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Investigation of the early effectiveness of an amino-alcohol based corrosion inhibitor using simulated pore solutions and mortar specimens

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Abstract

This study was carried out to determine effective modes of use of an amino-alcohol based mixed corrosion inhibitor. It was tested in fresh pore concrete simulating solutions. Their compositions and the practical procedures were chosen in order to simulate both curative and preventive modes of use. Effectiveness of the corrosion inhibitor was investigated through corrosion potential measurements, polarisation curves and microscopic observations. The best inhibiting capacity was noted when the inhibitor was introduced in the solution before the contamination with chlorides. Using this inhibitor as a curative mean gave a reduced effect especially when chlorides were present in the simulated pore solutions. The curative mode was tested in the case of mortar specimens. Its efficiency was demonstrated even in the case of chloride presence. For the mortar specimens, the reinforcement electrochemical behaviour was assessed through the corrosion potential measurements and the study of current density evolution.

Keywords: Inhibitor; Pore solution; Steel corrosion; Chloride; Mortar

1. Introduction

Several methods have been used in order to reduce the concrete reinforcement corrosion. They include cathodic protection, coatings, addition of the inhibitors to the concrete and a combination of these methods [1]. Corrosion inhibitors have been successfully used in steel pipelines, tanks etc, for many decades [1,2]. Their use in concrete field is more recent, but it is of an increasing interest [3–7] since it can be considered as a promising technique offering an easy practice with reduced costs. For this reason, a large range of inhibitors is, nowadays, available for the customer. However, there is still a controversy regarding the inhibitors protection efficiency [8]. Some authors report that they are not effective when concrete is under immersion conditions whereas others report that inhibitors are effective in reducing corrosion rate in concrete contaminated with chlorides [8]. The most frequently used technique is adding the inhibitors to the mixing water of concrete as admixtures for new structures. Calcium nitrite was the most extensively tested corrosion inhibitor [9]. Nitrite acts by stabilizing the passive film and its effectiveness had intensively been proved however environmental limitations have highly reduced its use [10]. Laboratory studies of the preventive inhibitive action carried out on monofluorophosphate (MFP) showed that a critical concentration ratio MFP/ chlorides greater than 1 had to be achieved; otherwise the reduction in corrosion rate was not significant [11]. Furthermore, in solutions based on

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$Ca(OH)_2$ MFP is reported to react with the calcium ion and as a result, its active substance disappears from solution due to precipitation.

The amino-alcohols are common inhibitors based on mixtures of alkanolamines and amines or alternatively on organic acids [4]. They were widely applied and rapidly established in the market since they are non toxic and cost attractive. Furthermore, amino-alcohols can be applied for different purposes. In fact, Wombacher et al. [12] reported that amino-alcohols based mixed inhibitors can be used either as concrete admixtures or in repair products for existing structures [12]. The transport mechanism through the concrete cover had been studied by Tritthart [13] who demonstrated that the amino-alcohol compound is not bound by cement but remains largely dissolved in the pore liquid which provides optimal conditions for high mobility. However, according to another study carried out by Tritthart [14] on cement paste samples, he found that in the case of surface application only a very small amount of amino-alcohol penetrated from mixed inhibitors which suggested that the penetration is inhibited by some mechanisms such as the clogging of the pores by solidification of other compounds of the mixed inhibitor.

The aim of this work, is to make an investigation on the best mode of use of an amino-alcohol based mixed inhibitor (Ferrogard 903). In order to get a rapid idea, the tests were carried out in saturated calcium hydroxide solutions polluted with 0.5 M sodium chloride; it simulates the fresh concrete's interstitial electrolyte [5,15]. The inhibitor action was assessed by electrochemical techniques. This paper presents an extension to current knowledge concerning mixed inhibitors being still a subject of discussion. The results sought would underline a close relationship inhibitor efficiency-mode of use especially in the case of simulated pore solutions. Furthermore, this paper would help to fill some doubts concerning the performance of the curative mode of use applied with a mixed inhibitor. In fact, studying the migration capacity of an inhibitor from the surrounding aggressive environment of a mortar specimen was not extensively treated in the literature contrary to other modes of use of mixed inhibitors such as surface impregnation or addition in the mixing water.

