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

L. SAIL, F. GHOMARI, A. BEZZAR, O. BENALI

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 the literature have been used: the sodium phosphate and the three different environs, the first one simulates the marine basis of phosphate and that didn't show effects of toxicity in inhibitory efficiency of the product tested. Two inhibitors to metal in an electrolytic solution in order to determine the first approach in the study of the inhibition of corrosion of a 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$_3$SiO$_5$ or C$_3$S 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]:

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

The excess of calcium released by the hydration 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$_2$O and K$_2$O 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:

\[ V = \Delta M / \Delta t \text{ (mg/h.cm²)} \]

\[ \Delta M = M_1 - M_2 \]

Where, \( \Delta M \) represents the difference between the initial mass \( M_1 \) and the final mass \( M_2 \) after a time \( \Delta t \) 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:

\[ \mu (\%) = \frac{V - V_{\text{inhibit}}}{V} \times 100 \]

Where \( V \) and \( V_{\text{inhibit}} \) 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 + CaSO₄ 2H₂O 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>
<thead>
<tr>
<th>Table I</th>
<th>Composition of Tested Steel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical elements</td>
<td>C</td>
</tr>
<tr>
<td>Composition (%)</td>
<td>7</td>
</tr>
<tr>
<td>Chemical elements</td>
<td>Ni</td>
</tr>
<tr>
<td>Composition (%)</td>
<td>0.114</td>
</tr>
</tbody>
</table>

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 initial and after 24 hours, a thermostat that keeps the electrolyte at constant temperature \( T = 25 \pm 0.2 \) °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 Na₃PO₄
- Potassium monohydrogen K₂HPO₄

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>
<thead>
<tr>
<th>Table II</th>
<th>Evolution of Corrosion Rates and Inhibition Efficiency of the Studied Steel in the Three Mediums</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (Mol/L)</td>
<td>( V_{\text{corr}} \times 10^{-3} ) (mg/h.cm²)</td>
</tr>
<tr>
<td>0</td>
<td>8,67</td>
</tr>
<tr>
<td>7,5 \times 10^{-5}</td>
<td>8,55</td>
</tr>
<tr>
<td>1 \times 10^{-4}</td>
<td>7,91</td>
</tr>
<tr>
<td>2,5 \times 10^{-4}</td>
<td>4,03</td>
</tr>
<tr>
<td>5 \times 10^{-4}</td>
<td>3,66</td>
</tr>
<tr>
<td>7,5 \times 10^{-4}</td>
<td>3,60</td>
</tr>
<tr>
<td>1 \times 10^{-3}</td>
<td>3,42</td>
</tr>
</tbody>
</table>

112
FIG I. EVOLUTION OF CORROSION SPEEDS ACCORDING TO THE CONCENTRATION OF THE INHIBITOR

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 \(7.5 \times 10^{-3}\); 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 \(7.5 \times 10^{-3}\) 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 1 especially 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

TABLEAU 3. EVOLUTION OF PH SOLUTIONS IN THE THREE MEDIUMS

<table>
<thead>
<tr>
<th>Concentration (Mol/L)</th>
<th>PH at t_0</th>
<th>PH at t_24h</th>
<th>PH at t_0</th>
<th>PH at t_24h</th>
<th>PH at t_0</th>
<th>PH at t_24h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>8.97</td>
<td>8.72</td>
<td>11.78</td>
<td>11.77</td>
<td>11.81</td>
<td>11.80</td>
</tr>
<tr>
<td>2.5x10^{-3}</td>
<td>11.17</td>
<td>11.15</td>
<td>12.29</td>
<td>12.26</td>
<td>12.32</td>
<td>12.28</td>
</tr>
<tr>
<td>1x10^{-2}</td>
<td>11.15</td>
<td>11.02</td>
<td>12.28</td>
<td>12.23</td>
<td>12.31</td>
<td>12.26</td>
</tr>
<tr>
<td>7.5x10^{-3}</td>
<td>11.11</td>
<td>10.97</td>
<td>12.26</td>
<td>12.21</td>
<td>12.28</td>
<td>12.22</td>
</tr>
<tr>
<td>2.5x10^{-3}</td>
<td>10.09</td>
<td>9.97</td>
<td>12.02</td>
<td>12.00</td>
<td>12.05</td>
<td>12.03</td>
</tr>
<tr>
<td>1x10^{-3}</td>
<td>9.78</td>
<td>9.55</td>
<td>11.91</td>
<td>11.9</td>
<td>11.97</td>
<td>11.97</td>
</tr>
<tr>
<td>7.5x10^{-4}</td>
<td>9.55</td>
<td>9.52</td>
<td>11.9</td>
<td>11.88</td>
<td>11.98</td>
<td>11.97</td>
</tr>
<tr>
<td>5x10^{-4}</td>
<td>9.52</td>
<td>9.51</td>
<td>11.89</td>
<td>11.86</td>
<td>11.9</td>
<td>11.87</td>
</tr>
<tr>
<td>2.5x10^{-4}</td>
<td>9.12</td>
<td>9.00</td>
<td>11.87</td>
<td>11.85</td>
<td>11.88</td>
<td>11.86</td>
</tr>
<tr>
<td>1x10^{-4}</td>
<td>9.05</td>
<td>8.88</td>
<td>11.81</td>
<td>11.78</td>
<td>11.84</td>
<td>11.82</td>
</tr>
<tr>
<td>7.5x10^{-5}</td>
<td>9.02</td>
<td>8.45</td>
<td>11.8</td>
<td>11.76</td>
<td>11.82</td>
<td>11.81</td>
</tr>
</tbody>
</table>

