Investigation of the protective effect of inorganic coating with corrosion inhibitors against deterioration of structural damages

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Abstract

The most widely used method for the protection of reinforced concrete and masonry is through coatings, either inorganic or organic. Inorganic coatings based on water glass present various advantages, which are very important when used in old structures. Their microcrystalline texture results in admirably aesthetic appearance and the lower absorption of sun radiation causes no change of coloration, consequently when repainting it is not possible to distinguish between old and new coating. They do not flake off, build up algae or microorganisms or have organic solvents, hence bringing out pollution. Inorganic coatings also react chemically with the concrete surface strengthening the substrate, as opposed to organic coatings, which need a stable substrate. However, they are less protective against chloride diffusion and carbonation than organic coatings. For that reason, inorganic coatings are combined with three different corrosion inhibitors based on calcium nitrite, aminoalcohols and alkanolamines. All these inhibitors can be used either as admixtures or applied on the surface of the construction. For the evaluation of the performance of the coating and the inhibitors in the presence of chloride ions, the following methods were used: measurement of the corrosion potential and the mass loss of the reinforcing bars, measurement of the carbonation depth in the mortars and the strain gauge technique for corrosion measurements. Results proved that when the inorganic coating is combined with the corrosion inhibitors, particularly as admixtures, there is a significant protective effect followed by lower corrosion rate.
1 Introduction

Reinforced concrete is a versatile, economical and successful construction material. Its alkalinity leads to a passive layer of saturated hydrated iron oxide forming on the steel surface. This layer is a dense impenetrable film, which prevents further corrosion of reinforcing steel [1]. However, corrosion remains the most frequent cause of concrete deterioration, as finally expansive corrosion products exert significant tensile forces within the concrete, contributing to the cracking and spalling of concrete cover [2]. The steel bars corrosion onset, the time interval before the attack starts and the rate at which it proceeds are dependent on factors influenced by the chemistry of cement, mineral additions, water binder ratio, curing and environmental conditions [3].

Surface coatings on concrete have become well established mainly to prevent the deterioration due to chemical and physical effects and to enhance or maintain the appearance. They offer an effective and consistent solution for the protection both of the concrete and the embedded steel, either for a new construction or for rehabilitating deteriorating concrete [4]. Inorganic coatings present various advantages, which are very important when used in old structures. They have microcrystalline texture with admirably aesthetic appearance and low absorption of sun radiation with no change of coloration, consequently in repainting it is not possible to distinguish between old and new coating. Furthermore, inorganic coatings do not flake off, build up algae or microorganisms or have organic solvents, therefore they do not bring out pollution. They react chemically with the concrete surface strengthening the substrate, as opposed to organic coatings, which need stable substrate [5].

Calcium nitrite is a well-known corrosion inhibitor (C.I.), which suppresses the anodic corrosion reaction and results in the creation and maintenance of a strong and stable passive film, even in the presence of chlorides [6]. N-N'-dimethylaminoethanol is chemisorbed from aqueous solutions onto oxidised steel surfaces, in chloride-contaminated environments. Its corrosion inhibition effect is explained by the fact that it displaces chlorides from the oxidised steel surface and forms a durable passivating film [7]. Migrating corrosion inhibitors based on alkanolamines are mixed inhibitors, which influence both the cathodic and the anodic process and upon contact with reinforcing steel they form a monomolecular protective layer [8].

The purpose of this study is to compare the effectiveness of corrosion inhibitors, either when added into the mortar mass or sprayed on its surface, when used simultaneously with an inorganic coating.

2 Experimental

2.1 Materials

Specimens were prepared using a cement type II/A-P, the chemical composition of which is shown in Table 1. Sand (BS 4550: Part 6) for type I specimens and pumice of 0-5 mm maximum grain dimension from Yali Island in S.E. Greece
for type II specimens were used as aggregates. Pumice’s chemical analysis is shown in Table 1. Steel bars from steel type S400 and tap water were used.

Three types of corrosion inhibitors for steel in concrete were used, either as admixtures, or sprayed on the surface before the application of the coating. Inhibitor-D is a 15% Ca(NO₂)₂-based solution. Inhibitor-F is based on partially neutralized aminoalcohols (N,N’-dimethylaminoethanol, DMEA). Inhibitor-M is based on alcanolamines. The coating applied on type II specimens was an inorganic silicate coating with main pigment TiO₂.

Table 1: Chemical analysis (%) of cement and pumice.

