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Na_2PO_3F AS INHIBITOR OF CORRODING REINFORCEMENT IN CARBONATED CONCRETE

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ABSTRACT

In the present paper a protective action of Na_2PO_3F from corrosion of steel concrete in carbonated environments is presented. The inhibitor effect has been followed using electrochemical techniques. Na_2PO_3F has been tested as a curative method penetrating from outside when the steel reinforcement is already corroding by carbonation of concrete cover. Results show that the product can reduce significantly an active corrosion through the use of drying and wetting cycles of the concrete cover with solutions having high concentration of Na_2PO_3F.

Introduction

A bibliography study shows that the widest experience with the use of inhibitors to protect rebar from corrosion has been developed in the case of chloride attack (1)(2)(3)(4)(5).In these experiments the only case taken into account is that of a preventing action by adding the inhibitor during the mixing of the concrete. However little is known about the chemistry and characteristics of inhibitors when they are introduced from outside into hardened concretes. Concrete properties vary and are subjected to environmental conditions (6).

Concrete carbonation, encountered mainly in structures 20–30 years old, is considered as one of the most important cause of rebar corrosion.

On the other hand, very few studies on the use of corrosion inhibitors have been done in the field of carbonation, except those developed by some of the authors of the present paper (7)(8). The inhibition ability of nitrites was studied, together with the preventing action against rebar corrosion due to likelihood of further carbonation of the concrete cover.

Inhibitors are generally considered as preventive method for rebars corrosion, but very litle attention has been given to the use of inhibitors as a remedial procedure, only a Japanese study (9) has been found in the literature.

Traditional repair methods usually start with the removal of the deteriorated zones and cleaning of the steel surface. This procedure is expensive and may damage the structural integrity when large areas have to be treated. In consequence, it looks of interest to study alternative remedial measures which avoid the need of an extensive concrete removal or rebar cleaning.

An alternative repair method is proposed in the present paper, consisting in the penetration of a corrosion inhibitor through the pores of the hardened concrete. This product is designed to reach the rebars to prevent or even stop active corrosion.

The aim of the present study is to evaluate the inhibiting ability of Na_2PO_3F when entering from outside for repassivation of the rebars suffering active corrosion due to concrete cover carbonation.

Previous work with the same product (10) demonstrates the inhibition properties of Na_2PO_3F, added to the mixing water against the corroding attack of chlorides. The ratio PO_3F^{-2}/Cl^- is preferencially ≥ 1. The inhibition was also detected when Na_2PO_3F penetrates form outside together with chlorides. The present paper deals particularly with the case of reducing already active corrosion.

Experimental Procedure

Solution Tests. Synthetic solutions were used to simulate those of concrete pores. The solutions were prepared with deionized water adding $Ca(OH)_2$ until saturation (pH = 12.6). Different amounts of Na_2PO_3F (also named MFP), as a corrosion inhibitor, were added to these solutions: 5 and 10% by weight (corresponding to 0.34 and 0.70 M concentration of the inhibitor).

These solutions were carbonated (reduction of the initial pH) by bubbling CO_2 through the solution until total carbonation (pH ~ 7) and depassivation of the rebars were detected. After carbonation, the corrosion process was left to develop for a certain time.

