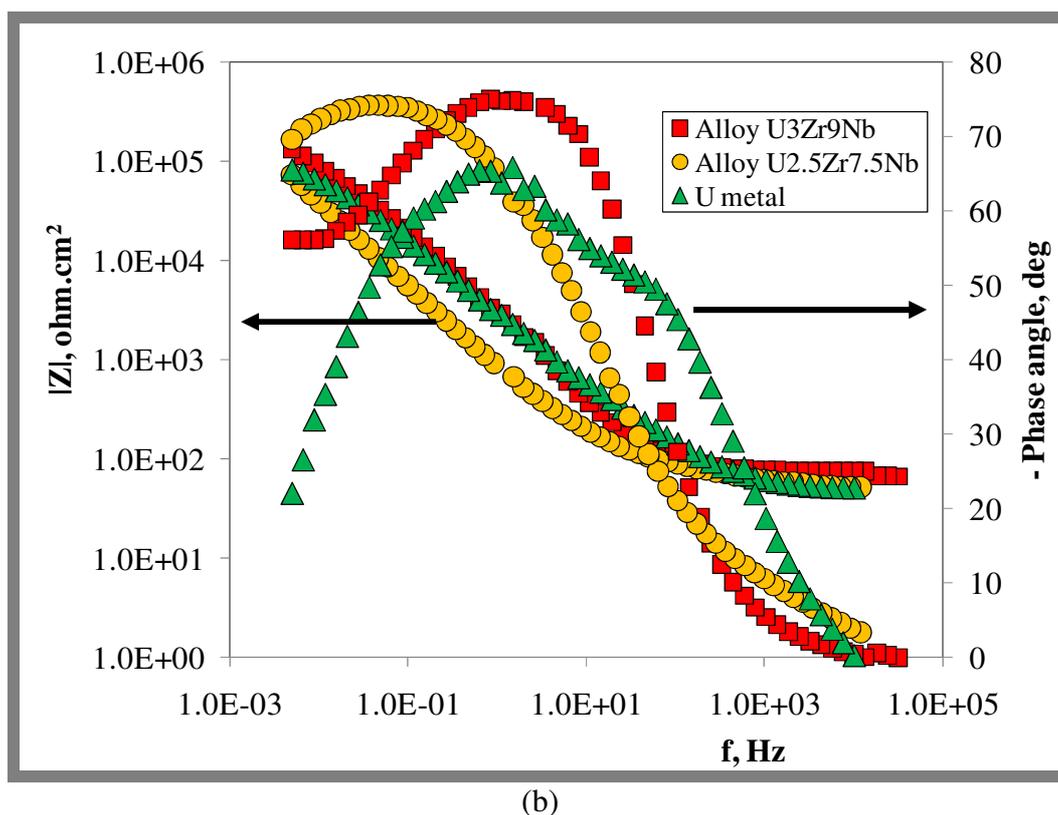
**Table 1. Corrosion potential and passive currents obtained from the potentiodynamic polarization curves of alloys U2.5Zr7.5Nb, U3Zr9Nb and uranium metal in deaerated solution of pH 7.**

Alloy	Corrosion potential, $V_{Ag/AgCl}$	Passive current density, $\mu A/cm^2$
U3Zr9Nb	-0.470	2.7
U2.5Zr7.5Nb	-0.650	2.4
U metal	-0.660	36

These results are also in accordance with electrochemical impedance measurements, shown in Figure 2, by the Nyquist and Bode diagrams. The diagrams indicate the presence of two semicircles, one at high frequencies and the other at low frequencies. They are better noticed in the Bode plot. The two semicircles correspond to two different electrochemical phenomena occurring at the interface metal-solution, probably the corrosion process and the occurrence of the electrical double layer. The uranium alloys showed higher impedance values than the uranium metal, indicating that the presence of alloying elements Nb and Zr increased the corrosion resistance of uranium.



