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

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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: 298K, 308K and 318K. The results obtained for the use of these three products show that the inhibitory efficacy is lower at 318K, than that detected at 308K and 298K of temperature. In addition, we find that the best inhibitory efficiency at 298K 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 measurements Efficiency.

INTRODUCION

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 an insoluble iron III phosphate that will clog the anodic surface and displace the cathodic reduction reaction (Oly, 2011).
The required concentration of passivate inhibitor, often of the order of 10^{-4} to 10^{-5} mol/l (Buchler, 2005), 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- (Helie, 2015).
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 (Khenadeki, 2013).

The variation of temperature affects the rate of corrosion. According to Liu and Weyer (1998), an increase in temperature increases the rate of corrosion. This result was confirmed in carbonated concrete and 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: 298K, 303K and 313K).

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.

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 based on 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, and then they are placed in a thermostatic bath while adjusting the desired temperature. After 24 hours, 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.

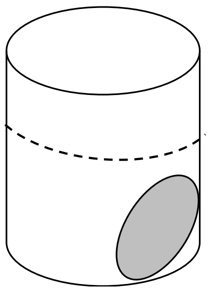


Fig.1. Position of steel sample.

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.

Table 1. Synthetic Medium of Concrete (Ghods et al., 2009; Moragues et al., 1987; Page and Vennesland, 1983).

1L Distilled water	$Ca(OH)_2$	NaOH	KOH	$CaSO_4$ $2H_2O$	NaCl
Wt (g/l)	2	0.4	0.56	0.27	30

Steel preparation

The steel used is circular shaped with a diameter of 27±1mm and 2±2mm of thickness. Sail et al. (2011) have detailed the procedure of gravimetric tests. The corrosion rate is determined by the following formula:

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

$\Delta M = M1 - M2$

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:

$$IE\,(\%) = \frac{Cr0 - Cr}{C_{ro}} .100 \quad (2)$$

Tested inhibitors

This study describes the corrosion behavior of steel immersed in synthetic concrete pore solutions contaminated by chlorides for three phosphate-inhibitors (Na_3PO_4, K_2HPO_4 and Na_2PO_3F), their molecular structure is given in figure 2. The optimal concentration, which provides maximum efficiencies for the three products cited, was extracted from a previous study (Sail, 2013) (Table 2).

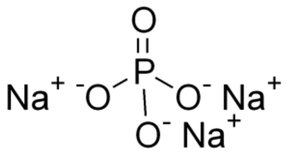
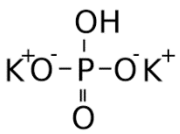
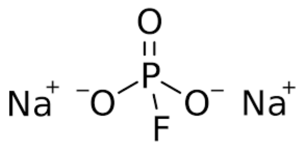
		
Sodium phosphate	Potassium Monohydrogenphosphate	Sodium monofluorophosphate

Fig.2. Molecular structure of the three tested inhibitors.

Table 2. Medium Concentrations.

Inhibitor	Na_3PO_4	K_2HPO_4	Na_2PO_3F
Concentration (mol/l)	$7.5\ 10^{-3}$	$2.5\ 10^{-3}$	$5\ 10^{-2}$

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: 298K, 303K and 318K for the 3 inhibitors.

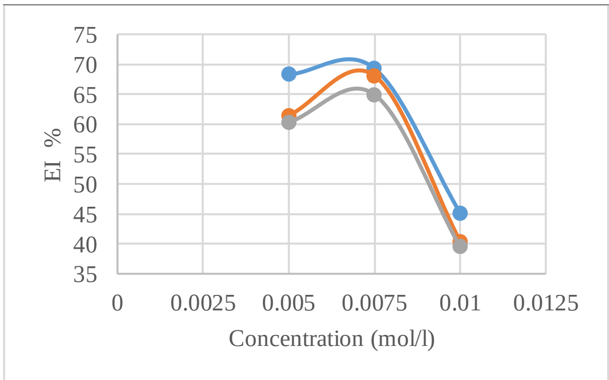
It can be seen from the results shown in table 3 that the corrosion rates decrease in the presence of the corrosion inhibitor, it reached the maximum at the optimal concentration, for the first inhibitor sodium phosphate Na_3PO_4 the maximum efficiency 69.28% was detected at a concentration of 7.5. 10^{-3} mol/l at 298K, we can see clearly that the inhibitory efficiency slightly decrease as a function of temperature increase. While for K_2HPO_4, the best efficiency 67.44% was detected at 298K 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 298K. 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 that increases the corrosion rate. Hunkeler (1994) has shown in his studies that the influence of temperature on the rate of corrosion is greater than that the resistivity of the concrete.

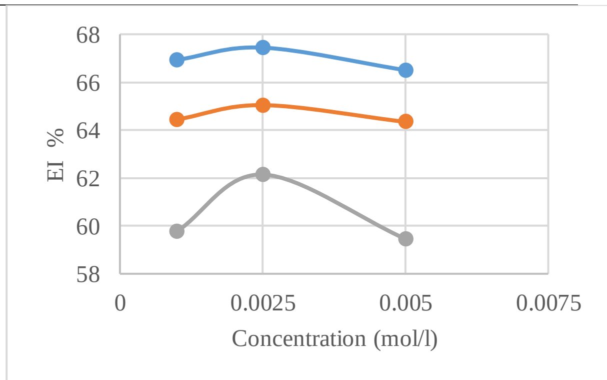
Figure 3 shows the evolution of inhibitory efficiencies as a function of temperature variation for different concentrations of tested inhibitors.

