Mass loss for assessment of the inhibitory efficiency of products to basis of phosphate

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Abstract — *The effect of variation of the corrosion levels has been studied experimentally by mass loss that proves to be a first approach in the study of the inhibition of corrosion of a metal in an electrolytic solution in order to determine the inhibitory efficiency of the product tested. Two inhibitors to basis of phosphate and that didn't show effects of toxicity in the literature have been used: the sodium phosphate and the potassium monohydrogenophosphate. Tests have been led in three different environs, the first one simulates the marine environment of the Mediterranean (3% NaCl), the second environ represents a solution of calcium hydroxide saturated $Ca(OH)_2$ simulates the solution of the pores of the concrete and the third one represents the synthetic environment of the concrete in the same conditions of temperature and relative humidity. Maximal value of the inhibitory efficiency has been treasured respectively formerly to 80%, 75% and 74% for the sodium phosphate in the three surroundings; while for the potassium monohydrogenophosphate, this efficiency has been evaluated at 65,5%, 66% and 51,5% in the same three surroundings of the study. The influence of the concentration as well as the effect of the PH have been interpreted.*

Key words: Concrete, Corrosion, Inhibitory, Phosphate, Mass loss.

INTRODUCTION

Concrete is a mixture of cement, aggregate (sand, gravel) and water. After setting, a porous medium consisting of granulate, hydrated cement and pore solution composed of water contained alkali metal ions, Ca^{2+}, OH^- which are characterized by a basic pH is formed. The hydration of cement occurs by dissolution of anhydrous solid, followed by precipitation of hydrates forming a mechanically strong structure. Tricalcium silicate, Ca_3SiO_5 or C_3S in cement nomenclature, is the main constituent phase in the Portland cement clinker. The hydration reactions formed portlandite $Ca(OH)_2$, noted CH as hexagonal platelets and calcium silicate hydrates, noted CSH[1]. Thus, by dissolving tricalcium silicate ion releases more calcium hydroxide and CSH as it consumes, the solution is enriched with these ions and becomes supersaturated with respect to calcium hydroxide which precipitates as portlandite which is the most soluble phase of hydrated cement [2]:

$$Ca^{2+} + 2OH^- \rightarrow Ca(OH)_2$$

The excess of calcium released by the hydratation reactions of cement, change into crystallized portlandite Ca $(OH)_2$. There is a high concentration of crystals of $Ca(OH)_2$ in the transition zone of the interface of cement-aggregate or around air bubbles. Portlandite formed during hydration of portland cement is partly causing the high pH of the pore solution (pH ~ 12.5) [3] responsible for the protection of reinforcement steel embedded in concrete. This protection reduces temporary corrosion of reinforced steel in concrete, but do not stop it permanently and we continue to detect pathologies of reinforced concrete structures due to rebar corrosion thus reducing their durability and whose rehabilitation requires a very important coast and specialists in this domain [4] with periodic maintenance of rehabilitated structures. Several methods are used to mitigate the effect of reinforcement corrosion in concrete, they include cathodic protection [5], surface treatments and the addition of inhibitors [6] in fresh concrete as adjuvants or impregnation surface for hardened concrete [7]. Corrosion inhibitors have demonstrated remarkable efficiency in the industry, the underground pipes [8], storage rooms, refrigerating rooms, etc.. The literature presents several studies of simulation in the laboratory representing the steel immersed in an environment where saturated calcium hydroxide as electrolytic solutions were used [9], [10] to simulate the environment present in the pores of the concrete well that solutions in the pores of concrete saturated with calcium hydroxide, Ca $(OH)_2$, also contain additional ions that vary depending on type of cement [11], [12]. Ionic species include major cations such as Ca^{2+}, Na^+ and K^+ and anions like OH^- and SO_4^{2-}. In addition, sodium and potassium ions come from alkali metal oxides such as Na_2O and K_2O in the existing portland cement and sulphate ions due to the addition of gypsum for cement production, or by contaminated aggregates, or the mixing water [13]. For our study, we opted for an experimental program includes tests for corrosion of steel in several synthetic media solutions simulating the concrete.

One method of evaluating the corrosion of a metal exposed to an electrolyte solution, the gravimetric measurements based on tests of mass loss remains a first approach to the study of corrosion inhibition of steel in an electrolyte solution. This method has simple implementation and does not require a large apparatus.

II- METHODS AND MEASUREMENTS

The mass loss measurements give us a direct estimate of the corrosion rate of steel immersed in the electrolyte solution in

the presence of aggressive agents in our case, the chloride ions.