(a)



**Figure 2. Nyquist (a) and Bode (b) diagrams of the impedance results obtained for alloys U2.5Zr7.5Nb, U3Zr9Nb and uranium metal in deaerated solution at pH 7.**

Based on the shape of the plots, it was proposed the model  $R_s(Q_1R_1)(Q_2R_2)$  to fit the data to an equivalent circuit. In this model  $R_s$  represents the solution resistance and  $Q_1R_1$  and  $Q_2R_2$  represent the two capacitance and resistor in parallel, which are related to the two electrochemical processes. In this work we assume that  $Q_1$  represents the capacitance of the double layer with  $R_1$  as the charge transfer resistance.  $Q_2R_2$  represents the capacitance and the polarization resistance associated with the corrosion process. Table 2 presents the results of the modeling. We can see that the resistance  $R_2$  of alloy U3Zr9Nb is higher than the resistance  $R_2$  for alloy U2.5Zr7.5Nb and that U metal showed the smaller resistance, indicating that the presence of Zr and Nb increased the corrosion resistance of uranium.

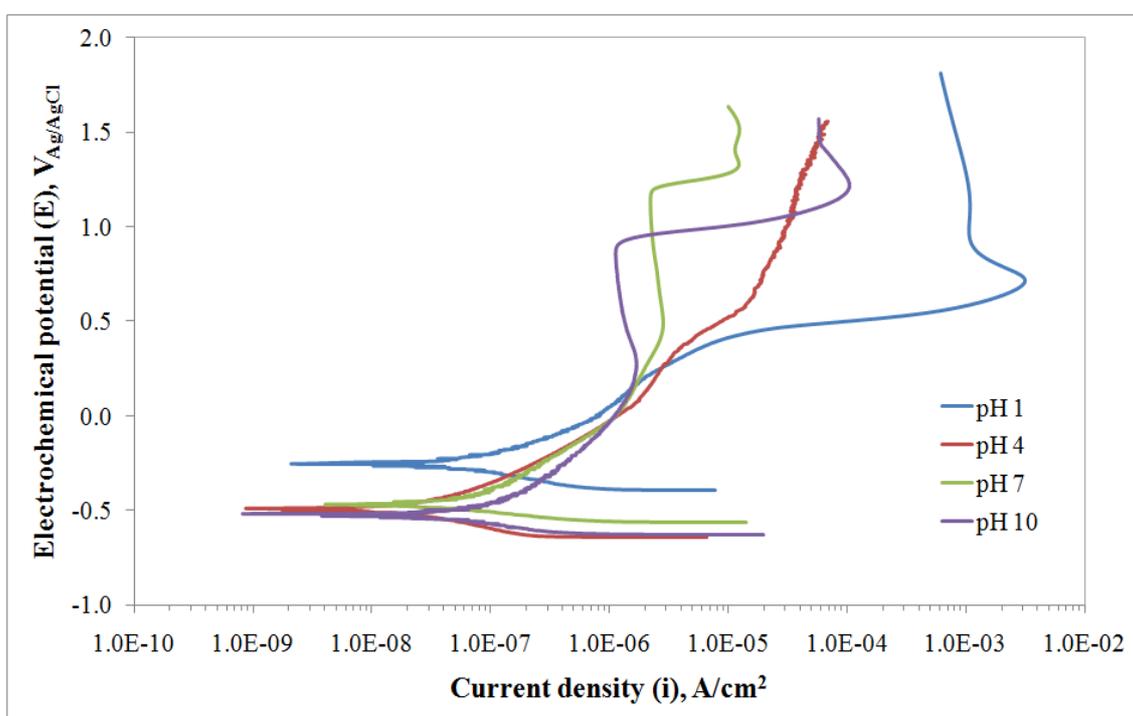
**Table 2. Fitting parameters for the model  $R(QR)(QR)$  applied to U2.5Zr7.5Nb, U3Zr9Nb and uranium metal in deaerated solution at pH 7.**