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>SO₃</th>
<th>LOI</th>
<th>CaOf</th>
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<tr>
<td>II/A-P</td>
<td>27.38</td>
<td>9.10</td>
<td>5.65</td>
<td>45.39</td>
<td>2.73</td>
<td>0.94</td>
<td>0.56</td>
<td>2.71</td>
<td>5.04</td>
<td>2.67</td>
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<td>Pumice</td>
<td>70.55</td>
<td>12.24</td>
<td>0.89</td>
<td>2.36</td>
<td>0.10</td>
<td>4.21</td>
<td>3.49</td>
<td>0.03</td>
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</table>

Mortar test specimens of type I for Strain Gauge measurements presented in Fig. 1 were partially immersed in a 3.5% NaCl solution up to 50 mm from their bottom.

The coating on type II specimens (Fig. 1) was applied by brush on the dried surface at two layers after a drying period between them of 24 h. The first layer was diluted using its respective solvent (0.3 l per kg) and the second layer was applied undiluted. The total consumption given by the producer equals 0.36 kg/m². Specimens were let dry for another 24 h and finally were partially immersed in 3.5% NaCl solution up to 20 mm from their bottom.

Proportions of materials used and specimens’ code names depending on the type of the inhibitor are given in Table 2.

Figure 1: Dimensions of specimens (mm).
Table 2: Categories of specimens.

<table>
<thead>
<tr>
<th>Code name</th>
<th>Cement</th>
<th>Sand / Pumice</th>
<th>Water</th>
<th>Inhibitor D</th>
<th>Inhibitor F</th>
<th>Inhibitor M</th>
<th>Coating</th>
</tr>
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<td>3</td>
<td>0.50</td>
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<td>...</td>
<td>...</td>
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<tr>
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<td>0.01</td>
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<td>...</td>
</tr>
<tr>
<td>SGF</td>
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<td>3</td>
<td>0.49</td>
<td>...</td>
<td>0.01</td>
<td>...</td>
<td>...</td>
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<tr>
<td>SGF’</td>
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<td>3</td>
<td>0.50</td>
<td>...</td>
<td>*</td>
<td>...</td>
<td>...</td>
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<tr>
<td>SGM</td>
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<td>3</td>
<td>0.49</td>
<td>...</td>
<td>0.01</td>
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<td>...</td>
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<tr>
<td>R</td>
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<td>3</td>
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<tr>
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<td>+</td>
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<tr>
<td>MI</td>
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<td>0.69</td>
<td>...</td>
<td>0.01</td>
<td>+</td>
<td></td>
</tr>
<tr>
<td>MO</td>
<td>1</td>
<td>3</td>
<td>0.70</td>
<td>...</td>
<td>*</td>
<td>+</td>
<td></td>
</tr>
</tbody>
</table>

* sprayed

2.2 Techniques

The SG technique is based on the stresses’ appearance caused by steel corrosion products, monitored by embedded in mortar specimens Strain Gauge extensimeters. Disturbing effects during the measurements, as ambient temperature and specimen’s volume changes, were compensated as described below [9].

The sensors used for measurement of corrosion rate of reinforcing steel are Strain Gauge (SG) type KM-30-120, of KYOWA. Two SG were embedded in type I mortar specimen during casting. Distance and directions between SG are shown in Fig.1. One of them (horizontally mounted) was used for the corrosion results measurement and the other (vertically mounted) for compensating the temperature and other parameters (creep, wetting) influencing specimen’s volume. A third auxiliary SG was also used as common for all experiments for temperature compensation of the electrical circuit. The test set-up, including a potentiostat (EG&G PAR Model 173) for applying the anodic potential, a Strain Gauge bridge-amplifier circuit and a common multimeter for SG resistance measurements is shown in the schematic diagram Fig. 2.

The application of the impressed anodic potential to the specimen by the potentiostat is performed by means of the working bar electrode, a 80X100X20 mm graphite auxiliary electrode and a reference saturated calomel electrode (SCE). Measurements and calculations were carried out according to the procedure described in a previous work [10].

During the exposure of type II specimens in the corrosive environment (partial immersion in 3.5% wt NaCl solution), the half-cell potential of steel bars was periodically measured versus a saturated calomel electrode (SCE).
Carbonation depth of the mortars in type II specimens was determined by the phenolphthalein method recommended by RILEM CPC-18.

The corrosion rate of reinforcing steel in type II specimens was determined by measuring the mass loss of the steel bars taken out of the broken specimens. The mass loss was calculated, as the average value of four bars, from the difference between the initial and the final mass of each steel bar.

3 Results and discussion

The comparative diagram obtained by SG technique for the SGR, SGD, SGF and SGM specimens containing corrosion inhibitors is illustrated in Fig.3 as a function of time. Specimens tested under similar conditions of fixed anodic potential are classified according to their corrosion behavior. The initial time is the moment of application of anodic potential to the specimen. In all cases there is an increase in SG values, related to corrosion. A good dynamic response of SG in the potential increases is also observed.