The corrosion rate was determined after 24h of immersion at a constant temperature equal to 25 ° C. It is calculated by the following formula:

$$V = \Delta M / S. t \ (mg/h.cm2) \qquad (1)$$
$$\Delta M = M1 - M2$$

Where, ΔM represents the difference between the initial mass M1 and the final mass M2 after a time t equal to 24h. S is the surface area exposed to the study solution. This value of the corrosion rate is the average of three tests under the same conditions for each concentration. The value of inhibition efficiency is given by the following formula:

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

Where V and V_{inhib} represents the corrosion rate without inhibitor and in the presence of inhibitor.

III- EXPERIMENTAL CONDITIONS

A. STUDY MEDIUMS

The mass loss tests were realized in three different environments according with literature:

Medium 1: Distilled Water + 3% NaCl

Medium 2: Distilled Water + 3% NaCl + Ca $(OH)_2$ at saturation.

Medium 3: Distilled Water + 3% NaCl + KOH + NaOH + $Ca(OH)_2$ + $CaSO_4$ $2H_2O$ saturation [14].

B- Material Selection

To realize the gravimetric measurements, we performed tests on a previously machined steel in the form of circular pieces of diameter 27 ± 2 mm and 2 ± 0.2mm of thickness, whose composition is shown in Table 1. These pieces are subjected to polishing at 400 rpm, with sandpaper grain size decreases up to 1000 degrees successively. Then rinsed with distilled water, degreased with acetone and dried using an electric dryer before being submitted for testing weight loss [15].

TABLE I
COMPOSITION OF TESTED STEEL

Chemical elements	C	Si	Mn	P	S	Cr	Mo
Composition (%)	7	0.271	1.25	0.0127	0.0402	0.05	0.01
Chemical elements	Ni	AL	Cu	V	Su	Fe	
Composition (%)	0.114	0.00363	0.29	0.0685	0.0177	97,65	

The mass loss tests have a simple implementation, the equipment needed to perform these measurements consist of an analytical balance, a pH meter in order to give us the pH and temperature of the tested solution at t tinitiale and after 24 hours, a thermostat that keeps the electrolyte at constant temperature T = 25 ± 0.2 ° C where we introduced 18

recipients of 100 ml and the volume of the electrolyte is 50 ml, for each test, two concentrations are studied.

C- Number of tests:

- 12 tests without inhibitors to verify the reproducibility of results.
- 07 concentrations for each inhibitor (do more if necessary).
- 03 tests trials for each concentration in the same medium.

D - Selection of Inhibitors:

Inhibitors used in the tests are derived from phosphate which doesn't show any toxic effects at slow or long term.
- Sodium Phosphate Na_3PO_4
- Potassium monohydrogen K_2HPO_4.

IV- EXPERIMENTAL PROCEDURE

After preparing steel for the initial mass measurements (polishing, rinsing with distilled water, degreasing with acetone, drying, determination of the diameter and thickness of each piece), we shall weigh as M1, then the Preparation of electrolyte solutions with concentrations for inhibitors. The pH of the solutions is measured after calibration of the device. The piece is then placed in an inclined position in the recipient and then closed compactly and introduced in the thermostat at T = 25 ° C.

After 24 hours: we Poured distilled water in numbered dishes, then we pull the recipients from the thermostat, we rinsed the pieces with distilled water, then brush them with acetone, without forgetting to measure the pH of the solution, after that we dried pieces using an electric dryer and then weighed the mass M2.

The corrosion is calculated by equation (1) and inhibition efficiency of each product is calculated using equation (2).

V- RESULTS AND DISCUSSION

A- 1st case: Sodium Phosphate:
- Corrosion rate

The evolution of corrosion rates and efficiencies in function of inhibitory concentrations of sodium phosphate is shown for each medium in the following table:

TABLE II.
EVOLUTION OF CORROSION RATES AND INHIBITION EFFICIENCY OF THE STUDIED STEEL IN THE THREE MEDIUMS

Concent (Mol/L)	Medium 1		Medium 2		Medium3	
	V_{cmoy} x10^{-3} (mg/h.cm^2)	μ (%)	V_{cmoy} x10^{-3} (mg/h.cm^2)	μ (%)	V_{cmoy} x10^{-3} (mg/h.cm^2)	μ (%)
0	8,67	/	4,44	/	2,97	/
7,5x10^{-5}	8,55	01,44	3,68	17,00	2,62	11,78
1x10^{-4}	7,91	08,82	3,67	17,12	2,5	15,82
2,5x10^{-4}	4,03	53,54	3,43	22,64	2,33	21,55
5x10^{-4}	3,66	57,81	3,11	29,84	2,08	29,97
7,5x10^{-4}	3,60	58,50	2,81	36,49	1,41	52,52
1x10^{-3}	3,42	60,55	2,23	52,03	1,37	53,87

