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Corrosion protection of steel in pumice lightweight mortar by coatings

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Abstract

The purpose of this work was to investigate the corrosion resistance of lightweight mortar exposed to corrosive environments. Widespread use of lightweight mortar is attributed to the several advantages it presents; nevertheless its durability is questionable, as far as the corrosion of reinforcing bars is considered, due to its high porosity. Lightweight mortar specimens were produced using two types of Greek cements as well as Greek pumice of volcanic origin; three different organic coatings and a varnish were applied on them. Specimens were either partially immersed in 3.5% NaCl solution or exposed outdoors. The anti-corrosive performance of these systems was investigated monitoring corrosion potentials and mass loss as well as carbonation and chloride diffusion. The results revealed that in all cases the use of protective coatings reduced significantly corrosion of rebars. Among the examined systems the best protection is offered by the aqueous acrylic dispersion containing titanium dioxide.

Keywords: Lightweight mortars; Pozzolanic cements; Organic coatings; Corrosion

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1. Introduction

In the cement and concrete industries the use of pozzolanic and cementitious materials has risen sharply during the last 50 years. Volcanic ashes, calcined clays and pulverized coal ash from thermal power plants are among the commonly used pozzolanic materials. The benefits derived from their use are functional, i.e. improved workability, economic, i.e. substantial energy and costs savings, and ecological, i.e. disposal of by-products [1]. Concrete containing a pozzolan typically provides lower permeability, reduced heat of hydration, reduced alkali-aggregate expansion, higher strengths at later ages and increased resistance to attack from sulphates in seawater or from other sources [2]. Despite the fact that the pozzolans react with the calcium hydroxide in concrete, the pH of the concrete is not significantly altered [3]. In the Greek market, I-35 cement is mainly used, which contains few pozzolanic materials, but II-35 cement also exists, which contains pozzolanic materials of natural and artificial origin (volcanic and fly ashes).

Additionally, there is a continuing worldwide trend towards lightweight concrete, because it has the advantages of good thermal insulation, of lower weight, of lower total mass of materials to be handled and of reduction of the cost of construction. The main natural lightweight aggregates are diatomite, pumice, scoria, volcanic cinders and tuff; except for diatomite, all of these are of volcanic origin [4]. Pumice mortars can be used in reinforced masonry, as they have the suitable rheological and mechanical properties [5]. In Greece pumice is extracted from a quarry in Yali Island.

There are two main causes of corrosion of steel in concrete, chloride attack and carbonation. These two mechanisms are unusual in that they do not attack the integrity of the concrete. Instead, aggressive chemical species diffuse through the pores in the concrete and attack the steel [6]. Consequently, a disadvantage of lightweight concrete is its high porosity, which could promote carbonation and corrosion of rebars. The obvious solution is to cut off the transportation path of aggressive agents by applying surface or barrier coatings on the mortar surface that can do this efficiently, effectively and economically [7,8].

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In this work, the durability of mortars prepared with types I-35 and II-35 and containing pumice (grading 0–5 mm) as fine aggregate was investigated in relation to that of the same mortars protected against corrosion by three different organic coatings as well as by a varnish, all applied on the surface of the mortar specimens.

2. Materials and techniques

The mortar specimens were prepared using two different Greek cement types, I-35 and II-35. The chemical composition of the cements is shown in Table 1.

In all specimens the aggregate used was the same, i.e. pumice from Yali Island in SE Greece. Its chemical analysis is shown in Table 2, while its gradation is given in Table 3.

Reinforcing steel bars of steel type S400 and tap water were used. Mix proportions aggregate/water/cement were kept constant and equal to 3/0.85/1. Each specimen was cast into a prismatic mould (80 × 80 × 100 mm), where four identical steel bars (100 × 12 mm) were embedded in the positions shown in Fig. 1. Specimens were stored at ambient conditions for 24 h, then cured in tap water for another 24 h, stored for an additional 24 h period at ambient conditions and thereafter the part shown in Fig. 1 was insulated with epoxy glue Araldite^{R}.

