Study of corrosion protection offered to concrete reinforcement by organic coatings and inhibitors

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Abstract

The application of organic coatings on concrete is the most widespread method for the protection of both the concrete and the steel reinforcement against weathering and corrosion, performing as well in decoration. Coatings prevent the access of harmful substances, mainly carbon dioxide and chlorides, from the environment into concrete. Exposure to sunlight, moisture and heat are the main factors influencing the durability of coatings and substrates. Corrosion inhibitors are also used in concrete to prevent corrosion, forming a protective film on the surface of the reinforcement and reducing chloride ion ingress into concrete. This study investigates reinforcement corrosion protection through organic coatings and corrosion inhibitors under accelerated conditions and assesses physicochemical properties of these coatings, such as liquid water permeability, water-vapor transmission rate and carbonation of concrete.

Key words. concrete reinforcement corrosion, organic coatings, corrosion inhibitors, protective ability, physicochemical properties of coatings

1. Introduction

Steel reinforcement in concrete is naturally protected against corrosion thanks to a thin iron oxide layer that forms on the steel surface and remains stable as long as the pH in the pores in concrete is alkaline. Corrosion initiates when this protective film is damaged owing to the diffusion of chlorides and to the carbonation of the concrete cover (Broomfield, 1997; Bertolini, 2004).

Among the various protective methods against reinforcement corrosion, organic coatings is the most universally used one, owing to the simplicity in application, flexibility, toughness, adhesion, chemical resistance and durability, serving as a barrier for isolating steel from moisture, chlorides, oxygen and carbon. However ultraviolet radiation and moisture affect their durability resulting from the mere surface discoloration to substantial loss of mechanical properties, which severely limits their performance (Seneviratne, Sergi and Page, 2000; Selvaraj, Selvaraj and Iyer, 2009).

Another common method for the protection of reinforcement is the use of corrosion inhibitors as admixtures to concrete to reduce the risk of corrosion. Alkanolamine-based corrosion inhibitors move through the pore structure of the concrete to reach the surface of reinforcing steel, where they form a protective film. They also reduce chloride ion ingress into concrete (Soylev and Richardson, 2008; Broomfield, 1999; Wombacher, Maeder and Marazzani, 2004).

The aim of this study is the comparative evaluation of five different types of organic coatings, as the only protective method or combined with a corrosion inhibitor, in the protection of steel reinforcement in mortar specimens exposed to highly corrosive conditions and the examination of physicochemical characteristics of these coatings.

2. Experimental

A variety of tests were performed, either on non-reinforced mortar specimens, where important physicochemical properties of the organic coatings were examined, or on reinforced mortar specimens, where the corrosion resistance of the reinforcement attributed to the influence of the organic coatings and the corrosion inhibitor was assessed.

2.1 Materials

In all cases mortar specimens were constructed using Portland cement (OPC) type CEM II 32.5, quarry sand of maximum grain size 4 mm and water from the Athens public network in standard proportions of 1:3:0.5 according to DIN 1164. An alkanolamine-based corrosion inhibitor was also used for the specimens' preparation in a percentage of 4% wt in replacement of water. Specimens were cast and cured according to a procedure described in the literature (Kalogeropoulou, et. all, 2014; Pantazopoulou, et. all, 2014).

Mortar specimens were coated with the five different organic protective coatings: a two-pack epoxy coating (**E**), a two-pack polyurethane coating (**P**), a nanotechnology coating (**N**), an acrylic emulsion (**A**) and an elastomeric acrylic dispersion (**R**) (Table 1). Uncoated specimens (**O**) were used as reference. The coating procedure for all coatings involved three layers, applied by brush, with 24h intervals between them: firstly the appropriate for each coating primer was applied on the dried surface of the specimen, to achieve the best adhesion between coating and mortar. Then the first layer of the organic coating and finally the second layer perpendicularly to the first one were applied. Coated mortar specimens were stored in the laboratory for at least 7 days, so as coatings were dried and all quantity of solvents evaporated.