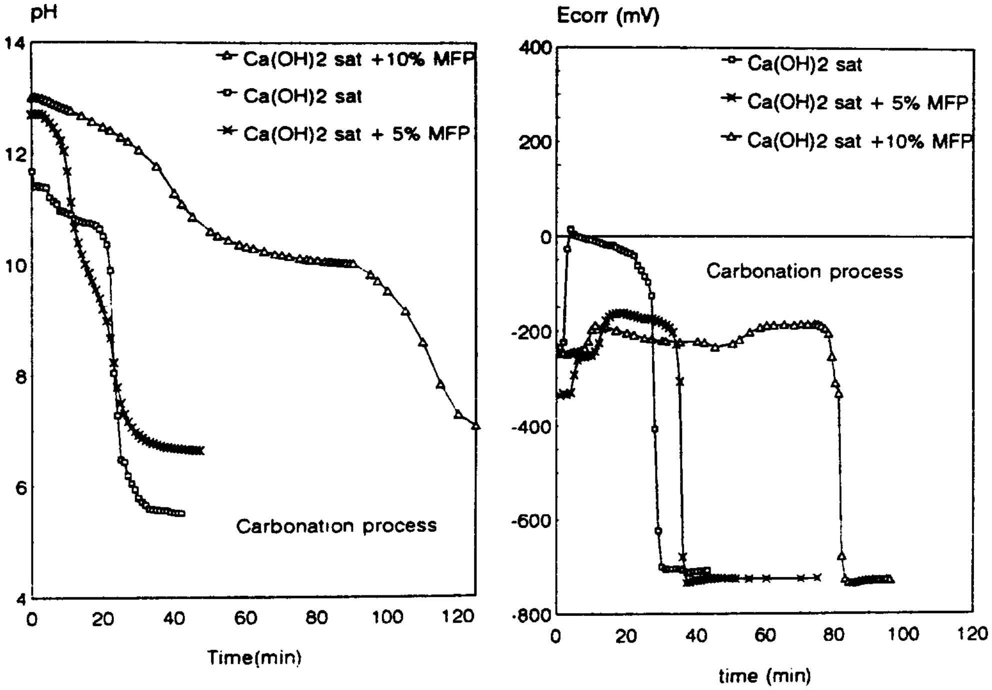
Afterwards, 5% Na_2PO_3F (MFP) were added to the solutions without inhibitor to check the inhibition effect in the corrosion process.

The type of corrosion cell used was described previously (11). Two reinforcing bars and a carbon rod acting as counter electrode were immersed in each solution. Polarization Resistance (Rp), Corrosion Potential (Ecorr) and Impedance measurements were monitored during a period of 30 days.

Mortar Tests. Mortar specimens of 8 × 5.5 × 2 cm in size similar to those described in reference (10) were fabricated with an OPC cement. A cement/sand (c/s) ratio of 1/3 and water/cement (w/c) ratios of 0.4, 0.5 and 0.6 were used.

The procedure followed with all specimens was:

1. 28 days curing period in a chamber at 100% R.H. and 20 ± 2°C.
2. Preconditioning of specimens before carbonation, holding them for some time in a chamber at 50% R.H., until sufficient drying.
3. Then the specimens were rapidly carbonated in a CO_2^- filled chamber at 60% R.H., until depassivation of rebars was detected and mortars were completely carbonated.
4. The active corrosion of specimens was maintained for several months, holding them partially submerged in water to guarantee the development of corrosion products (rust).
5. The inhibiting ability of Na_2PO_3F was tested by means of dry and immersion cycles, submerging the corroding specimens in a 20% (MFP) solution. Two types of cycles were tested, and they were distinguished as "short" and "long" treatments.
   a) "Short" treatment: One cycle of drying the specimens 3 days at 105°C followed by, 2 days of immersion in the solution at room temperature. This treatment was used in the mortar c/s = 1/3 and w/c = 0.5.



FIGS. 1 AND 2.

Ecorr of rebars (left) and pH evolution (right) during the carbonation process of simulated pore solutions with MFP addition.

b) "Long" treatment: Several cycles of drying the specimens at 50°C for 7 days followed by immersion in the MFP solution at room temperature for 2 days. The number of cycles were five for the specimen with c/s = 1/3 and w/c = 0.5 and ten cycles for the specimens with c/s = 1/3 and w/c = 0.4 or 0.6.

