

## Some factors affecting on the behavior of steel electrode in citric acid solutions.

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### Abstract

Potential-time curves are constructed for the steel electrode in naturally aerated citric acid solutions devoid of and containing some aggressive and inhibitive compounds.  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions cause the destruction of passivity and initiation of pitting corrosion. The rate of oxide film growth by citric acid and oxide film destruction by  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions follows a direct logarithmic law as evident from the linear relationships between the open-circuit potential and the logarithm of immersion time. Urea, phenylhydrazine and 1,2-phenylenediamine compounds inhibit the pitting corrosion of steel. The rate of oxide film healing and thickening increases with their concentrations. In presence of constant inhibitor concentration, the efficiency of pitting inhibition increases in the order: (weak) urea < phenylhydrazine < 1,2-phenylenediamine (strong).

**Key words:** Steel, Citric acid, Oxide film thickening, Aggressive, Corrosion, Inhibition.

### I. Introduction

Iron and its alloys (e.g. steels) are always exposed to the action of acids in industry [1]. Processes in which acids play a very important part are acid pickling, industrial acid cleaning, cleaning of oil refinery equipment, oil well acidizing and acid descaling [1, 2]. The exposures can be most severe but in many cases, corrosion inhibitors are widely used in the industry to prevent or to reduce the corrosion rates of metallic materials in these media.

**Corrosion:** Corrosion is the gradual physiochemical destruction of materials by the action of environment. It is also known as the deterioration of materials or its properties because of reaction with its environment. The word corrosion comes from the Latin word "corroder", which means to gnaw away. It usually begins at the surface of a material and occurs because of the spontaneous tendency of the materials to return to their thermodynamic stable state or to one of the forms in which they were originally found. Metals are generally prone to corrosion because most of them occur naturally as ores, which is the most stable state of low energy and there is a net decrease in free energy  $\Delta G$  from metallic to oxidized state [3].

Acid corrosion inhibitors find vast application in the industrial field as components in acid descaling, oil well acidizing, acid pickling, acid cleaning, etc. Most of the efficient corrosion inhibitors used in industry are organic compounds having multiple bonds and hetero atoms like N, O, S through which they are adsorbed on the metal surface [4-11]. The influence of such organic compounds on the corrosion of steel in acidic solution has been investigated by several researchers [12-14]. The

inhibition property of these compounds is attributed to their molecular structure [15].

Citric acid is the natural organic acid produced in oranges and other citric fruits. It is generally regarded as safe for use in food products. It is a common material used in many food and beverages sold on the market. This means that citric acid is compatible with the environment and can usually be blended into sanitary sewage systems with environmental agency approval. The electrochemical behavior of steel electrode immersed in citric acid solutions has been followed and discussed using potential measurements under open-circuit conditions [16]. The effect of increasing concentrations, temperature of solution and addition of some organic compounds are also investigated. It is found that, the steel electrode can be passivated in naturally aerated solutions of citric acid and the rate of oxide film growth follows a direct logarithm law, as evident from the linear relationship between the open-circuit potential and the logarithm of immersion time. The rate of oxide film growth decreases by raising the solution temperature. The addition of some organic compounds as urea, phenylhydrazine and 1,2-phenylenediamine decrease the destruction of the passive film and thus increase the inhibition process [16].

The aim of the present work is to shed more light on the effect of chloride and sulphate ions on the rate of oxide film formed on a steel electrode in citric acid solutions. The effect of increasing concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions and temperature changes (25-55°C) on the rate of oxide film healing and destructed are examined. The effect of addition of some organic compounds such as urea, phenylhydrazine and 1,2-

phenylenediamine on the stability of the oxide film formed is also examined.

## II. Experimental

The steel electrodes were made from steel samples produced by the Egyptian Mill steel Company (Helwan- Cairo) and having the following chemical composition:

C	Si	Mn	P	S	Fe
0.32	0.24	0.89	0.024	0.019	98.507

mass %

The steel electrodes were fixed to borosilicate glass tubes with epoxy resin so that the total exposed surface area was 1.33 cm<sup>2</sup>. Electrical contacts were achieved through thick copper wires soldered to the ends of the steel rods not exposed to the solution. Before being used, the steel electrodes were abraded into uniform surfaces by a grinding machine (model Jean Wirtz TG 200, Germany) using successive 0-, 00- and 000-grades emery papers, rinsed with acetone and finally washed with triply distilled water before immersing in the test solution.

The potential of the steel electrode was measured in naturally aerated 0.5 M citric acid solutions to the nearest mV on a Wenking potentiometer Type PPT 70 relative to the saturated calomel electrode (SCE). The steady-state potentials were considered as those values which did not change by more than 1 mV in 10 minutes. Furthermore, the effect NaCl and Na<sub>2</sub>SO<sub>4</sub> on the passivity of steel electrode in citric acid solution was investigated. Addition of some organic inhibitors including urea, phenylhydrazine and 1,2-phenylenediamine on the behavior of steel in citric acid was also investigated. Scanning electron micrographs for steel samples, after immersion in the tested solutions for 2 h, were undertaken using a Jeol scanning electron microscope, JSM-T 100(Japan).

Electrolytic solutions were prepared from analytical grade reagents and triply-distilled water. Solutions of citric acid with different concentrations were prepared by dissolving the corresponding quantitative weights of solid citric acid in the appropriate volumes of distilled water. The effect of adding variable concentrations of NaCl, Na<sub>2</sub>SO<sub>4</sub> ranged from 1x10<sup>-4</sup>M to 1M was tested in the presence of definite concentration of citric acid as 0.5M. The addition of increasing concentrations of urea, phenyl hydrazine and 1,2-phenylenediamine were prepared with a tested concentration of citric acid 0.5M and the adjusted concentration of aggressive Cl<sup>-</sup> ion as 0.1M. The cell has a double wall jacket through which water, at the adjusted temperature, was circulated. Measurements were carried out at a constant temperature 25± 0.1°C, except those related to the effect of temperature. The cell temperature was controlled using an ultra-thermostat type polyscience (USA). The main joint of

the cell contains openings for both the steel electrode and the reference electrode (SCE). The effect of temperature on 0.5M citric acid + 0.1M Cl<sup>-</sup> ions was carried out at (25°C - 55°C). No trails were made to measure the oxygen content of the solution.