Mortar specimens were coated by a varnish consisting of isomerised latex resin (LV) (density 1.2 g/cm^3, coverage 5–7 m^2/l, pH 7.9) or by three different types of coatings. The first one among them consisted of an isomerised latex resin containing as main pigments Fe_2O_3 and Fe_3O_4 (LF) (density 1.35 g/cm^3, coverage 6–8 m^2/l, pH 8.7), the second one was an aqueous acrylic dispersion containing as main pigments Fe_2O_3 and Fe_3O_4 (AF) (density 1.35 g/cm^3, coverage 6–8 m^2/l, pH 8.7) and the third one was an aqueous acrylic dispersion having as main pigment TiO_2 (AT) (density 1.32 g/cm^3, coverage 6–8 m^2/l, pH 8.5). Specimens without coating were also used as reference ones (C) (Table 4). In all cases one layer of coating was applied on the specimens surface by brush. Then specimens were stored to dry at ambient conditions for 24 h. The dry film thickness was about 40 μm. Finally, from each type of specimens some were partially immersed up to 2/10 of their height in 3.5% NaCl solution for a total period of 8 months, while some others were exposed outdoors for a total period of 36 months. The iron oxides pigment used was a by-product of the oxygen convertor slag of the ferronickel industry in Greece. It was used after being washed, dried and ground to powder [9].

Table 3
Gradation of pumice

Special besser 0–5 mm		
Grain size (mm)	Retained %	
	Ideal	Tolerance
6.40	0	0
4.76	2	0.5–4
4.00		
2.38	32	28–36
1.19	22	19–25
0.60	13	11–15
0.30	9	7–11
0.15	7	5.5–8.5
PAN	15	12–17

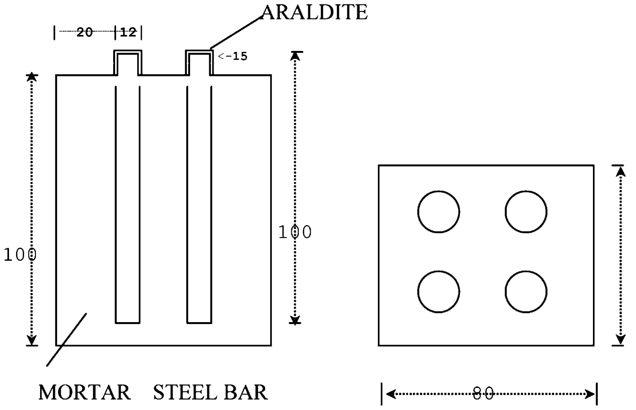

Fig. 1. Schematic representation and dimensions (mm) of mortar specimens.

The protection offered by the coatings as well as the durability of mortars were evaluated by monitoring the

Table 1
Chemical composition of cements

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	CaO_f	LOI	Specific surface (cm^2/g)
I-35	21.64	5.85	4.60	58.10	2.63	0.51	0.30	2.61	1.11	3.80	3300
II-35	27.38	9.10	5.65	45.39	2.73	0.94	0.56	2.71	2.67	5.04	3900

Table 2
Pumice chemical composition (%)

SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	LOI	Undetermined	Bulk density (kg/m^3)
70.55	12.24	0.89	2.36	0.10	4.21	3.49	0.03	5.51	0.62	720

Table 4
Type of specimens

Specimens		Coating			
		Latex varnish	Latex + Fe_xO_z	Acrylic dispersion + Fe_xO_z	Acrylic dispersion + TiO_2
C	No				
LV		+			
LF			+		
AF				+	
AT					+

half-cell potentials and mass loss of steel rebars, carbonation depth of the mortars and diffusion of chloride ions.

The corrosion potentials of steel in the specimens partially immersed in 3.5% NaCl solution were measured according to ASTM C876–87, using a saturated calomel electrode (SCE) as a reference electrode.

The corrosion rate of the rebars was determined by measuring their mass losses at predetermined exposure time intervals in the corrosive environments. The difference between the masses of the clean rebar before and after the exposure is defined as the mass loss. Corrosion products were removed from the steel surface according to ISO/DIS 8407, both before the construction of the specimens and after the removal of the broken, by biaxial loading, mortar pieces.

The carbonation depth time development of mortars was measured in a vertical section of broken specimens using phenolphthalein method [10].

Diffusion of chloride ions through the pumice mortars was determined using a device, in which cylinders (thickness 5 mm, $\Phi = 20$ mm), made from coated or uncoated mortars, were placed in contact with two glass tubes, one on each side. The first was filled with 3.5% NaCl solution and the second with distilled water. Samples from the distilled water compartment were taken at fixed time intervals and the amount of chlorides diffused through the mortar cylinders was determined by titration [11].