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.
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 1 that 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 PO₄³⁻ 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 Monohydrogenophosphate:

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

<table>
<thead>
<tr>
<th>Medium 1</th>
<th>Medium 2</th>
<th>Medium 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concent (Mol/L)</td>
<td>V₁₁₀⁺ (mg/h.cm³)</td>
<td>µ (%)</td>
</tr>
<tr>
<td>0</td>
<td>8.67</td>
<td>/</td>
</tr>
<tr>
<td>2.5x10⁻²</td>
<td>4.21</td>
<td>51.44</td>
</tr>
</tbody>
</table>

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
The concentration of $2.5 \times 10^{-3}$. According to the literature [19], sodium monohydrargenophosphates $\text{Na}_2\text{HPO}_4$, present real-inhibiting properties because the ion Na has inhibitory properties more than the potassium ion [18], the ion $\text{PO}_4^{3-}$ played an important role in the overall process of inhibition. The inhibitory action of phosphate is made proved in the case of the reducing corrosion of iron or steel in neutral aerated [18].

**Figure IV. Evolution of pH according to the concentrations of potassium monohydrogenophosphate** for:

a) **Medium 1**, b) **Medium 2**, c) **Medium 3**

![Graphs showing pH evolution for different mediums](image)

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 $2.5 \times 10^{-2}$, 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 $7.5 \times 10^{-3}$, 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 medium 1, a considerable change of pH is reported, from a concentration of $2.5 \times 10^{-4}$, mainly to the growth of corrosion products and the formation of protective layers that are mixtures of insoluble ferric phosphate and $\text{Fe}_2\text{O}_3$ and their interaction with the corrosion inhibitor added to electrolyte study.

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 $7.5 \times 10^{-3}$ for the first inhibitor, whereas for the second inhibitor, it is 65.40% at a concentration of $2.5 \times 10^{-4}$. In medium 2, the inhibition efficiency of sodium phosphate was 75.22% at a concentration of $7.5 \times 10^{-3}$, and for potassium monohydrogenophosphate, it is 65.99% at a concentration of $2.5 \times 10^{-4}$ 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 $\text{C}_7\text{H}_6\text{NaO}_2$
- Potassium thiocyanate $\text{KSCN}$
- Sodium tetraborate $\text{Na}_2\text{B}_4\text{O}_7$
- Thiourea $\text{CH}_4\text{N}_2\text{S}$

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

**TABLE VI.**

<table>
<thead>
<tr>
<th>C (Mol/l)</th>
<th>$7.5 \times 10^{-4}$</th>
<th>$2.5 \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mediums</strong></td>
<td><strong>M 1</strong></td>
<td><strong>M 2</strong></td>
</tr>
<tr>
<td>Sodium Benzoate</td>
<td>5.79 x $10^{-5}$</td>
<td>2.82 x $10^{-5}$</td>
</tr>
<tr>
<td>Potassium Thiocyanate</td>
<td>4.78 x $10^{-5}$</td>
<td>2.83 x $10^{-5}$</td>
</tr>
<tr>
<td>Sodium Tetraborate</td>
<td>6.58 x $10^{-5}$</td>
<td>2.58 x $10^{-5}$</td>
</tr>
<tr>
<td>Thiourea</td>
<td>7.58 x $10^{-5}$</td>
<td>3.85 x $10^{-5}$</td>
</tr>
</tbody>
</table>

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 this four products (sodium benzoate, potassium thiocyanate, sodium tetraborate) and Thiourea) for a thorough study of corrosion in different mediums. The advantage of this method is to quickly determine the corrosion kinetics for the various tested products. These tests should be supplemented by electrochemical tests to evaluate the corrosion 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 $2.5 \times 10^{-3}$, 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 were selected for 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 inhibitory effect of the ion $\text{PO}_4^{3-}$ was revealed for the first two products tested. In medium 1, the inhibition efficiency reached a value of 80.17% at a concentration of $7.5 \times 10^{-3}$ by adding sodium phosphate, for potassium monohydrogenophosphate, it reached 65.40% at a concentration of $2.5 \times 10^{-3}$. In medium 2, this value was 75.22% at a concentration of $7.5 \times 10^{-3}$, and 65.99% at a concentration of $2.5 \times 10^{-4}$ 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 the 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 ($\text{pH}$ 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**


**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:


**BIOGRAPHIES**

**First A. Author (M’76-SM’81-F’87)** and the other authors should include biographies at the end of the paper. Usual biography information includes birth date and place, education, employments, and memberships in other professional societies. It is also appropriate to include research interests, professional activities and awards that have been received. Copy and paste this paragraph, with picture, for additional authors.