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Temperature Influence on Inhibitory Efficiency of Three Phosphate Inhibitors by Mass Loss

Latefa Sail

Abstract

The effect of temperature on steel samples immersed in concrete pore solutions contaminated by chlorides incorporating three inhibitors based on phosphate (Na_3PO_4, K_2HPO_4, and Na_2PO_3F) was studied by gravimetric measurements at several ranges: 298, 308, and 318 K. The results obtained for the use of these three products show that the inhibitory efficacy is lower at 318 K than that detected at 308 and 298 K of temperature. Also, we find that the best inhibitory efficiency at 298 K was detected for Na_2PO_3F (75.80% at 0.05 mol/l of concentration) followed by K_2HPO_4 (65.05% at $2.5\ 10^{-3}$ mol/l) and then Na_3PO_4 (61.48% at $7.5\ 10^{-3}$ mol/l).

Keywords: temperature, concrete pores, corrosion inhibitors, phosphate, gravimetric measurement efficiency

1. Introduction

Corrosion of reinforcement in concrete is one of the most dangerous pathologies that attack reinforced concrete structures; the means of protection against corrosion are varied and expensive. During this last decade, a new alternative has been adapted which is the application of corrosion inhibitors either as an adjunct to the mass of fresh concrete or by impregnation on the facing of hardened concrete. Several families of corrosion inhibitor products have been developed to prove their protective effect against steel reinforcement corrosion initiated by the penetration of chlorides through the pores of concrete. The best known are phosphates, borates, silicates and carbonates. One of the peculiarities of these ions is that their hydrolysis releases hydroxide ions which will have the effect of increasing the pH of the medium and thus passivating the steel. Moreover, in the presence of oxygen, the anions will form with the metal cation a very insoluble iron III phosphate which will clog the anodic surface and displace the cathodic reduction reaction [1].

The required concentration of passivative inhibitor, often of the order of 10^{-4} to 10^{-5} mol/l [2], it depends in fact on many factors such as temperature, pH, the presence of depassivating ions such as chlorides or reducing agents such as sulfur S_2 [3].

Temperature is one of the factors that can alter the behavior of a material in a corrosive environment. It can modify the metal-inhibitory interaction in a medium [4].

The variation of temperature affects the rate of corrosion. According to Liu and Weyer [5], an increase in temperature increases the rate of corrosion. This result was confirmed in carbonated concrete and also that subject to aggressive environments like chloride ions penetration.

The objective of this research is based on the analysis of the evolution of the inhibitory efficiencies of three phosphate inhibitors (Na_3PO_4, K_2HPO_4 and Na_2PO_3F) as a function of the temperature variation: 298, 303 and 313 K.

2. Methods and measurements

In this section, gravimetric tests were performed to characterize the influence of temperature on inhibition efficiency for the three phosphate inhibitors used in this study.

2.1 Gravimetric measurements

These measurements consist in determining the weight loss of a steel sample subjected to specified conditions of temperature and relative humidity; they are calculated on the basis of three tests to determine the average. The steel sample is polished with abrasive paper ranging from 120 up to 1000 grades using a polisher at a speed of 500 rpm, then rinsed in distilled water, dried with an electric dryer then we weigh the mass M1.

The steel samples are introduced into beakers containing 50 ml of electrolytic solution in an inclined position as shown in **Figure 1**, hermetically closed, then they are placed in a thermostatic bath while adjusting the desired temperature, after 24 h, the samples are removed from beakers then, rinsed in distilled water, degreasing is carried out with acetone and then dried with the electric dryer, after that we weigh the mass M2.

2.2 Study medium

The medium of this study is a concrete synthetic medium which simulates concrete pores contaminated by 3% of chlorides given in **Table 1**.

Figure 1.
Position of steel sample.

1 l distilled water	Ca(OH)$_2$	NaOH	KOH	CaSO$_4$ 2H$_2$O	NaCl
Wt (g/l)	2	0.4	0.56	0.27	30

Table 1.
Synthetic medium of concrete [6–8].

