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The effect of phosphate corrosion inhibitor on steel in synthetic concrete solutions

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Abstract. The study of the corrosion inhibition of armatures made of steel conceived for reinforced concrete by sodium phosphate is the aim object of our experimental tests. Gravimetric and electrochemical measurements were carried in three different Mediums contaminated by chlorides (3% NaCl) with addition of increasing concentrations of sodium phosphate. Inhibitory efficiency reached 80% at an optimal concentration of $7{,}5 \times 10^{-3}$M, the results obtained using the gravimetric measurements are in good agreement with those obtained by electrochemical methods. However, the monitoring of the pH evolution after 24h shows in the three studied environments, that the pH decreases slightly at 24 hours from the initial pH at t_0, due to the presence of corrosion products which change the state of the final solution. Also, scanning electron microscopy revealed the existence of layers of apatite on the metal surface previously treated with the sodium phosphate which confirms the formation of a protective film around the surface of the metal.

Keywords: concrete;corrosion; efficiency; inhibitory; phosphate.

1. Introduction

Reinforced concrete is the widely used building material in the world because of its advantages like: comfort, aesthetics, flexibility, stability, strength and durability. The deterioration mechanism which affects the reinforced concrete and requires the largest maintenance cost is the corrosion of steel reinforcement. With good reinforced concrete quality, steel corrosion is unlikely, even in the presence of sufficient moisture and oxygen, this is due to the formation of a protective film of oxides (the passive film) in the highly alkaline environment (Elsenen 2002). However, this passive film may deteriorate and thus corrosion by carbonation is triggered due to the penetration of carbon dioxide (CO_2) in the concrete, then, the alkalinity of the environment decrease; or by the presence of high concentrations of aggressive ions which are mainly chlorides (Andrade *et al*. 2011).

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The incorporation of corrosion inhibitors in concrete (Ormellese *et al*. 2005). is among the methods of fight against corrosion of steel bars concrete. This is a new approach to control corrosion in reinforced concrete structures. Corrosion inhibitors have shown remarkable efficiency in the oil industry, underground pipes (Boummersbach 2005), storage areas, cooling chambers, etc. These are organic or inorganic chemicals products that are added to the mixing water or ground fresh concrete or by impregnating used on hardened concrete (Batis *et al*. 2001), in order to reduce or completely stop corrosion (Virmanj *et al.* 2008); they have proven over these past two decades a remarkable effectiveness against corrosion of reinforcement concrete Cafferty (2010). Sodium nitrite was used among the first corrosion inhibitors of steel (Gonzalez 1998). In 1958, the Soviet Union, used sodium nitrite in the products of autoclave and have innovated the use of $Ca(NO_2)_2$ as a strategy for protection against corrosion caused by salt icing. Japan and the United States used also $Ca(NO_2)_2$ during the 1970s (Soylev 2006). The first patent was granted in 1977 to a company for commercial application of inhibitors based of nitrites (DE Rinco 2002).

2. State of the art

If we examine the bibliography relating to the corrosion inhibition of iron or steels immersed in sea water or solutions of sodium chloride with inorganic compounds, we found that chromates and nitrites used separately or in binary mixtures are among the most effective. However, the concentrations required are very high (the order of several grams per liter), which severely limits their ability to use because of their recognized degree of toxicity (Duprat *et al*. 1983). This problem incited researchers to found other inhibitor products without altering the environment.

Research showed that sodium phosphate (Na_3PO_4) prevents pitting corrosion of steel in simulated pore solutions in concrete if its concentration is higher than chloride's (Dhouibi *et al.* 2003). The inhibitory action of phosphates or polyphosphates is also permissible in the case of the fight against corrosion of iron or steel in neutral aerated, the concentrations required are much lower than the previous (Duprat *et al.* 1983). However, its effectiveness is partially lost if the compound is added directly into the concrete (Dhouibi *et al*. 2003) .

Interest has been taken through several searches for coating steel by phosphatation process before its introduction into the concrete (Simescu 2002), but these methods are based on the immersion of steel in phosphoric acid solutions which can alter the properties of concrete.

Further research were based on the pretreatment of steel by inhibiting solution of sodium phosphate at 0.5 M at defined immersion times 2h and 72h (Etteyeb *et al*. 2006), the inhibition efficiency was then confirmed; the test results clearly showed that pretreatment offer high inhibitory properties as a consequence of the formation of a protective layer on the metal surface, which prevents access of aggressive corrosion. The stability of the passive layer seems to depend on the time of immersion in the phosphate inhibitory solution (Etteyeb *et al*. 2007).

The literature presents several simulation studies in laboratory representative of steel immersed in an electrolytic medium where solutions of saturated calcium hydroxide were used (Saremi 2002, Blanco *et al.* 2006) to simulate the medium present in the pores of the concrete; but the solutions into the pores of concrete saturated with calcium hydroxide, $Ca(OH)_2$, also contain differ ions depending on the type of cement (Moragues *et al*. 1987, Page *et al.* 1983). The major ionic species include cations such as Ca^{2+}, Na^{+}, K^{+} and anions such OH^- and SO_4^{2-}. In addition, potassium and sodium ions result from alkali metal oxides, such as Na_2O and K_2O that exist in the portland cement and sulphate ions due to the addition of gypsum for cement production, or by contaminated aggregates, or the mixing water (Neville 2005).

For our study, we opted for an experimental program including corrosion tests of steel in solutions simulating several synthetic concrete mediums. The experimental tests were conducted in three different environments: the first simulates the marine environment of the Mediterranean, it contains 3% NaCl (Paradis *et al.* 2006, Huet 2005), The second medium is the simulated concrete pore environment containing $Ca(OH)_2$ to saturation (AbdelAala *et al.* 2009, Dhouibi *et al.* 2003, Dillard *et al.* 1991) this is the first approach to the study of corrosion of reinforcement in concrete, it begins with the simulation of concrete mid pores of the saturated calcium hydroxide (Luo 2006, Vézina 1997). The third environment of our study is the synthetic medium concrete which approach the alkaline environment of concrete (Ghods *et al.* 2009, Mammoliti *et al.* 1996).