Table 3. Evolution of inhibitory efficiencies (%) as a function of temperature variation.

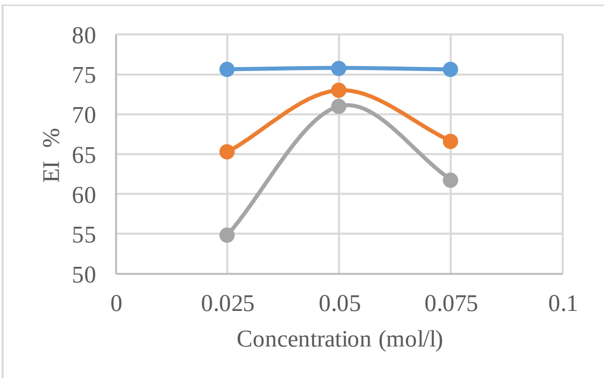
C(mol/l)	298K Cr. 10^{-3} (mg/h.cm^2)	298K IE %	303K Cr. 10^{-3} (mg/h.cm^2)	303K IE %	313K Cr. 10^{-3} (mg/h.cm^2)	313K IE %	
0	1.4	/	2.5	/	3.1	/	
5. 10^{-3}	0.444	68.28	0.964	61.44	1.231	60.29	Na_3PO_4
7.5. 10^{-3}	0.43	69.28	0.798	68.08	1.0875	64.92	
10^{-2}	0.768	45.14	1.49	40.4	1.8764	39.47	
0	1.4	/	2.5	/	3.1	/	K_2HPO_4
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	
0	1.4	/	2.5	/	3.1	/	Na_2PO_3F
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	



Na_3PO_4



K_2HPO_4



Na_2PO_3F

Fig.3. Evolution of inhibitory efficiencies as a function of temperature variation for different concentrations of Na_3PO_4, K_2HPO_4 and Na_2PO_3F.

Figure 3 illustrate 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 (Khenadeki, 2013)
The variation in temperature affects the rate of corrosion. This result was also detected in previous researches (Liu and Weyer, 1998).

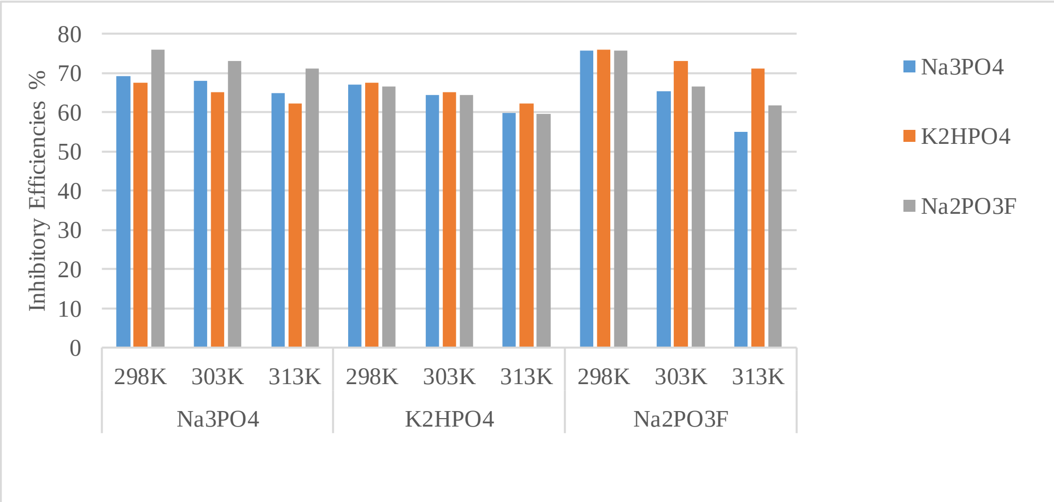


Fig.4. Evolution of inhibitory efficiencies as a function of temperature variation.

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 slightly as a function of temperature increase. As a result, the maximum inhibitory efficacy at T 298K, 303K and 318K 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 (Sail, 2013).
Indeed, sodium monofluorophosphate has been the subject of several studies (Douche-Portanguen et al., 2004; Pujol Lesueur, 2004; Duprat et al., 1983), it has proven remarkable inhibitory properties especially in the case of its use in zinc phosphate baths (Zimmermann et al., 2004; Kashyap , 2008; Simescu, 2008)
The variation of the temperature influences the rate of corrosion and consequently the mechanism of the inhibition (Khouikhi, 2007). According to Liu and Weyer (1998), an increase in temperature increases the rate of corrosion.

CONCLUSION

Direct measurements of both corrosion rates and inhibitory efficiencies as a function of inhibitor concentrations, have confirmed that sodium monofluorophosphate (Na_2PO_3F) offers the best corrosion protection under study conditions (temperature 298K, 303K and 313K); its inhibitory efficiency has exceeded 70% for these temperatures.
This inhibitor has been the subject of several previous studies (Douche-Portanguen et al., 2004 ; Soylev et al., 2006; Farcas et al., 2002; Talamge and Biemer, 1987; Wang et al., 1999), its effectiveness against corrosion has been confirmed especially when used in a carbonated concrete (Alonso et al., 1996; Vézina, 1997; Benzina et al., 2007; Duprat et al., 1983; Dhouibi et al., 2003) and then 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.

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