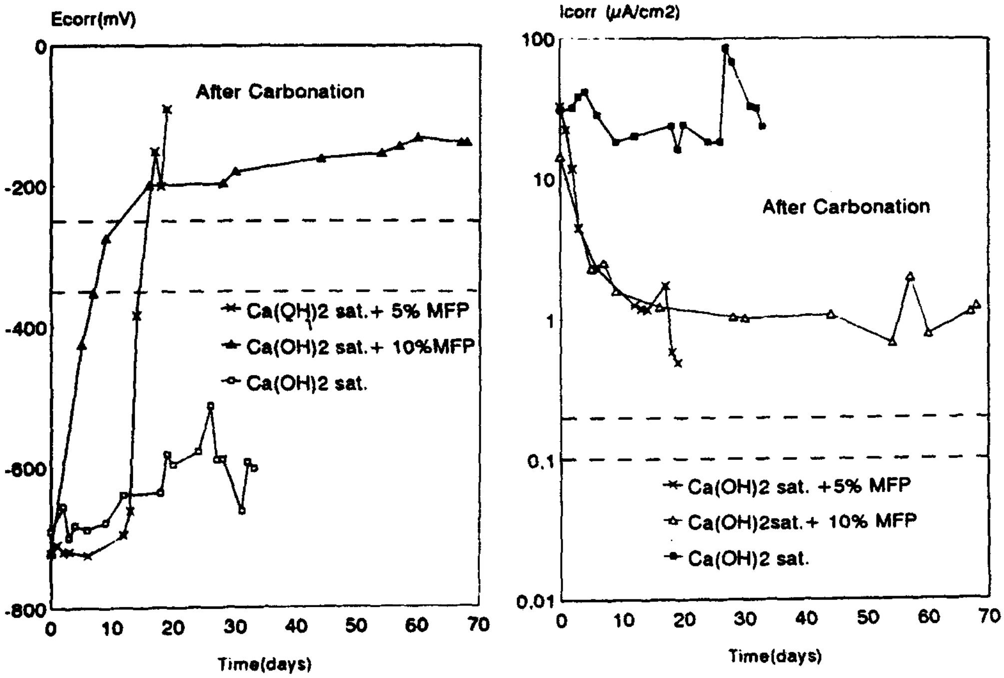
6. Finally the efficiency of the treatment was tested in the specimens with c/s = 1/3 and w/c = 0.5 keeping them in partial water immersion for about 30 days at room temperature.

Corrosion potential and polarization resistance were the electrochemical techniques used for corrosion monitoring in these tests.

Techniques of Corrosion Monitoring. As mentioned above, in the solutions and in the mortar specimens the corrosion process was studied by electrochemical techniques.

In both systems, the Corrosion Potential (Ecorr) was determinated through a saturated calomel electrode as reference. The instantaneous corrosion rate values (Icorr) were obtained from the Polarization Resistance measurements (Rp) according to Stern and Geary equation (12): Icorr = B/Rp. The values of the B constant used were 26 mV when the specimens were actively corroding and 52 mV when they were in a passive state, as used in previous work (13).

Impedance measurements were taken only for $Ca(OH)_2$ satured solutions without and with 5% MFP before and after carbonation. The frequency range used was 10 mHz–50 KHz keeping deviations of the corrosion potential less than 20mV.



FIGS. 3 AND 4.

Ecorr (mV) SCE (left) and Icorr (μA/cm^2) (right) after the carbonation of simulated pore solutions with MFP addition.