The aim of this experimental study is to test by gravimetric and electrochemical efficiency of sodium phosphate in the inhibition of steel corrosion as a function of the addition of different concentrations of inhibitor in solutions simulating several synthetic concrete environments contaminated by chlorides. Monitoring the evolution of the pH solutions at initial time "*t*" and after 24 hours was carried out in the three different environments in gravimetric study.

3. Methods and measures

3.1 Gravimetric measurements

Gravimetric measurements based on the mass loss tests give us a direct estimate of the corrosion rate of steel immersed in the electrolyte solution in the presence of aggressive agents which are in this case, the chloride ions. Solutions of sodium phosphate are prepared by adding a specific concentration to the considered medium; after 10 mn of stirring, the solution is ready.

The corrosion rate is determined after 24 hours of immersion at a constant temperature 25°C. It is calculated by the formula 1

$$V = \frac{\Delta M}{S.t} \qquad (\mathrm{mg/cm^2.h}) \qquad (1)$$

$$\Delta M = M_1 - M_2$$

Where: ΔM, represents the difference between the initial mass M_1 and the final mass M_2 after a time "t" equal to 24h.

S, is the surface of the metal exposed to the solution of study.

This value of the corrosion rate is the average of three tests under the same conditions for each concentration. The value of the inhibition efficiency is given by the formula 2

$$EI_G(\%) = \frac{V - V_{inhib}}{V}.100 \qquad (2)$$

where, V and V_{inhib} represents speeds of corrosion in absence and in presence of inhibitor respectively.

3.2 Electrochemical Measurements

Electrochemical techniques are the more comprehensive study since it based on the phenomenon of corrosion and electrochemical process. The quantitative aspect of these techniques (polarization curves, electrochemical impedance spectroscopy) allows access to reaction rates and values of the physical parameters describing the state of the system (Laamari *et al*. 2010).

Electrochemical tests were conducted in a Pyrex cell equipped with a conventional assembly with three electrodes connected to a potentiostat Galvanostat attached at a software EC-Lab.

3.2.1 Open circuit potential OCP

The values of the open circuit potential (noted Ecorr) were measured and plotted with reference to a saturated calomel electrode, a platinum electrode as an auxiliary electrode and a working electrode with a surface area, S = 1.13 cm^2. All tests were performed at open circuit potential after 3 hours of immersion in the corrosive electrolyte solution (Alexandre *et al*. 2011).

3.2.2 Polarization curves

The polarization curves, intensity - potential of the metal/solution (log(I) = f(E)) are obtained by potentiodynamic mode; the potential applied to the sample varied continuously with a scan rate speed of 0.1 mV / s from -100 to 1000 mV$_{VS}$.
The inhibitory efficiency is expressed by the formula 3

$$EI_i(\%) = \frac{I_{0corr} - V_{corr}}{I_{0corr}}.100 \qquad (3)$$

I_{corr} and I_{0corr} designed respectively corrosion courant densities in presence and absence of inhibitors.

3.2.3Electrochemical impedance spectroscopy EIS

Electrochemical impedance diagrams: Niquist diagrams, Bode impedance spectra and phase angles, were plotted for different environments corrosion potential by imposing a variable frequency between 0.05 Hz and 100 kHz with sinusoidal voltage amplitude of 10mV.

In the field of corrosion, EIS allows precise determination of the corrosion rate even in the case where the metal is coated with a protective layer. The EIS also allows the evaluation of the inhibition rate (Lebrini, 2005); the inhibition efficiency is determined by the formula 4:

$$EI_R(\%) = \frac{R_t - R_{t0}}{I_t}.100 \qquad (4)$$

Where R_t and R_{t0} represent respectively the charge transfer resistance in presence and absence of inhibitors.

3.3 Analytical measurements

3.3.1 Scanning electron microscopy SEM

The steel surface morphology previously immersed in a solution of Na_3PO_4 at optimal concentration for 7 days was analyzed in the three environments studied by SEM, while comparing with steels immersed in the corrosive solution without inhibitors.

3.3.2 X-ray diffraction XRD

XRD tests were conducted on steel previously rinsed in the three environments studied in the absence and presence of inhibitor: Na_3PO_4

4. Experimental conditions

4.1 Studied mediums

Gravimetric measurements, electrochemical and analytical procedures were carried out in three different environments at temperature T = 25° C (Benali et al 2007, Larabi et al 2005) according to the literature reviews:

- Medium 1: Distilled water + 3% NaCl
- Medium 2: Distilled water + 3% NaCl + $Ca(OH)_2$ at saturation[2g/l].
- Medium 3: Distilled water + 3% NaCl + $Ca(OH)_2$ at saturation [2g/l].+ KOH [0,4g/l].+ NaOH [0,56g/l].+ $CaSO_4 2H_2O$ [0,27g/l]. (Ghods *et al*. 2009).

4.2 Choice of material

We conducted weight loss tests on previously machined steel in the form of circular pieces with Ø 27 ± 2 mm and 2 ± 0.2 mm of thickness; whose composition is shown in Table 1. These parts are subjected to polishing at a speed of 400 t / m, with a decreasing particle size abrasive paper up to 1000 grade successively. Then rinsed in distilled water, degreased with acetone and dried using an electric dryer before being introduced for testing mass loss (Benali *et al*. 2007). For electrochemical measurements, tests were performed on the same type of steel with a diameter equal to 12 mm.

5. Results and discussion

5.1 Gravimetric measurements

Evolution of corrosion speeds, inhibitory efficiencies and pH in accordance with inhibitor concentrations for each medium is shown in Fig. 1.

The results show that the corrosion rate decreases gradually according to the increase of the inhibitor concentration in the three study Mediums, which converges with the results obtained in the literature in spite of the difference between studied environments and the steel used (Larabi et al, 2004).