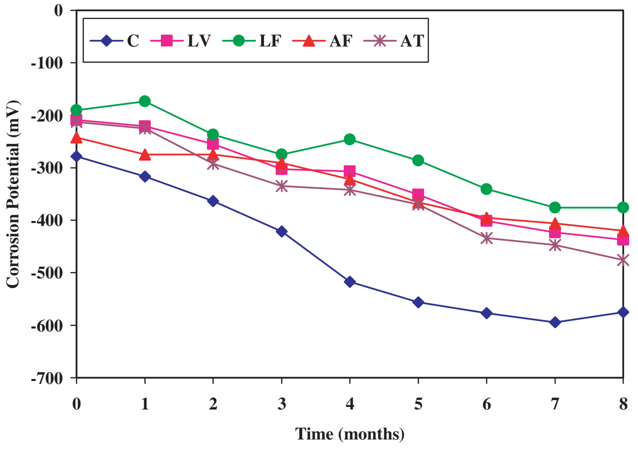

Fig. 2. Half-cell potentials on steel rebars in I-35 cement specimens.

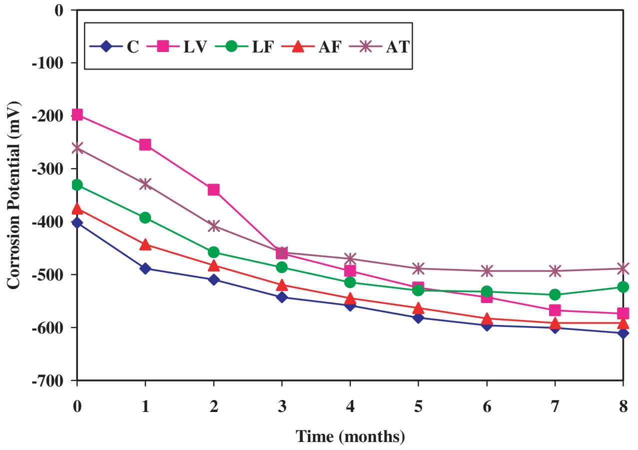

Fig. 3. Half-cell potentials on steel rebars in II-35 cement specimens.

3. Results and discussion

The corrosion trend of the samples was estimated by monitoring the corrosion potential vs. exposure time (Figs. 2 and 3). During the 8 months of exposure the potential values range between −200 and −600 mV SCE. Just after the immersion in the NaCl solution, I-35 cement specimens exhibit corrosion potential values ranging between −190 and −240 mV SCE for coated specimens, whereas that of the uncoated ones equals −280 mV SCE. Then a decay of E_{cor} to more electronegative values is observed, which is faster for uncoated specimens. After about 6 months of exposure, all the specimens reach to a more or less stable E_{cor} value ranging between about −350 mV SCE for LF specimens and −450 mV SCE for AT specimens, while that of uncoated ones is equal to about −580 mV SCE. The steeper decay of E_{cor} of the uncoated specimens and their more electronegative final E_{cor} value imply an increase in the electrochemical activity of the system, that can be attributed to an increased corrosion of the steel rebars. The differences between coated specimens are not pronounced and thus they do not permit a clear qualitative prediction of differences in the protective performance of the four types of coatings used. As it concerns specimens with II-35 cement, from the beginning of the exposure all coated specimens present more electropositive E_{cor} values than the reference ones and more electronegative values than the corresponding I-35 cement specimens. Thereafter, a steep decay during the first 3 months of exposure is observed, followed by a tendency for stabilization to a plateau value of about −500 to −590 mV SCE. In this case the observed earlier arrival of E_{cor} to plateau values, as well as the more electronegative values of E_{cor} compared to those of I-35 cement specimens is an indication of probable more serious corrosion problems, or respectively less protection effectiveness of the coatings used on II-35 cement specimens.

From the mass loss measurements for all types of specimens (Figs. 4 and 5) it is obvious that coated specimens performed better than the reference ones, as a result of the decrease of the surface porosity offered by the coatings and consequently of the slowness down of the entrance of the aggressive agents. Additionally, these measurements validated that corrosion is greatly influenced by the cement type. As it is shown in Figs. 4 and 5, the specimens prepared with cement I-35 resisted better against corrosion than the ones prepared with II-35 cement. In the case of I-35 cement, an indicative ranking of the anti-corrosive performance of the various coatings is the following: AT > LF > AF > LV, i.e. the acrylic dispersion with titanium dioxide pigment offered the best protection. Titanium dioxide generally affects the durability of coatings in two distinct and opposing ways: i.e. as a strong UV-absorber, it protects the paint film and as an UV-activated oxidation catalyst, it degrades binders [12]. Nevertheless, the superiority of the coating with TiO_2 pigment could be explained by its better gradation analysis (100% ⩽ 1 μm) [13], compared to that of the iron oxide pigment (100% ⩽ 16 μm) [14]. As it is known, iron oxides have high density, excellent light fastness as well as chemical resistance [12]. However, the iron oxide pigment used in this work, as mentioned above, was a by-product of a Greek ferronickel industry. This is the probable cause of the inferior performance of the iron oxide coatings compared to that of the titanium dioxide coatings. The absence of pigment in the formulation of the isomerised latex resin could explain the lowest protection level offered by this coating. The above order of ranking remains the same for II-35 cement specimens, but after 8 months of exposure in the corrosive environment, their mass losses are almost double compared to those of I-35 cement specimens.