2.3 Steel preparation

The steel used is circular shaped with a diameter of 27 ± 1 and 2 ± 2 mm of thickness, and the procedure of gravimetric tests is detailed in [9]. The corrosion rate is determined by the following formula:

$$Cr = \Delta M/S.t \; (mg/h.cm^2) \tag{1}$$

$$\Delta M = M1 - M2 \tag{2}$$

Hence, ΔM represents the difference between the initial mass M1 and the final mass M2 after a time "t" equal to immersion time by hours. "S" is the surface of the metal exposed to the electrolytic solution.

This value of the corrosion rate is the average of three tests carried out under the same conditions for an optimal concentration at a definite time. The value of the inhibitory efficiency is given by the following formula:

$$IE \; (\%) = \frac{Cr0 - Cr}{C_{r0}}.100 \tag{3}$$

3. Tested inhibitors

This study describes the corrosion behavior of steel immersed in synthetic concrete pore solutions contaminated by chlorides for three phosphate-inhibitors (Na$_3$PO$_4$, K$_2$HPO$_4$ and Na$_2$PO$_3$F), their molecular structure is given

Sodium phosphate   Potassium Monohydrogenphosphate   Sodium monofluorophosphate
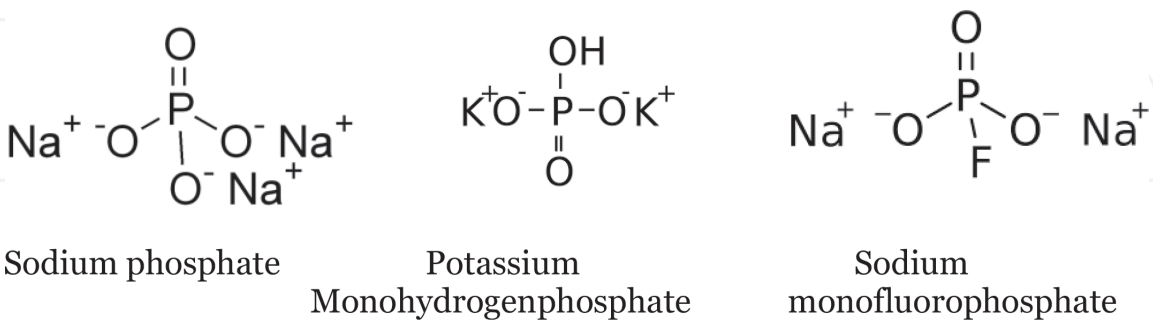
Figure 2.
Molecular structure of the three tested inhibitors.

Inhibitor	Concentration (mol/l)
Na$_3$PO$_4$	7.5×10^{-3}
K$_2$HPO$_4$	2.5×10^{-3}
Na$_2$PO$_3$F	5×10^{-2}

Table 2.
Medium concentrations.

in **Figure 2**. The optimal concentration which provides maximum efficiencies for the three products cited was extracted from a previous study [10] (see **Table 2**).

4. Results and discussions

Table 3 records the mass loss results, relating to the evolution of corrosion rates as well as the inhibitory efficiencies as a function of the temperature variation: 298, 303 and 318 K for the three inhibitors.

It can be seen from the results shown in **Table 3** that the corrosion rates decrease in the presence of the corrosion inhibitor, it reached the maximum at the optimal concentration, for the first inhibitor sodium phosphate Na_3PO_4 the maximum efficiency 69.28% was detected at a concentration of 7.5×10^{-3} mol/l at 298 K, we can see clearly that the inhibitory efficiency slightly decrease as a function of temperature increase. Likewise for K_2HPO_4, the best efficiency 67.44% was detected at 298 K for a concentration of 2.5×10^{-3} mol/l, also, the increase of temperature affects the inhibitory efficiency which decrease following temperature increasing, the same remark was recorded for Na_2PO_3F the maximal efficiency 75.8% was detected at 298 K. This phenomenon can be explained by the fact that the anodic processes (oxidation components of steel) and cathodic (proton reduction in acidic medium) are thermally activated.

This results in a current of exchange which increases the corrosion rate. Hunkeler [11] has shown in his studies that the influence of temperature on the rate of corrosion is greater than that the resistivity of the concrete.