According to Fig. 1, it is found that the corrosion rate decreases to attain an optimal concentration which is $7,5 \times 10^{-3}$M; from this point, the corrosion rate increases. At this optimum of concentration, the inhibition efficiency of Sodium Phosphate in Medium1 (distilled water + 3% NaCl) reaches a value of 80%, in the simulated environment of concrete, this value is 75%, while in the synthetic medium of concrete, the value is in the order of 74%.

The inhibition efficiency is even lower in the alkaline medium than in the medium simulating the Mediterranean Sea (Medium 1). The metal is attacked by chloride ions and phosphate ions diffusion is faster to reach the surface of the steel in question. In contrast, in alkaline mediums 2 and 3, the electrolyte solution has a basic nature because of the passive film barrier that surrounds the steel, the diffusion of chloride ions is much slower and consequently leads to the destruction of the passive film (Laferrière 2006); therefore the phenomenon of corrosion occurs. The corrosion rate of the steel without inhibitor application is clearly small compared to medium 1 especially for the estimated time is 24 hours, where the inhibition of corrosion in these environments is less. pH

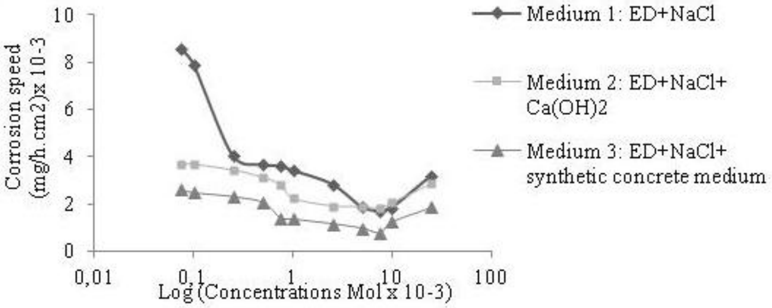
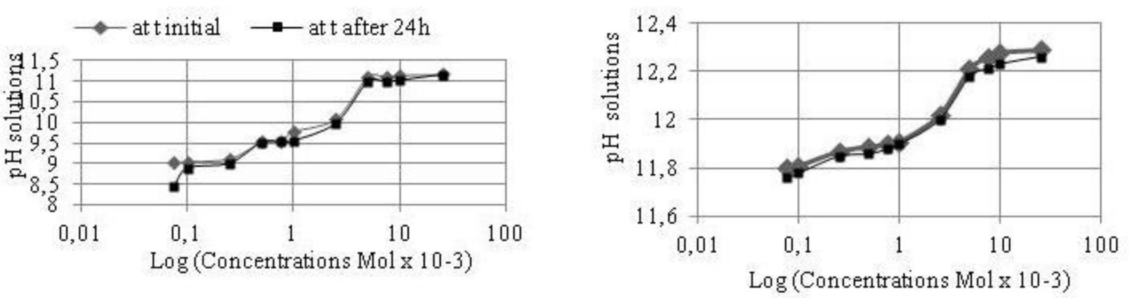
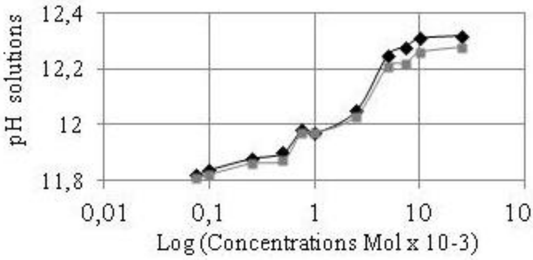


Fig. 1 Evolution of corrosion speeds according with sodium phosphate concentrations by Mass Loss



a) Medium 1 b) Medium 2



c) Medium 3

Fig. 2 Evolution of pH according with sodium phosphate concentrations

of treated solutions was taken directly at t initial and after 24 hours once calibrating the device. Referring to Fig. 2, ranges of pH in Medium 1 are inserted between 8.75 and 11.17, in Medium 2, the pH ranges are from 11.77 to 12.29, however, in Medium 3, pH of synthetic solutions is included in the interval from 11.81 to 12.32 (Mediums 2 and 3 are alkaline basic). The kinetics of corrosion affects pH of the solutions: we distinguish in the three studied environments, that the pH after 24 hours decreases compared to the initial pH, due to the presence of corrosion products that change the state of the final solution (Bensoltane 2005).

5.2 Adsorption isotherms

The relation between the amount of adsorbed species on the surface of the material and the activity of this species in the liquid or gaseous phase in contact with the material is called the

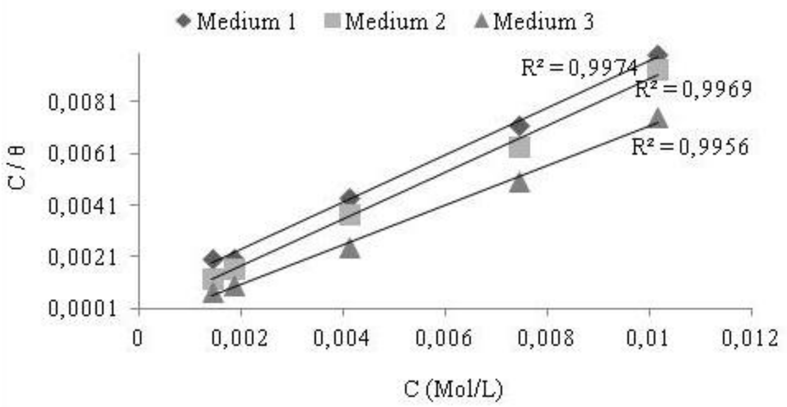


Fig. 3 Variation of C/θ depending on the concentration of Sodium phosphate

adsorption isotherm. When a corrosion inhibitor is added to a corrosive environment, its adsorption at the interface metal - solution occurs according to different adsorption isotherms, the best known is the Langmuir adsorption isotherm. Assuming that the inhibitor reacts per simple adsorption by blocking the active sites of the metal, the corrosion rate is proportional to the apparent ratio of the covered area θ by the inhibitor, and the no covered area (1-θ) (Khouikhi 2007).