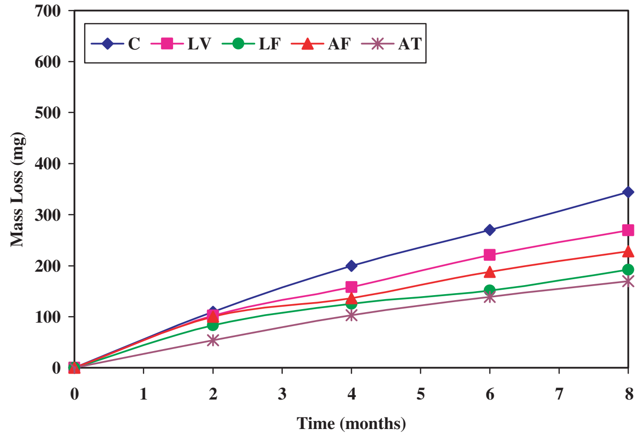

Fig. 4. Mass loss of steel rebars vs. immersion time for I-35 cement specimens. Corrosive environment: partial immersion in 3.5 wt.% NaCl solution.

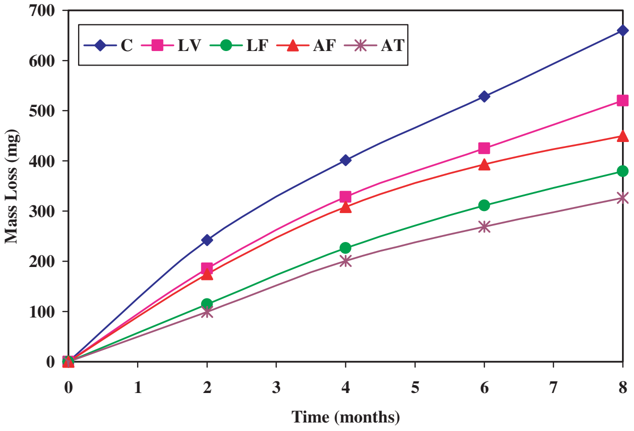

Fig. 5. Mass loss of steel rebars vs. immersion time for II-35 cement specimens. Corrosive environment: partial immersion in 3.5 wt.% NaCl solution.

Carbonation depths measured on broken specimens, partially immersed in NaCl solution, are shown in Figs. 6 and 7. The observed high values of carbonation depth can be attributed to the high porosity of such type of mortars as the one used in this work. Values up to that level have been measured previously in relative specimens [15]. As it is observed, carbonation depth of II-35 cement specimens is the double of I-35 cement specimens. This could be attributed to the pozzolanic character of II-35 cement specimens, as it is known that pozzolanic cements suffer from carbonation earlier than OPC cements [16]. Also, from Figs. 6 and 7 comes out that all coatings reduce significantly the carbonation depth, and consistent to the above-mentioned remark, this reduction is more pronounced in the case of II-35 cement specimens. In this case after 8 months of exposure in the corrosive environment, specimens coated with AT present carbonation depth values that are by 80% reduced in relation to that of the uncoated specimens, while even specimens with the LV coating exhibit values that are by 50% reduced. The corresponding reduction in carbonation depths of I-35 cement speci-

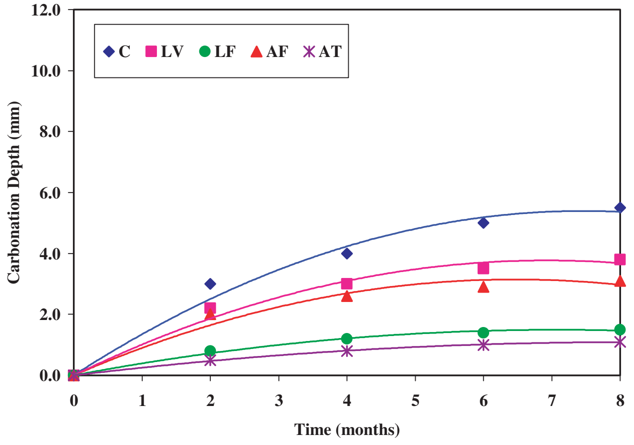

Fig. 6. Carbonation depth vs. time for I-35 cement specimens. Corrosion environment: partial immersion in 3.5 wt.% NaCl solution.