$2,5x10^{-3}$	2,84	67,26	1,91	56,98	1,17	60,6
$7,5x10^{-3}$	1,72	**80,17**	1,10	**75,22**	0,78	**73,73**
$1x10^{-2}$	1,85	79,48	1,76	60,36	1,25	57,91
$2,5x10^{-2}$	3,20	63,1	2,85	35,81	1,87	37,03

FIG I. EVOLUTION OF CORROSION SPEEDS ACCORDING TO THE CONCENTRATION OF THE INHIBITOR
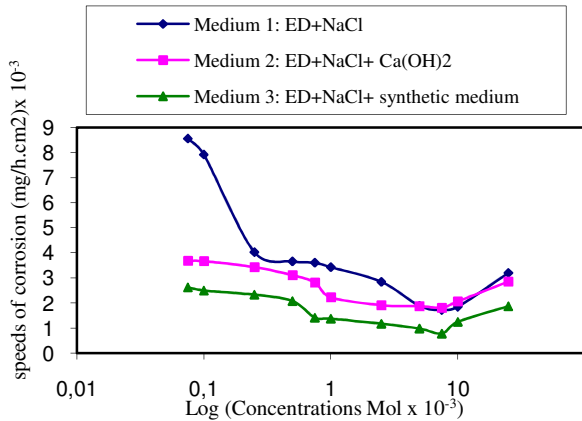
- *Ph*

The evolution of the treated solutions pH according to the concentrations of sodium phosphate is shown for each medium in this table:

TABLEAU 3. EVOLUTION OF PH SOLUTIONS IN THE THREE MEDIUMS

Concent (Mol/L)	Medium 1		Medium 2		Medium 3	
	PH at t_0	PH at t_{24h}	PH at t_0	PH at t_{24h}	PH at t_0	PH at t_{24h}
0	8,97	8,72	11,78	11,77	11,81	11,80
$2,5x10^{-2}$	11,17	11,15	12,29	12,26	12,32	12,28
$1x10^{-2}$	11,15	11,02	12,28	12,23	12,31	12,26
$7,5x10^{-3}$	11,11	10,97	12,26	12,21	12,28	12,22
$2,5x10^{-3}$	10,09	9,97	12,02	12,00	12,05	12,03
$1x10^{-3}$	9,78	9,55	11,91	11,9	11,97	11,97
$7,5x10^{-4}$	9,55	9,52	11,9	11,88	11,98	11,97
$5x10^{-4}$	9,52	9,51	11,89	11,86	11,9	11,87
$2,5x10^{-4}$	9,12	9,00	11,87	11,85	11,88	11,86
$1x10^{-4}$	9.05	8,88	11,81	11,78	11,84	11,82
$7,5x10^{-5}$	9,02	8,45	11,8	11,76	11,82	11,81

The results show that the corrosion rate decreases gradually following the increase of the concentration of inhibitor in the three study mediums, which converges with the results obtained in the literature although the different environments and steel used [16].

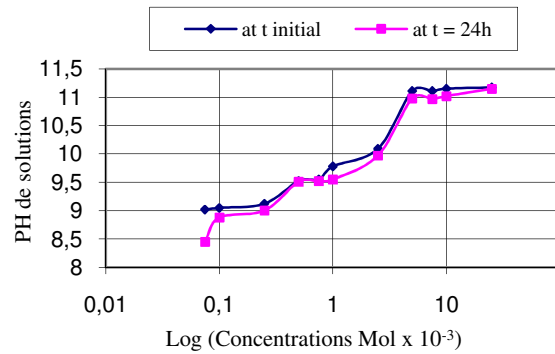From Figure 1, we find that the corrosion rate decreases until it reaches an optimal concentration about 7.5 $x10^{-3}$; at this point, the corrosion rate's increases. The inhibition efficiency of sodium phosphate in the medium 1 (distilled water + 3% NaCl) reaches a value of 80% at a concentration of 7.5 x 10^{-3} mol / l in the simulated environment of concrete, this value is 75%, while in the synthetic medium of concrete, inhibitory effectiveness of sodium phosphate is in the order of 73.7% for the same concentration.