The effectiveness of inhibition depends on:

- The recovery rate of the metal surface by the inhibitor molecules,
- The fixing of the inhibitor molecules at the metal surface,
- The complex stability.

The Langmuir adsorption model assumes the existence on the surface of a fixed number of sites identical energetically. Each site can adsorb only one particle. In addition, the model assumes that interactions between adsorbed particles are negligible.

The recovery rate θ for different concentrations is determined from gravimetric measurements by the Eq. (5)

$$\theta = 1 - \frac{V_{inhib}}{V} \tag{5}$$

Assuming that the adsorption of the inhibitor follows the Langmuir adsorption isotherm, the recovery rate of the metal surface is given by the relation 6

$$\theta = \frac{KC_{inhib}}{1 + KC_{inhib}} \tag{6}$$

Assuming that the adsorption of the inhibitor follows the Langmuir adsorption isotherm, the recovery rate of the metal surface is given by the following relation in Eq. (6)

K: equilibrium constant of the adsorption process

C_{inh}: the inhibitor concentration

Rearrangement of this equation gives

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{7}$$

Fig. 3, show the variation of C/θ depending on the concentration of Sodium phosphate in the three study mediums.

We can observe from Fig. 3, that the curves are linear in all the three tested mediums, which confirm, that the adsorption of corrosion inhibitor on surface steel follows the Langmuir isotherm model in the three study mediums; by forming a monolayer film which contributes to the steel corrosion inhibition.

The values of the adsorption coefficients Kads obtained by extrapolating the straight axis C/θ and the free enthalpy of adsorption ΔG_{ads} are given in Table 2.

ΔG_{ads} is determined by eq. 8

$$K_{ads} = 1/55{,}5 \exp^{(-\Delta Gads / RT)} \tag{8}$$

R: constant perfect gas
T: temperature of the electrolyte
55.5: Concentration of water in solution (mol/l)

Negative values of ΔG_{ads} indicate spontaneity of the adsorption process and the stability of the adsorbed layer on the metal surface. Usually, the values of ΔG_{ads} near to - 20 kJ. mol^{-1} or less negative, are related to the electrostatic interactions between the charged molecules and the metal charge (physical adsorption), while those near to -40 kJ.mol^{-1} or more negative confirm a charge transfer between organic molecules and the metal surface (chemisorption) (Laamari *et al.* 2010).

ΔG_{ads} value calculated for the sodium phosphate in Medium 1, which is close to - 20 kJ/mol leaves suggest that this is a mechanism based on physical adsorption, while for the other two mediums, adsorption is chemical.

5.3 Electrochemical measurements

Although mass loss tests give us a direct measure of the evolution of corrosion speeds and inhibitor effectiveness of the tested product; electrochemical measurements are needed to determine the corrosion parameters (E_{corr}, I_{corr}, R_t, etc.) and compare them with the results obtained by gravimetric method.

According to electrochemical measurements performed on the same steel used for gravimetric study immersed in a corrosive solution containing 3% NaCl at different concentrations of Na_3PO_4, we find that the optimum concentration is 7,5 × 10^{-3}M in the three mediums studied which converge with the results obtained by gravimetric method (Benali *et al.* 2007).

5.3.1 Open circuit potential OCP

From the results shown in Fig. 4 about the open circuit potential of samples exposed to three mediums, we find that E_{corr} is different in the three study environments in the absence of inhibitors. In Medium 1 which simulate the marine environment, the potential begins to decrease until it reaches a value of -600 mV, indicating the onset of corrosion phenomenon (Jamil *et al.* 2005); in Medium 2, which simulates the concrete pore solution (Hachani *et al.* 1992), there is a slight decrease in E_{corr} which stabilizes around -520 mV; while for the Environment 3 (synthetic concrete medium), E_{corr} remains almost constant at -560mV. In the literature (Jamil *et al.* 2003), the change

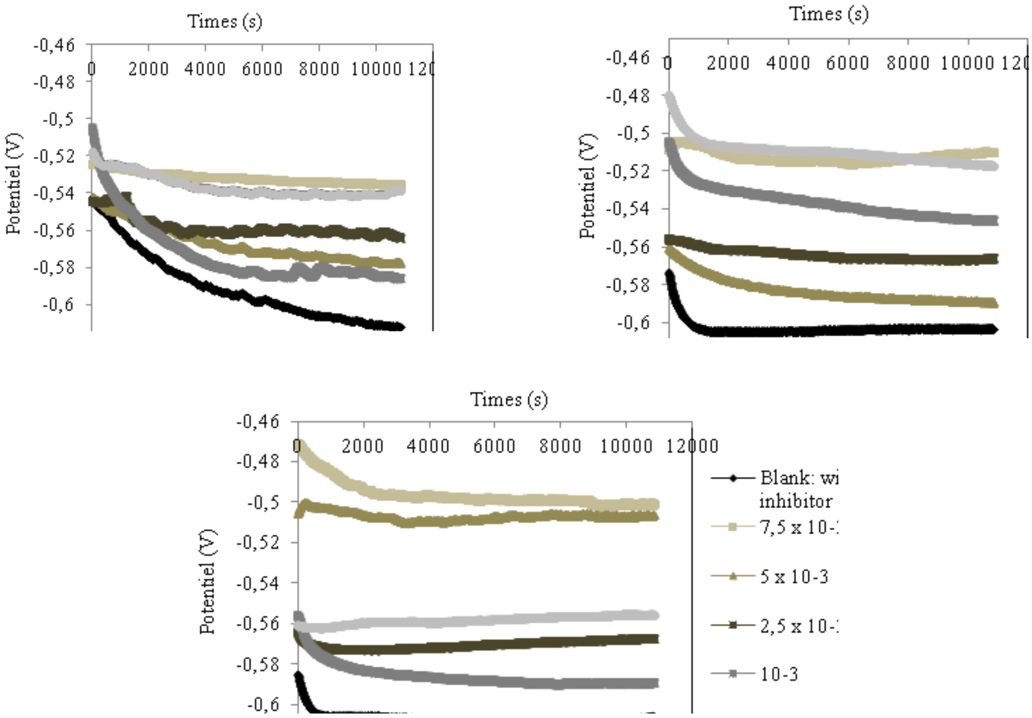


Fig. 4 OCP curves in function of Na_3PO_4 concentrations

in potential to the anode side is attributed to the spontaneous adsorption of inhibiting film on the metal surface, where the trend towards the potential values more positive as shown in Medium 2 and 3.