2. Experimental

2.1. Tests in solutions simulating the electrolyte present in the pores of fresh concrete

In order to get a first idea about the action of the inhibitor, tests were carried out in solutions simulating different states of the electrolyte present in the concrete pores: four different solutions were considered. Their compositions and the practical procedures have been chosen to simulate two different modes of use: preventive and curative. Solution S_0 was a saturated calcium hydroxide solution containing a chloride concentration of 0.5 mol/l: it represented a contaminated electrolyte contained in the pores of fresh concrete [15]. In order to simulate a curative mode of use of the inhibitor, solution S_1 was considered. It was initially identical to solution S_0, but its composition was changed after 24 h by adding the inhibitor. Concerning solution S_2, it was a saturated calcium hydroxide solution containing the inhibitor. After 24 h, it was added with sodium chloride (Table 1). This way of proceeding represents a preventive mode of use.

Solution S_3 was, also, a saturated calcium hydroxide solution containing simultaneously sodium chloride and the inhibitor. S_3 was considered to simulate an initial use of the inhibitor in a contaminated concrete environment.

For all solutions, NaCl was present at a concentration of 0.5 mol/l whereas the inhibitor was introduced with a coefficient of dilution equal to 1 ml/50 ml [16]. These solutions were slowly agitated and maintained at a temperature of 25 ± 1 °C.

Tested steel specimens were cut from rebars used for concrete reinforcement. Their cross section surfaces were polished with emery paper and degreased in acetone then with distilled water. The end of each specimen was masked with resin to give a known exposed area of about $28.26\ mm^2$. It was welded to a copper wire in order to ensure electrical contacts for electrochemical tests. The content of accessory components of steel is as follows: C 22%, Mn 8.9%, Si 24%, S 1.6%, and P 4.6%.

In order to control the electrochemical behaviour of steel in aggressive environments and to check the action

Table 1
Simulating solution compositions and their pH values

Solutions	$t = 0$			$t = 24$ h		
	Contents	Concentrations	pH	Substance added	Concentration	pH
S_0	$Ca(OH)_2$ NaCl	Saturated 0.5 mol/l	12.4	–		
S_1	$Ca(OH)_2$ NaCl	Saturated 0.5 mol/l	12.4	Inhibitor	20 ml/l	12.3
S_2	$Ca(OH)_2$ Inhibitor	Saturated 20 ml/l	12.1	NaCl	0.5 mol/l	12.1
S_3	$Ca(OH)_2$ NaCl Inhibitor	Saturated 0.5 mol/l 20 ml/l	12.3	–		

of the inhibitor, different electrochemical tests have been performed: the measure of the free corrosion potential E_{corr} with time of immersion and polarisation curves: the reference electrode was a saturated calomel one and the counter electrode was a platinum one. Cathodic and anodic plots have been drawn after 48 h of immersion using a scan rate of 0.1 mV/s. At the end of the tests, the electrode sections were examined with an optical microscope.

2.2. Tests on mortar specimens

In order to investigate the inhibitor efficiency for mortar under immersion conditions which can represent the state of some repairable structure elements, experimental work was also carried out on mortar specimens. They were prismatic with $4 \times 7 \times 28$ cm^3 dimensions, each embedding a 6 mm diameter steel bar having a length of 24 cm. After being polished and rinsed with distilled water, each rebar was connected, at its middle, to a copper wire in order to ensure electrical contact. The connection zone was protected with resin. The rebar was placed in the center. Hence, it was protected by a mortar thickness of approximately 2 cm. The mortar proportioning was as follows: cement 450 g, sand 1350 g, water 270 ml, this mix design involved a water to cement ratio of 0.6. Mortar was vibrated in the moulds using a laboratory vibrating table. The major chemical cement composition is illustrated in Table 2.