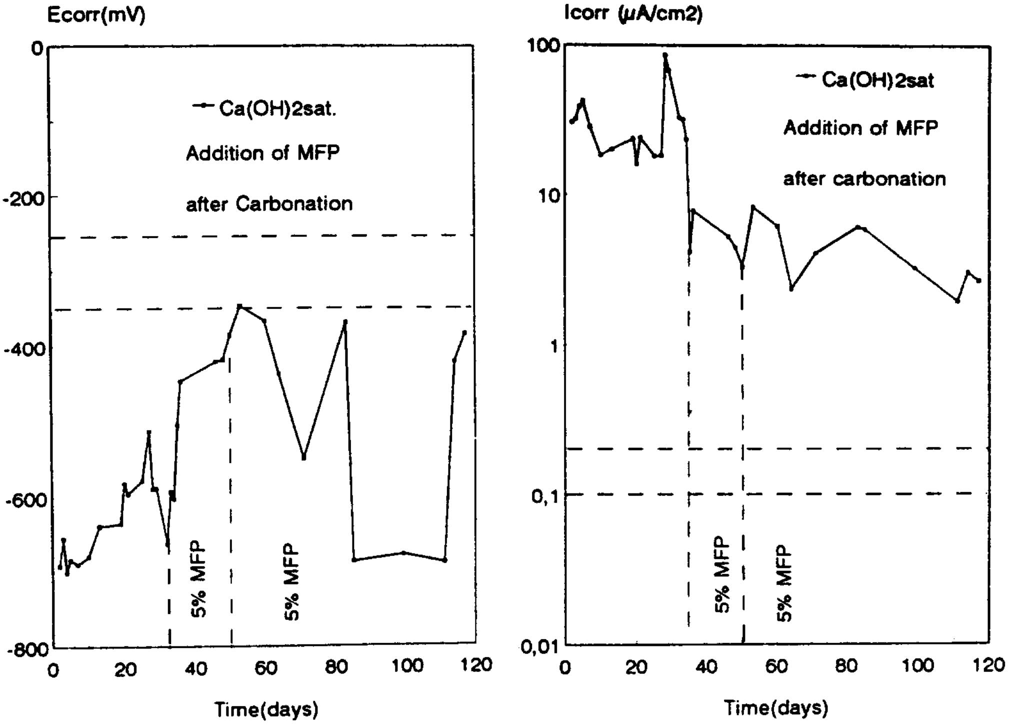
Results

Solutions. During the carbonation process of solutions prepared with Ca(OH)$_2$ sat. and different Na$_2$PO$_3$F additions, (0,5 or 10% MFP) the pH changes in the solution and Ecorr on the rebar were monitored. Other electrochemical techniques could not be applied, due to the continuous changes of Ecorr during the carbonation process.

Figure 1 shows the changes in Ecorr, according to the Nernst equation, during the first minutes of CO$_2$ flow. These changes are due to the lowering of the pH. The increase of Ecorr was higher when no Na$_2$PO$_3$F was added. In the case of 5 and 10% Na$_2$PO$_3$F additions, the changes occurred in two steps, possibly due to the formation of different type of phosphates and carbonates/bicarbonates having a buffer effect. Figure 2 represents the evolution of the pH, showing the two steps decay in presence of MFP.

The further sharp decay to very negative Ecorr values (near to -700 mV SCE) takes place at different times depending on the amount of Na$_2$PO$_3$F employed. This is attributed to the moment of rebar depassivation which occurs later when 10% MFP is used, and only after reaching the pH = 7. This pH limit for rebar depassivation agrees with that found in (14).

Once rebars were depassivated, and after total carbonation of the solutions, Ecorr and Icorr measurements were also monitored in the same solution. Results are shown, respectively, in Figures 3 and 4. When no Na$_2$PO$_3$F was used very active corrosion occurs (around 30 μA/cm^2). This behaviour correlate with Ecorr values, remaining around -600 mV even after 30 days of testing.



FIGS. 5 AND 6.

Ecorr (mV SCE) (left) and Icorr (µA/cm^2) (right) evolution on the inhibition effect of MFP added to carbonated pore solutions.

However, with 5 and 10% Na_2PO_3F additions, Ecorr evolves again to more positive values, (-200 mV) and Icorr levels change after few days reaching values of 1 µA/cm^2 at 20 days. For 10% addition the test was extended until 70 days and it was appreciated that the Icorr does not decrease significantly with time.

In the case of the carbonated solution with no initial Na_2PO_3F addition, 5% of Na_2PO_3 was added after 30 days or active corrosion (Figures 5 and 6); the Ecorr then changes to -400 mV and Icorr decreases from high levels (30 µA/cm^2) and stabilizes around 1–3 µA/cm^2. After 20 days another 5% MFP was added. In this case, no significant change was observed either in Ecorr or Icorr measurements. Further additions of MFP to a carbonated solution do not change significantly the neutral conditions: from pH = 7 at 0% MFP to pH = 8 after first 5% addition of MFP and 8.5 after second 5% addition.