## III. Results and discussion

### 3.1. Effect of chloride and sulphate ions on the behavior of the steel electrode in naturally aerated citric acid solution

The curves in Fig. 1(A and B) represent the variation of the open-circuit potential, E, of the steel electrode with time in naturally aerated solutions of 0.5 M citric acid devoid of- and containing increasing concentrations of NaCl and Na<sub>2</sub>SO<sub>4</sub>, respectively. Inspection of the curves of this figure reveals that the steady-state potentials, E<sub>st</sub>, of the steel electrode in aggressive ions-free citric acid solutions are invariably approached from negative values following the immersion of the electrode in solution. The ennobling of the steel electrode potential when immersed in naturally aerated citric acid solutions denotes that the pre-immersion oxide film carried by the metal surface is not sufficient to impart passivity [17, 18]. Healing and thickening of the film continue until passivity is reached. The open-circuit potential of the electrode reaches steady values after a time ranging from 100 to 120 min. This finding can be explained on the basis of the continuous growth of the oxide film on the electrode surface. On further inspection of the curves present in Fig. 1(A and B), three different behaviors of the steel electrode could be recognized depending on the type and the concentration of aggressive anion present. Thus: (i) In the presence of lower concentrations of both ions, the steady-state potential is approached from negative values and becomes less active the higher the concentration of the aggressive chloride and sulphate ions. This behavior indicates the continuous repair of the oxide film on steel surface to an extent which decreases with increasing anions concentration. In this range of aggressive ions concentration, the process of oxide film healing and growth by citric acid predominates that of film destruction by the aggressive ions.(ii) On further increasing of the concentration of the aggressive anions, above a threshold value which depends on the anion type, the open-circuit potential of the steel electrode after reaching a certain noble value, which depends also on anion type and concentration, starts to move into the negative direction to reach a new steady value which becomes more active the higher the concentration of the aggressive anions. This behavior is assumed to be due to a competitive process which involves oxide film healing and growth by the inhibiting citric acid and oxide film destruction by the aggressive anions. As the concentration of the

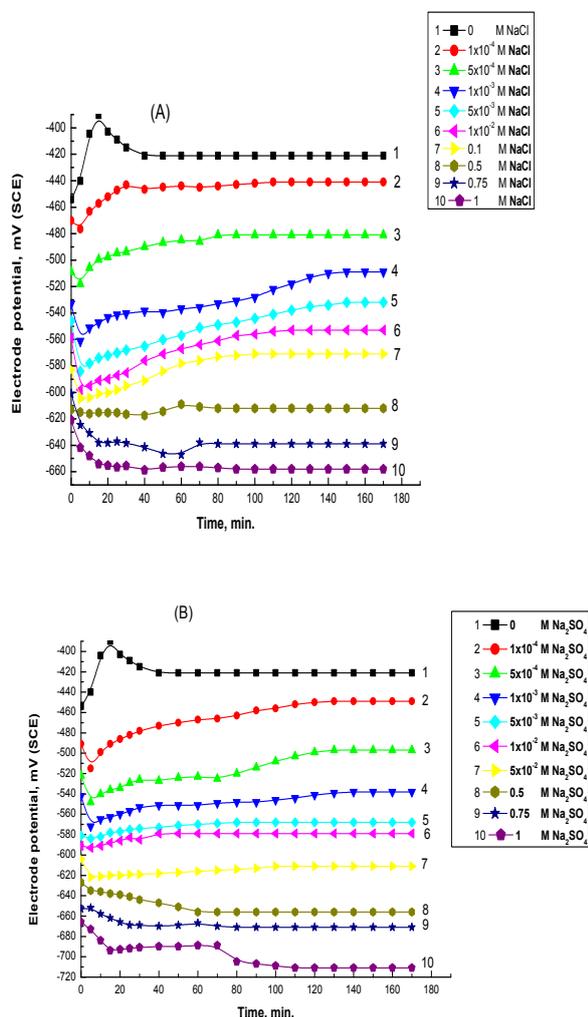


Fig.1 (A and B) Variation of the open circuit potential, E, of the steel electrode with time in solutions of 0.5 M citric acid in presence of increasing addition of (A) NaCl and (B) Na<sub>2</sub>SO<sub>4</sub>.

latter ions increases, oxide film destruction predominates oxide film healing and growth. (iii) At still higher concentrations of the aggressive ions (1 M solution), the final steady-state potentials are reached from less negative values and become more active the higher the concentration of the aggressive anions. The shift of the open-circuit potential of the steel electrode to more negative values is related to the destruction and the continuous dissolution of the protective passive film by the present aggressive anions with the initiation of localized attack, the extreme of which is pitting corrosion.

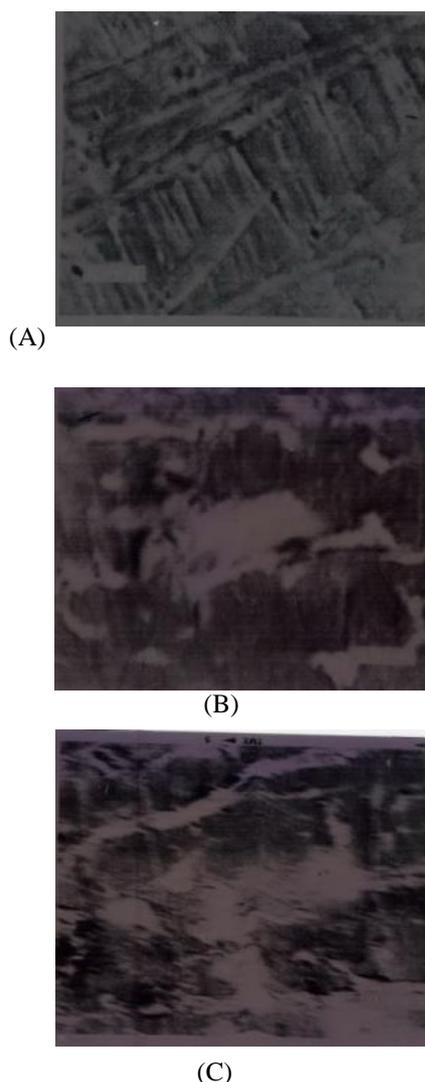


Fig. 2. SEM micrographs of steel electrode surface after immersion for a period of 2 h in (A) 0.5 M citric acid (free) and 0.5 M citric acid in presence of (B) 0.1 M Cl<sup>-</sup> ions and (C) 0.1 M SO<sub>4</sub><sup>2-</sup> ions, respectively.