The inhibition efficiency is even lower in the alkaline environment then in the simulated Mediterranean Sea (medium 1). The metal is attacked by the chloride ions and the diffusion of phosphate ions is faster to reach the surface of the steel in question. In contrast, in alkaline media 2 and 3, the basic nature of electrolyte solution formed a protective barrier of the passive film around the steel, the diffusion of chloride ions is much slower and consequently leads to the destruction of the passive film [17] and therefore the corrosion appears. The corrosion rate of steel without application of inhibitor is clearly low compared with the medium 1especially for the estimated time which is 24 hours, hence the inhibition of corrosion in these environments is less.
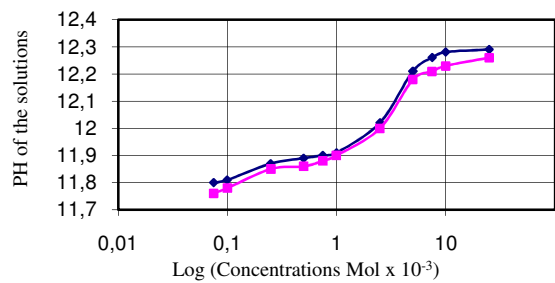
The curves illustrating the evolution of PH for each medium are plotted separately in order to visualize the difference between the initial pH and after 24 h.

FIGURE II. EVOLUTION OF PH ACCORDING TO THE CONCENTRATIONS OF SODIUM PHOSPHATE) FOR: A) MEDIUM 1, B) MEDIUM 2, C) MEDIUM 3
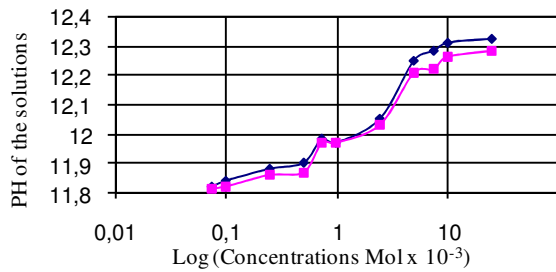
a)

b)

c)

$1x10^{-2}$	3,45	63,9	2,85	35,82	1,67	43,77
$7,5x10^{-3}$	3,13	60,21	2,75	38,06	1,51	49,16
$2,5x10^{-3}$	3,08	63,32	2,58	41,89	1,44	**51,51**
$1x10^{-3}$	3,02	23,3	2,04	54,05	1,6	46,13
$2,5x10^{-4}$	3	**65,40**	1,51	**65,99**	2,04	31,31
$1x10^{-4}$	7.6	11.76	4,62	42,34	2,45	17,51

FIGURE III.
EVOLUTION OF CORROSION RATES ACCORDING TO POTASSIUM MONOHYDROGENOPHOSPHATE CONCENTRATIONS IN THE THREE MEDIUMS

- *Ph*
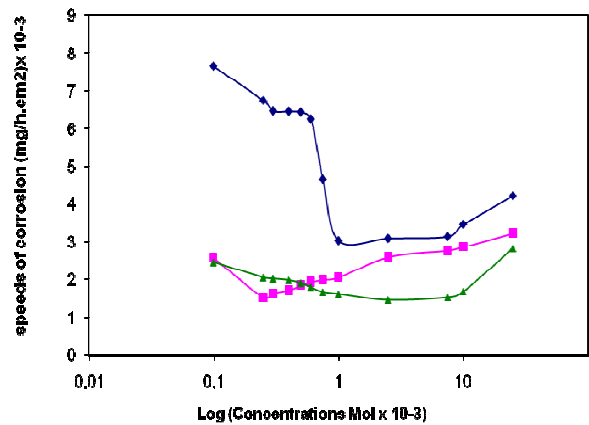
The evolution of the treated solutions pH according to the concentrations of potassium monohydrogenophosphate is shown for each medium in this table:

TABLE IV.
EVOLUTION OF PH SOLUTIONS IN THE THREE MEDIUMS

Concent (Mol/L)	Medium 1		Medium 2		Medium 3	
	PH at t_0	PH at t_{24h}	PH at t_0	PH at t_{24h}	PH at t_0	PH at t_{24h}
$2,5x10^{-2}$	8,09	9,33	11,99	12,02	11,98	12
$1x10^{-2}$	8,23	9,32	11,98	12,02	12,04	12,05
$7,5x10^{-3}$	8,45	9,3	11,71	11,7	11,76	11,75
$2,5x10^{-3}$	8,49	9,33	12,01	12,01	12,04	12,04
$1x10^{-3}$	8,6	9,25	12,07	12,08	12,07	12,12
$2,5x10^{-4}$	8,71	9,15	12,28	12,27	12,27	12,27
$1x10^{-4}$	9,16	9,02	12,3	12,28	12,28	12,29

The pH of treated solutions was taken directly at initial and after 24 hours after the calibration device, the pH range in the medium 1 is inserted in the range of 8.45 and 11.17, in medium 2, the rate of pH ranging between 11.76 to 12.29, for the medium 3, the pH of synthetic solutions is included in the range of 11.80 and 12.32 (mediums 2 and 3 are basic alkaline mediums). The corrosion initiation begins during the destruction of the passive film protects the steel against corrosion, and the chloride ions attack the metal surface rapidly in the propagation phase of corrosion, resulting in the presence of several points corrosion (pitting), which is clearly visible after observing the surface state at the end of our pieces in medium 1 in absence of inhibitor. We observe from Fig 1that the kinetics of corrosion affects the pH solutions, this is distinguished in the three studied mediums where the pH decreases after 24 hours according to the pH at t initial, this is due to the presence of corrosion products which change the state of the final solution.