S/N	Code	Product	Characteristics
1	E	Epoxy	Two-pack epoxy paint with amine hardener, density 1,55 kg/Lt, spreading rate 6 m^2/kg (100 μm), solids 95% w/v.
2	P	Polyurethane	Two-pack polyurethane with aliphatic isocyanic hardener, density 1,20-1,40 kg/Lt, spreading rate 9-11 m^2/ Lt (50μm).
3	N	Nanotechnology	Siloxane paint, density 1,60 kg/Lt, solids 50% w/v, spreading rate 8,6 m^2/Lt.
4	A	Acrylic emulsion paint for exterior use	Acrylic dispersion, density 1.46±0.05 g/ml, solids 61±2.5% w/w, pH 8.4±1, spreading rate 9±1 m^2/Lt (2 coats).
5	R	Elastomeric insulating acrylic paint	Acrylic dispersion, undiluted for final coat, density 1.35 g/ml, solids 60±2% w/w, spreading rate 2±1 m^2/Lt.
1	EA	Epoxy primer (coatings 1-2)	Two-pack epoxy primer, A:B-2:1 w/v with hardener, solids 58% w/v, density 0,99 kg/Lt, spreading rate 10 m^2/Lt.
2	AA	Acrylic water-based primer (coating 3)	Density 1kg/Lt, solids 25,9% w/v, dilution up to 1:4 with water, spreading rate 8-32 m^2/Lt.
3	SA	Styrene-acrylic primer (coatings 4-5)	Copolymers of styrene and acrylic resins, density 0.85 g/ml, solids 26±2% w/w, spreading rate 7.5-8.5 m^2/Lt.

Table 1. Categories of organic coatings and primers – technical characteristics.

2.2 Evaluation of physicochemical properties of coatings

Liquid water transmission rate of each coating was determined according to standard BS EN 1062-3:2008 *"Paints and varnishes - Coating materials and coating systems for exterior masonry and concrete - Part 3: Determination of liquid water permeability*", where the liquid water permeability coefficient *w* ($kg/m^2 \cdot h^{1/2}$) was calculated.

Water-vapor transmission rate V ($g/m^2 \cdot d$) was also defined according to standard EN ISO 7783-2:1999 *"Coating materials and coating systems for exterior masonry and concrete - Part 2: Determination and classification of water-vapor transmission rate (permeability)".*

Finally, **carbonation depth** was measured on cylindrical mortar specimens coated with the 5 organic coatings and placed in accelerated carbonation chamber for a total period of eight weeks, according to the standard BS EN 13295:2004 *"Products and systems for the protection and repair of concrete structures - Test methods - Determination of resistance to carbonation"*. Measurements were performed in accordance with the standard BS EN 14630:2006 *"Products and systems for the protection and repair of* *concrete structures - Test methods - Determination of carbonation depth in hardened concrete by the phenolphthalein method".*

2.3 Corrosion Testing

The **Strain Gauge** (SG) technique was used for short-term evaluation of corrosion behavior of reinforcement in mortar specimens. This technique is based on the appearance of swelling strain near the steel reinforcement and is measured by embedded SG sensors in mortar specimens. The mortar test specimens for the SG measurements were in the form of 80 mm x 80 mm x 100 mm prisms. Reinforced specimens were immersed up to the middle of their height in 3.5% wt NaCl solution. Acceleration of the corrosion process was accomplished by the application of anodic potential. The duration of the test depended on specimens' resistance to corrosion and it was terminated by the mortar cracking caused by steel corrosion. The gravimetric **mass loss** of reinforcing steel bars of the above specimens was estimated according to ISO 8407:2009 *"Corrosion of metals and alloys - Removal of corrosion products from corrosion test specimens*", as the difference between the initial and the final mass of the bars determined after removing corrosion products from the bars (Kalogeropoulou, et. all, 2014; Pantazopoulou, et. all, 2014).