Fig. 4 a shows the evolution of open circuit potential of steel samples immersed in Medium 1 after addition of increasing concentrations of inhibitor. We note that the potential identified for these samples decreases significantly until reaching values of -570, -580 and -600mV for concentrations: 2,5. 10^{-3}, 10^{-3} and without inhibitors respectively. The best potential value detected is -528mV appropriate to a concentration of 7,5 x 10^{-3}M of Na_3PO_4. It can be deduced that the concentration significantly affects the evolution of the potential (Etteyeb *et al.* 2007). In Figs. 4 (b) and (c), we see that the corrosion potential decreases slightly compared to Medium 1, it's mainly due to the presence of an alkaline medium (pH > 11). We also note that the trend of the corrosion potential towards positive values is not really strong, it's definitely depend on the tests times, because, the inhibitory effect is not necessarily justified during the early hours, if we consider complex reactions that occur, taking into account the alkalinity factor of these two environments.

5.3.2 Linear polarization curves

Fig. 5 represent cathodic and anodic polarization curves of steel immersed in the three study environments contaminated by chlorides to 3% NaCl in the absence of inhibitor.

From the results of Fig. 5, we observe a decrease in the anodic and cathodic currents in the

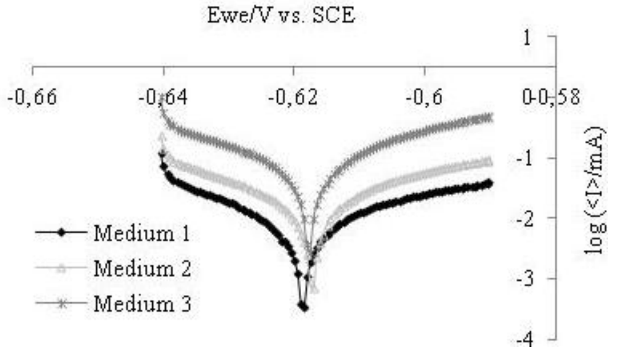
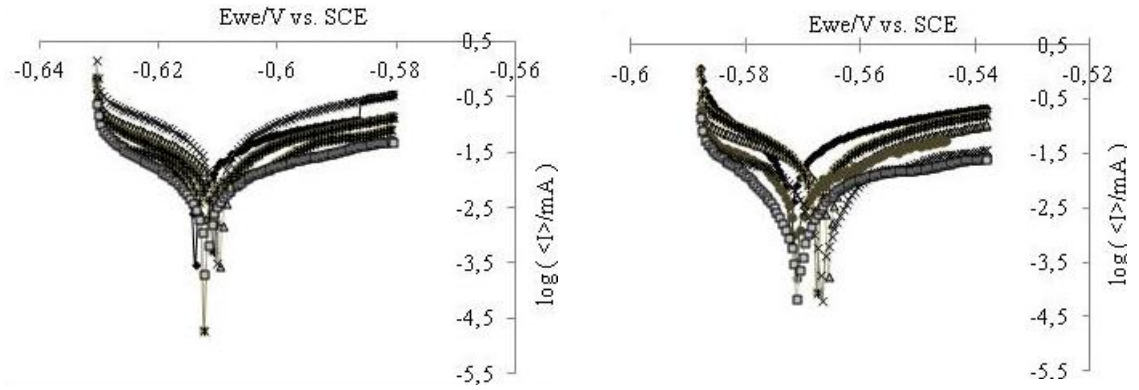
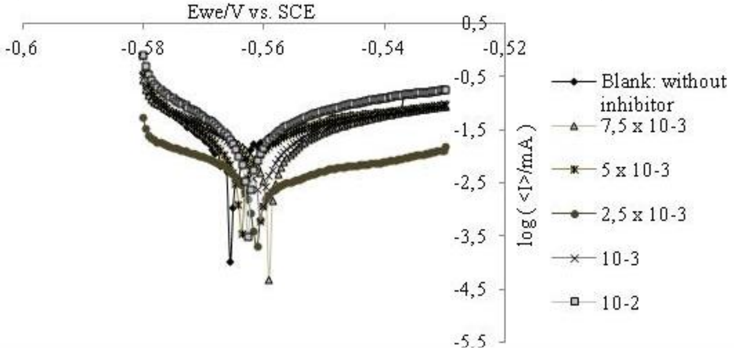


Fig. 5 Linear polarization curves in the three mediums in absence of inhibitor



a) Medium 1 b) Medium 2



c) Medium 3

Fig. 6 Linear polarization curves as function of the concentration of Na_3PO_4

environments simulating the concrete pores (Medium 2) due to the alkalinity of the solution, and therefore the presence of a passive film around steel (Dhouibi *et al.* 2003). This decrease is even more important in Medium 3, which simulates the synthetic medium of concrete, due to the presence of a significant amount of calcium hydroxide and relatively minor amounts of alkaline elements such as sodium and potassium which offer concrete high alkalinity with a pH up to 12 to 13(Virmanj *et al.* 2008).

Electrochemical parameters identified from these curves are given in Table 3.