In some cases impedance measurements were also carried out. In Figure 7 the results after some days of carbonation are given for the solutions with 5% and without MFP addition. The diameter size of the semicircle was higher when the inhibitor was added which indicates the inhibitor effect of MFP in carbonated conditions.

Once the tests were finished the corrosion products were observed. A black oxide (covered the rebar surface), as well as a some brown oxides. After cleaning the oxides, a generalized attack was detected.

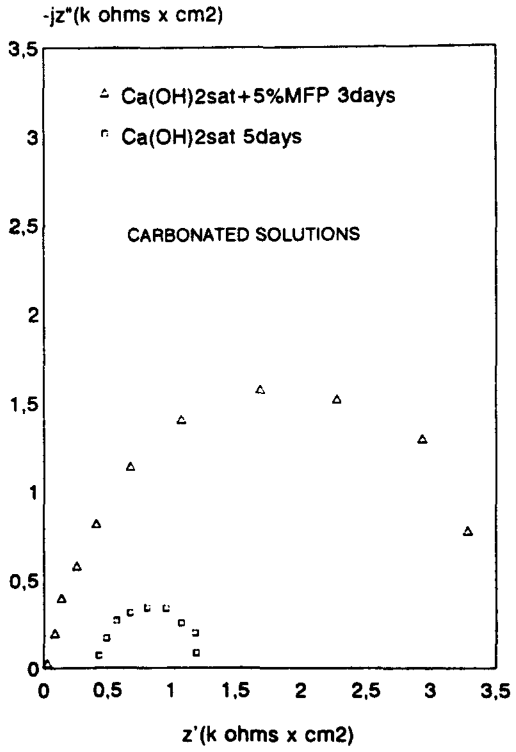


FIG. 7.
Impedance results of carbonated pore solutions with MFP.

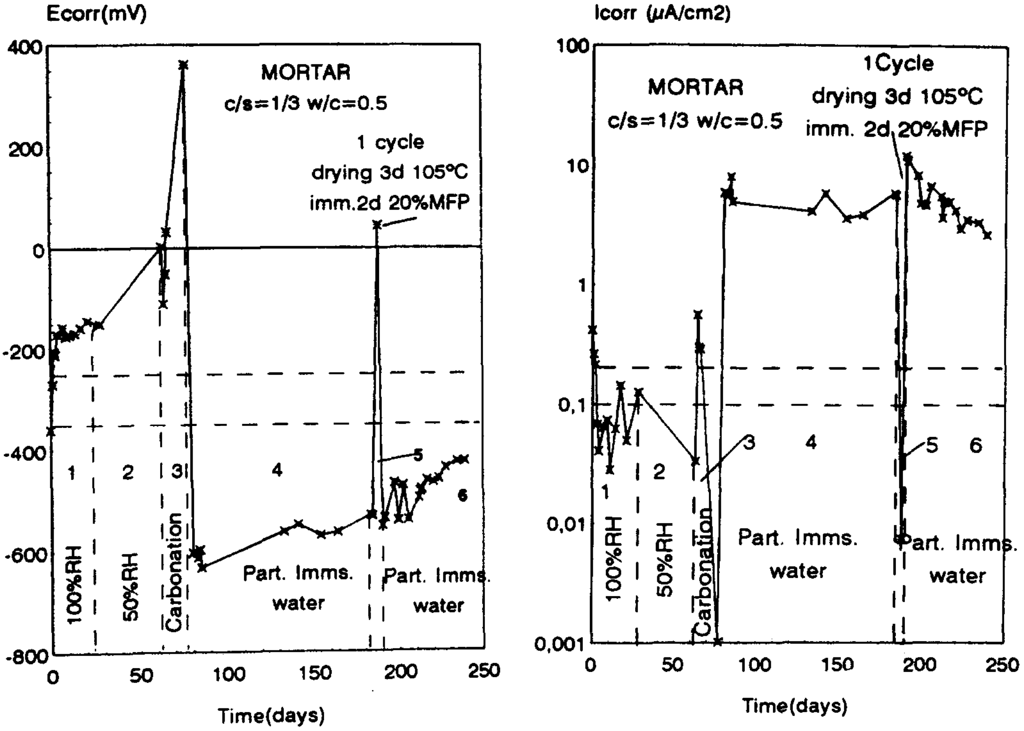
Mortar Tests. After the common treatment of carbonation applied to all the specimens, (already described in the experimental section) and once the rebars were actively corroding, the specimens were submitted to the action of dry and immersion cycles with the inhibitor.