Long-term corrosion testing was also performed using cylindrical mortar specimens (L=100 mm, d=10 mm), with one axially embedded B500C steel bar (L=100 mm, d=10 mm), partially immersed in 3.5% wt. NaCl solution for 18 months. The **corrosion potential** of steel in coated and uncoated specimens was measured according to ASTM C876 – 91 (1999) "*Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete*", using a Silver/ Silver Chloride Electrode (SSCE) as reference electrode.

In these specimens potentiodynamic **linear polarisation** measurements, according to ASTM G59 – 97 (2009) "*Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements",* were carried out using a 263A EG&G model potentiostat / galvanostat and data were analyzed by the corresponding software Power Suite. The experimental setup consisted of three electrodes, where the steel bar was the working electrode, the reference electrode was Silver/ Silver Chloride Electrode and the auxiliary electrode consisted of two cylindrical graphite rods in contact with the mortar specimen. The linear polarization plot was performed in a range of ±20mV from the Open Circuit Potential (OCP) at a scanning rate of 0.1mV/s. The electrochemical mass loss of the steel reinforcement was calculated from the values of corrosion current through the Faraday's Law.

Finally, the corrosion rate of the steel reinforcements in the cylindrical mortar specimens partially immersed in 3.5% wt. NaCl solution for 18 months was determined by measuring the **mass loss** of the bars, according to ISO 8407:2009.

3. Results and discussion

The results of liquid water transmission and water-vapor transmission rate are presented in Tables 2 and 3 respectively. Classification of the coatings according to EN 1062-3 and EN ISO 7783-2 respectively is also given. The best performance in terms of water permeability is demonstrated by epoxy and polyurethane coatings, which is expected since they are chemical reaction coatings for industrial use and special applications. The rest of the coatings present greater water permeability values. Regarding water-vapor transmission rate, conventional (elastomeric, acrylic) and nanotechnology coatings present much higher values and consequently they are ideal for indoor and outdoor concrete applications. It should be noted that the optimal behavior for an organic coating is the simultaneous achievement of high water-vapor transmission rate and low water permeability (Al-Tholaia, Azad and Ahmad, 2014; Adler, 1994). Coatings with these properties prevent the ingress of water and all the factors that water may carry, while allowing the escape of water-vapor from the interior of the wall creating a sealing membrane which "breathes".

Coating	Liquid Water Transmission Rate w (kg/m^2·h$^{1/2}$)	Classification EN 1062-3
E	0,06	Class III (low)
P	0,02	Class III (low)
N	0,20	Class II (medium)
A	0,60	Class I (high)
R	0,30	Class II (medium)

Table 2. Mean values of water permeability for each organic coating.

Coating	Water-Vapor Transmission Rate V (g/m^2·d)	Classification EN ISO 7783-2
E	25	Class II (medium)
P	20	Class II (medium)
N	618	Class I (high)
A	180	Class I (high)
R	215	Class I (high)

Table 3. Mean values of water-vapor transmission rate for each organic coating.

Results of carbonation depth for all specimens after 4 and 8 weeks of exposure are presented in Table 4 and the (%) protection against the non-coated specimens after 8 weeks of exposure is presented in Figure 1. Epoxy and polyurethane coatings provide the best protection, whereas aqueous dispersion coatings offer a satisfying level of protection. The nanotechnology coating provides a low and negligible degree of protection.

Coating	Carbonation Depth (mm) 4 weeks of exposure	Carbonation Depth (mm) 8 weeks of exposure
E	0	2,0
P	0	1,0
N	7,5	11,5
A	4,0	6,5
R	7,0	9,0
O	8,0	12,0

Table 4. Carbonation depth of mortars.

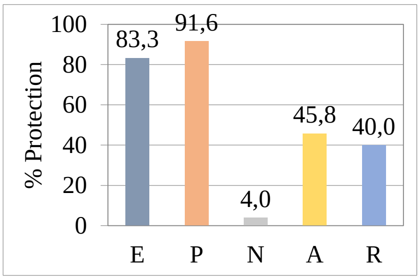

Figure 1. (%) protection against carbonation for all specimens after 8 weeks of exposure.