Figure 3 shows the evolution of inhibitory efficiencies as a function of temperature variation for different concentrations of tested inhibitors.

	298 K		303 K		313 K	
C (mol/l)	Cr 10^{-3} (mg/h.cm^2)	IE %	Cr 10^{-3} (mg/h.cm^2)	IE %	Cr 10^{-3} (mg/h.cm^2)	IE %
Na_3PO_4						
0	1.4	—	2.5	—	3.1	—
5×10^{-3}	0.444	68.28	0.964	61.44	1.231	60.29
7.5×10^{-3}	0.43	69.28	0.798	68.08	1.0875	64.92
10^{-2}	0.768	45.14	1.49	40.4	1.8764	39.47
K_2HPO_4						
0	1.4	—	2.5	—	3.1	—
10^{-3}	0.4629	66.93	0.8889	64.44	1.2478	59.77
2.5×10^{-3}	0.4558	67.44	0.8737	65.04	1.1737	62.14
5×10^{-3}	0.4689	66.5	0.89126	64.34	1.251	59.45
Na_2PO_3F						
	1.4	—	2.5	—	3.1	—
2.5×10^{-2}	0.3411	75.63	0.8675	65.29	1.3976	54.91
5×10^{-2}	0.3386	75.8	0.6749	73	0.8986	71.01
7.5×10^{-2}	0.3414	75.61	0.8344	66.62	1.1842	61.8