Fig. 2(A–C) represent the scanning electron micrographs of the steel electrode samples immersed for 2 h in naturally aerated 0.5 M citric acid solutions devoid of and containing 0.1 M of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions, respectively. Inspection of these micrographs shows only the abrasion lines in aggressive ion free citric acid solutions, Fig. 2(A). However, in the presence of chloride and sulphate ions, Fig. 2(B and C), fine pits were formed, some of which expanded equally laterally as well as inwardly to give some large attacked areas. Inside these large areas traces of the corrosion products are observed.

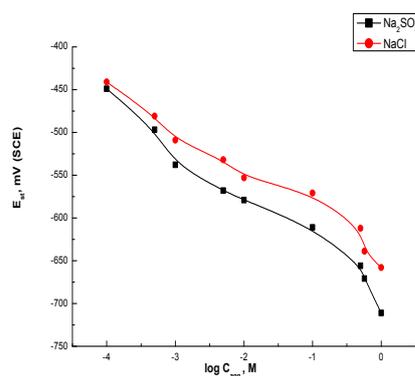


Fig.3. Variation of the steady state potential,  $E_{st}$ , with  $\log C_{agg}$ , for steel electrode in 0.5 M citric acid in different concentration of NaCl and  $Na_2SO_4$ .

The curves in Fig. 3 represent the variation of the steady-state potential,  $E_{st}$ , of the steel electrode in solutions of 0.5 M citric acid, with the logarithm of the molar concentration of  $Cl^-$  and  $SO_4^{2-}$  ions. Sigmoidal S-shaped curves are obtained which reveal that the initiation of pitting corrosion on the steel by chloride and sulphate ions takes place by the way of an adsorption mechanism. The way by which the open-circuit potential of the steel electrode,  $E$ , approaches the final steady-state values in solutions of citric acid devoid of- and containing increasing concentrations of the aggressive  $Cl^-$  and  $SO_4^{2-}$  ions is of interest. As can be seen from the curves in Fig. 4(A and B),  $E$  varies linearly with the logarithm of the immersion time,  $t$ , in minutes according to [17,18–24]:

$$E = a_1 + b_1 \log t \quad (1)$$

where  $a_1$  and  $b_1$  are constants. The value of the constant  $b_1$  decreases with increasing the aggressive ions concentration. This behavior indicates that oxide film thickening and/or destruction on the steel electrode, under the prevailing experimental conditions, follows a direct logarithmic growth law. A brief review of the oxidation theories indicates that no sound theory of general applicability exists for the direct logarithmic oxidation kinetics of metals at low temperatures [25, 26].

The linearity of the open-circuit potential with the logarithm of time during oxide film growth has been modeled by several investigators. In general, the growth of oxide films is controlled by the diffusion of ions and electrons under the influence of gradients in their concentration and electric potential [25–29]. A generic model describing the kinetics of oxide film growth on metals, at low temperatures, under the effect of a high electric field was proposed by Cabrera and Mott [28]. This model is based on the

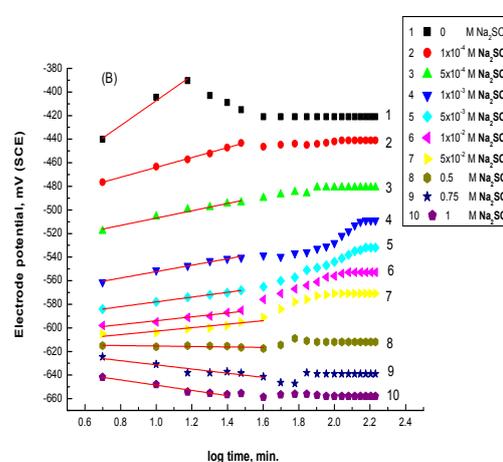
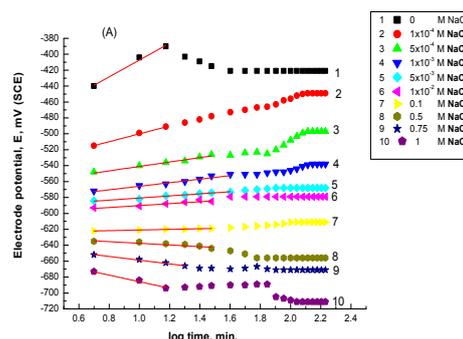


Fig.4 Variation of the open circuit potential,  $E$ , of the steel electrode immersed in 0.5 M citric acid in presence of increasing addition of (A) NaCl and (B)  $Na_2SO_4$  respectively, with the logarithm of immersion time.

assumption that cation migration occurs under the influence of a potential build up across the growing oxide film and explains the logarithmic kinetics of oxide film thickening on copper and iron [29]. Shimizu et al. [27] explained the linear relationships between the open-circuit potential and time on the basis that electron tunneling through the growing oxide is the rate determining step for the cathodic process. Burstein and Organ [23, 24], on the other hand assumed that oxide film growth follows the high field equation [27–32], while others [33,34] proposed the direct logarithmic equation to describe the kinetic form of the linear increase of potential with the logarithm of time. All iron oxides tend to be non-stoichiometric. With the exception of  $\alpha-Fe_2O_3$ , the structure of iron oxides may be visualized as cubic close packed arrays of oxide ions with certain number of  $Fe^{2+}$  and/or  $Fe^{3+}$  ions distributed among the octahedral and tetrahedral interstitial sites in the oxide lattice [19]. Abd El Kader and Shams El Din [18], assumed that only under the influence of strong electric field, of the order of magnitude of  $RT/ZF$  per atom layer of the oxide, can detectable ionic currents flow. With this

high field strength, Ohm's law does not apply, and ion transport is governed by the familiar Guntherschulze & Betz relationship [31].