Alloy	$R_s$ (ohm.cm <sup>2</sup> )	$Q_1$ (S.s <sup>n</sup> .cm <sup>-2</sup> )	$n_1$	$R_1$ (ohm.cm <sup>2</sup> )	$Q_2$ (S.s <sup>n</sup> .cm <sup>-2</sup> )	$n_2$	$R_2$ (ohm.cm <sup>2</sup> )
U3Zr9Nb	85.8	0.000105	0.86	34,100	0.000147	0.89	504,000
U2.5Zr7.5Nb	45.5	0.002633	0.35	3,000	0.000278	0.87	460,000
U metal	50,0	0,000146	0,79	108.8	0,000083	0,76	103,000

### 3.2. Influence of Solution pH

Figure 3 presents the potentiodynamic polarization curves for alloy U3Zr9Nb in deaerated solutions at four different pH's: 1, 4, 7 and 10. The curves show that at pH 1 the alloy was more intensely corroded, which can be verified by the higher anodic currents it presented. At pH 10 the alloy showed a higher corrosion resistance.

Table 3 illustrates the corrosion potentials and passive currents obtained for the alloy U3Zr9Nb at each pH. At pH 1 the alloy corroded intensely but reached constant current values of about  $1.2 \text{ mA}\cdot\text{cm}^{-2}$ . This region is associated with film growth, but due to the high current density, this film is not protective and the current is referred to as a film-limited current density.



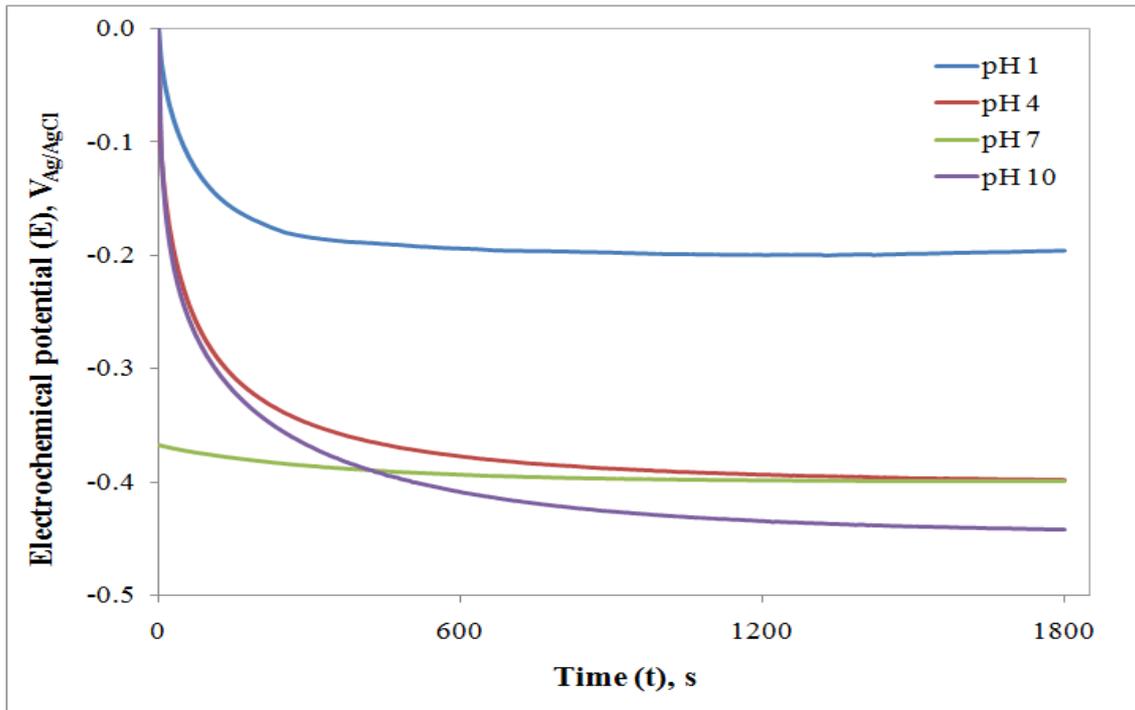
**Figure 3. Polarization curves of alloy U3Zr9Nb in deaerated solutions at pH 1, 4, 7 and 10.**

