The use of a Phosphate-Based Migrating Corrosion Inhibitor to Repair Reinforced Concrete Elements Contaminated by Chlorides

Francesca Tittarelli, Alessandra Mobili, Tiziano Bellezze
Department of Materials and Environment Engineering and Physics (SIMAU), Università Politecnica delle Marche (UNIVPM), UdR INSTM, Via Brecce Bianche, 60131 Ancona, Italy

Abstract: The use of sodium monofluorophosphate (MFP) was experimented as migrator inhibiting treatment against corrosion of reinforced concrete elements induced by chlorides. The results show that sodium monofluorophosphate, applied by surface impregnation, is able to slow down reinforcement corrosion only for reinforcing steel bars with concrete cover not thicker than 1 cm. This limitation is most probably due to the difficulty, with the type of application adopted, in making MFP to reach concentrations high enough to inhibit the corrosive process at greater depths from the impregnation surface.

Keywords: Concrete, Inhibitor, Reinforcement corrosion, Surface treatment

1. INTRODUCTION

Aggressive ions, such as sulphates and chloride ions in polluted area and coastal zone [1]-[2]-[3], promotes concrete deterioration and corrosion of embedded reinforcements. Methods proposed for corrosion mitigation in reinforced concrete structures include cathodic protection, where current is impressed to polarize the reinforcement or a sacrificial anode is placed to protect the rebar [4]; galvanised reinforcement, which provides protection through sacrificial corrosion [5]-[6]-[7], and stainless steel rebar, which is highly corrosion resistant but very expensive [8]; concrete protection through surface treatments which make concrete less susceptible to water saturation [9]-[10], or penetrating natural bioactive agents [11] and corrosion inhibitors. In particular, corrosion inhibitors are chemical products that, when added to the concrete mixture, can prevent or delay corrosion of steel reinforcing bars embedded in concrete structures [12]. More recently, the possible use of inhibitors as a rehabilitation method to slow down or to inhibit the active corrosion process in reinforced concrete structures is very promising. In this case, inhibiting products can be directly applied on steel reinforcing bars after concrete cover removal during restoration work, or they can even be put in contact with the reinforcing bars as corrosion inhibiting admixtures added to the restoring mortar and/or concrete. Inhibitor solutions can also be used by means of direct impregnation on the concrete surface to be treated or, finally, by means of electrophoretic methods. Among the inhibitors studied to delay steel reinforcement active corrosion in concrete, sodium monofluorophosphate...
(MFP) has aroused particular interest as a migrating inhibitor in concrete surface treatments for restoration. The fluorophosphate ion [13]-[14] seems to slow down reinforcement dissolution and to catalyse the formation of a passive protective film on reinforcing bars. Mechanical consolidation of the treated cementitious matrix, due to the precipitation of apatite, has also been observed. These two combined effects seem to retard steel reinforcement active corrosion and even to hinder further penetration of aggressive agents. Moreover, the absence of undesirable effects caused by concrete treatment with MFP and its absolute harmlessness have made MFP a very promising corrosion inhibitor, such that it was used in the restoration work of the Towers of Carouge and the Bridge of Peney in Geneva.

However, it is necessary to underline that, in spite of the beneficial effects of corrosion inhibitors currently reported in the literature, unanimous agreement does not exist on their real effectiveness, particularly due to some experiments showing that their use actually increases corrosive phenomena.

Therefore, this work was aimed to verify the effectiveness of MFP use to slow down active corrosion of steel reinforcing bars during concrete structures restoration. The need for further investigation is justified by poor experience achieved with this type of inhibitor on real concrete structures, since most of the experimental results, available to date, were obtained on cementitious systems simulating concrete, with application techniques not always feasible in current restoration practice.

2. Experimental

2.1 Specimens

Prismatic reinforced concrete specimens were manufactured (10×10×40 cm) by mixing cement (CEM II/A-L 42.5 R according to European Standards), natural aggregates and water with a w/c = 0.7. In this way a rather porous concrete matrix was obtained, able to allow faster induction of the steel reinforcement corrosion process in order to better underline the effectiveness of the corrosion inhibitor, if any. Each concrete specimen was reinforced with 4 steel ribbed bars (d = 10 mm) embedded at the corners of the specimen cross section (Fig. 1). Two different concrete covers, respectively equal to 1 and 2 cm, were adopted.