$$i_a = K_a \exp(\beta H) \quad (2)$$

where  $K_a$  and  $\beta$  are constants, and  $H$  is the effective field strength. Under open circuit conditions,  $i_a$  can originate from the specific adsorption of the present anions on the oxide covered metal [18]. This creates image charges of the same magnitude but of opposite sign at the oxide/metal interface, sufficient to promote ion transfer through the oxide to the film/solution interface. The field strength depends on the nature and charge of the anions, and to a lesser extent on its concentration. Assuming, however, that all the potential differences in the electrical chain: Cu (connecting lead)/Steel electrode/Fe oxides/citric acid solution/SCE-Cu (connecting lead) other than the one across the oxide film, are constant and small, the field strength  $H$  of Eq. (2) is substituted by the term  $E/\delta$ , where  $E$  is the measured potential relative to the reference half cell, and  $\delta$  is the thickness of the oxide film. The oxidation of Fe in aerated citric acid solutions leads exclusively to the increase in the thickness of the oxide film on the steel surface. At the initial stages of oxide growth, the increase in  $\delta$  necessitates a corresponding equivalent change in potential,  $E$ , so as to keep the field strength constant. Following this reasoning, one can apply Eq. (3), derived theoretically by Abd El Kader and Shams El Din [18], which describes the variation of the open-circuit potential of the metal,  $E$ , with time,  $t$ , via:

$$E = \text{const.} + 2.303 \delta^- / \beta \log t \quad (3)$$

where  $\delta^-$  represents the rate of oxide film thickening per unit decade of time, and  $\beta$  is a constant which is identified as [35]:

$$\beta = (nF/RT) \alpha \delta' \quad (4)$$

where  $\alpha$  is the transfer coefficient similar to that encountered in normal electrochemical reactions [21], ( $0 < \alpha < 1$ ), and  $\delta'$  is the width of the energy barrier surmounted by the ion during transfer. Assuming that the thickening of the oxide film on the steel surface occurs by way of the diffusion of the  $\text{Fe}^{2+}$  ions to the oxide/metal interface, so that "n" in Eq. (4) amounts to 2 and  $\alpha$  acquires a value of 0.5 and  $\delta'$  the value of 1 nm, the constant  $\beta$  acquires the value of 39 nm/V. From the slopes of the straight lines of Fig. 4(A and B), relating the variation of  $E$  with  $\log t$ , the values of the rate of oxide thickening,  $\delta^-$ , in naturally aerated 0.5 M citric acid solutions in absence and presence of increasing concentrations of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions have been calculated. Further inspection of the curves present in Fig. 4 (A and B) and reveals that the open-circuit potential of the steel electrode varies, in all cases, linearly with the logarithm of the immersion time,  $t$ , until reaching the final steady-state values. Three different behaviors could also be recognized

depending on the anion type and concentration. Thus, in presence of lower concentrations of  $\text{Cl}^-$ ,  $E$  varies with  $\log t$  according to Eq. (1). The slope,  $b_1$ , of the straight line portion of the curves decreases with increasing the concentration of the aggressive anions due to a decreased rate of oxide film growth. The extent of this decrease becomes noticeable with the increase in the concentration of the  $\text{Cl}^-$  anions, Fig. 4(A). Similar behavior is found in presence of  $\text{SO}_4^{2-}$  ions of concentrations up to 1 M, Fig. 4(B). However, in presence of moderate concentrations of  $\text{Cl}^-$  ions,  $E$  remains more/or less independent of the immersion time until reaching the final steady potential. This behavior could be attributed, as previously noted, to a competitive process of oxide film growth by citric acid and oxide film destruction by the aggressive ions [19]. On the other hand, in the presence of higher concentrations of both  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions,  $E$  varies with  $\log t$  according to:

$$E = a_2 + b_2 \log t \quad (5)$$

where  $a_2$  and  $b_2$  are constants. Table 1 shows the values of the constant  $a_2$  and  $b_2$  for both  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  anions in 0.5 M citric acid solutions. The values of the constant  $b_2$  depend on both the type and the concentration of

**Table 1**

The values of the constants  $a_2$ ,  $b_2$ , A and B for  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  anions in 0.5M citric acid

Constant	$\text{Cl}^-$	$\text{SO}_4^{2-}$
$a_2$ (mV)	-646	-704
$b_2$ (mV)	-41.385	-22.178
A	0.461	0.256
B	-0.263	-0.231

the aggressive anions. For one and the same anion,  $b_2$  decreases with increasing the concentration of the added ions due to a decreased rate of oxide film thickening or increased rate of oxide film destruction. However, the values of the intersection of these parallel straight lines,  $a_2$ , reflect the specific aggressiveness of each anion towards oxide film destruction which decreases in the order: (strong)  $\text{SO}_4^{2-} > \text{Cl}^-$  (weak) [36]. The same trend was also observed from the variation of the final steady-state potentials,  $E_{st}$ , with the concentration of the aggressive anions, Fig. 3(A and B). From the slopes of the straight lines of Fig. 4(A and B), the values of the rate of oxide film thickening,  $\delta^-$ , in presence of the aggressive ions could be determined [19]. In Fig. 5 and Table 1 the rate of the oxide film thickening on the steel surface in naturally aerated 0.5 M citric acid solutions are plotted, as function of the logarithm of the molar concentration of the aggressive  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  anions. Parallel straight lines are obtained satisfying the relation:

$$\text{Rate of oxide film thickening} = A + B \log C_{agg} \quad (6)$$

where A and B are constants. In Table 1, the values of the constants A and B are also depicted. The constant A represents the rate of oxide film destruction in presence of 1 M of the aggressive Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> ions. From these relations, it is quite clear that the rate of oxide film thickening is decreased while the rate of oxide film destruction is increased with increasing

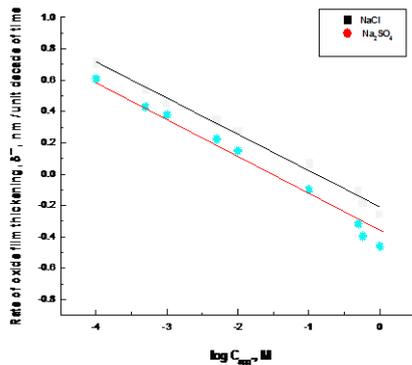


Fig. 5. Rate of oxide film thickening in 0.5 M acetic acid in presence of Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions.

the concentration of the present aggressive anions. The nearly constant value of the slope, B of the straight lines of Fig. 5 indicates that the mechanism of oxide film destruction and dissolution by Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup> anions is the same.

