



## NITRATE ION EFFECTS ON THE NICKEL CORROSION AND PASSIVATION BEHAVIOUR IN 0.5 M H<sub>2</sub>SO<sub>4</sub> SOLUTIONS

Gabriela Elena BADEA,<sup>a</sup> Simona DZITAC,<sup>b</sup> Camelia PORUMB,<sup>c</sup>  
L. POPPER<sup>d</sup> and Teodora BADEA<sup>e\*</sup>

<sup>a</sup>Department of Energy Engineering and Management, Faculty of Energy Engineering, University of Oradea

<sup>b</sup>Electroenergetica Department, Faculty of Energy Engineering, University of Oradea, University of Oradea

<sup>c</sup>Department of Theoretical Disciplines, Faculty of Fine Arts, University of Oradea

<sup>d</sup>UNESCO Department, Faculty of Energy Engineering, University of Oradea  
Universitatii no.1, Oradea -410087, Roumania

<sup>e</sup>Department of Analytical Chemistry, Faculty of Environment Engineering,

<sup>f</sup>Sapientia University, Libertății 1, Miercurea Ciuc-530290, Roumania

Received August 28, 2009

The corrosion and passivation electrochemical parameters for nickel in deaerated 0.5 M H<sub>2</sub>SO<sub>4</sub> in presence of various nitrate ion concentrations (10<sup>-3</sup>-1 M) were evaluated on basis of the anodic and cathodic potentiostatic polarization curves. The nitrate ion is an accelerator of the nickel corrosion in acid solutions both in active and in passive state. The nickel corrosion potential shifts to positive potential value with 28 mV at a nitrate concentration increase of ten times. The corrosion current density in presence of 1 M KNO<sub>3</sub> is over 40 times more than in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution without nitrate. The active-passive transition region increased with 200 mV and the critical passivation current and passive current densities showed an exponential increase in presence of 1 M KNO<sub>3</sub>.

### INTRODUCTION

The electrochemical behaviour of the polycrystalline nickel in acid media depends, among other variables on the composition and pH of the electrolyte.<sup>1-8</sup> In the sulphate acid solutions, the nickel active-passive transition is characterized by two current peaks, of which high decreases with pH increase.<sup>1, 2</sup> The first peak is attributed to the formation at the electrode surface of a pre-passive film of Ni(OH)<sub>2</sub> that acts as an inhibition membrane on the metal dissolution, but which cannot induce the passive state. The current increase to form the second peak is due to the activation action of the anions that shift the OH<sup>-</sup> anion and promote the metal dissolution.<sup>1, 6</sup>

The anodic behaviour of nickel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions is modified by anions: SO<sub>4</sub><sup>2-</sup>, Cl<sup>-</sup>, Br<sup>-</sup>, I<sup>-</sup>, both in the active and in the passive state, in

different modes depending on their nature and concentration.<sup>3</sup> The sulphate anion (≥ 0.5 M) determined a significant decrease of the critical current, but also an increase of the passive current. In presence of the chloride (10<sup>-2</sup> M) and bromide (10<sup>-1</sup>M) the passive nickel dissolved in pitting, and at more concentrations (10<sup>-1</sup>M Cl<sup>-</sup> and 1 M Br<sup>-</sup>) Ni did not show passivity. The iodide ions had an inhibition effect on the nickel dissolution in active state, while in the passive region it take placed the oxidation of iodide to iodine.

In the organic acid solutions the nickel anodic behaviour is characterized by the active-passive transition, but in various parameters, depending on their nature and concentrations.<sup>4, 6, 8</sup>

The purpose of this work is to elucidate the role of the nitrate ion in the corrosion and passivation behaviour of the polycrystalline nickel in sulphuric acid solutions.

\* Corresponding author: badea\_t@yahoo.com

## EXPERIMENTAL

Measurements were performed in a conventional three compartments electrochemical cell separated by fritted glass disks. Nickel of 99.9 purity was used as working electrode. The geometrical area was of 2.3 cm<sup>2</sup>. A platinum sheet was used as counter electrode and a saturated calomel electrode (SCE) as reference electrode.

The working electrode surface was polished successively with 1000 and 1200-grade emery papers, washed with acetone, rinsed with distilled water and electrochemical polished in sulphuric acid solution for 1 minute, followed by washing with double distilled water. Before the measurement, the electrode surface was activated by cathodic polarization at -0.8 V/SCE.