The comparative diagram obtained by the SG technique for all specimens is illustrated in Figure 2 as a function of time. The better corrosion resistance of specimens P and E is evident when compared to the other specimens and consequently the final classification in anticorrosive behaviour is P and E, A, R, N and O. Measurements obtained by the SG technique as a function of time for specimens IN, IA and IR with the corrosion inhibitor are illustrated in Figure 3. The better corrosion resistance of these specimens is evident when compared to the specimens without the corrosion inhibitor.

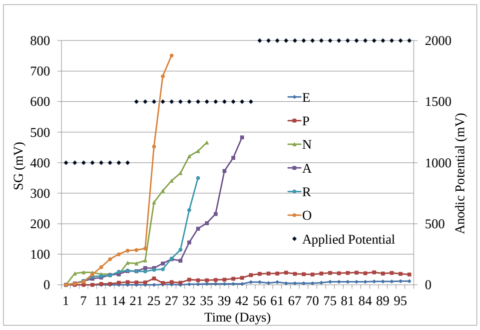

Figure 2. SG values vs. time for all specimens.

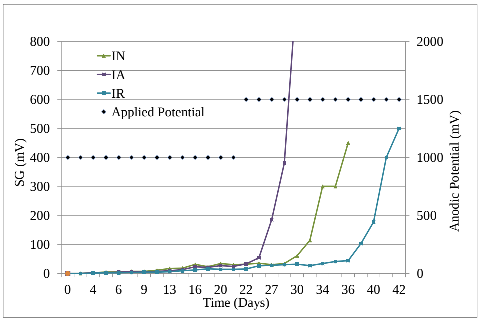

Figure 3. SG values vs. time for specimens with corrosion inhibitor.

The results of reinforcement mass loss for SG specimens are presented in Figures 4 and 5. The absolute values of the mass losses of steel reinforcement at the period of time from the beginning of the anodic potential application till the specimens' breaking are presented against the reduced per day mass loss values. As shown in Fig.4 the classification of specimens' durability against corrosion is P and E, A, R, N and O. Moreover from Fig.5 is obvious that the incorporation of the alkanolamine-based inhibitor resulted in better corrosion resistance of specimens than that of the specimens without corrosion inhibitor.

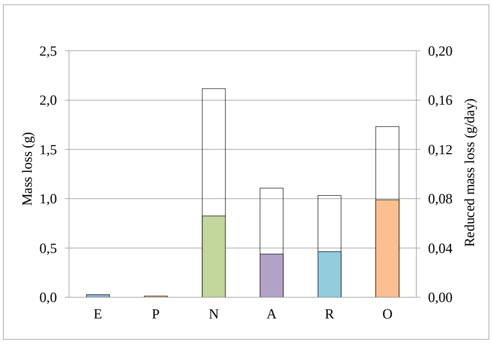

Figure 4. Mass loss of steel reinforcement in SG specimens.

Figure 5. Mass loss of steel reinforcement in SG specimens with corrosion inhibitor.

According to the standard ASTM C876 – 91 “*Standard Test Method for Half-Cell Potentials of Uncoated Reinforcing Steel in Concrete*”, the values of the corrosion potential measured indicate the situation of the reinforcement in mortar specimens at the time of the measurement. As seen from the diagram in Figure 6, the specimens with the polyurethane coating exhibited the best behavior showing minimum corrosion activity throughout the whole exposure period, followed by the epoxy specimens that showed fairly greater likelihood of corrosion. The elastomeric, acrylic and nanotechnology coatings presented lower values of corrosion potential, which implied greater corrosion activity, but potentials were nevertheless lower than that of the reference specimens. The presence of the corrosion inhibitor generally led to an increase of the corrosion potential, as seen from Figures 6 and 7, which indicates better protection of reinforcement against corrosion than in the absence of inhibitor. In the case of polyurethane and epoxy coatings, throughout the whole exposure time, corrosion potentials remained in the range of -50mV ÷ -100mV, which means a reduced susceptibility to corrosion.