Effect on the Type of Cycle Employed. "Short" and "Long" treatments with Na_2PO_3F were used with specimens having c/s = 1/3 and w/c = 0.5. Before the drying/immersion cycles, the specimens had high corrosion levels as can be appreciated in step 4 in Figures 8, 9, 10 and 11, with Ecorr around -600 mV and Icorr in the range of 5–7 $\mu A/cm^2$.

The "short" treatment shown in figures 8 and 9 (step 5 in figures) keeps after the immersion in Na_2PO_3F, Ecorr values similar to the initial ones around -600 mV, and the Icorr values even suffer a small increase although a certain decrease is appreciated when kept in partial immersion (step 6 in figures).

The "long" treatment results are shown in figures 10 and 11 (step 5). Considering the situation immersion in the inhibitor, the Ecorr (figure 10) slowly moves towards more positive values and the Icorr also decreases, (figure 11), after ten cycles (one of them in water) to around -200 mV and 0.3–0.4 $\mu A/cm^2$ respectively.

After both, "short" and "long" treatments, the specimens were kept again partially immersed in water (step 6 in figures) to determine the corrosion response after treatment.



FIGS. 8 AND 9.

Penetration of MFP (1 immersion/drying cycle) through carbonated mortar. Ecorr (left) and Icorr (right) results.

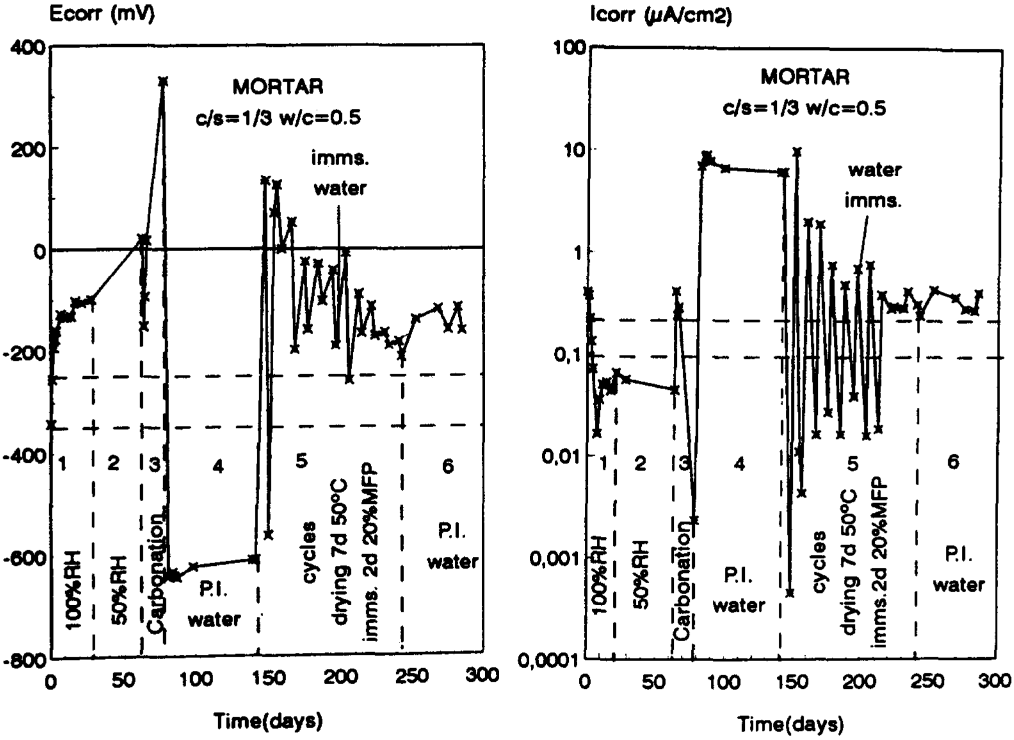
It was appreciated, that in case of one cycle treatment (short) the Ecorr value stays around -500 mV and Icorr around 3 μA/cm^2 even after 50 days treatment. The specimen submitted to several cycles (long) remain in the range of -100 mV or 0.3 μA/cm^2. The "long" treatment seems to be the most effective.