According to Fig 2., the pH of solutions in medium 1 reaches at 11.17, we notice a change in pH at C0 (without inhibitor) and C (2.5 x10-3) is due essentially to the basic nature of Sodium phosphate, the action of the phosphate ion PO_4^{-3} on the effect of inhibition of the steel studied is in agreement with results obtained in the literature [18]. The inhibitory effect is partially due to the alkalinity of the corrosive medium (pH between 11 and 12.1). The phosphate ions are directly involved in inhibiting the anodic reactions of corrosion and promote the formation of protective layers with mixed insoluble compounds with iron ions [19].

B- *2nd case: Potassium Monohydrogénophosphate:*
  - *Corrosion rate*

The evolution of corrosion rates and efficiencies in function of inhibitory concentrations of Monohydrogénophosphate is shown for each medium in the following table:

TABLE III.
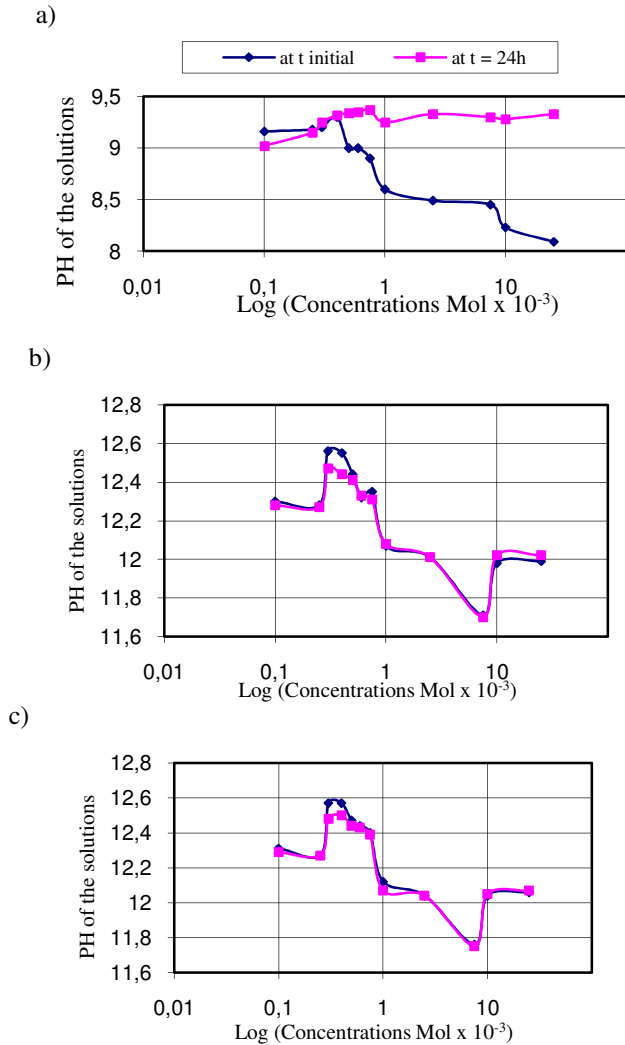**EVOLUTION OF CORROSION RATES AND INHIBITION EFFICIENCY OF THE STUDIED STEEL IN THE THREE MEDIUMS**

Concent (Mol/L)	Medium 1		Medium 2		Medium 3	
	$V_{cmoy} x10^{-3}$ (mg/h.cm²)	μ (%)	$V_{cmoy} x10^{-3}$ (mg/h.cm²)	μ (%)	$V_{cmoy} x10^{-3}$ (mg/h.cm²)	μ (%)
0	$8,67^3$	/	4,44	/	2,97	/
$2,5x10^{-2}$	4,21	51,44	3,21	27,70	2,82	5,05

The second inhibitor studied is potassium monohydrogenophosphate; the inhibition of corrosion was monitored in the three mediums mentioned above. It is found that the corrosion rate decreases with the concentration of inhibitor. For medium 1, the inhibition efficiency reaches a value of 65,4 for a concentration of 2.5 x10⁻⁴, in the medium 2, this value is about 65.99 at the same inhibitor concentration, while for the medium 3, the inhibition efficiency is 51,51 at a

concentration of 2.5 x10-3. According to the literature [19], sodium Monohydrpgénophosphates Na_2HPO_4, present real-inhibiting properties because the ion Na has inhibitory properties more than the potassium ion [18], the ion PO_3F_2 played an important role in the overall process of inhibition. The inhibitory action of phosphate is made in proved in the case of the reducing corrosion of iron or steel in neutral aerated [18].