### 3.2. Effect of temperature

The curves of Fig.6A, represent the variation of the open-circuit potential of the steel electrode, E, with time in naturally aerated 0.5 M citric acid + 0.1M NaCl at temperatures varying between 25 and 55°C. Inspection of the curves of this figure reveals that raising the solution temperature is accompanied by a marked effect on the value of the steady state potential, E<sub>st</sub>. The latter varies with temperature in according with the straight line of Fig. 7(A).

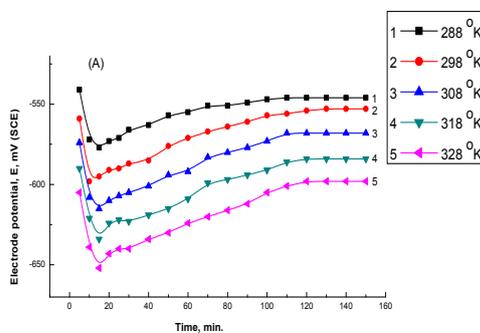


Fig. 6. (A) Variation of the open circuit potential, E, of the steel electrode with time in 0.5 M citric acid + 0.1 M NaCl at different temperatures.

It is quite clear that raising the temperature decreases the initial rate of oxide film growth or enhances the corrosion of the steel and the extent of

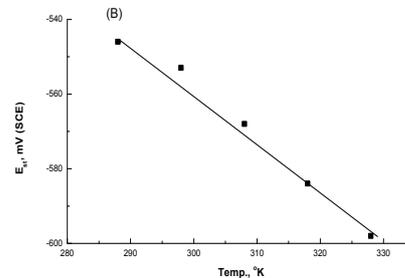


Fig. 6. (B) Variation of the steady state potential, E<sub>st</sub>, with temp. °K, for steel electrode in 0.5 M citric acid containing 0.1 M Cl<sup>-</sup> ions.

corrosion promotion increases with raising the temperature, as reflected by the shifting of the final steady potential in the negative direction. This could be attributed to the decrease of solution viscosity and the consequent increase in the mobility of ions with raising the solution temperature [26].

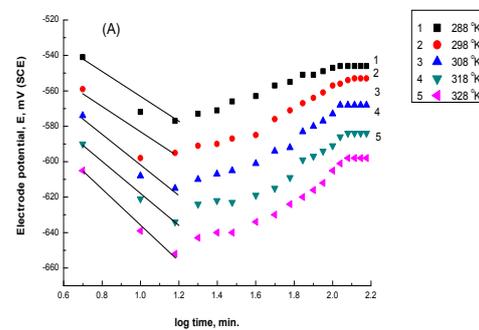


Fig. 7. (A) Variation of the open circuit potential, E, of the steel electrode in 0.5 M citric acid solutions + 0.1 M NaCl at different temperatures with logarithm the time, t.

The straight lines present in Fig. 7(A) relate the variation of the open-circuit potential of the steel-electrode with the logarithm of the immersion time, t, in aerated 0.5 M citric acid solutions+ 0.1M NaCl at temperatures varying between 25 and 55°C, respectively. The slopes of these straight lines decrease with raising the temperature. The calculated values of the initial rate of oxide film thickening on the steel electrode, at varying temperatures, are plotted as function of 1/T (K<sup>-1</sup>) in Fig. 7 (B). From the straight line of this figure; one can concluded that, the rate of oxide film destruction increases with raising of temperature.

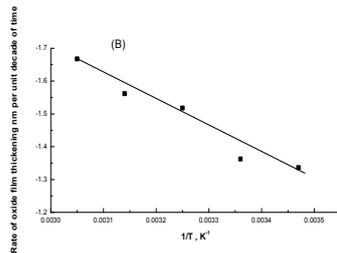


Fig. 7. (B) Variation of the rate of oxide film thickening,  $\delta^-$ , of the steel electrode in 0.5 M citric acid solutions containing 0.1 M NaCl with  $1/T, K^{-1}$ .

### 3.3. Effect of addition of some organic compounds on the behavior and kinetics of oxide film growth on the steel electrode

Increasing concentrations of urea, phenylhydrazine and 1,2 phenylenediamine, are used to inhibit the pitting corrosion of the steel in naturally aerated 0.5 M citric acid solution in presence of 0.1 M Cl<sup>-</sup> ions as pitting corrosion agent. The open-circuit potential of the steel electrode is followed as function of time and inhibitor concentration till steady-state potentials are reached. The curves in Fig. 8 (A and B) represent such behavior in presence of urea and 1,2-phenylenediamine compounds, as examples of the other used additives. Inspection of the curves in Fig. 8 (A and B) and the likes reveals two different actions of these additives which depend on their type and concentration. Thus, in presence of low concentrations of these compounds, the steady-state potentials,  $E_{st}$ , are approached from negative values and shift to the noble direction to reach values which are more positive the higher the concentration of the additives. However, after a certain time, which increases with increasing the additives concentration, the open-circuit potentials,  $E$ , shift suddenly and directly into the negative direction to reach steady-state values which are less active the higher the inhibitor concentration. This behavior could be attributed to a competitive process, involving oxide film healing and thickening by the inhibitor anions and oxide film destruction by the aggressive Cl<sup>-</sup> ions. In this range of the inhibitors concentrations, oxide film destruction predominates oxide film repair and thickening. Higher concentrations of the additives, on the other hand, cause the potential  $E$  to shift directly into noble direction to reach steady-state values which are more positive the higher the inhibitor concentration indicating oxide film healing and thickening. The curves of Fig. 9 represent the variation of the steady-state potential,  $E_{st}$ , of the steel electrode, in 0.5 M citric acid + 0.1M Cl<sup>-</sup> ions, as a function of the logarithm of the molar concentration of the added inhibitive compounds. Like s-shaped curves are obtained indicating the domain of oxide

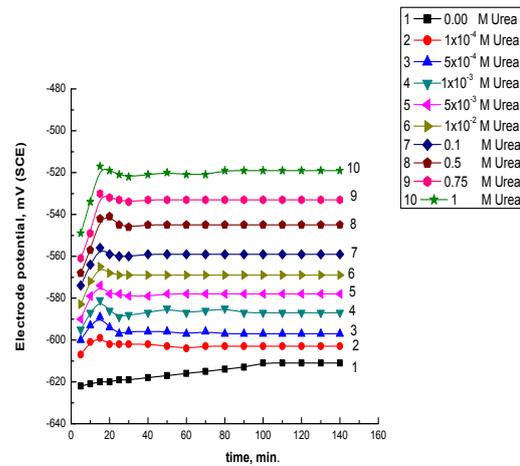


Fig. 8(A) Variation of the open circuit potential,  $E$ , of the steel electrode with time in 0.5 M citric acid + 0.1 M NaCl in presence of increasing additions of Urea