The observation of the bars at the end of the test shows the presence of black and yellow brown oxides. A general attack was detected in the rebars after the end of both treatments.

"Long" Treatment and Porosity of Mortar. In order to explore the penetration ability of Na_2PO_3F the porosity of the mortar was modified by using different w/c ratios: 0.4, 0.5 and 0.6. The three specimens were carbonated as usual and actively corroding as indicated by the Ecorr (-500 or -600 mV) and the Icorr (0.4–7 μA/cm^2) values before inhibition.

Results after being submitted to MFP treatment are presented in figures 12 and 13, for Ecorr and Icorr, respectively. In these figures only results after the immersion cycles are considered in order to better appreciate the corrosion activity.

In all cases the trend of the potential was to evolve towards more positive values indicating the reduction of activity; this was also confirmed by Icorr measurements. However the process is slow and does not seem to be influenced significantly by the porosity of mortar. The faster



FIGS. 10 AND 11.

Ecorr mV SCE (left) and Icorr (µA/cm^2) evolution of rebar in carbonated mortar. Penetration of MFP through immersion/drying cycles.

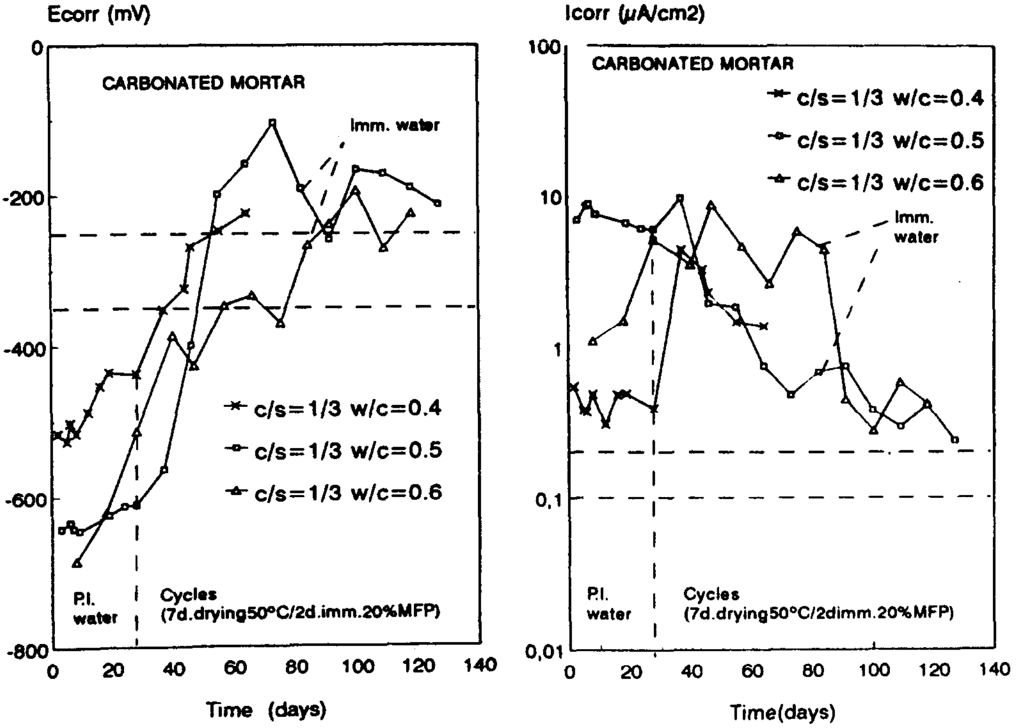
reduction of corrosion was found with w/c = 0.5, but at the end of treatment efficiency is similar to the specimen with w/c = 0.6.