Table 3.
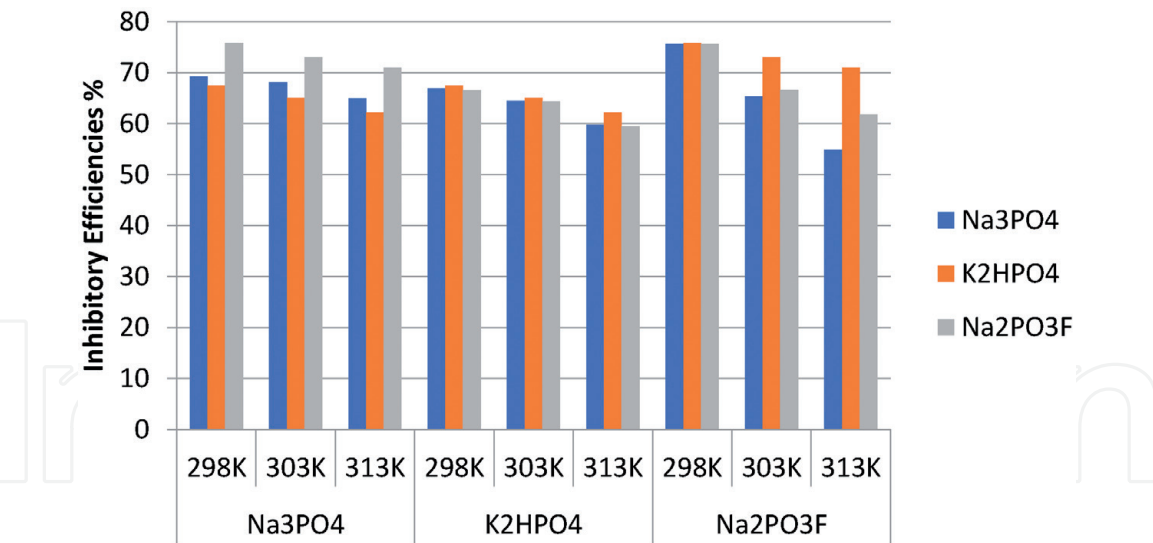*Evolution of corrosion rates and inhibitory efficiencies as a function of temperature variation.*
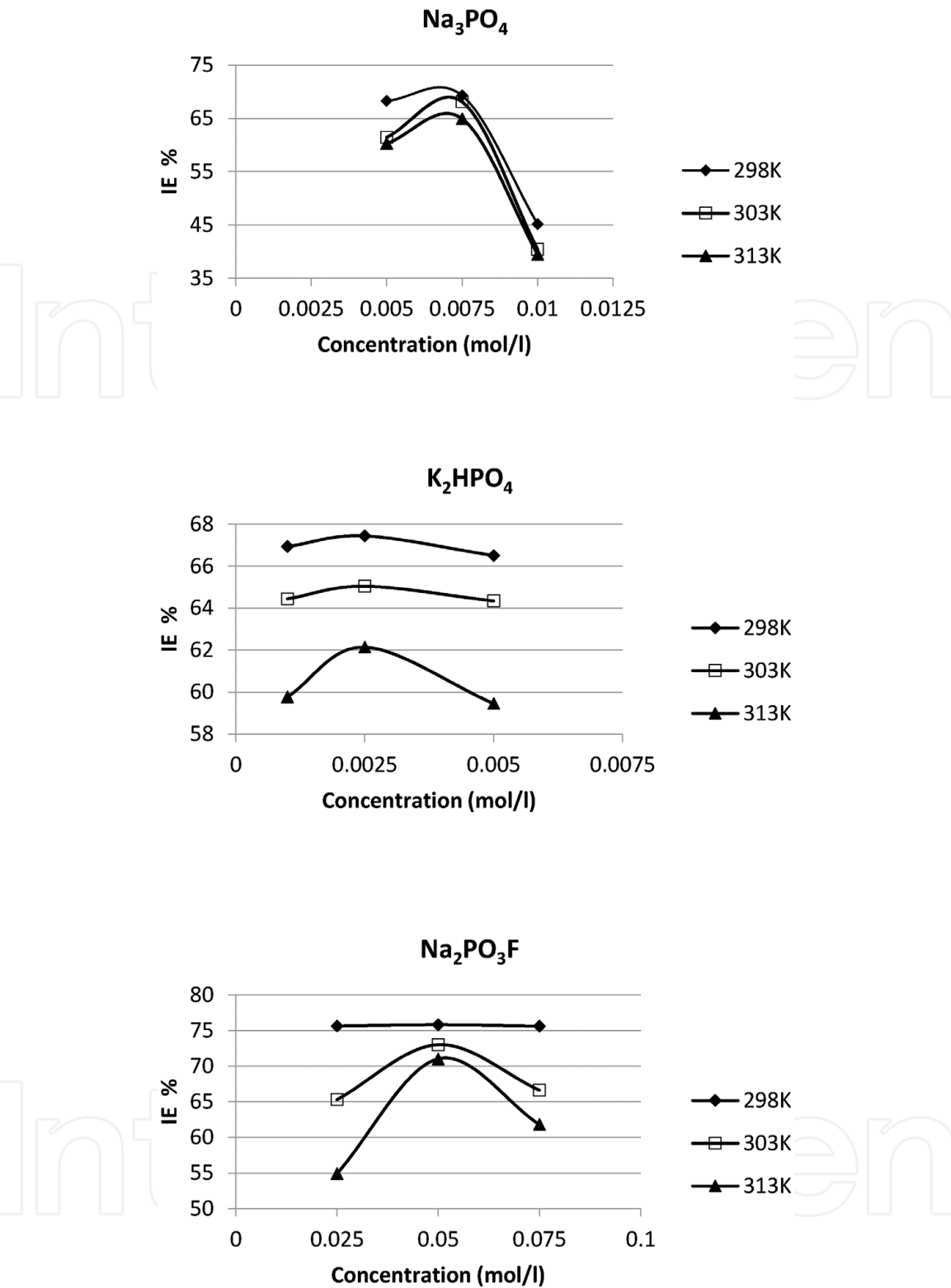
Figure 3.
Evolution of inhibitory efficiencies as a function of temperature variation for different concentrations of Na₃PO₄, K₂HPO₄ and Na₂PO₃F.

Figure 3 illustrates the influence of temperature variation on the inhibitory efficacy of the three phosphate-based inhibitors. Certainly, temperature is one of the factors that can alter the behavior of a material in a corrosive environment. It can modify the metal-inhibitory interaction in a given environment [4].

The increase in temperature causes the instability of inhibitory molecules and also reduces the inhibitory efficacies which was detected in previous researches [5].