After 24 h of setting, the mortar specimens were removed from the molds and cured in water for 28 days. After, they were immersed, during six months, in a sodium chloride solution with a concentration of 0.5 mol/l. They underwent, successively, wet–dry cycles. The duration of each cycle was of 48 h: 24 h of wetting followed by 24 h of drying carried out in a drying oven at a temperature equal to 40 °C. Then, some specimens were placed in an aqueous solution called S added with the inhibitor at the concentration of 1 ml/50 ml (1 ml of inhibitor per 50 ml of solution). The others were maintained in a solution called S′ containing both NaCl and the inhibitor. S′ was obtained by mixing two aqueous solutions: the first containing the inhibitor (1 ml of inhibitor/50 ml of distilled water) and the second containing sodium chloride (0.5 mol NaCl/liter of distilled water).

Mortar reinforcement corrosion was monitored by measuring the steel potential and the anodic current densities deduced from chrono-amperometry plots: the retained corrosion current density was the value corresponding to the plateau of the graph [17]. These measurements were carried out using a three electrode corrosion cell: the reference was a saturated calomel electrode, a stainless steel plate (18% Cr, 10% Ni) was used as a counter electrode and it was simply placed on the surface of the specimen. The working electrode which was the steel reinforcement was connected to the circuit through the electrical wire.

3. Results and discussion

3.1. Solutions

Fig. 1 shows the changes of steel potential E_{corr} in all solutions within the first 24 h. Solution S_1 did not contain yet the inhibitor, its composition and the potential values measured were therefore equal to those of S_0. As expected, the potential of the steel immersed in these aggressive solutions shifted to most negative values. Solution S_2 contained the inhibitor, but no NaCl whereas S_3 contained both the inhibitor and NaCl. Therefore the steel became passive in solution S_2 and its potential shifted to much less negative values. The shift of steel potential in solution S_3 towards somewhat less negative values indicates a certain positive effect of the inhibitor.

Fig. 2 illustrates the steel potential evolution during 48 h both in solutions S_1 and S_2. Steel potential E_{corr} shifted to a less negative value due to the inhibitor addition to solution S_1. This value was maintained constant during 24 h revealing a reduced corrosion activity. However, in solution S_2, NaCl addition resulted in a decrease of the steel potential to more negative values despite the inhibitor presence.

The polarization curves recorded after 48 h of immersion in the different solutions tested are gathered in Fig. 3.

The relative position of potential curves corresponding to the blank solution S_0 and to solutions added with inhibitor introduced in different ways showed that whatever is the mode of its introduction (preventive: S_2 or curative: S_1), its effectiveness can be obviously noticed. In fact, it has an influence on reducing the anodic dissolution of steel: for all solutions and giving a fixed value of the potential E, the corrosion current densities are clearly inferior to the value relative to the blank solution S_0. As for the cathodic action, it was not clear in the interval of potential chosen [8].

Fig. 4 shows the macrophotographies of the specimens after 48 hour immersion in the solutions S_0, S_1, S_2 and S_3. On the specimen immersed in S_2, the surface was corrosion free. Some corrosion points were present on the specimens maintained in S_1 and S_3. The specimens immersed in S_0 solution were decisively corroded.

These observations confirmed the inhibiting effect as it was showed through the E_{corr} ennoblement. The absence of corrosion traces on specimens tested in S_2 solution showed that the inhibitor was more efficient when it was

Table 2
Major chemical components of cement (% of cement)

Element	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	K_2O	I R	Na_2O	Loss on ignition
Percentage of mass	17.38	3.86	3.22	60.75	1.26	2.41	0.74	2.96	0.69	2.6