from this point, the pH begins to increase to a value of 12.05 which corresponds to a concentration of 10^{-2} Mol / l, we may notice a slight pH stability. For the medium1, a considerable change of pH is reported, from a concentration of 2.5 x10^{-4}, mainly to the growth of corrosion products and the formation of protective layers that are mixtures of insoluble ferric phosphate and Fe_2O_3 and their interaction with the corrosion inhibitor added to electrolyte study.

FIGURE IV. EVOLUTION OF PH ACCORDING TO THE CONCENTRATIONS OF POTASSIUM MONOHYDROGENOPHOSPHATE) FOR:

A) MEDIUM 1, B) MEDIUM 2, C) MEDIUM 3

a)

b)

c)

FIGURE V.
EVOLUTION OF CORROSION RATES ACCORDING TO THE CONCENTRATIONS OF THE TWO INHIBITORS IN THE THREE MEDIUMS.
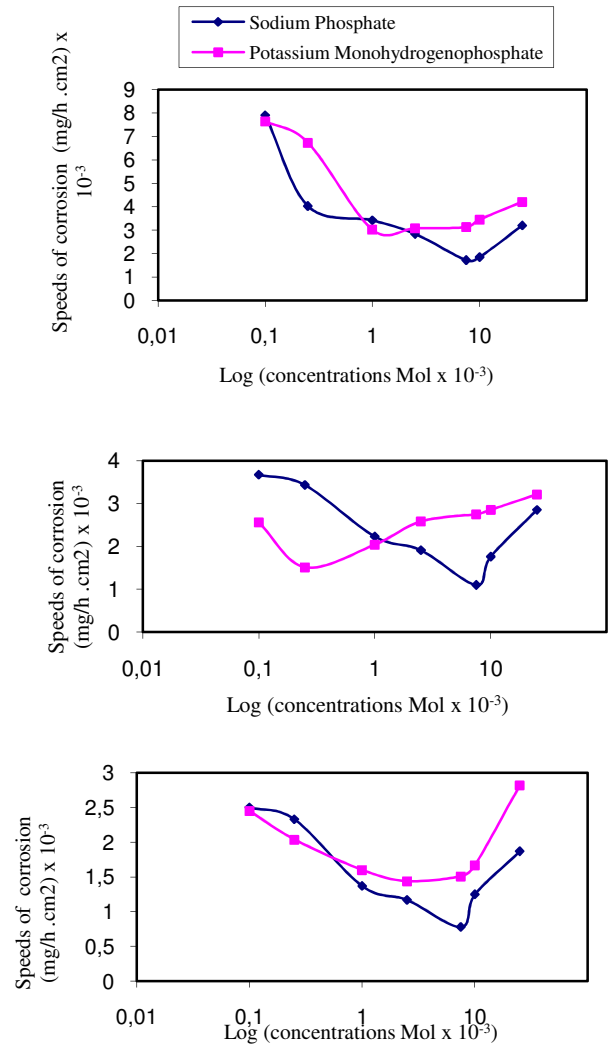
For the second inhibitor tested: potassium monohydrogenophosphate, the pH range observed is include in the interval [8.09 and 9.33] for medium 1, [11.7 and 12.27] for the medium 2 and [11.75 to 12.29] for the medium 3.

We note that the gradual addition of the inhibitor from a concentration of 10^{-4}, up to 2.5 x10^{-2}, reduces the pH of the solution in the medium 1, in the medium 2 the pH decreases depending on the concentration of potassium monohydrogenophosphate until a concentration of 7.5 x10^{-3},

According to the analysis of the three curves shown above, we note that the inhibition of corrosion of sodium phosphate is more greater than potassium monohydrogenophosphate. In medium 1, the inhibition efficiency reached a value of 80.17% at a concentration of 7.5 x10^{-3} for the first inhibitor, whereas for the second inhibitor, it is 65.40% at a concentration of 2,5x10^{-4}. In medium 2, the inhibition efficiency of sodium phosphate was 75.22% at a concentration of 7.5 x10^{-3}, and for potassium monohydrogenophosphate, it is 65.99% at a concentration of 2,5x10^{-4} in the medium 3, the value of this

efficiency is 73.73% for sodium phosphate in the same concentration previously reported, and reached a value of 51.51% for potassium monohydrogenophosphate.