The average corrosion rates are calculated from the tendency lines of SG curves. Specimens F exhibit the lowest corrosion tendency (slope 2.4911), behaviour that is somewhat better than that of specimens D (slope 3.1362). Specimens M show lower corrosion tendency (slope 3.9012) than the reference ones (slope 4.8622).
The way of corrosion inhibitors' application is an important factor of the protection of steel bars against corrosion. The sprayed on the surface of specimens inhibitor acts after a period of time needed for its diffusion through the mortar till the rebar. On the contrary, the inhibitor added in the mortar mass during casting is available from the beginning [11]. The results of the test of specimens SGF, SGF' and SGO as reference (Fig.4) confirm the lower protection of steel in the case of sprayed inhibitor SGF', compared with the incorporated inhibitor SGF.
The corrosion trend of all specimens was evaluated by monitoring the corrosion potential versus exposure time (Fig. 5). During the ten months of exposure the potential values range between -100 mV and -630 mV. Just after the immersion in the NaCl solution, all specimens exhibit low initial corrosion potential values. Then a decay of $E_{\text{cor}}$, to more electronegative values is observed and after about four months of exposure, all types of specimens reach to a more or less stable $E_{\text{cor}}$ value, ranging between $-550$ mV and $-630$ mV. The more electronegative final $E_{\text{cor}}$ value implies an increase in the electrochemical activity of the system, that can be attributed to an increased corrosion of the steel rebars. However, the differences between uncoated and coated specimens are not well defined and thus they do not permit an unambiguous qualitative prediction of differences in the protective performance of the three types of inhibitors used.

The results of mass loss measurements for reference specimens, coated ones and coated specimens with the three types of inhibitors as admixtures are presented in Fig. 6, whereas these with the relevant ones but with the three inhibitors sprayed on the surface of the specimens are presented in Fig. 7. It is obvious that coated specimens perform better than the reference ones, as a result of the decrease of the surface porosity offered by the coatings and consequently of the retardation of the entrance of the aggressive agents. Additionally it is validated that corrosion is greatly influenced by the inhibitor type and the way of its application. As it is shown in Figs. 6-7, the mass loss values are lower by about 10% when inhibitors are added as admixtures than when they are sprayed. The coating alone offers a degree of protection of about 10%, inhibitor M of 15-25%, whereas inhibitors D and F of 35% to 60%.
Carbonation depths measured on broken specimens, partially immersed in NaCl solution, are shown in Fig. 8. As it is observed, there is a reduction to the carbonation depth due to the application of the coating. A further low reduction if offered by the corrosion inhibitor D, which can be attributed to the presence of more Ca$^{2+}$ in the mortar mass, helping thus keep the pH levels high.

The application of inorganic coatings on reinforced mortar presents many advantages, as described above. The disadvantage of low protection against chloride ingress and carbonation can be raised by the concurrent use of corrosion inhibitors.
The inhibiting effect of nitrite ions on steel corrosion induced by chlorides is attributed to the formation of a stable passive layer on the reinforcement, avoiding all the metastable intermediate forms, according to the following reaction, $2\text{Fe}^{2+} + 2\text{OH}^- + 2\text{NO}_2^- \rightarrow 2\gamma\text{-FeOOH} + 2\text{NO}_3^-$. Thus the nitrite ions compete with chloride ions for the ferrous ions at the anode. Nitrite ions must be present in sufficient quantities and come in immediate contact, by diffusion, with the structure in order to provide protection. The mechanism is similar, either when the inhibitor is added in the mixture or when sprayed on the surface [6].

Amines, alkanolamines and their salts with organic and inorganic acids have been described and patented for various applications, such as the protection of steel in cementitious matrices. Experiments have shown that aminoalcohols chemisorb from aqueous solutions onto oxidised steel surfaces. The thickness and the composition of the adsorbate phase depend upon the composition and the concentration of the aminoalcohols solutions. The adsorbate phase is formed even if chlorides are present. The corrosion inhibition effect is explained by the fact that aminoalcohols displace, due to their strong bonding, ionic species from the oxidised steel surface, in particular chlorides which cause corrosion and forms a durable passivating film [7].

Migrating corrosion inhibitors influence both the cathodic and the anodic process by the formation of a protective monomolecular layer at the steel surface, as they diffuse from the surface through the concrete mass surrounding the steel [8].

4 Conclusions

Based on the measurements and test results obtained in this study, the following conclusions can be drawn.
Unprotected mortar specimens exhibited the worst properties resulting in the higher corrosion rate of the reinforcing steel bars.

The inorganic coating provided low protection of reinforced mortar under aggressive corrosive exposure.

The application of corrosion inhibitors by spraying on the surface of mortar, along with the use of the inorganic coating, produced a good anticorrosive performance.

A significant higher level of protection was the result of the simultaneous use of the coating with the corrosion inhibitors, when used as admixtures in the mortar.

References