**Table 3. Corrosion potential and passive currents obtained in the potentiodynamic polarization test of alloy U3Zr9Nb in deaerated solutions at pH 1, 4, 7 and 10.**

pH	Corrosion potential, $V_{\text{Ag}/\text{AgCl}}$	Passive current density, $\mu\text{A}/\text{cm}^2$
1	-0.25	1,200*
4	-0.49	14
7	-0.47	2.8
10	-0.52	1.5

\* film-limited current density

Figure 4 illustrates the evolution of the open circuit potential with time. The curves show that the potential stabilized quickly in less than 20 minutes. Table 4 shows a comparison between the potential values obtained in the open circuit potential and potentiodynamic polarization tests. We can see that the OCP and the corrosion potentials presented similar values, indicating stability of the system.

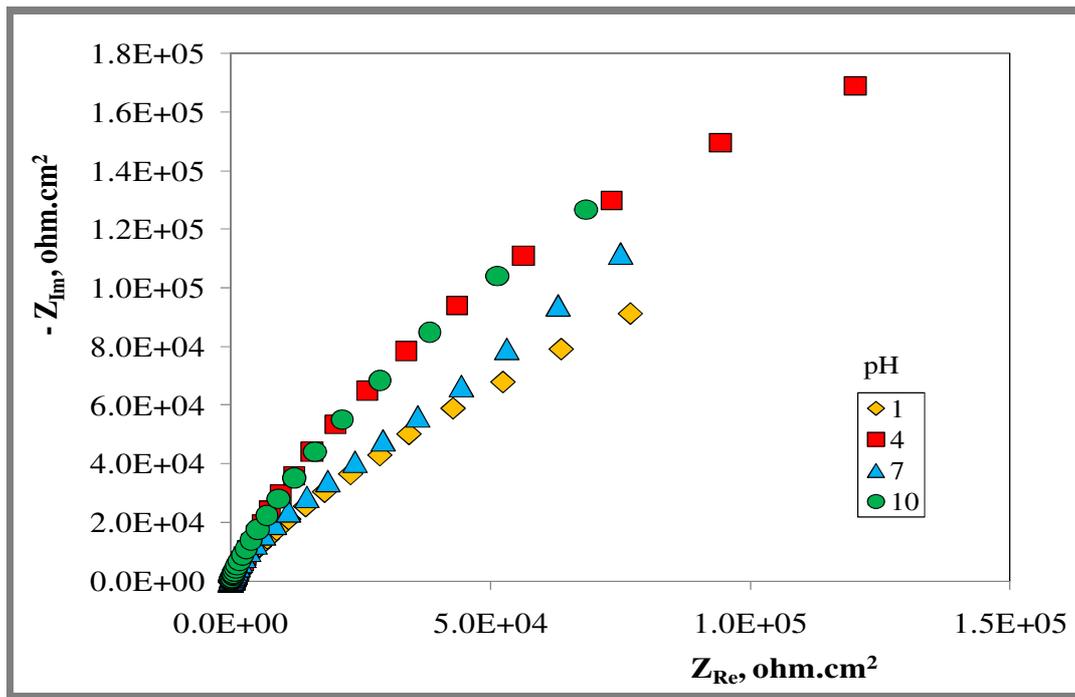


**Figure 4. Evolution of open circuit potential with time for alloy U<sub>3</sub>Zr<sub>9</sub>Nb in deaerated solutions at pH 1, 4, 7 and 10.**