Other inhibitors products were tested in this study to evaluate their efficiency and inhibitory effect and then to compare with the two inhibitors studied. We've selected the following products:

• Sodium benzoate $C_7H_5NaO_2$
• Potassium thiocyanate KSCN
• sodium tetraborate $Na_2B_4O_7$
• Thiourea CH_4N_2S

The evolution of corrosion rates versus concentrations was found for only two points for each inhibitor and illustrated below.

TABLE VI.
EVOLUTION OF CORROSION RATES IN THE THREE MEDIUMS

C (Mol /l)	$7,5 \times 10^{-4}$			$2,5 \times 10^{-3}$		
Mediums	**M 1**	**M 2**	**M 3**	**M 1**	**M 2**	**M 3**
sodium Benzoate	$5,79 \times 10^{-3}$	$2,82 \times 10^{-3}$	$2,79 \times 10^{-3}$	$5,15 \times 10^{-3}$	$2,61 \times 10^{-3}$	$2,67 \times 10^{-3}$
potassium Thiocyanate	$4,78 \times 10^{-3}$	$2,83 \times 10^{-3}$	$2,56 \times 10^{-3}$	$4,3 \times 10^{-3}$	$2,24 \times 10^{-3}$	$2,44 \times 10^{-3}$
Sodium Tetraborate	$6,58 \times 10^{-3}$	$2,58 \times 10^{-3}$	$2,08 \times 10^{-3}$	$5,94 \times 10^{-3}$	$2,28 \times 10^{-3}$	$1,95 \times 10^{-3}$
Thiourea	$7,58 \times 10^{-3}$	$3,85 \times 10^{-3}$	$1,92 \times 10^{-3}$	$7,45 \times 10^{-3}$	$3,44 \times 10^{-3}$	$1,79 \times 10^{-3}$

According to the corrosion inhibition tests by mass loss for this four products (sodium benzoate, potassium thiocyanate, sodium tetraborate and Thiourea), we observe a layer of corrosion products on the surface of metal by adding high concentrations of inhibitor ($2,5.10^{-3}$). Also, the color of the solution of the medium turns yellow (which justifies the severe aggression of steel). This is the result of the attack of metal by the chloride ions, which must assess the rapport between inhibitors ions and Cl^- ions [18], the optimal concentration required for inhibition of corrosion Steel shall be estimated. after analysis of inhibition processes through the results from Table 6, we conclude that the sodium phosphate in both mediums 1 and 3 marked a remarkable efficiency in relation to sodium benzoate and sodium tetraborate. While at a concentration of $2,5.10^{-3}$, sodium tetraborate gave higher inhibition than the two other products. For Thiourea, the inhibitory effect was not detected after 24 hours of immersion. These tests should be supplemented by electrochemical tests to evaluate the corrosion kinetics for the various tested products. The advantage of this method is to quickly determine the effectiveness of the product and its reliability in preparation for a thorough study of corrosion in different mediums.

V. CONCLUSION

According to tests based on gravimetric measurements of mass loss made on several inhibitor products: phosphate derivatives (sodium phosphate and potassium monohydrogenophosphate the following conclusions were adopted:

• Sodium phosphate scored a good inhibition efficiency against the potassium monohydrogenophosphate, this has been reported before starting the calculation of corrosion rates for each product and this is related to the condition of the solutions after 24 h of immersion. The corrosion rate decreases with inhibitor concentrations to achieve optimal value (optimal concentration), from this point the corrosion rates begin to rise spontaneously. potassium monohydrogenophosphate gave a lower efficiency compared to that obtained by sodium phosphate [5], for this reason, we tested other products based on sodium Na^+ (sodium benzoate, sodium tetraborate) and potassium ion K^+ (potassium thiocyanate, potassium monohydrogenophosphate) to visualize the differences in inhibition efficiency in the presence of sodium and potassium [18].

• The inhibitory effect of the ion PO_4 was revealed for the first two products tested. In medium 1, the inhibition efficiency reached a value of 80.17% at a concentration of 7.5 $x10^{-3}$ by adding sodium phosphate, for potassium monohydrogenophosphate, it reached 65.40% at a concentration of 2.5 $x10^{-4}$. In medium 2, this value was 75,22% at a concentration of 7,5. 10^{-3}, and 65.99% at a concentration of 2.5 $x10^{-4}$ for the two inhibitors products respectively, in medium 3 The value of this efficiency is 73.73% for sodium phosphate in the same concentration previously reported, and reached a value of 51.51% for potassium monohydrogenophosphate.