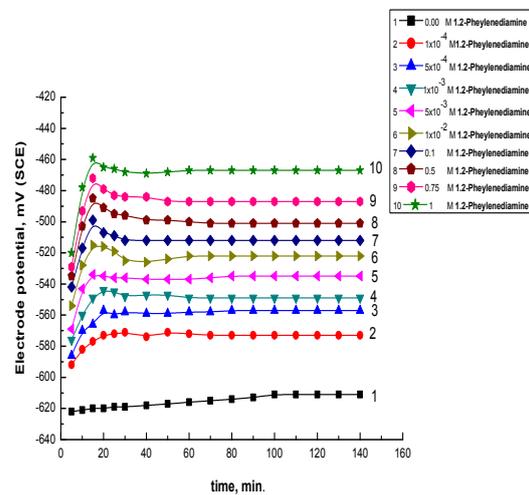


Fig. 8 (B) Variation of the open circuit potential,  $E$ , of the steel electrode with time in 0.5 M citric acid + 0.1 M NaCl in presence of increasing additions of 1,2-Phenylene diamine

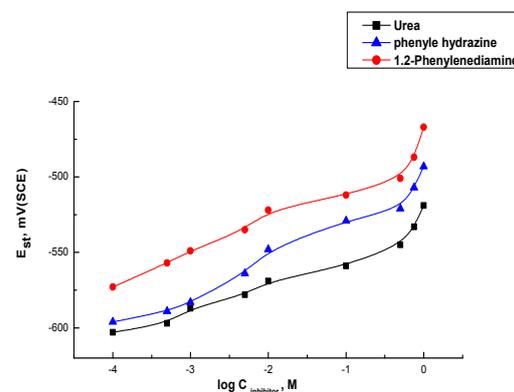
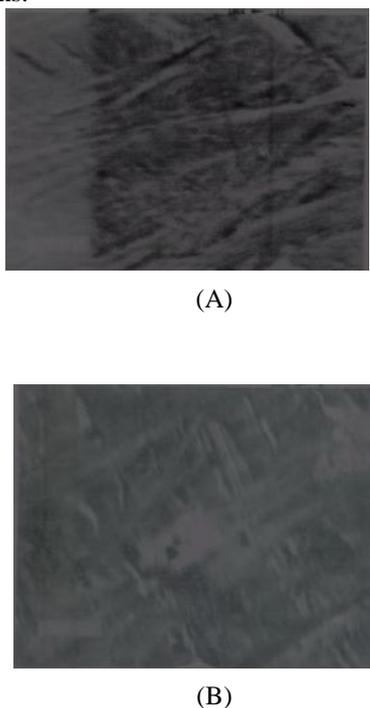


Fig. 9. Variation of the steady state potential,  $E_{st}$ , of steel electrode in 0.5 M citric acid + 0.1M NaCl in presence of studied inhibitors.

film destruction and initiation of pitting corrosion in presence of the inhibiting compounds

in concentrations below  $1 \times 10^{-3}$  M. When the concentration of these compounds reaches  $1 \times 10^{-2}$  M, oxide film repair and thickening predominates over oxide film destruction and passivation of steel surface takes place. Referring to the S-shaped curves present in Fig. 9, it is assumed that whatever the actual inhibiting action of each of the present additive compounds, they are all first adsorbed on the active sites of the oxide film covered steel surface in competition with  $\text{Cl}^-$  ions [32, 37–40]. When their concentration exceeds a threshold value, passivation of the surface is completed.

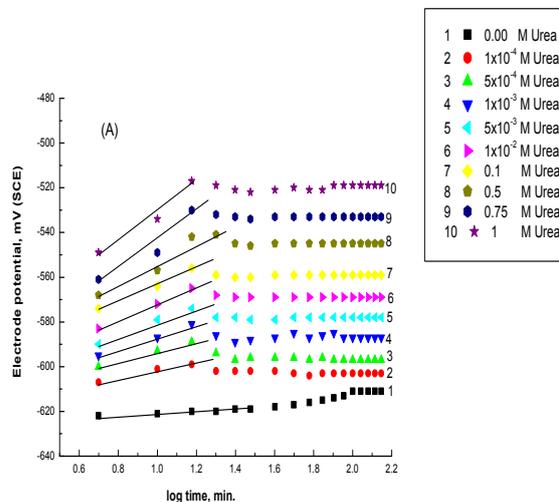
Fig. 10 (A and B) represents SEM micrographs for the surface of the steel electrodes attacked in solutions of 0.5M citric acid + 0.1M NaCl in presence of 1M of urea and 1,2-phenylhydrazine, respectively, as examples of the other inhibiting additives. Inspection of these micrographs shows that urea and 1,2-phenylhydrazine compounds act as good inhibitors for pitting corrosion of steel by  $\text{Cl}^-$  ions. The number and size of the pits formed are remarkably decreased relative to that observed in inhibitor free solutions, Fig. 2(B). There are no large corroded areas as those observed in inhibitors free solutions.



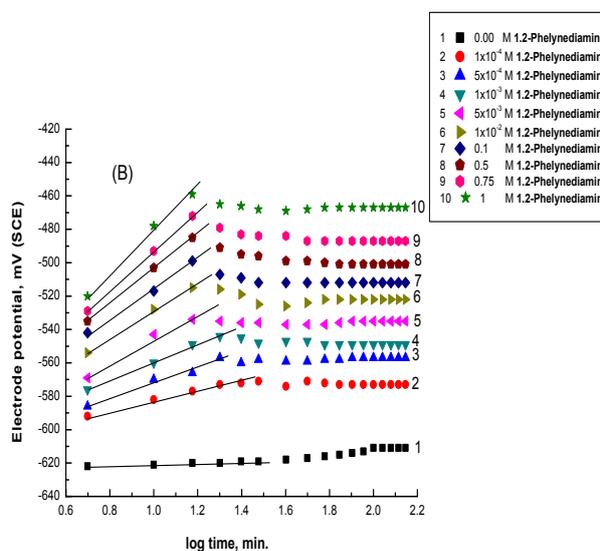
**Fig. 10.** SEM micrographs of steel electrode surfaces immersed for a period of 2 h in 0.5M citric acid + 0.1M NaCl in presence of (A) 1M urea and (B) 1M 1,2-phenylenediamine, respectively.