![Fig. 1. Reinforced concrete specimen.](image)

All the specimens were air cured for 1 month at room temperature before their exposure to weekly wet-dry cycles (2 days wet followed by 5 days dry) in 3.5% NaCl solution to induce the corrosive process.
2.2 Tests

The corrosion risk of reinforcement embedded in the concrete specimens was evaluated by means of free corrosion potential measurements with a saturated calomel electrode (SCE) as reference. The kinetic of the corrosion process was monitored by polarisation measurements (adopting B = 26 mV as Stern-Geary constant). By using an external graphite bar as counter-electrode, the polarisation resistance was measured through the galvano-dynamic method as average value calculated between the anodic and cathodic ones.

The following graphs report the average electrochemical values obtained by measuring four reinforcing bars embedded in the same specimen during the full immersion period.

Once the electrochemical data and the autoptic examination of the steel reinforcement, extracted by splitting the specimens, assessed that the corrosive process had started, half of the specimens was submitted for 10 days to daily surface impregnation treatment with 20% MFP aqueous solution, whilst the other half, as reference, was contemporarily submitted to impregnation with tap water only. Then, all the specimens were stored at room conditions for 7 days.

Subsequently, all the specimens were newly exposed to wet-dry cycles with tap water. Electrochemical monitoring of the corrosion behaviour was continued in order to verify if washing out could affect the effectiveness in time of the MFP impregnation treatment.

At the end of the experimentation, chloride ion penetration through concrete cover was quantitatively evaluated by means of free chlorides determination (UNI Standard 9944). At the same time, quantitative analysis of MFP impregnation was carried out by means of emission spectrophotometric analysis (AES-ICP) on cement paste samples removed at different depths from the concrete specimen surface.

Finally, to further evaluate the electrochemical behaviour, at the end of the test, the concrete specimens were split in order to assess reinforcing bar corrosion by visual observation.

3. DISCUSSION OF TEST RESULTS

Fig. 2a shows free corrosion potential of reinforcing steel bars with 1 cm concrete cover, as a function of time, before and after MFP treatment. The reported trend can be compared with that obtained from the corresponding specimens treated with water and shown in Fig. 2b.

![Fig. 2. Free corrosion potential of the reinforcing steel bars embedded with 1 cm concrete cover in the specimens treated with MFP (a) and water (b).](image-url)
It is evident that without MFP treatment (Fig. 2b) the potential maintains at a constant value of about -600 mV/SCE, which is typical of active corrosion. After the inhibitor application (Fig. 2a) the free corrosion potential seems, indeed, to shift toward passivation values (E = ~ -500 mV/SCE).

The corrosion rate measurements (Fig. 3) confirm the free corrosion potential trend. As a matter of fact, the corrosion rate of the reinforcing bars embedded in the reference concrete specimens without inhibitor treatment (Fig. 3b) continuously rises up to values of about 70 µm/year, whilst, after the MFP treatment, the corrosion rate slowly decreases to values as low as a few µm/year (Fig. 3a).

![Fig. 3. Corrosion rate of the reinforcing steel bars embedded with 1 cm concrete cover in the specimens treated with MFP (a) and water (b).](image-url)
In the case of thicker concrete cover (2 cm) the results obtained after the inhibitor application were not as promising. In this case, in fact, after the inhibitor application, significant improvement in corrosion resistance of steel reinforcement in terms of either free corrosion potential (Fig. 4a) or corrosion rate (Fig. 4b), were not observed.

This electrochemical behaviour was also confirmed by autoptic evaluation carried out on the reinforcing steel bars extracted from the concrete specimens after their splitting. Indeed, the steel corroded area appeared appreciably lower on reinforcing bars with 1 cm concrete cover extracted from the specimens treated with MFP (Fig. 5) than that observed on the reinforcing bars either embedded with 2 cm concrete cover (Fig. 6) or in the reference specimens treated with water (Fig. 7).

This result may probably be due to the fact that with the application used, it was impossible to achieve high enough MFP concentrations at 2 cm depth to effectively counteract chloride induced corrosion.

![Fig. 4. Free corrosion potential of the reinforcing steel bars embedded with 2 cm concrete cover in the specimens treated with MFP (a) and water (b).](image)

![Fig. 5. Autoptic evaluation of reinforcing steel bars embedded with 1 cm concrete cover in the specimens treated with MFP.](image)
In order to obtain further evidence for the above mentioned hypothesis, chloride and MFP profiles in the concrete cover were determined by quantitative analysis. Tables 1 and 2 respectively show quantitative determinations of free chlorides and MFP at different depths from the reinforced concrete specimens surface.