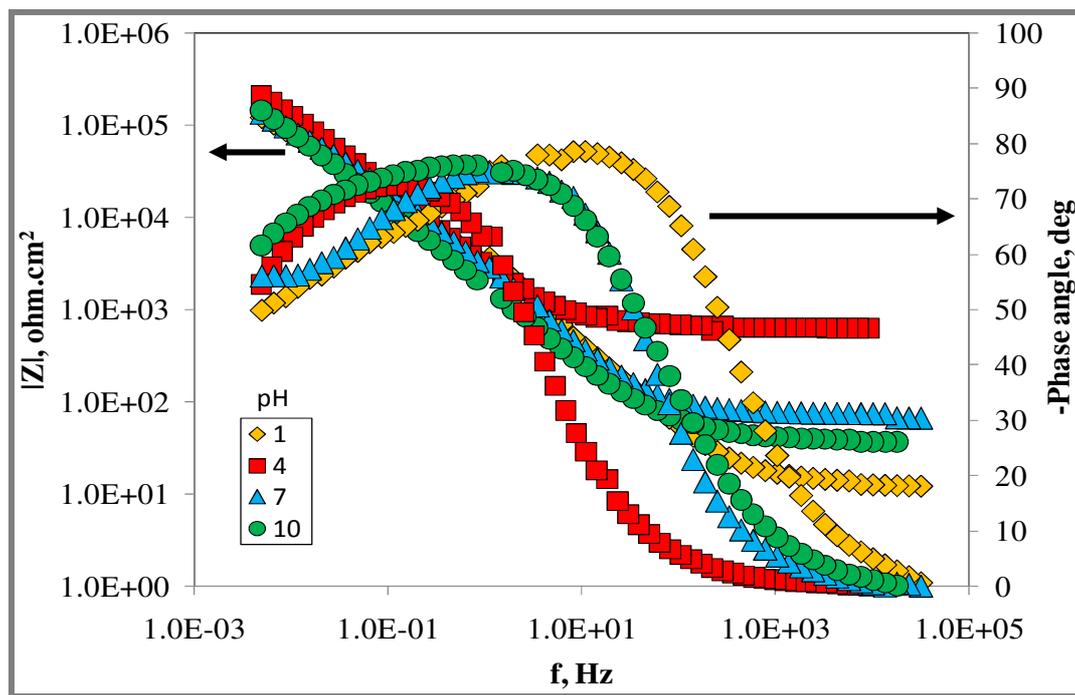
**Table 4. Comparative of the potential values obtained with the open circuit potential and potentiodynamic polarization tests of alloy U<sub>3</sub>Zr<sub>9</sub>Nb in deaerated solutions at pH 1, 4, 7 and 10.**

pH	Open circuit potential, V <sub>Ag/AgCl</sub>	Corrosion potential, V <sub>Ag/AgCl</sub>
1	-0.20	-0.25
4	-0.40	-0.49
7	-0.40	-0.47
10	-0.45	-0.52

The results of electrochemical impedance of alloy U<sub>3</sub>Zr<sub>9</sub>Nb for the different values of pH are shown in Figure 5, by the Nyquist and Bode diagrams.



(a)



(b)