The curves in Fig. 11(A and B) represent the variation of the open-circuit potential, E, of the steel electrode with the logarithm of the immersion time, t, in naturally aerated 0.5 M citric acid solution containing 0.1 M  $\text{Cl}^-$  ions, upon the addition of

increasing concentrations of urea and 1,2-phenylenediamine compounds, respectively. Similar curves are also obtained in presence of phenylhydrazine compound as pitting corrosion inhibitors (curves not shown here).



**Fig. 11(A)** Variation of the open circuit potential, E, of the steel electrode with logarithm of immersion time in 0.5 M citric acid + 0.1 M NaCl in presence of increasing additions of Urea.



**Fig. 11(B)** Variation of the open circuit potential, E, of the steel electrode with logarithm of immersion time in 0.5 M citric acid + 0.1 M NaCl in presence of increasing additions of 1,2-Phenylenediamine.

Inspection of the curves present in Fig. 11(A and B) and the like reveals that, in all solution concentrations studied, E varies with log t until reaching the steady-state potentials according to the relation:

$$E = a_3 + b_3 \log t \quad (7)$$

where  $a_3$  and  $b_3$  are constants. Following the attainment of the steady potentials, two types of

behaviors could be recognized. Thus, in presence of low concentrations of the additive anions, the open-circuit potentials drop into the negative direction to reach new steady-state values which become less active the higher the concentration of the present inhibitors. When the concentration of the additives reaches  $1 \times 10^{-2}$  M or more, the potentials move into the positive direction to reach steady-state values which are also more noble the higher the additives concentration. The slope  $b_3$  of the straight line portion of the  $E-\log t$  curves is slightly increased with increasing the inhibitor concentration indicating oxide film growth rather than film destruction.

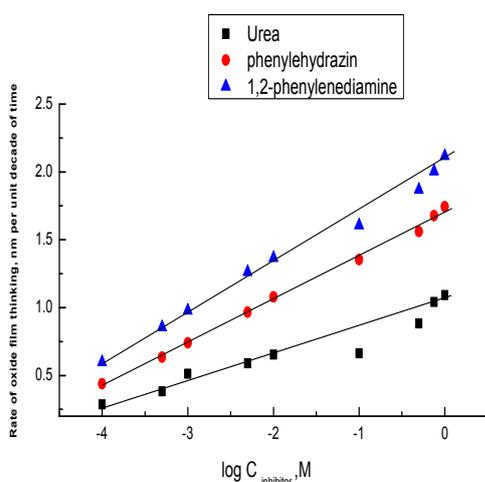


Fig. 12. Variation in the rate of oxide film thickening,  $\deltā$ , of the steel electrode in 0.5 M citric acid + 0.1M NaCl with the logarithm of the inhibitors concentrations.

From the slopes of the  $E-\log t$  curves in Fig. 11(A and B) and the like, the rate of oxide film thickening,  $\deltā$ , is calculated. In Fig. 12, the variation of the rate of oxide film thickening with the logarithm of the molar concentration of the added inhibitors is depicted. As can be seen, the rate of the oxide film thickening changes linearly with the logarithm of the molar concentration of the inhibitors,  $C_{\text{inh}}$ , according to: Rate of oxide film thickening =  $k + n \log C_{\text{inh}}$  (8) where  $k$  and  $n$  are constants given in Table 2. The constant  $k$  represents the rate of oxide film thickening (nm/unit decade of time) in presence of 1 M inhibitors. The slope  $n$  increases with increasing the concentration of organic additives. From the values of the constants  $k$  and  $n$  of Eq. (8), Table 2, the efficiency of the studied compounds as corrosion inhibitors of steel decreases in the order: (strong) 1,2-phenylenediamine > phenylhydrazin > urea (weak).

Table 2

The values of the constants  $k$  and  $n$ .

Inhibitor	K(nm/unit decade of time)	n
Urea	0.237	0.999
phenylhydrazin	0.275	1.701
1,2-phenylenediamine	0.441	2.042

#### IV. Summary and conclusions

From measurements of the open-circuit potential of the steel electrode in naturally aerated citric acid solutions devoid of- and containing increasing concentration of  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  as aggressive agents and 1,2-phenylenediamine, phenylhydrazin and urea as inhibitors, the following conclusions could be drawn:

- (i) The rate of oxide film thickening in citric acid solutions devoid of- and containing  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  ions follows a direct logarithmic law as evident from the linear relationships between the open-circuit potential and the logarithm of immersion time.
- (ii) Threshold concentrations of both  $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  anions decrease the rate of oxide film thickening and finally cause the destruction of passivity and initiation of visible pits.
- (iii) urea, phenylhydrazin and 1,2-phenylenediamine, compounds inhibit the pitting corrosion of steel by  $\text{Cl}^-$  ions. The rate of oxide film healing and thickening in presence of these compounds increases with their concentrations and varies linearly with the logarithm of the inhibitor concentrations. The efficiency of these anions as pitting corrosion inhibitors decreases in the order: (strong) 1,2-phenylenediamine > phenylhydrazin > urea (weak).

#### References

- [1.] Gardner G.I, Nathan C. C. Ed, (2000), "Corrosion inhibitors", NACE, p.156.
- [2.] Abd El Rehim S.S, Ibrahim M.A.M and Khalid K.F,(2001), The Inhibition of 4 - (2'-amino-5' Methylphenylazo) anti pyrine on corrosion of mild steel in HCl solution. Material Chemistry and Physics, 70, p.268.
- [3.] Ogunleye I. O., Adeyemi G. J and Oyegoke A.O.V. Effect of grape fruit juice on the corrosion behaviour of mild steel in acidic medium ., Am. J. Sci. Res., 2011, 2(4): 611-615.
- [4.] Reinhard G and Rammet U 1985 in Proceedings 6th European symposium on corrosion inhibitors (Ferrara: Ann. University)p. 831.
- [5.] Abd El-Rehim S S, Ibrahim M A M and Khaled K F 1999 J. Appl. Electrochem. 29 593.