### Table 1. Free chlorides content at different depths from the surface of the reinforced concrete specimens exposed to the aggressive environment.

| Depth (cm) | Free chlorides (% by cement weight) |
|------------|-------------------------------------|
| 0-1        | 0.98                                |
| 1-2        | 1.01                                |
| 2-3        | 0.84                                |
| 3-4        | 0.80                                |

### Table 2. MFP content at different depths from the surface of the reinforced concrete specimens treated by MFP impregnation.

| Depth (cm) | MFP (% by cement weight) |
|------------|--------------------------|
| 0-1        | 12.15                    |
| 1-2        | 0.19                     |
| 2-3        | -                        |
| 3-4        | -                        |

As can be noticed in Table 1, whatever the depth from the concrete surface, chloride concentrations certainly exceed the minimum threshold (0.4% by weight of cement) reported in the literature as the one necessary to induce the corrosive process, by exposing the reinforced concrete specimens to the aggressive environment.
Table 3. MFP/Cl molar ratio at different depths from the surface of the reinforced concrete specimens.

| Depth (cm) | MFP/Cl |
|-----------|--------|
| 0-1       | 3.00   |
| 1-2       | 0.05   |
| 2-3       | -      |
| 3-4       | -      |

In any case, the results obtained show that only at 1 cm concrete cover the molar ratio MFP/Cl (Tab. 3) is significantly greater than 1. According to the literature [14], this value represents the minimum value needed to make the inhibitor effective in counteracting chloride induced corrosion.

4. CONCLUSIONS

- Sodium monofluorophosphate, used as a migrating inhibitor by means of impregnation on reinforced concrete surface, is able to slow down reinforcement corrosion induced by chlorides.
- However, in this work, sodium monofluorophosphate appears to be effective only for reinforcing steel bars with concrete cover not thicker than 1 cm.
- This limitation can be likely ascribed to the difficulty in making MFP to reach concentrations high enough to inhibit the corrosive process at greater depths from the impregnation surface, with the type of application adopted.

REFERENCES

[1] F. Tittarelli, G. Moriconi, “The effect of silane-based hydrophobic admixture on corrosion of reinforcing steel in concrete,” Cement and Concrete Research, vol. 38, pp. 1354-1357, 2008.
[2] A. Bonazza, G. Vidorni, I. Natali, C. Ciantelli, C. Giosuè, F. Tittarelli, “Durability assessment to environmental impact of nano-structured consolidants on Carrara marble by field exposure tests,” Science of the Total Environment, vol. 575, pp. 23-32, 2017.
[3] I. Ozga, A. Bonazza, E. Bernardi, F. Tittarelli, O. Favoni, N. Ghedini, L. Morselli, C. Sabbioni, Diagnosis of surface damage induced by air pollution on 20th-century concrete buildings, Atmospheric Environment, vol. 45 (28), pp. 4986-4995, 2011.
[4] M. Dugarte, A.A. Sagüés, Accounting for Temperature Effects on an Evolving Galvanic Anode Cathodic Protection System for Steel in Concrete, Corrosion, vol. 72 (11), pp.1462-1469, 2016.
[5] G. Roventi, T. Bellezze, G. Giuliani, C. Conti,“Corrosion resistance of galvanized steel reinforcements in carbonated concrete: Effect of wet-dry cycles in tap water and in chloride solution on the passivating layer,” Cement and Concrete Research, vol. 65, pp. 76-84, 2014.
[6] G. Roventi, T. Bellezze, E. Barbaresi, R. Fratesi, “Effect of carbonation process on the passivating products of zinc in Ca(OH)2 saturated solution,” Materials and Corrosion, vol. 64, pp. 1007-1014, 2013.
[7] T. Bellezze, G. Roventi, E. Barbaresi, N. Ruffini, R. Fratesi, “Effect of concrete carbonation process on the passivating products of galvanized steel reinforcements,” Materials and Corrosion, vol. 62, pp. 155-160, 2011.
[8] F. Tittarelli, M. Carsana, M.L. Ruello, “Effect of hydrophobic admixture and recycled aggregate on physical-mechanical properties and durability aspects of no-fines concrete,” Construction and Building Materials, vol. 66, pp. 30-37, 2014.