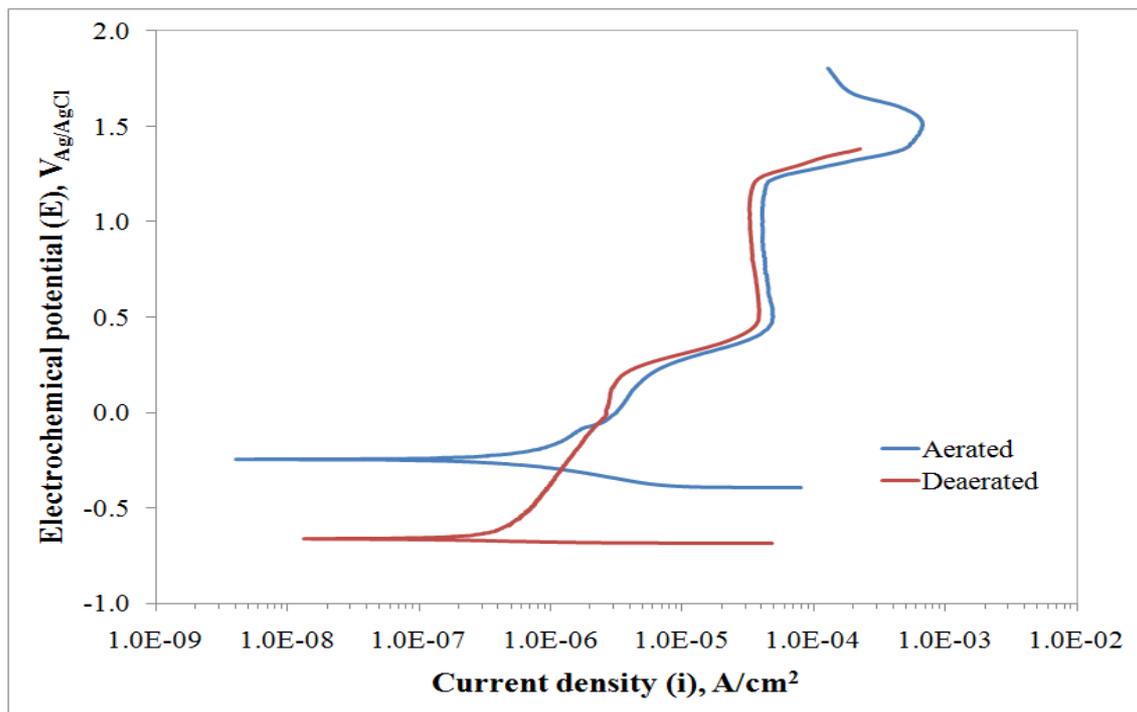
**Figure 5. Nyquist (a) and Bode (b) diagrams of the impedance results obtained for alloy U3Zr9Nb in deaerated solutions at pH 1, 4, 7 and 10.**

The impedance results show that the alloy U3Zr9Nb had a higher impedance at pH 10 and lower impedance at pH 1, indicating that at these two pH values, the alloy had major and minor corrosion resistance, respectively. The apparent higher impedance value of pH 4 may have been masked by the high resistance value of the solution (around 650 ohm.cm<sup>2</sup>), which was not compensated during the tests. At pH 1, 7 and 10, the solution resistance is lower, not affecting the results considerably.

### 3.3. Influence of Solution Aeration

Figure 6 shows the potentiodynamic polarization curves for the samples of uranium metal in pH 7 aerated and deaerated solutions. From literature [5], it is expected that uranium metal has higher corrosion resistance in aerated solutions than in solutions without dissolved gases. Figure 6 shows that this behavior was verified during tests, in which the uranium in aerated solution has a higher corrosion potential than in deaerated solution. This is related to the corrosion product formed at each condition of aeration. Hyperstoichiometric UO<sub>2</sub> is formed in aerated solution, while near-stoichiometric UO<sub>2</sub> is formed in deaerated solution [5].

Table 5 illustrates the corrosion potentials and passive currents obtained for the uranium metal for each condition of aeration. In deaerated conditions the uranium sample showed a higher degree of passivation.