- [6.] Quraishi M A and Jamal D 2002 J. Appl. Electrochem. **32** 425
- [7.] EmregulKaan C, KurtaranRaif and AtakolOrhan 2003 Corros. Sci. **45** 2803.
- [8.] Khaled F, Babic-Samardzija K and Hackerman N 2004 J. Appl. Electrochem. **34** 697.
- [9.] Wang Hui-Long, Liu Rui-Bin and XinJian 2004 Corros. Sci. **46** 2455.
- [10.] Bentiss F, Lebrini M and Lagrenee M 2005 Corros. Sci. **47** 2915.
- [11.] ZorSibel, Dogan Pinar and YaziciBirgul 2005 Corros. Rev. **23**217
- [12.] Quraishi M A, Jamal D and Singh R N 2002 Corrosion **58** 201.
- [13.] Popova A, Christov M, Raicheva S and Sokolova E 2004 Corros. Sci. **46** 1333.
- [14.] Vishwanatham S and Anil Kumar 2005 Corros. Rev. **23** 181.
- [15.] Mora-Mendoza J L, Chacon-Nava J G, Zavala-Olivares G, Gonzalez-Nunez M A and TurgooseS, 2002 Corros. Eng. **58** 608.
- [16.] S.M. Abd El-Haleem, A. Diab, AzaaAbd El-Megeed and M. Elgharabawy., *IJMTER*, **2** (8)(2015) 188.
- [17.] S.M. Abd El Haleam, E.E. Abd El Aal, S. Abd El Wanees, A. Diab, in: Taiba International Chemistry Conference, Al Madinah, Saudi Arabia, March 23–25,2009, p. 272.
- [18.] J.M. Abd El Kader, A.M. Shams El Din, Film thickening on nickel in aqueous solutions in relation to anions type and concentration, *British Corrosion Journal* **14** (1979) 40–45.
- [19.] E.E. Abd El Aal, S.M. Abd El Haleem, Kinetics of oxide film growth and
- [28.] N. Cabrera, N.F. Mott, Theory of the oxidation of metals, *Reports on Progress in Physics* **12** (1948) 163–184.
- [29.] H.H. Uhlig, *Corrosion and Corrosion Control*, J.W. & Sons Inc., N.Y., London, 1971. 189.
- [30.] E.J.W. Verwey, Electrolytic conduction of a solid insulator at high fields the formation of the anodic oxide film on aluminium, *Physica***2** (1935) 1059–1063.
- [31.] A. Guntherschulze, H. Betz, Die Bewegung der Ionen in Gittern von Isolatoren bei extremen elektrischen Feldstärken, *Zeitschrift für Physik***92** (1934) 367–374.
- [32.] G.T. Burstein, A.J. Davenport, The current–time relationship during anodic oxide film growth under high electric field, *Journal of the Electrochemical Society* **136** (1989) 936–941.
- [33.] C.Y. Chao, F. Liu, D.D. Macdonald, Point defect model for anodic passive films, destruction on iron surface in carbonate solutions, *Corrosion Engineering Science and Technology* **43** (2008) 219–224.
- [20.] C.M.A. Brett, I.A.R. Gomes, J.P.S. Martins, The electrochemical behaviour and corrosion of aluminium in chloride media, the effect of inhibitor anions, *Corrosion Science* **36** (1994) 915–923.
- [21.] H.A. El Shayeb, F.M. Abd El Wahab, E.A. El Meguid, Electrochemical behavior of molybdenum electrodes in various aqueous and buffered solutions and their use in titration, *British Corrosion Journal* **36** (2001) 215–220.
- [22.] E.E. Abd El Aal, Oxide film formation on zinc in borate solutions under open circuit, *Corrosion Science* **50** (2008) 41–46.
- [23.] G.T. Burstein, R.J. Cinderey, Evolution of the corrosion potential of passivating aluminium surfaces, *Corrosion Science* **33** (1992) 475–492.
- [24.] G.T. Burstein, R.M. Organ, Repassivation and pitting of freshly generated aluminium surfaces in acidic nitrate solution, *Corrosion Science* **47**(2005)2932–2955.
- [25.] F.P. Fehlner, N.F. Mott, Cabrera–Mott mechanism for oxidation of metals, *Oxidation of Metals* **2** (1) (1970) 59–99.
- [26.] D.J. Young, M.J. Dignam, “Logarithmic” kinetics in thin film tarnishing, *Oxidation of Metals* **5** (5) (1972) 241–249.
- [27.] K. Shimizu, K. Kobayashi, G.E. Thompson, G.C. Wood, Contribution to the paper on evolution of the corrosion potential of repassivating aluminium surfaces by G.T. Burstein and R.J. Cinderey, *Corrosion Science* **34** (1993) 701–704. *Journal of the Electrochemical Society* **128** (1981) 1187–1194.
- [34.] N. Sato, M. Cohen, The Kinetics of anodic oxidation of iron in neutral solution, *Journal of the Electrochemical Society* **111** (1964) 519–536.
- [35.] K.J. Vetter, in: H. Fisher, K. Hanfe, W. Wederholt (Eds.), *Passivierende Filme und Deckschichten*, Springer Verlag, Berlin, 1956, p. 72.
- [36.] J.M. Abd El Kader, A.A. El Warraky, A.M. Abd El Aziz, Corrosion inhibition of mild steel by sodium tungstate in neutral solution. Part 1: Behaviour in distilled water, *British Corrosion Journal* **33** (1998) 139–144.
- [37.] A.M. Shams El Din, S.M. Abd El Haleem, Variation of the potential of the zinc electrode in relation to the concentration of the aggressive anions, *Werkstoff und Korrosion***25** (1974) 571–577.

- [38.] S.M. Abd El Haleem, Initiation and inhibition of pitting corrosion in alkali solutions under potentiostatic polarization conditions, *Werkstoffe u. Korrosion***30** (1979) 631–637.
- [39.] M.A. Deyab, S.S. Abd El Rehim, Inhibitory effect of tungstate, molybdate and nitrite ions on the carbon steel pitting corrosion in alkaline formation water containing  $\text{Cl}^-$  ion, *Electrochimica Acta***53** (2007) 1754–1760.
- [40.] Z.F. Foroulis, M.J. Thubrikar, Contribution to the study of the critical pitting potential of oxide covered aluminum in aqueous chloride solutions, *Werkstoffe u. Korrosion***26** (1975) 350–355.