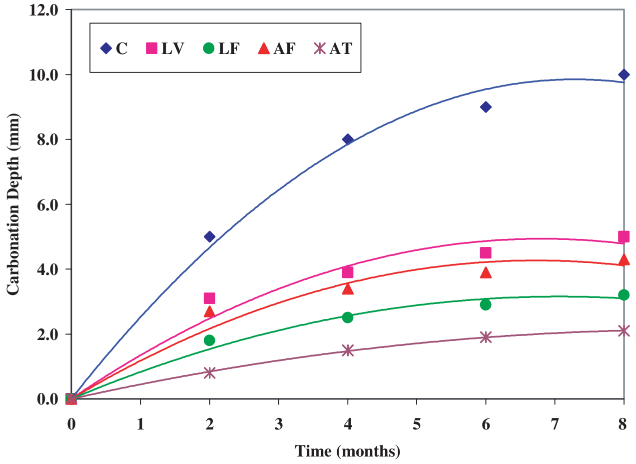

Fig. 7. Carbonation depth vs. time for II-35 cement specimens. Corrosion environment: partial immersion in 3.5 wt.% NaCl solution.

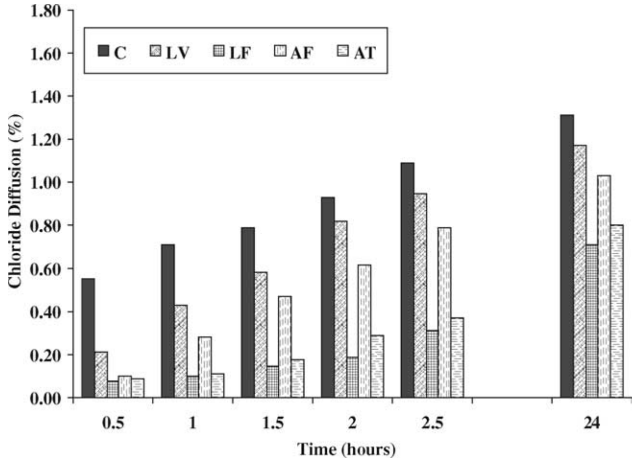

Fig. 8. Chloride diffusion through I-35 cement cylinders.

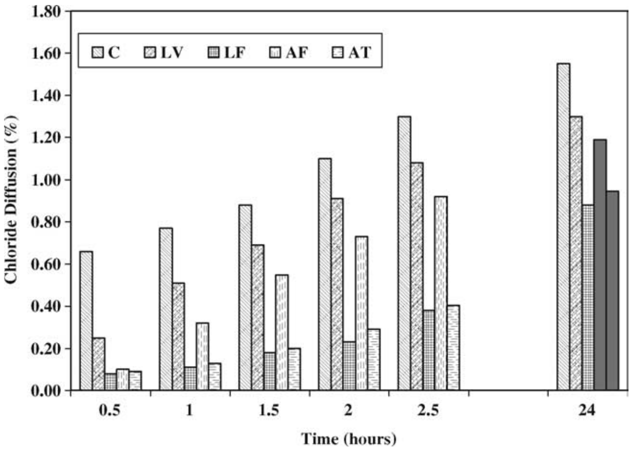

Fig. 9. Chloride diffusion through II-35 cement cylinders.

mens is 80% and 30%, respectively. The comparison of the differences in protective behaviour of these coatings as it results from the mass loss measurement, with those of the carbonation depth points out that the coatings under examination are more effective in preventing the penetration of carbon dioxide than the intrusion of chloride ions.

In order to confirm the above observation, the diffusion of chloride ions through mortar cylinders in a 24-h experiment was measured (Figs. 8 and 9). All coatings inhibit the chloride diffusion, especially at the beginning of the exposure. In both cement specimens mortars coated with LF and AT coatings present the lowest diffusion of chloride ions, with small differences between them indeed, result that is in accordance with the mass loss measurements. The amounts of chloride ions diffused through mortars with both cements do not present great differences, fact that validates the before-mentioned suggestion that carbonation is the predominant factor of corrosion in these lightweight pumice specimens.