Figs. 6 (a), (b) and (c) illustrates cathodic and anodic polarization curves of the steel immersed in the three studied mediums according to different concentrations of Na_3PO_4. The test temperature is T=25°C. Table 5 shows the values of corrosion current density (I corr), corrosion potential (Ecorr) and the corrosion rate (Corr) comparing with the reference sample without inhibitor. We find that for different concentrations added, the corrosion currents are relatively lower than for blanc samples, also for the potential, we see a slight decrease which signifies precipitation of inhibitory molecules (Won Song 2006). Moreover, Manna (2009) concluded that when the potential is low (less than 700 mV,) it generates a low corrosion current and hence this phenomenon justifies a good inhibition. Scimesciu (Simescu 2008) also confirmed that the corrosion potentials of steels treated with phosphate are more negative than those untreated and that the presence of phosphate gives the steel a character of galvanized steel.

If we compare the evolution of the corrosion rate, in Blanc solution 0.116 mmpy with addition of different concentrations; there is a remarkable reduction justifies the beneficial effect of the adding Na_3PO_4, until reaching an optimal concentration of 7,5 $\times 10^{-3}$M, further than no inhibition of the corrosion is proven.

5.3.3 Niquist Impedance diagrams

The corrosion behavior of steel immersed in Blanc solutions in the three mediums has been studied by EIS measurements at T=25°C. Niquist diagrams presented in Fig. 7 have the forms of arcs; the diameter is greater in Medium 3 indicating protection against corrosion (Dhouibi *et al.* 2006) due to the high alkalinity of the medium. While, in impedance diagram obtained from Medium 1, the semi-circle is flattened, it is due to the severe attack of the steel surface (Lafont *et al.* 2005), the corrosion products will appear on the entire surface.

The equivalent circuit used for this system is presented in Fig. 8.

Rs: resistance of the electrolyte, Rct: charge transfer resistance and Cdl: double layer capacity of the film.

The equivalent circuits representing the state of the system are as follows

R1+C1/R2/C3/R3+Q3; shown in Fig.10, where:

R1: Electrolyte Resistance (Rs), R2: charge transfer resistance (Rct)

C1: double layer film Capacity (Cdl), C3: Faradien Capacity

R3: Faradien Resistance, Q3: CPE (constant phase element)

According to the results derived from impedance curves for steel immersed in Blank solutions in the three environments studied, we find that the charge transfer resistance is higher in Medium 2 and 3 indicating protection against corrosion in the presence of the passive film, whereas the decrease of Cdl values indicate a state of passivation.

Niquist diagrams shows the existence of two spectrums, where the regression calculation demand an equivalent circuit of the type: Rs+Cdl/Rct/Cf/Rf+Q.

According to the results extrapolated from electrochemical measurements about the influence of Na_3PO_4 concentration on the global process of corrosion inhibition. The charge transfer resistance remains a key parameter to define the inhibitory efficiency of the tested product. It was found that this resistance is even greater for a concentration of 7,5 X 10^{-3}M, therefore we can deduce that this is the optimal concentration. Moreover, the double layer capacity of the film decreases with the increase in the charge transfer resistance (Benali *et al.* 2007), this phenomenon

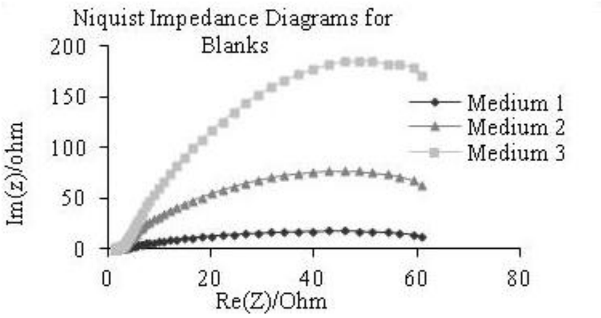


Fig. 7 Niquist impedance curves Blanks

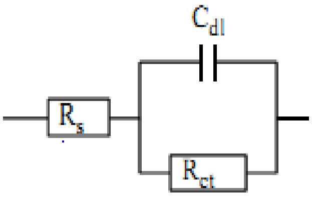
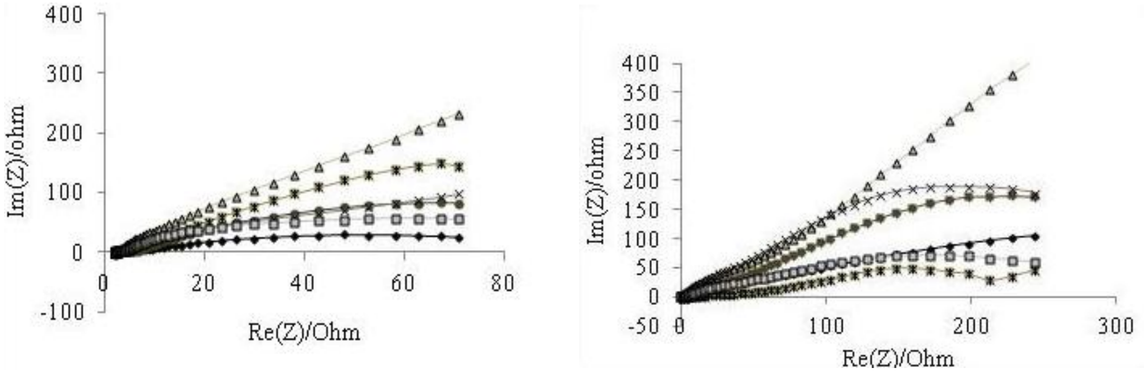
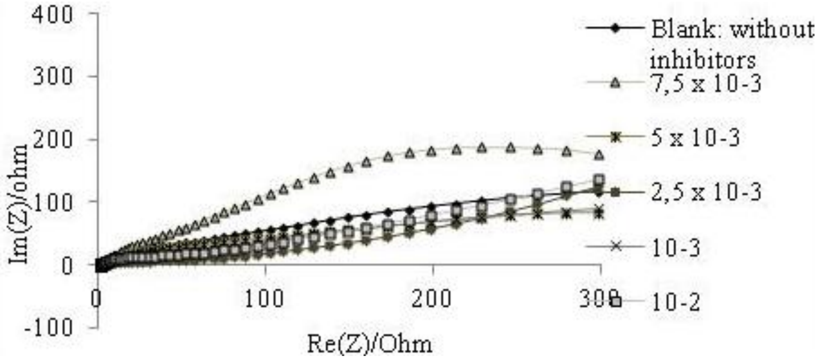