[9] Y. Cai, P. Hou, C. Duan, R. Zhang, Z. Zhou, X. Cheng, S. Shah, The use of tetraethyl orthosilicate silane (TEOS) for surface-treatment of hardened cement-based materials: A comparison study with normal treatment agents, Construction and Building Materials, Vol. 117 (1), pp 144-151, 2016.

[10] P. Scarfato, L. Di Maio, M.L. Fariello, P. Russo, L. Incarnato, Preparation and evaluation of polymer/clay nanocomposite surface treatments for concrete durability enhancement, Cement and Concrete Composites, vol. 34 (3), pp. 297-305, 2012.

[11] P. Scarfato, E. Avallone, L. Incarnato, L. Di Maio, Development and evaluation of halloysite nanotube-based carrier for biocide activity in construction materials protection, Applied Clay Science, vol. 132-133 (1), pp. 336-342, 2016.

[12] H. Verbruggen, H. Terryn, I. De Graeve, Inhibitor evaluation in different simulated concrete pore solution for the protection of steel rebars, Construction and Building Materials, vol 124, pp 887-896, 2016.

[13] D. M. Bastidas, M. Criado, S. Fajardo, A. La Iglesia, J.M. Bastidas, Corrosion inhibition mechanism of phosphates for early-age reinforced mortar in the presence of chlorides, Cement and Concrete Composites, vol. 61, pp 1-6, 2015.

[14] C. Andrade, C. Alonso, M. Acha, B. Malric, Preliminary testing of Na2PO3F as a curative corrosion inhibitor for steel reinforcement in concrete, Cement and Concrete Research, vol. 22, pp. 869-881, 1992.

Francesca Tittarelli, graduated in Chemistry with honour, PhD in Materials Engineering, Associate Professor at UNIVPM in the field Materials Science and Technology. She teaches Material Science and Technology for Civil and Environmental Engineering. Since 2012 is associated to the Institute of Atmospheric Sciences and Climate of the National Research Council of Italy (CNR-ISAC). She published more than 150 papers on durability and sustainability of materials for Engineering. She is referent of COSMONET "Concrete Structures Monitoring Network" developed after the patent "Monitoring system for preventative maintenance of reinforced concrete structures." AN2005A000045’. For UNIVPM, she is member of the Academic Board of the PhD Program in Industrial Engineering, the Scientific Council of the Center for Research and Service in Nanostructures Microscopy (CISMIN), the Scientific Council of the Center for Research and Service Engineering Apparatus Motor (CIAM), the Joint Commission. She is founder professor of the Center for Research and Service SMALL (SMArt Living Lab) of UNIVPM and member of the relative board. She is UNIVPM representative in the INSTM board and in the EIP on Raw Material “C&D-WRAM”. She is member of AIMAT, INSTM, ACI, RILEM. She is invited member of ATINER. She is member of the Italian SC5 Consultation Board, she is member of the HDB RILEM Technical Committee. She is referee for several international scientific journals and Evaluator of Projects for Italian MIUR and Romanian National Council.

Alessandra Mobili has a Master Degree in Building Engineer - Architecture at Polytechnic University of Marche (UNIVPM) of Ancona,
Italy. She is a civil engineer and has a PhD in “Materials, Environmental and Territorial Engineering”. From April 2015 to July 2015 she was visiting PhD student at Vrije Universiteit Brussel (VUB) of Brussels, Belgium. Actually she is working in the area of innovative building materials and their sustainability. She is concrete technologist. The actual research is about the study and the development of innovative and environmentally friendly materials for building applications prepared also by re-cycling industrial by-products. Furthermore, her research work is focused on the field of geopolymeric materials for rehabilitation and restoration of ancient and modern buildings.

Tiziano Bellezze was graduated with honours in Chemistry at the University of Parma (Italy) in 1995, discussing a thesis in the field of theoretical chemistry. He took the PhD in Materials Engineering at the University of Bologna (Italy) in 2000, discussing a thesis in the fields of Corrosion Science. The PhD thesis won the prize ‘Fondazione Oronzio De Nora 2001’ given by the Electrochemical Division of the Italian Society of Chemistry. Since 2007, Tiziano Bellezze is Researcher at the Polytechnic University of Marche (Italy). He is member of Italian Corrosion Technical Committee within the Italian Metallurgical Association (AIM). Furthermore, he is member of European Federation of Corrosion (EFC) though AIM, member of Italian Association of Materials Engineering (AIMAT) and member of National Interuniversity Consortium of Materials Science and Technology (INSTM). He is author of more than 100 papers in the field of Corrosion Science.
Corrigendum:
Francesca Tittarelli et al 2017 IOP Conf. Ser.: Mater. Sci. Eng. 225 012106

The use of a Phosphate-Based Migrating Corrosion Inhibitor to Repair Reinforced Concrete Elements Contaminated by Chlorides

The published references are not correct.