It can be seen from **Figure 4** that inhibitory efficiencies are highest in the optimum concentration for all the studied temperature ranges, although they decrease

Figure 4.
Evolution of inhibitory efficiencies as a function of temperature variation.

slightly as a function of temperature increase. As a result, the maximum inhibitory efficacy at T 298, 303 and 318 K deduced using gravimetric measurements was confirmed by sodium monofluorophosphate (Na_2PO_3F), followed by potassium monohydrogenphosphate (K_2HPO_4) and thirdly sodium phosphate (Na_3PO_4).

These results are in good agreement with previous research that used the same inhibitory products [10].

Indeed, sodium monofluorophosphate has been the subject of several studies [12–14], and it has proven remarkable inhibitory properties especially in the case of its use in zinc phosphate baths [15–17].

The variation of the temperature influences the rate of corrosion and conse-quently the mechanism of the inhibition [18]. According to Liu and Weyer [5], an increase in temperature increases the rate of corrosion.

5. Conclusions

Direct measurements of both corrosion rates and inhibitory efficiencies as a function of inhibitor concentrations, have confirmed that sodium monofluoro-phosphate (Na_2PO_3F) offers the best corrosion protection under study conditions (temperature 298, 303 and 313 K); its inhibitory efficiency has exceeded 70% for these temperatures.

This inhibitor has been the subject of several previous studies [12, 19–22], its effec-tiveness against corrosion has been confirmed especially when used in a carbonated concrete [14, 23–26] and also than for concrete solutions contaminated by chlorides.

We can also conclude that increase of temperature affects inhibitory efficiencies, which is in good concordance with literature. For inhibitors based of phosphate, the increase of temperature has a slight influence on the inhibitory efficiency for the study temperatures, moreover, at higher temperatures, the molecular activation will be greater, which leads to an increase in corrosion rates.

Acknowledgements

Conflict of interest

My 'research areas' focus on corrosion prevention and repair by inhibitors.

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References

[1] Oly M. Contribution à l'évaluation des capacités des glycérophosphates pour la maintenance dans le béton armé, [thesis]. France: University of Toulouse; 2011

[2] Buchler M, Corrosion inhibitors for reinforced concrete, in Corrosion Reinforced Concrete Structures. In: H. Böhni. Switzerland: Formerly Swiss Federal Institute of Technology; 2005. pp. 190-214

[3] Helie M. Matériaux métalliques— Phénomènes de corrosion, Edition Ellypses. Val of Essonne: University of Evry; 2015. ISBN: 9782340004023

[4] Khenadeki A. Etude théorique et expérimentale de l'effet d'inhibition de la corrosion d'un acier au carbone par les dérivées de base de Schiff en milieu acide chlorhydrique [thesis]. Algeria: University of Tlemcen; 2013

[5] Liu T, Weyer RW. Modeling the dynamic corrosion process in chloride contaminated concrete structures. Cement and Concrete Research. 1998;**28**(3):365-379. DOI: 10.1016/S0008-8846(98)00259-2

[6] Ghods P, Isgor OB, Mcrae B, Millar T. The effect of concrete pore solution composition on the quality of passive oxide films on black steel reinforcement. Cement and Concrete Composites. 2009. DOI: 10.1016/j.cemconcomp.2008.10.0032-11

[7] Moragues A, Macias A, Andrade C. Equilibria of the chemical composition of the concrete pore solution. Part I: Comparative study of synthetic and extracted solutions. Cement and Concrete Research. 1987;**17**(2):173-182. DOI: 10.1016/0008-8846(87)90100-1

[8] Page CL, Vennesland O. Pore solution compositions and chloride binding capacity of silica fume cement paste. Materials and Structures. 1983;**16**(1):19-25. DOI: 10.1007/BF02474863.