• The pH of treated solutions was taken directly at t initial and after 24 hours, the pH range in medium 1 is inserted between 8.45 and 11.17; in medium 2, the rate of pH ranging between 11.76 to 12.29, for the medium 3, the pH of synthetic solutions is included in the range of 11.80 and 12.32, The inhibitory effect is partly due to the alkalinity of the corrosive medium (pH between 11 and 12.1). The phosphate ions are directly involved in inhibiting the anodic reactions of corrosion and promote the formation of protective layers with mixed insoluble compounds with iron ions.

REFERENCES

[1] E.Guillon, « Durabilité des matériaux cimentaires - Modélisation de l'influence des équilibres physico-chimiques sur la microstructure et les propriétés mécaniques résiduelles », Thèse de Doctorat, 2004.

[2] J P. Ollivier, A. Vichot, « La durabilité des bétons, Association technique de l'industrie des liants hydrauliques », 2008.

[3] M. Codina, « Les bétons à bas pH Formulation, caractérisation et étude à long terme », Thèse de Doctorat, 2007.

[4] J. Joceline(Setra), G. Taché (CEBTB), « Réhabilitation du béton armé dégradé par la corrosion », AFGC, 2003.

[5] P.Pedeferri, "Cathodic protection and cathodic prevention, Construction and Building Materials", *Ed. Elsevier,* Vol. 10, N° 05, 1996, pp. 391-402.

[6] B. Ormellese, M. Berra, F. Bolzonib, T. Pastore, "Corrosion inhibitors for chlorides induced corrosion in reinforced concrete structures", *Cement and concrete research , Ed. Elsevier*, Vol. 36, 2006, pp. 536-547.

[7] A. Batis, A. Routoulas, E. Rakanta, "Effects of migrating inhibitors on corrosion of reinforcing steel covered with repair mortar", *Cement & Concrete Composites, Ed. Elsevier*, Vol. 25, 2001, pp 109–115

[8] P. Boummersbach, « Evolution des propriétés d'un film inhibiteur de corrosion sous l'influence de la température et des conditions hydrodynamiques », Thèse de Doctorat, 2005.

[9] M. Saremi, E. Mahallati, "A study on chloride-induced depassivation of mild steel in simulated concrete pore solution", *Cement and concrete research, Ed. Pergamon*, Vol. 32, 2002, pp. 1915-1921.

[10] G. Blanco, A. Bautista, H. Takenouti, "EIS study of passivation of austenitic and duplex stainless steels reinforcements in simulated pore solutions", *Cement & Concrete Composites, Ed. Elsevier*, Vol. 28, 2006, pp. 212–219

[11] A. Moragues, A. Macias, C. Andrade, "Equilibria of the chemical composition of the concrete pore solution. Part I: comparative study of synthetic and extracted solutions". *Cement & Concrete Research, ,*Vol. 17, N° 12, March 1987, pp. 173-182.,

[12] CL. Page, O. Vennesland, "Pore solution compositions and chloride binding capacity of silica fume cement paste" , *Material & Structures*, Ed. Springer, Vol. 16, 1983.

[13] AM. Neville, "Properties of concrete". 4th ed. Prentice, 2005.

[14] P. Ghods P., O B Isgor, B. Mcrae, T. Millar, "The effect of concrete pore solution composition on the quality of passive oxide films on black steel reinforcement", *cement and concrete composites*, Ed. Elsevier, Vol. 31, N° 1, 2009, pp. 2-11.

[15] O. Benali, L. Larabi, M. Traisme, L. Gengembre, Y. Harek, "Electrochimical, theorical and XPS studies of 2-mercapto-1-methylimidazole adsorption on carbon steel in 1 M HCLO4", *Applied surface science,* Ed. Elsevier, Vol. 253, N° 14, 2007, pp. 6130-6139.

[16] L. Larabi, Y. Harek; "Effect of iodide ions on corrosion inhibition of mild stell in 0,5 M H_2SO_4 by Poly(4-vinylpyridine) P4VP", *Portugalie Electrochimica Acta*, Ed. Elsevier, Vol. 22, N° 16, 2004, pp. 227-247.

[17] F. Laferrière, "Capteur chimique à fibres optiques pour la mesure des ions chlore dans le béton à un stade précoce », Thèse de Doctorat, 2006.

[18] M. Duprat, A. Bonnel, F. Dabosi ; « Les monofluorophosphates de zinc et de potassium en tant qu'inhibiteurs de la corrosion d'un acier au carbone en solution de NaC1 a 3% », *journal of applied electrochemistry*, Ed. Springer, Vol. 13, N° 3, 1983, pp. 317-323.

[19] S. Bensoltane; « Etude électrochimique d'acier de gazoduc API-5L X60 dans le milieu environnant et leur protection par polyphosphate », Thèse de Magister, 2005.

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