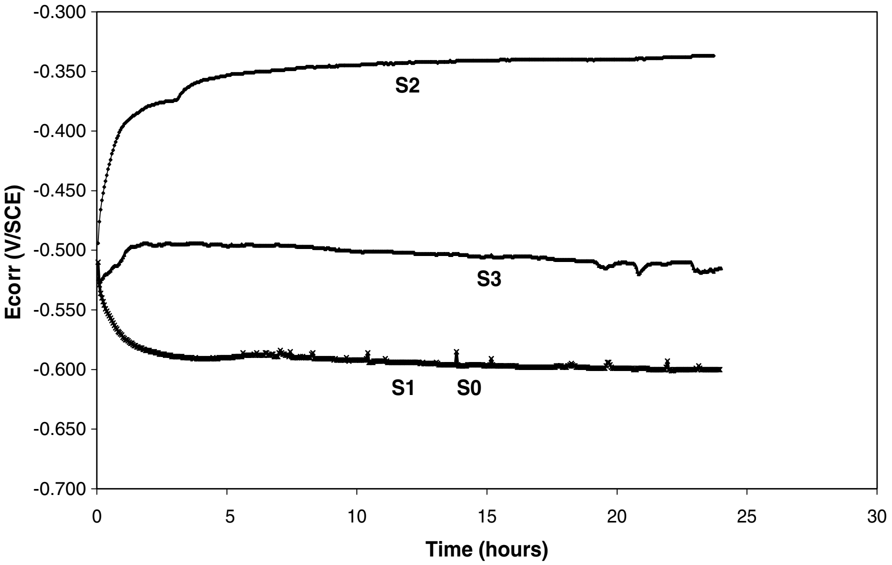

Fig. 1. Evolution of the corrosion potential relative to the steel electrodes immersed in the different solutions: S_0, S_1, S_2 and S_3.

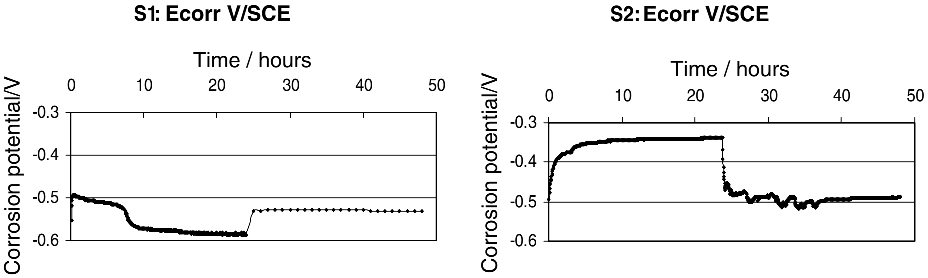

Fig. 2. Evolution of the corrosion potential relative to the steel electrodes immersed in solutions: S_1 and S_2 during 48 h.