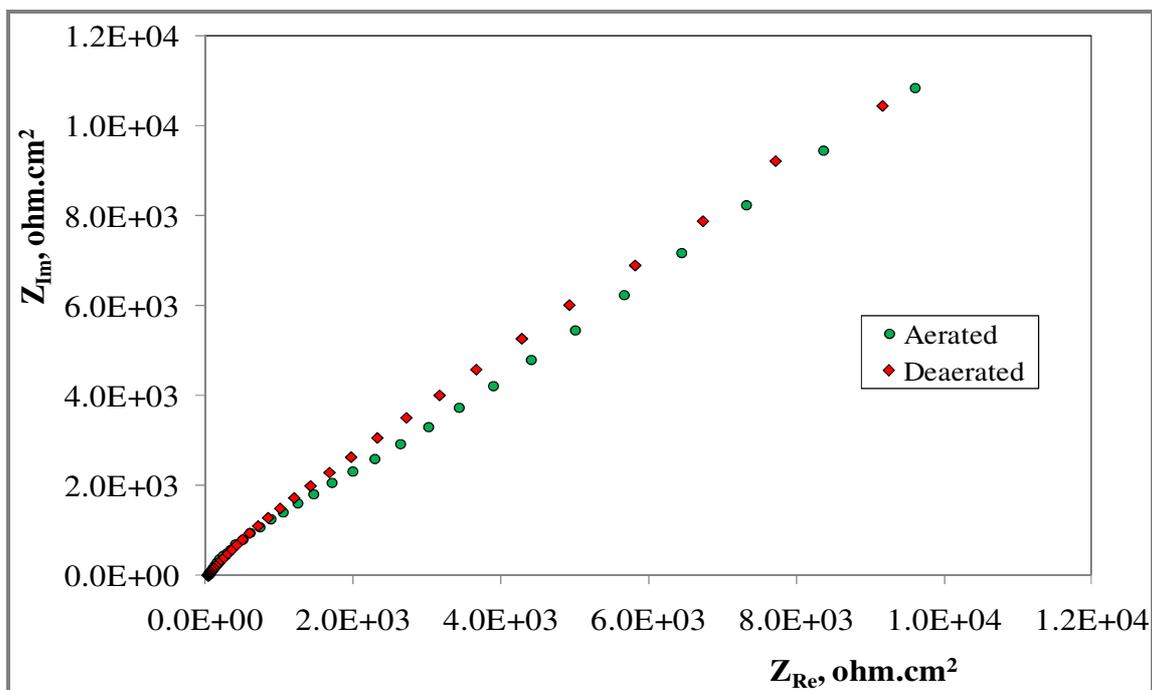


**Figure 6. Polarization curves of uranium metal in aerated and deaerated solutions at pH 7.**

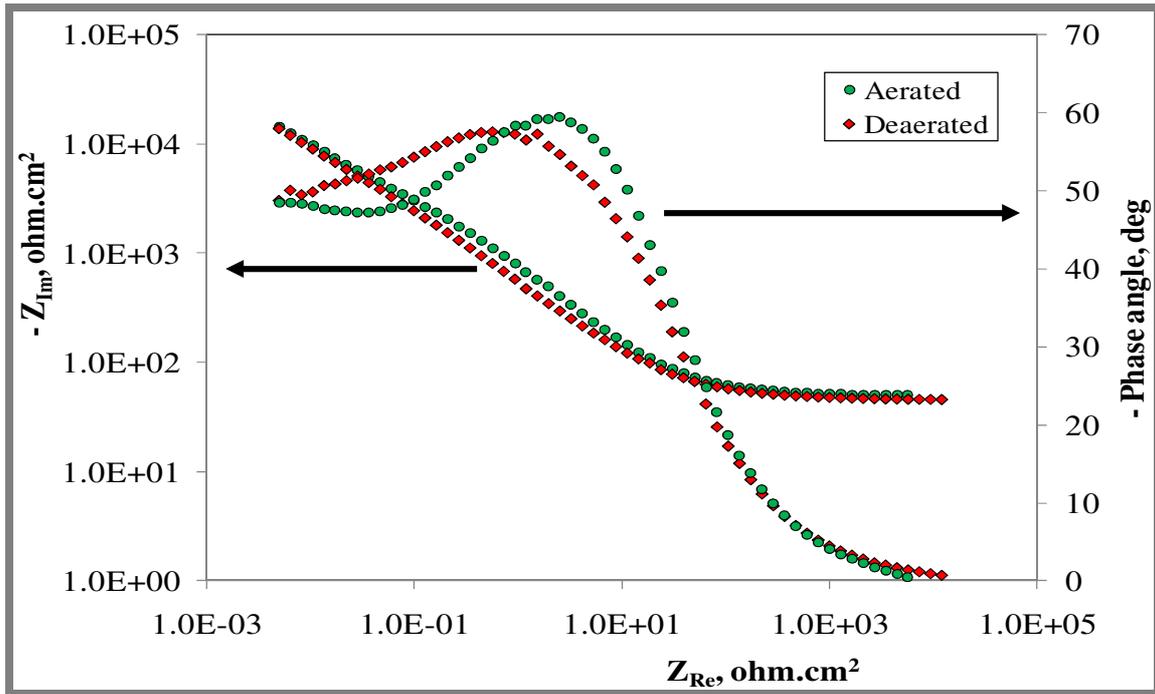
**Table 5. Corrosion potential and passive currents obtained in the potentiodynamic polarization tests of uranium metal in aerated and deaerated solutions at pH 7.**