Fig. 8 Equivalent electrical circuit



a) Medium 1 b) Medium



c) Medium 3

Fig. 9 Niquist impedance diagrams depending on Na_3PO_4 Concentrations

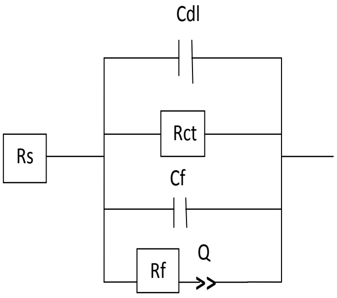


Fig. 10 Equivalent electrical circuit

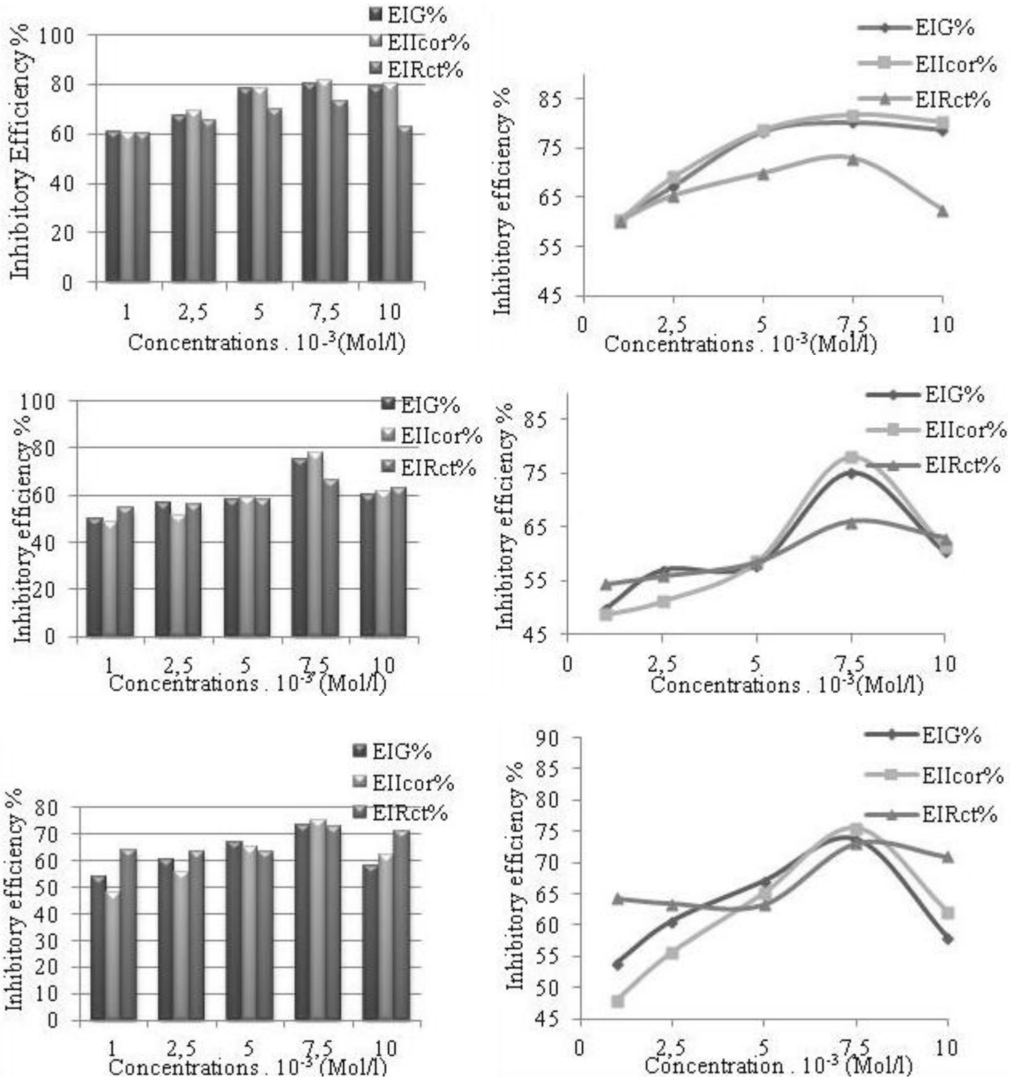


Fig. 11 Inhibitory efficiencies obtained by gravimetry, EIS and linear polarization for Na_3PO_4 in: a) Medium 1, b) Medium 2, c) Medium 3

is mainly due to the decrease of the local dielectric constant and rising of the electrical double layer thickness; thus suggesting that the molecules of the inhibitor act by adsorption on the metal /solution.

Faradien resistance Rf represents the response of the system when the disturbance frequency is much lower than the surface concentration; increases slightly the same as Rct, this resistance is associated with the stability of the film formed in the presence of inhibitor (Etteyeb *et al.* 2007).

To compare the inhibitory efficiencies obtained using the three methods examined for each inhibitor tested; we plotted histograms explaining the results shown in Table.6.

Fig.11 includes diagrams of Na_3PO_4 inhibitory efficiencies in the three study Mediums using electrochemical and gravimetric measurements.

Through diagrams related to the evolution of inhibitory efficiencies based on concentrations of Na_3PO_4 shown in Fig.11, in the three studied Mediums by electrochemical measurements: impedance spectroscopy and polarization resistance and gravimetric. It was found that the inhibitory efficiencies increase in the same direction by the three methods studied to achieve the optimum concentration which is $7.5.\ 10^{-3}$. A slight difference is observed between the diverse methods, this difference is due to the short duration of immersion for electrochemical measurements, equal to 3h and 24h for gravimetric measurements. Indeed, there's a protective film formation more important in the case of gravimetric measurements with immersion time of 24 hours. This explains the difference between the values obtained (Lebrini 2005).