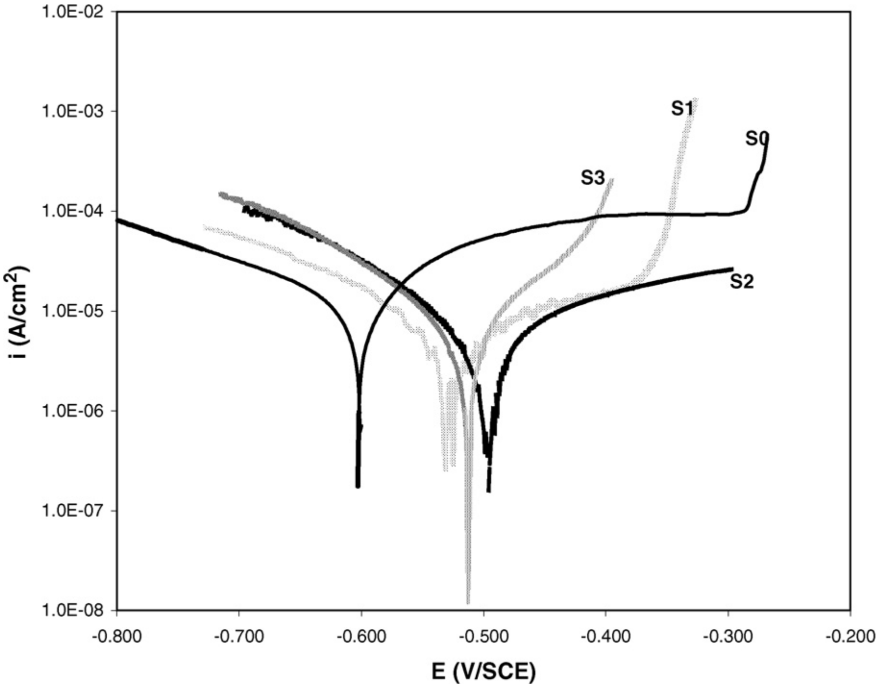

Fig. 3. Potential curves corresponding to the specimens immersed in solutions: S_0, S_1, S_2, and S_3.

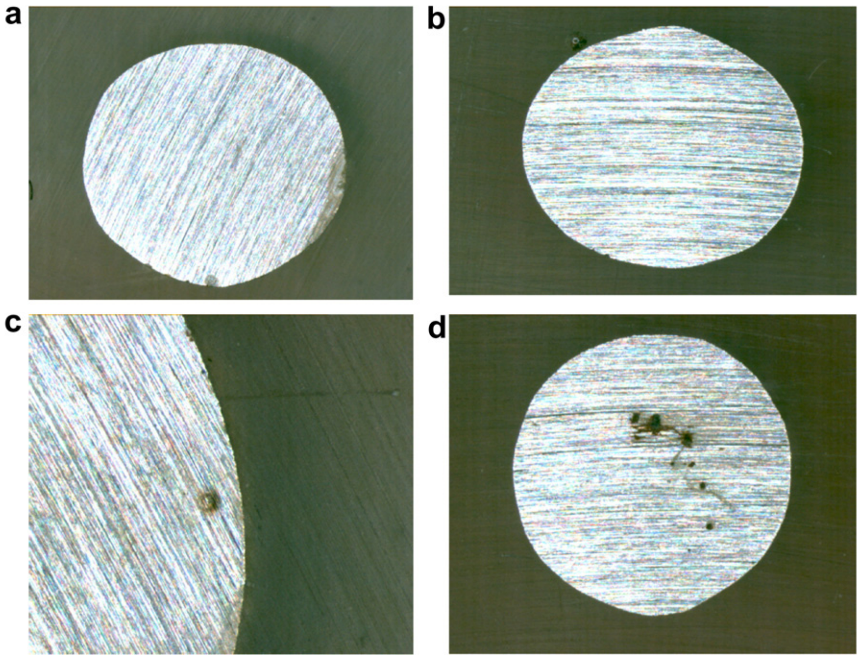

Fig. 4. Microscopy photos (6×) of the electrode surfaces after immersion in the different solutions. (a) Electrode surface after immersion in solution S_1, (b) electrode surface after immersion in solution S_2, (c) electrode surface after immersion in solution S_3 and (d) electrode surface after immersion in solution S_0.

used in a preventive mode which means when it was initially introduced in the chloride absence.

The polarization curves show that when the inhibitor was added at the beginning (S_2: preventive mode) before the chloride addition, the electrode was maintained passive up to −250 mV/SCE. The stabilization effect on the passive layer of the inhibitor was evident, but less pronounced, when the inhibitor was added after 24 h immersion of electrodes in solution containing chlorides (S_1: curative mode) or in S_3 solution.

These results show that the best inhibitor effectiveness, in simulated pore solutions, was obtained when it was used as a preventive inhibitor. This observation is confirmed by the macrophotography of Fig. 4 of the electrode surface immersed in S_2 solution.

During the first 24 h, the inhibitor contributed to the formation of a stable passive layer which resisted to the successive aggressive action of chloride ions, as the E_{corr} measurements confirmed (Fig. 2).