The solutions were prepared using chemically pure reagents and double distilled water. Before measurements the solutions were deaerated with purified nitrogen time of one hour. All measurements were made at room temperature (23±1°C).

A PS 2 potentiostat was employed for the polarization measurements, using stepwise technique of 40 mV/1 min. for cathodic curves and of 40 mV/3 min. for anodic curves. The corrosion potential was measured after 10 minutes from break of the cathodic treatment. The corrosion rate was determined by Stern<sup>9</sup> method – extrapolation of the cathodic Tafel line at the corrosion potential.

## RESULTS AND DISCUSSION

### Cathodic polarization curves

The cathodic polarization curves on extended potential range (a) and in the Tafel region (b) of the nickel in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions in presence of various concentrations of the nitrate ion are given in Fig.1.

The cathodic process is controlled by charge transfer polarisation at low current densities and by diffusion polarization at high current densities. The hydrogen ion concentration being constant, the modifications of the cathodic curves in presence of nitrate ion are determined by the nitrate ion reduction. The nitrate ions act as oxidizing agents in corrosion process that explains the variation of the corrosion electrochemical parameters with their concentration (Table 1).

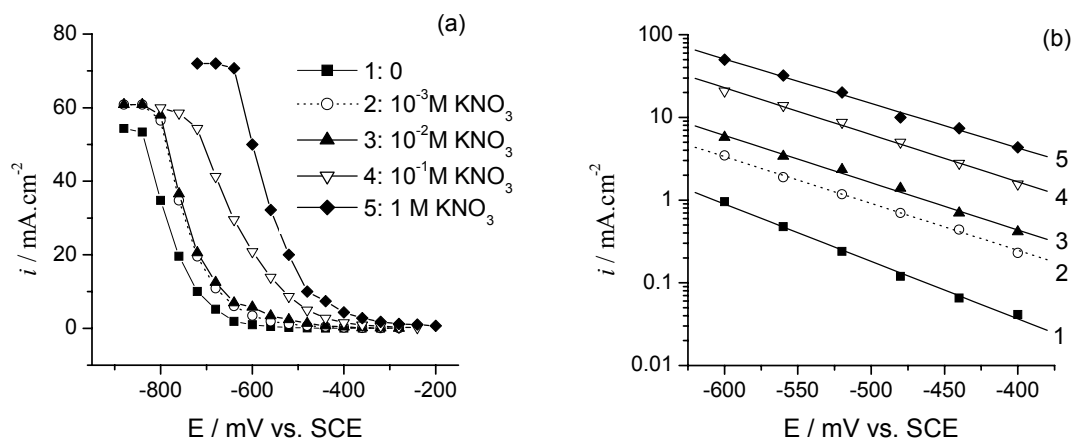


Fig. 1 – Cathodic polarization curves for Ni in 0.5 M H<sub>2</sub>SO<sub>4</sub> deaerated solutions without and in presence of the various concentrations of potassium nitrate: (a) on extended potential range; (b) in Tafel potential region.

Table 1

Nitrate ion effects on the nickel corrosion parameters in 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions

Solution↓	Parameters→	$E_{cor}$ V/SCE	$b_{cl}$ mV.decade <sup>-1</sup>	$\alpha$	$i_{cor}$ $\mu\text{A.cm}^{-2}$	$r_{cor}$ g.m <sup>-2</sup> .h <sup>-1</sup>
0.5 M H <sub>2</sub> SO <sub>4</sub> (a)		-0.280	-144	0.410	5.36	0.0059
(a) + 10 <sup>-3</sup> M KNO <sub>3</sub>		-0.245	-177	0.333	33	0.3612
(a) + 10 <sup>-2</sup> M KNO <sub>3</sub>		-0.215	-175	0.337	38	0.4160
(a) + 10 <sup>-1</sup> M KNO <sub>3</sub>		-0.185	-176	0.335	106	1.1604
(a) + 1 M KNO <sub>3</sub>		-0.163	-186	0.317	228	2.4960

A linear dependence between corrosion potential,  $E_{cor}$ , and logarithm of nitrate ion concentration was found with a slope:

$$\frac{E_{cor}}{\log c_{NO_3}} = 28\text{mV.decade}^{-1} \quad (1)$$

The cathodic Tafel slopes increase in presence of nitrate ions comparative with background solution but varies insignificant with their concentration. In presence of the nitrate ion, the charge transfer coefficients are lower than 0.5 that is in accordance with the implicating of some adsorption processes in the nitrate reduction reaction.<sup>8</sup>

In presence of the nitrate ions the corrosion current increases the more and the concentration. Thus the corrosion current increases of 6 times at an addition of 1mM  $\text{KNO}_3$  and of over 40 times if addition is 1 M  $\text{KNO}_3$  in the background solution. The obtained corrosion rate in presence of 1 M  $\text{KNO}_3$  decreases nickel corrosion resistance with two resistance groups, from the thirist group – stable materials, in background solution at the fifth group – less stable materials,.