Please replace with:

[1] V. Corinaldesi, G. Moriconi, F. Tittarelli, “Thaumasite: evidence for incorrect intervention in masonry restoration”, Cement & Concrete Composites, vol. 25 (8), pp. 1157-1160, 2003.
[2] I. Ozga, N. Ghedini, C. Giosuè, C. Sabbioni, F. Tittarelli, A. Bonazza, “Assessment of air pollutant sources in the deposit on monuments by multivariate analysis”, Science of the total environment, vol. 490, pp. 776-784, 2014.
[3] I. Ozga, A. Bonazza, E. Bernardi, F. Tittarelli, O. Favoni, N. Ghedini, L. Morselli, C. Sabbioni, “Diagnosis of surface damage induced by air pollution on 20th-century concrete buildings”, Atmospheric Environment, vol. 45 (28), pp. 4986-4995, 2011.
[4] M. Dugarte, A.A. Sagüés, “Accounting for Temperature Effects on an Evolving Galvanic Anode Cathodic Protection System for Steel in Concrete”, Corrosion, vol. 72 (11), pp.1462-1469, 2016.
[5] M. Carsana, F. Tittarelli, L. Bertolini, “Use of no-fines concrete as a building material: strength, durability properties and corrosion protection of embedded steel”, Cement and Concrete Research, vol. 48, pp. 64-73, 2013.
[6] Y. Cai, P. Hou, C. Duan, R. Zhang, Z. Zhou, X. Cheng, S. Shah. “The use of tetraethyl orthosilicate silane (TEOS) for surface-treatment of hardened cement-based materials: A comparison study with normal treatment agents”, Construction and Building Materials, Vol. 117 (1), pp 144-151, 2016.
[7] P. Scarfato, L. Di Maio, M.L. Fariello, P. Russo, L. Incarnato, “Preparation and evaluation of polymer/clay nanocomposite surface treatments for concrete durability enhancement”, Cement and Concrete Composites, vol. 34 (3), pp. 297-305, 2012.
[8] G. Moriconi, F. Tittarelli, V. Corinaldesi, “Review of silicone-based hydrophobic treatment and admixtures for concrete”, The Indian Concrete Journal, vol. 76, pp. 637-642, 2002.
[9] F. Tittarelli, “Effect of low dosages of waste GRP dust on fresh and hardened properties of mortars: Part 2”, Construction and Building Materials, vol. 47, pp. 1539-1543, 2013.
[10] P. Scarfato, E. Avallone, L. Incarnato, L. Di Maio, “Development and evaluation of halloysite nanotube-based carrier for biocide activity in construction materials protection”, Applied Clay Science, vol. 132-133 (1), pp. 336-342, 2016.
[11] H. Verbruggen, H. Terryn, I. De Graeve, “Inhibitor evaluation in different simulated concrete pore solution for the protection of steel rebars”, Construction and Building Materials, vol 124, pp 887-896, 2016.
[12] D. M. Bastidas, M. Criado, S. Fajardo, A. La Iglesia, J.M. Bastidas, “Corrosion inhibition mechanism of phosphates for early-age reinforced mortar in the presence of chlorides”, Cement and Concrete Composites, vol. 61, pp 1-6, 2015.
[13] C. Andrade, C. Alonso, M. Acha, B. Malric, “Preliminary testing of Na2PO3F as a curative corrosion inhibitor for steel reinforcement in concrete”, Cement and Concrete Research, vol. 22, pp. 869-881, 1992.

[14] M. Collepardi, L. Coppola, C. Corradetti, R. Fratesi, G. Moriconi, “Use of nitrite salt as corrosion inhibitor admixture in reinforced concrete structures immersed in seawater”, In: Admixtures for concrete - Improvement of properties, Ed. by E. Vazquez, Chapman and Hall, London, U.K., 279-288, 1990.