When the inhibitor was added in solutions containing chloride ions (S_1 and S_3), its effect was lower. The chloride ions have interfered on the formation of the film on the steel surface [8,12].

3.2. Mortar slabs

The mortar specimens have been immersed, during six months, in the solutions added with NaCl at the concentration of 0.5 mol/l. Then, they were transferred to the chloride free but inhibitor containing solution S. The blank specimen was maintained in the 0.5 M sodium chloride solution. Electrochemical behaviour of steel was monitored through the measure of the steel potential and the anodic current density I_{corr} every two months.

3.2.1. Action of solution S (added with the inhibitor) on the corrosion of rebars of the mortar specimens

Transferring the mortar specimens to the solution S resulted in ennobling the steel potential values (Fig. 5) and in stopping the increase of the anodic current densities moreover in returning it into a decrease (Fig. 6). These electrochemical data indicated an initiation and a going on of the inhibiting effect. Furthermore, they revealed the diffusion action of the investigated product while it was diluted in water with a dilution coefficient equal to 1/50. This quantity was sufficient to slow down the existing corrosion process.

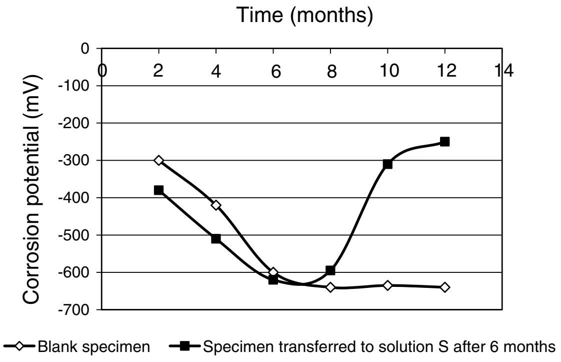

Fig. 5. Evolution of steel potential of rebars embedded in mortar specimens immersed in solution with added chlorides and then in solution S.

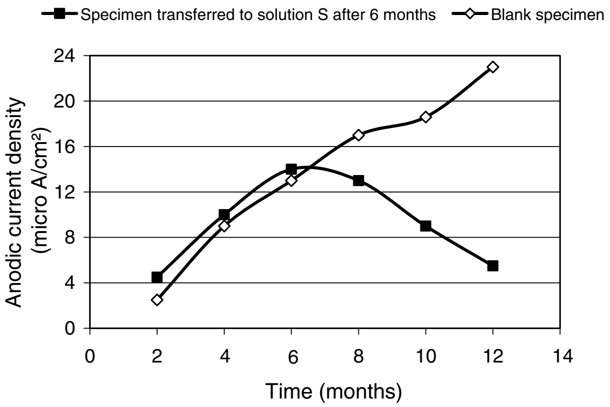

Fig. 6. Evolution of anodic current density of rebars embedded in mortar specimens immersed in the solution with added chlorides and then in solution S.

3.2.2. *Action of solution S′ (mixture containing chlorides and the inhibitor) on the corrosion of rebars of the mortar specimens*

For these specimens, monitored at the same dates indicated above, the action of the inhibitor can also be rapidly noted through the increase of the potential to less negative values and the decrease in anodic current densities as illustrated in Figs. 7 and 8 [18]. This finding was confirmed by the visual observations which showed reduced corroded zones compared to the case of the blank specimen. Hence, it seemed that the presence of chlorides did not disturb the action of the inhibitor. This behaviour can be attributed to its capability of binding chloride ions when it was diluted at 1 ml/50 ml of a mixture containing chlorides.

The inhibiting efficiency detected in the case of mortar specimens, controlled after a six month immersion in chloride containing solution, can be explained by the ability of diffusion that allowed a film formation before reaching high chloride concentration around the steel surface. In one hand, and with taking as reference the results found in solutions, it is possible to say that the product allowed the good inhibition due to its action of binding chloride ions present in the pore mortar solution. This action occurred before that the concentration around the steel rebar reached high values: it was the preventive effect. This interpretation is in a good agreement with the results found in the case of simulating solution S_2 where the preventive mode of use was applied.