Several immersion and drying cycles are needed to significantly reduce the corrosion activity (to Ecorr values around -200 mV and Icorr around 0.3 µA/cm^2).

Discussion

The more common practice is to use corrosion inhibitors a preventive method. Almost no experience has been reported of the possible addition of inhibitors to concrete structures which have shown corrosion activity. The impregnation of damaged concrete surface with an inhibitor is being tested in Japan (9) using nitrite. The impregnation method has been focused to the case of chloride attack, but no experience has been found in the literature regarding treatment of carbonated concrete.

Removal of contaminated concrete and patch repairs are generally the methods employed to treat corrosion damage structures. However, to eliminate the whole of the affected concrete cover is expensive. The method proposed in this paper, using MFP as a corrosion inhibitor penetrating through contaminated concrete, may be a simple and less expensive solution.



FIGS. 12 AND 13.

Ecorr mV SCE (left) and Icorr (μA/cm^2) (right) in carbonaated mortar with various w/c ratios. Results after immersion cycles, 2 days in 20% MFP solution.

The inhibition action of Na_2PO_3F against chloride corrosion was tested in a previous paper (10). In that case, the penetration of Na_2PO_3F through hardened mortar together with chlorides was also tested. The interest was to protect old structures from further chloride corrosion. It was appreciated that a certain delay on corrosion initiation in presence of chloride occured.

In this paper the main objective has been to study the ability of Na_2PO_3F to act against active corrosion produced by the carbonation of the concrete (neutral values of pH without chlorides). A more significant inhibiting action than with chlorides is found.

Regarding the possible inhibiting mechanism, the action of Na_2PO_3F detected seems similar to that proposed for phosphates. Na_2PO_3F hydrolyses in aqueous and neutral media to form orthophosphate and fluoride through a process like (15):

$$Na_2PO_3F + H_2O \rightleftharpoons F^- + H_2PO_4^- + HPO_4^{-2}$$

Therefore, the inhibiting action of Na_2PO_3F may be attributed to the formation of phosphates, and so the anodic formation of a passive layer of Fe_3O_4, γFe_2O_3 and $FePO_4 \cdot H_2O$ (16) (3) (17). This mechanism implies an anodic behaviour, although some authors (18) also consider certain cathodic behaviour. This last possibility could explain the cathodic polarization of the potential and the slight increase on corrosion rate detected in some occasions after the addition of MFP.

XRD analysis made on mortar previously impregnated with MFP indicated the presence in the forms of NaH PO_4 or $NaHPO_3F$.

The effect of the MFP concentration on the inhibiting action in neutral conditions, increases with concentration. In simulated carbonated pore solutions, the increasing addition of Na_2PO_3F reduces the corrosion rate by more than one order of magnitude. However, corrosion values of Icorr lower than 0.2 $\mu A/cm^2$ has not been detected even with the slow addition of 10% Na_2PO_3F.

It is more difficult to slow down corrosion when the inhibitor has to act against an active corrosion process. The different state of the surface of the steel covered with rust and the possible reduction of iron oxides could be the reasons for the lowered effectiveness of the inhibitor and the need for higher concentrations.

Concerning the penetrating methods employed, "short" and "long", it has been proven that the effectiveness increases with the number of immersion/drying cycles, probably due to increases in the concentration of inhibitor reaching the rebar. The size and distribution of the pores also influences the penetration process.

Practical applications of MFP to real structures has shown that MFP penetrates even more than 30 mm. The penetration depends on capillary absortion. Number of applications and time between saturations of concrete with the MFP also determine the depth of penetration.

Conclusions

1. Na_2PO_3F acts as a corrosion inhibitor in neutral media at least in the test conditions used.
2. Na_2PO_3F may be used as a corrosion inhibitor to reduce significantly the corrosion rate of corroding rebars in carbonated concrete.
3. Dry and immersion cycles seem a suitable method to allow the penetration of Na_2PO_3F, although high concentrations and long treatments are needed to significantly reduce active corrosion.

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