Condition	Corrosion potential, $V_{Ag/AgCl}$	Passive current density, $\mu A/cm^2$
Aerated	-0.25	49
Deaerated	-0.66	5.0

The impedance results for the two conditions used, aerated and deaerated, are shown in Figure 7 (a) and (b), by the Nyquist and Bode plots. Two semicircles can be seen for both solution conditions, what can be assigned to two different electrochemical processes. Using our proposed model  $R_s(Q_1R_1)(Q_2R_2)$  to fit the data to an equivalent circuit, we got the parameters showed in Table 6. We can see that the resistance  $R_2$  for the aerated condition is higher than the resistance  $R_2$  for the deaerated condition, indicating that the corrosion resistance of uranium is higher for the aerated condition.



(a)



(b)

**Figure 7. Nyquist (a) and Bode (b) diagrams of the impedance results obtained for uranium metal in aerated and deaerated solutions at pH 7.**

**Table 6. Fitting parameters for the model R(QR)(QR) applied to uranium metal in aerated and deaerated solutions at pH 7.**

Condition	$R_s$	$Q_1$	$n_1$	$R_1$	$Q_2$	$n_2$	$R_2$
Aerated	49.7	0.00052	0.78	2175	0.00083	0.73	55,000
Deaerated	45.6	0.00078	0.68	3787	0.00127	0.81	43,700

#### 4. CONCLUSIONS

In this work the uranium alloys U2.5Zr7.5Nb, U3Zr9Nb and uranium metal samples were tested against corrosion using by means of open circuit potential measurements, impedance measurements and anodic polarization curves. The results obtained allow us to conclude that:

- The electrochemical tests used in this work were appropriate to evaluate the corrosion behavior of uranium alloys and uranium metal samples.
- The alloys U3Zr9Nb and U2.5Zr7.5Nb presented similar corrosion behavior when tested in a deaerated solution at pH 7 at room temperature. At the same conditions, uranium metal presented much higher tendency to corrosion. The alloying elements Zr and Nb caused an increase in the corrosion resistance of uranium. The order of corrosion resistance was:  $U < U_{2.5Zr7.5Nb} < U_{3Zr9Nb}$ . The uranium alloys and uranium samples passivated in the test solution with higher values for the uranium passive currents.

- It was verified that the corrosion behavior of the uranium alloy U3Zr9Nb was affected by the solution pH. At the most acidic solution the sample corroded intensely and the film formed on the surface did not have a protective character. The order of resistance to corrosion of the samples tested in deaerated solutions at different pH values were pH 1 < pH 4 < pH 7 < pH 10.
- The aeration of the solution increased the corrosion resistance of the uranium metal samples when tested at pH 7. This was verified by the higher corrosion potential in aerated solution and also by the impedance measurements.
- Alloy U3Zr9Nb showed higher corrosion resistance, according to impedance measurements and potentiodynamic anodic polarization tests.

## 5. ACKNOWLEDGMENTS

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