5.4 Analytical measurement

5.4.1 Scanning electron microscopy SEM

Analysis by scanning electron microscopy were performed using a microscope branded "Hitachi TM-1000" on steel samples of 2.7 cm of diameter, immersed in solutions of optimal inhibitor concentrations for 7 days in the three Mediums of our study; in order to identify the nature of the precipitated products and morphology of the film formed on steel while comparing with steels immersed in the three Mediums without the addition of inhibitor “Blanks”.

Figs. 12 and 13 illustrate the results of SEM surface analysis, we find that:

- For samples immersed in a corrosive solution in absence of inhibitor, the surface was in free corrosion. Also, we note the presence of corrosion points on parts immersed in Medium 1, in the absence of inhibitors, these pieces were corroded conclusively.
- The existence of rust layers and accumulation of corrosion products on the metal surface; we show also, tearing of metal particles due to corrosion in the samples without inhibitor.
- The absence of traces of corrosion on the samples tested in solutions in the presence of
- inhibitor, in Mediums 2 and 3. We also note the presence of a thin protective layer of white products composed of ferrite and calcium hydroxide.
- Presence of scraped regions due to the polishing of parts especially in the case of addition of inhibitors. The above phenomenon indicates that the Na_3PO_4 provides better protection against corrosion, thus confirming the results obtained by electrochemical and gravimetric analyzes.
- Sodium phosphate showed a corrosion resistance of the steel in the two solutions simulating the pores of concrete by the examination of the steel surface, which was not corroded.
- SEM tests showed the existence of apatite layers on the metal surface previously treated with sodium phosphate which confirms the formation of a protective film around the surface of the metal, although this layer is not necessarily uniform, it is located in parts of the surface.

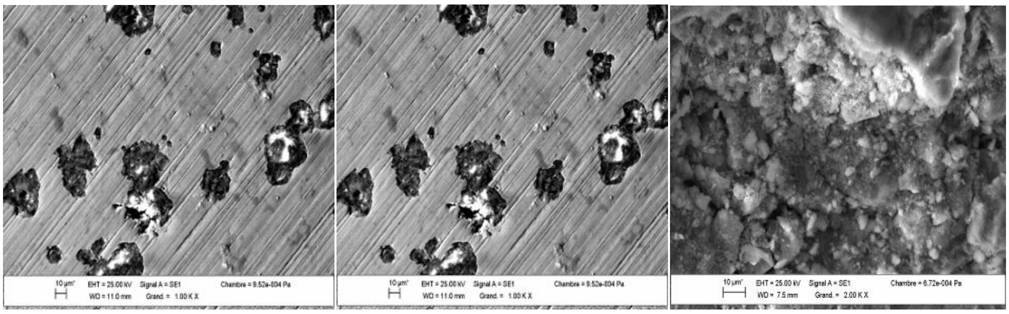


Fig. 12 SEM of steel rinsed in solutions in the absence of inhibitor for 7d

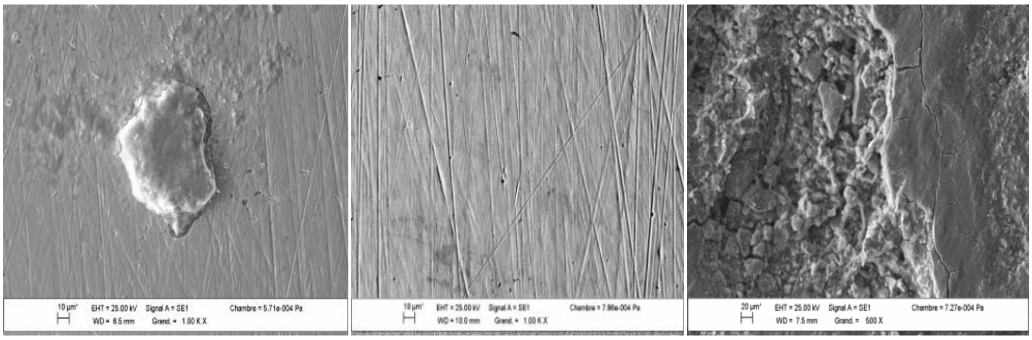


Fig. 13 SEM of steel rinsed in Na_3PO_4 Cop

6. Conclusion

Analysis of the results obtained through the electrochemical and gravimetric measurements of steel immersed in three separate study environment contaminated by chlorides (3% NaCl) with the addition of a corrosion inhibitor Na_3PO_4 allowed us to retain following conclusions:

- The inhibition efficiency increases with inhibitor concentration until it reaches a value of 80% at an optimal concentration of $7{,}5 \times 10^{-3}$M, the results obtained using the gravimetric measurements are in good agreement with those obtained by electrochemical methods.
- Kinetics of corrosion affects the pH solutions, it can be distinguished in the three studied environments, that the pH decreases slightly at 24 hours from the initial pH at t_0, due to the presence of corrosion products which change the state of the final solution. (Bensoltane 2005).
- To validate the hypothesis that the action of phosphate ions based on a mechanism action by simple adsorption at the metal surface, thus blocking the active sites, we tried to correlate the experimental results to the drawing of the isotherms adsorption. Indeed, in the three environments studied, we found that the inhibitor adsorption on the metal surface obeys to the Langmuir adsorption isotherm.
- The scanning electron microscopy revealed the existence of layers of apatite on the metal surface previously treated with the sodium phosphate which confirms the formation of a protective film around the surface of the metal, although this layer is not necessarily uniform across the surface of the metal, it is located in parts of the surface.
- Phosphates are known to inhibit the dissolution of iron and stabilizing ferrihydrites by adsorbing on goethite and other hydrated iron oxides II. (Nobel Pujol Lesueur 2004).

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