The protective efficiency of all the coatings on lightweight mortar specimens was confirmed in a long-term outdoors exposure. Mass losses for I-35 and II-35 cement specimens exposed outdoors for 36 months are shown in Fig. 10. The AT coated specimens still present, as in the case of partial immersion in NaCl solution, the lowest mass loss followed by the LF coated ones, although differences between uncoated I-35 cement specimens and II-35 cement specimens are smaller. This is also valid for the carbonation depths of these specimens after 36 months of outdoors exposure (Fig. 11).

From the results obtained so far it can be deduced that specimens with cement type II-35 suffer from greater corrosion in both corrosive environments than specimens with cement type I-35. II-35 cement contains more pozzolan than I-35 cement and is expected to protect steel better, because, as stated in the literature, pozzolanic cements have a protective effect on

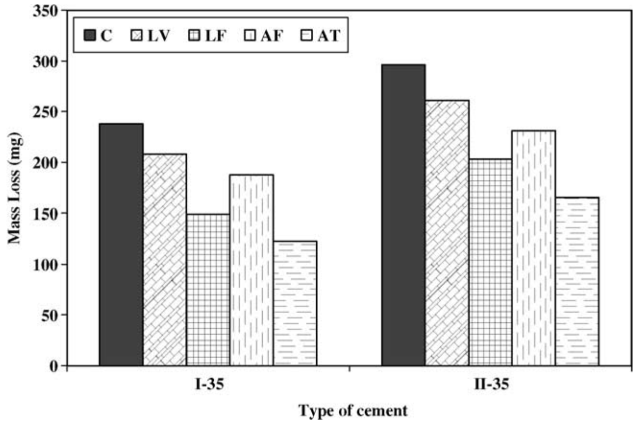

Fig. 10. Mass loss of steel rebars in I-35 and II-35 cement specimens after 36 months of outdoor exposure.

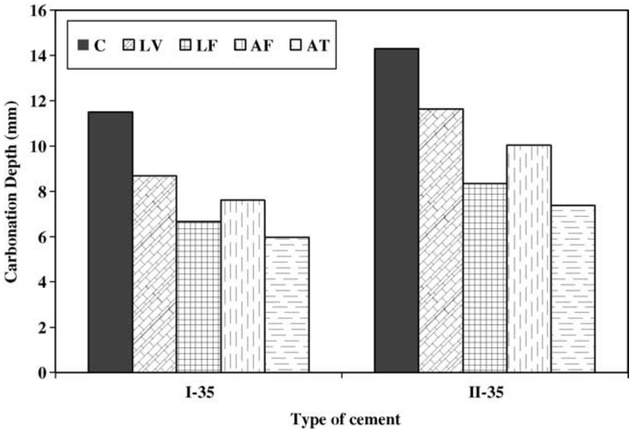

Fig. 11. Carbonation depth of I-35 and II-35 cement specimens after 36 months of outdoor exposure.

corrosion, when chloride ions are present [17]. However, in the case of porous aggregates, like pumice, chlorides can penetrate also through the aggregate pores, resulting in increased chloride concentration near the steel bar, fact that counterbalances the effect of the differences of the cement types. As it also known, pozzolanic cements suffer from carbonation earlier than OPC cements [16], which is in accordance with the results of this work. As a consequence, in the presence of both corrosive agents, steel bars in specimens with II-35 cement are more susceptible to corrosion. Nevertheless, in all cases, the application of coatings resulted in the protection of the steel bars.

4. Conclusions

Experiments on the corrosion resistance of reinforced mortar specimens prepared with two types of Greek cement and lightweight aggregate, coated with four different organic formulations and exposed in two corrosive environments, yielded the following conclusions:

1. The type of cement influences the durability of reinforced mortar specimens. Specimens prepared with I-35 cement (low pozzolanic content) present lower corrosion rate of steel rebars and carbonation depths than those prepared with II-35 cement (high pozzolanic content).
2. In pumice lightweight mortars, protective coatings reduce significantly the reinforcing steel bars corrosion, as they decrease the surface porosity and consequently slow down the diffusion of the aggressive agents. The protective effectiveness of an acrylic dispersion with TiO_2 pigment was the greatest one, resulting in a reduction of 50% of the steel bars corrosion rate and carbonation depth, compared to those of the uncoated specimens.
3. When the specimens are partially immersed in NaCl solution, carbonation, caused by atmospheric CO_2 on the water-free part of the mortar, seems to be the predominant factor of the corrosion, while chloride ions diffusion seems to affect less the efficiency of the coatings.

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