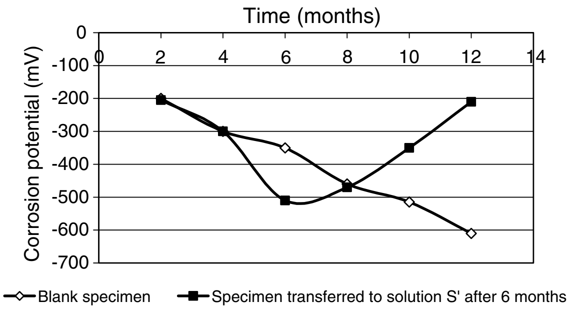

Fig. 7. Evolution of steel potential of rebars embedded in mortar specimens immersed in the solution with added chlorides and then in solution S′.

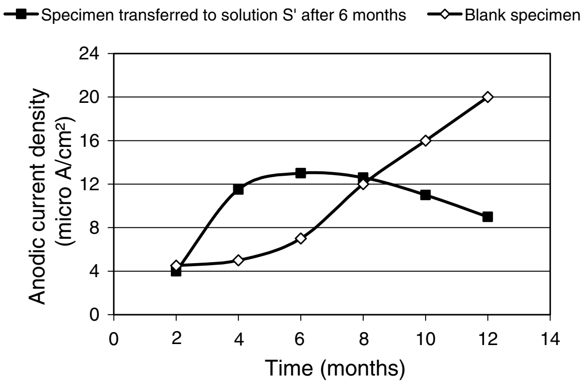

Fig. 8. Evolution of anodic current density of rebars embedded in mortar specimens immersed in the solution with added chlorides and then in solution S′.

On the other hand, the electrochemical techniques indicated the corrosion of the steel rebars after the six month immersion in the aggressive solution. The same techniques and the visual observation showed less corroded zones after a successive immersion in the inhibitor containing solutions: this illustrated the inhibitor curative effect. In fact, Tritthart [13] reported that organic inhibitors were described as fast-penetrating ones. Similar results were obtained by Jamil et al. [19] where the penetration of an amino-alcohol based inhibitor was studied in the case of different mortar thicknesses. It seemed that resistance of the protective film increased with time, being independent of the mortar thickness. Furthermore, the coupling of the preventive and the curative effect was strongly underlined by Nmai [20] who noted that acting by a two fold mechanism is the principle characteristic of the multi-functional organic inhibitors.

The same results let to note that the inhibitor curative action in simulated pore solutions seemed to be less pronounced then the one in mortar. For this reason, from a specimen being immersed during six months in the aggressive solution, some mortar was extracted from the steel-mortar interfacial zone which is the contact zone between mortar and steel rebar. After analysis, it was found that the chloride concentration in the cement filtrate was equal to 0.018 mol/l corresponding to a chloride to cement ratio equal to 2.82%. This low chloride concentration value, compared to the one adopted in simulated pore solutions which is equal to 0.5 mole/l, explains the better inhibiting result obtained in the case of mortar specimens.

4. Summary and conclusions

This investigation was conducted in order to check the most efficient mode of use of an amino-alcohol based mixed corrosion inhibitor both in the two cases of simulating solutions and real mortar specimens. In order to get a rapid result, tests were, first, carried out in simulated pore solutions: the inhibitor showed an acceptable inhibitive action when it was introduced before the chlorides. In the case of mortar specimens, it was obviously noticed, contrary to the case of simulated pore solutions, that the inhibitor was effective even with the presence of chlorides: the curative mode of use is efficient since the inhibitor reacted against existing corrosion and was able to slow down its progression in the two cases of presence or absence of chlorides. The inhibitor efficiency greatly depended on the environment and the way of use. Its dilution at 1 ml/50 ml in water can be considered as a suitable mean that can insure diffusion in the case of mortar specimens with standard mix.

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