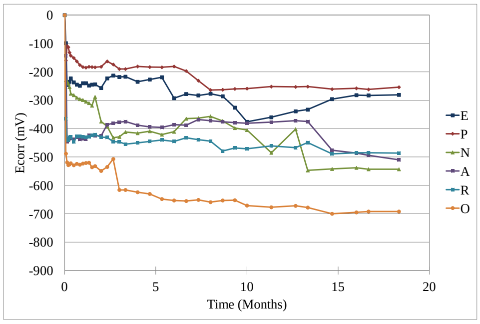

Figure 6. Average values of corrosion potential vs. exposure time for reinforced mortar specimens **without** corrosion inhibitor.

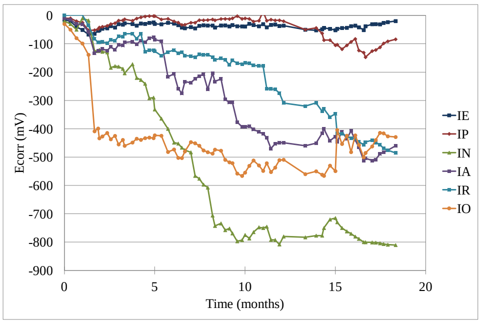

Figure 7. Average values of corrosion potential vs. exposure time for reinforced mortar specimens **with** corrosion inhibitor.

Corrosion potentials in elastomeric and acrylic coatings are rapidly reduced to values less than -350 mV, indicating that there is greater than 90% probability that reinforcing steel corrosion is occurring in that area at the time of measurement, while in the presence of inhibitor this reduction is slower. The reference specimens with inhibitor present potentials 200mV higher than those without inhibitor. Finally, the values of corrosion potential in the nanotechnology specimens in both cases (with and without inhibitor) indicate strong tendency for corrosion almost from the beginning and no improvement is observed due to the presence of the inhibitor. This fact, combined with the peeling of these specimens observed during the exposure to the corrosive environment, demonstrates that nanotechnology colors are not suitable for use in aqueous environments with chlorides.

The electrochemical mass loss of the steel reinforcement calculated from the values of corrosion current measured on cylindrical reinforced mortar specimens partially immersed in 3.5 wt% NaCl solution for 18 months are presented in Figures 8 (without corrosion inhibitor) and 9 (with corrosion inhibitor).

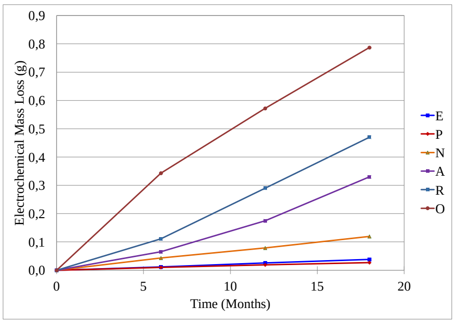

Figure 8. Electrochemical mass loss vs. time for reinforced mortar specimens **without** corrosion inhibitor partially immersed in 3.5 wt% NaCl for 18 months.

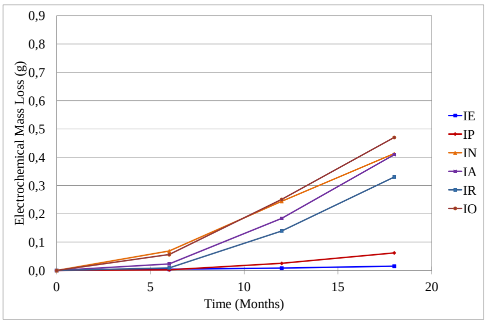

Figure 9. Electrochemical mass loss vs. time for reinforced mortar specimens **with** corrosion inhibitor partially immersed in 3.5 wt% NaCl for 18 months.