[9] Sail L, Ghomari F, Bezzar A, Benali O. Mass loss for assessment of the inhibitory efficiency of products to basis of phosphate. Canadian Journal on Environmental, Construction and Civil Engineering. 2011;**2**(5):111-117. Availabe from: http://www.ampublisher.com/June%202011/ECCE-1106-018-Mass-loss-for-assessment-of-the-inhibitory.pdf

[10] Sail L. Etude de la performance d'inhibiteurs de corrosion à base de phosphate pour les constructions en béton armé [thesis]. Algeria: Tlemcen; 2013

[11] Hunkeler F. Grundlagen der korrosion und der potential messing baustahlbetonbauten, ASTRA Brücken unter halts for schung. Zürich: Verein Schweizer Strassen fachleute (VSS); Report No. 510; 1994

[12] Douche-Portanguen A, Prince W, Lutz T, Arliguie G. Detection or quantitative analysis of a corrosion inhibitor, the sodium monofluorophosphate, in concrete. Cement and Concrete Composites. 2005;**27**(6):679-687. DOI: 10.1016/j.cemconcomp.2004.11.002

[13] Pujol Lesueur VN. Etude du mécanisme d'action du monofluorophosphate de sodium comme inhibiteur de la corrosion des armatures métalliques dans le béton [thesis]. Paris, France: University of Pierre et Marie Curie; 2004

[14] Duprat M, Bonnel A, Dabisi F. Les monofluorophosphates de zinc et de potassium en tant qu'inhibiteurs de la corrosion d'un acier au carbone en solution de NaCl à 3%. Journal of Applied Electrochemistry. 1983;**13**:317-323

[15] Zimmermann D, Mun~oz AG, Schule JW. Formation of Zn-Ni alloys in the phosphating of Zn layers. Surface & Coatings Technology. 2005;**197**(2): 260-269. DOI: 10.1016/j.surfcoat. 2004.07.129

[16] Kashyap A. Effects of water chemistry, temperature, gaseous cavitation et phosphate inhibitors on concrete corrosion [Master]. USA: University of Virginia; 2008

[17] Simescu F. Elaboration des revtements de phosphates de zinc sur armature à béton. Etude de leur comportement à la corrosion en milieu neutre et alcalin [thesis]. France: University of Lyon; 2008

[18] Khouikhi F. Etude de l'efficacité de deux inhibiteurs de corrosion dans les milieux multiphasiques (Eau, huile et gaz) [thesis]. Boumerdes, Algeria: University of M'Hamed Bougara; 2007

[19] Soylev TA, Richardson MG. Corrosion inhibitors for steel in concrete. State-of-the-art report. Construction and Building Materials. 2008;**22**(4):609-622. DOI: 10.1016/j. conbuildmat.2006.10.013

[20] Farcas F, Chaussadent T, Fiaud C, Mabille I. Determination of the sodium monofluorophosphates in a hardened cement paste by ion chromatography. Analytica Chimica Acta. 2002;**472**(1-2):37-43. DOI: 10.1016/S0003-2670(02)00978-9

[21] Talamge JM, Biemer TA. Determination of potassium nitrate and sodium monofluorophosphate in the presence of phosphate and sulphate by high resolution ion chromaltography. Journal of Chromatography. 1987;**410**:494-499. DOI: 10.1016/S0021-9673(00)90084-0

[22] Wang P, Li SF, Lee HK. Simultaneous determination of monofluorophosphate and fluoride in toothpaste by capillary electrophoresis. Journal of Chromatography. 1999. DOI: 10.1016/S0021-9673(96)00926-0

[23] Alonso C, Andrade C, Argiz C, Malric B. Na_2PO_3F as inhibitor of corroding reinforcement in carbonated concrete. Cement and Concrete Research. 1996;**26**(3):405-415. DOI: 10.1016/S0008-8846(96)85028-9

[24] Vézina D. Performance des inhibiteurs de corrosion, direction des laboratoires et chaussées. Technical Newsletter. 1997;**2**:3

[25] Benzina Mechmeche L, Dhouibi L, Ben Ouezdou M, Triki E, Zucchi F. Investigation of the early effectiveness of an amino-alcohol based corrosion inhibitor using simulated pore solutions and mortar specimens. Cement and Concrete Composites. 2008;**30**:167-173. DOI: 10.1016/j. cemconcomp.2007.05.007

[26] Dhouibi L, Triki E, Salta M, Rodrigues P, Raharinaivo A. Studies on corrosion inhibition of steel reinforcement by phosphate and nitrite. Materials and Structures. 2003;**36**(8):530-540. DOI: 10.1007/ BF02480830