### Anodic polarization curves

The anodic behaviour of Ni in 0.5 M  $\text{H}_2\text{SO}_4$  deaerated solutions in the absence and in the presence of various nitrate concentrations is shown in Fig. 2. The nitrate ion effect on the nickel anodic behaviour is relative insignificant at low concentration ( $\leq 10^{-2}$  M  $\text{KNO}_3$ ); at more concentration the shape of the anodic curves is much different from those in the background solution. At the addition of  $10^{-1}$  M  $\text{KNO}_3$ , on the anodic curve appears two peaks in the active-passive transition region. In presence of 1 M  $\text{KNO}_3$ , a high limiting current appears and the transition potential region increases with over 200 mV comparative with 0.5 M  $\text{H}_2\text{SO}_4$  solution.

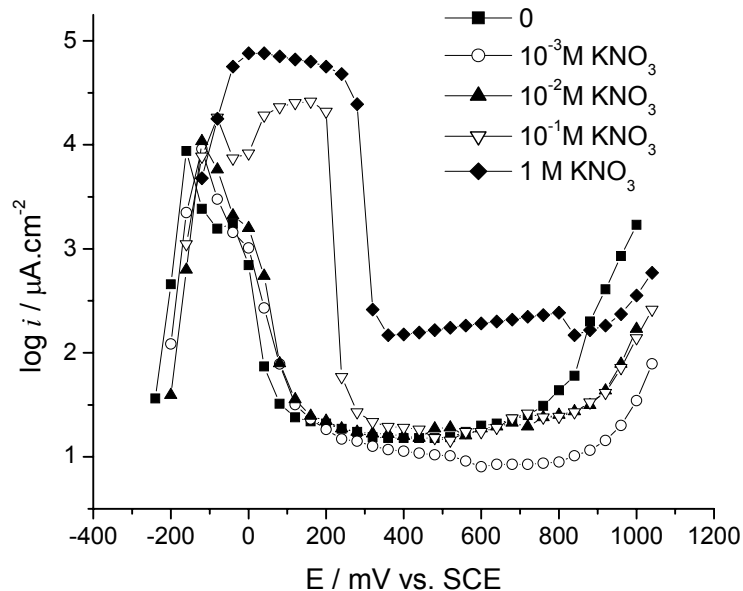


Fig. 2 – Anodic potentiostatic polarization curves of the Ni in 0.5 M  $\text{H}_2\text{SO}_4$  in deaerated solutions in absence and in presence of various concentration of  $\text{KNO}_3$ .

The critical current density of passivation,  $i_{cr}$ , and the passive current density,  $i_p$ , show an exponential growth with nitrate ion concentration, according to Fig.3. In presence of 1 M  $\text{KNO}_3$ ,  $i_{cr}$  and  $i_p$  increase with about one magnitude order. This behaviour of the nickel indicates an activator role of the nitrate anions, of which effects are significant especially at concentrations  $\geq 0.1$  M  $\text{KNO}_3$ . The adsorption of the  $\text{NO}_3^-$  ions on specific sites may to shift the  $\text{OH}^-$  anions promoting the metal dissolution and thus determining the increase

of the dissolution currents and of the transition potential region.

The obtained results may be explained on the basis of the literature data concerning to the mechanism of the nickel dissolution and passivation.<sup>1, 5, 8, 11, 12</sup> At the anodic polarization of Ni in aqueous solutions, on its surface have take place the successive, simultaneous and concurrent reactions. These may lead to the dissolution or passivation of nickel; in accordance to the following probable mechanism:

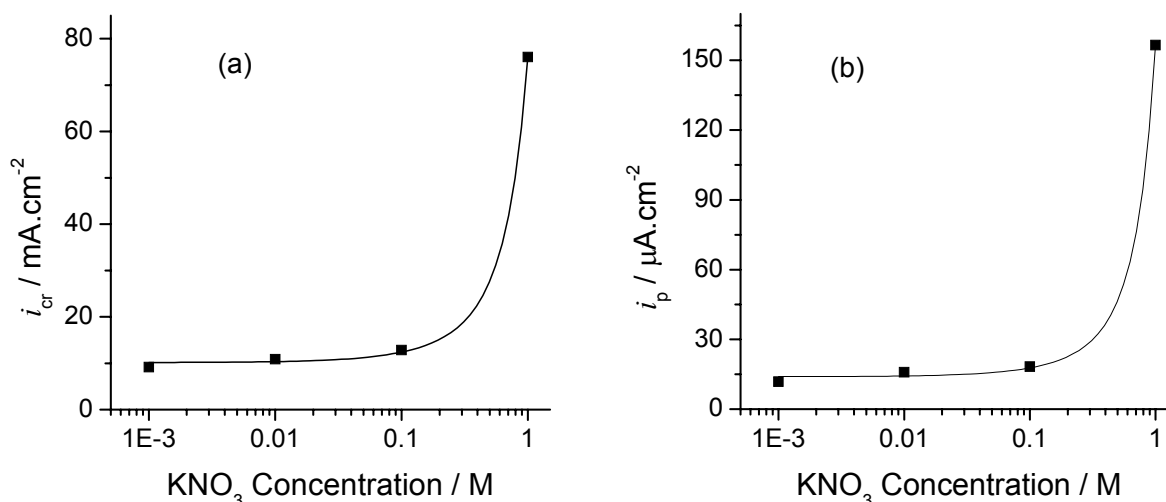
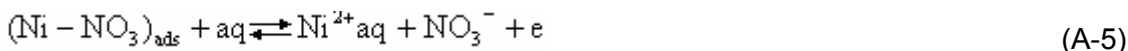


Fig. 3 – Exponential growth of  $i_{cr}$  (a) and  $i_p$  (b) with nitrate ion concentration for Ni in deaerated 0.5 M H<sub>2</sub>SO<sub>4</sub> solutions. (The  $i_p$  value corresponds to potential of 400 mV/SCE).

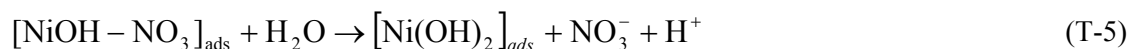
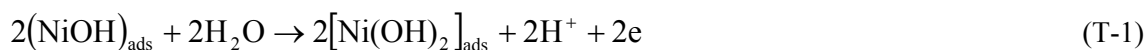
Active dissolution (A)



The reaction (A-4) and (A-5) make to increase the nickel dissolution rate so more and the high nitrate ion concentration. The active dissolution of the nickel corresponds to the total reaction (A)

obtained by summarizing of the reactions (A-1)-(A-5).

Active-passive transition (T):



At the high current density the nickel dissolution reaction is mass transfer controlled and  $[\text{Ni}(\text{OH})_2]_{\text{ads}}$  it forms on electrode surface that acting as inhibiting membrane leads at the anodic current decrease or at the dissolution rate limiting. The nitrate ions interacts with nickel hydroxide film, shifts the  $\text{OH}^-$  from pre-passive film conform to the reaction (T-2) - (T-5) determining the increase of the current peak and of the active-passive transition potential range (curves 4, 5 from Fig.2). The total reaction (T), obtained by summarizing the reactions (T-1)-(T-5) explains the high current densities recorded for anodic curves in presence of 0.1 or 1 M  $\text{KNO}_3$ , when beside of formation of the nickel hydroxide take places and nickel dissolution.

Passivation (P):



Conversion of the precursor film  $[\text{Ni}(\text{OH})_2]_{\text{ads}}$ , having ionic conduction, in an oxide film with electronic conduction, conform to the reaction (P) is accompanied by a sharp decrease of the dissolution rate, the nickel passing in the stable passive state. However, at the concentration of 1 M  $\text{KNO}_3$  the stability of the passive film is significant reduced, the passive current density being high. It is possible that adsorbed nitrate ions at high concentrations to form pores in passive film, which favours the nickel dissolution.

## CONCLUSIONS

The nitrate ions presence in 0.5 M  $\text{H}_2\text{SO}_4$  deaerated solutions had accelerator effects on the

corrosion and on the anodic dissolution rate of the nickel. In presence of 1 M  $\text{KNO}_3$ , the corrosion current density increased of over 40 times and an exponential growth of the critical current density of the passive current density obtained versus background solution. In active state the nitrate ion acts as depolarizer in the corrosion process and in the passivation process as activator shifting the  $\text{OH}^-$  ion from the passive film.

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