Moreover the results of reinforcement mass loss for all cylindrical mortar specimens after long-term partial exposure to the corrosive environment of 3.5 wt% NaCl solution (6, 12 and 18 months of exposure) are shown in Figures 10 and 11 without and with corrosion inhibitor, respectively.

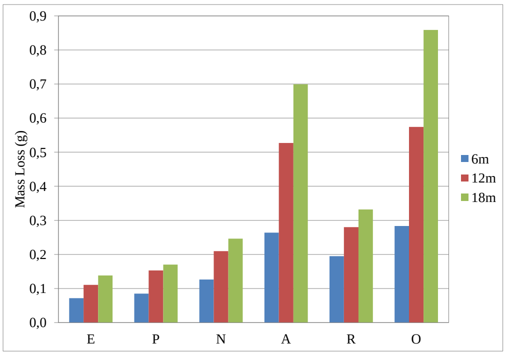

Figure 10. Reinforcement mass loss for mortar specimens **without** corrosion inhibitor after 6, 12 and 18 months partial immersion in 3.5 wt% NaCl solution.

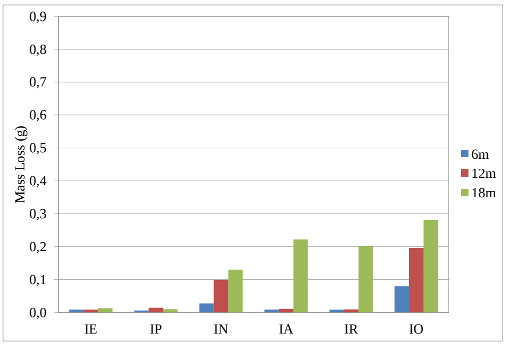

Figure 11. Reinforcement mass loss for mortar specimens **with** corrosion inhibitor after 6, 12 and 18 months partial immersion in 3.5 wt% NaCl solution.

From the results of electrochemical and gravimetric mass loss of the reinforcement in cylindrical mortar specimens throughout the whole exposure period in the corrosive environment, it is observed that all the organic coatings protected the reinforcement against corrosion. The two-component coatings (epoxy E and polyurethane P) gave significantly lower electrochemical mass loss rates than the uncoated reference specimens and much better compared to the other coatings (acrylic A, elastomeric R and nanotechnology N), the acrylic one being the less effective. This demonstrates that the coatings E and P present a strong barrier to the diffusion of water and chlorides towards the reinforcement.

The presence of the corrosion inhibitor further improved the protection of reinforcement against corrosion in coated specimens, with the exception of the nanotechnology coating. In the sodium chloride solution nanotechnology specimens with inhibitor suffered from peeling which resulted in higher values of electrochemical mass loss than those in specimens without corrosion inhibitor (Figures 8 and 9). The presence of imperfections in the coating film significantly affects the electrochemical measurements, as the electric field lines between the steel and the auxiliary electrode pass through them, altering the values of electrochemical parameters. On the contrary, given that these regions are very small compared to the overall surface of the steel, this effect does not appear in mass loss measurements, as shown in Figures 10 and 11.

4. Conclusions

The results of this study confirm the protective action of all organic coatings against corrosion of the embedded reinforcement, whereas epoxy and polyurethane coatings present an exceptional performance. In accelerated corrosion conditions the nanotechnology coating presents reduced protective ability. The corrosion inhibitor further improves the protection of reinforcement against corrosion in coated specimens, with the exception of the nanotechnology coating, which seems to perform poorly in aqueous environments. Polyurethane and epoxy coatings present very low water-vapor transmission rate and liquid water permeability. The two acrylic emulsions present fairly good behavior towards moisture. Finally the nanotechnology coating presents an improved behavior compared to all other coatings systems regarding water-vapor transmission rate and liquid water permeability. Epoxy and polyurethane coatings provide the best protection against carbonation, as well as aqueous dispersions which offer a satisfying level of protection, whereas the nanotechnology coating provides a low and negligible protection rate.

Acknowledgements

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