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Corrosion protection investigation of reinforcement by inorganic coating in the presence of alkanolamine-based inhibitor

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Abstract

Corrosion of reinforced concrete structures is a major problem throughout the world, demanding significant amounts for repair and rehabilitation. Corrosion protection is commonly performed by coating the concrete or by using corrosion inhibitors. This paper describes the comparative evaluation of the effectiveness of an acrylic dispersion and an inorganic coating on silicate basis, of an alkanolamine-based corrosion inhibitor and of their combination, on reinforced mortar specimens partially immersed in 3.5% NaCl solution. The following techniques were used: strain gauges, measurements of the corrosion potential, the mass loss and the EIS of the reinforcing bars and measurements of the chloride diffusion and the carbonation depth in mortars. Results demonstrate that the simultaneous use of the alkanolamine-based corrosion inhibitor with the inorganic coating offers a protection degree comparable to that of the acrylic dispersion, which performs best in the presence of both chloride ions and carbon dioxide.

Keywords: Reinforcement corrosion; Corrosion protection; Carbonation; Chloride; Anticorrosive coating; Alkanolamine-based corrosion inhibitor; Strain gauges

1. Introduction

The use of reinforcing steel to improve the physical properties of concrete has been an accepted practice for many years. Concrete provides a protective alkaline environment around steel. However, corrosion can be initiated either when the hardened cement paste carbonates to the cover depth reducing alkalinity, or when chlorides migrate through the concrete cover and build up in sufficient quantities to break down the passive oxide layer formed when the steel is first cast into concrete. As the steel corrodes, the rust occupies a volume two to four times greater than the parent steel, resulting in bursting stresses that ultimately crack and spall the concrete cover. Traditional methods of protection include cathodic protection, coatings, addition of inhibitors to the concrete, or a combination of these methods [1].

Coatings applied to the concrete surface offer an effective and reliable solution for the protection of concrete and the embedded reinforcing steel, either for new construction or for rehabilitation of deteriorated concrete [2]. The use of protective surface coatings is generally applied for both conventional and lightweight concrete with or without the presence of chloride ions [3,4]. A protective surface coating demands good adhesion on the concrete, high durability, UV and weather resistance, prevention of water ingress, high resistance against carbon dioxide diffusion, low chloride permeability but water vapour permeability [5]. The different types of surface coatings that can be used for the protection of reinforced concrete include inorganic coatings on silicate basis, acrylic emulsions, epoxy resin and chlorinated rubber [6].

Corrosion inhibitors have been used successfully in steel pipelines, tanks, etc., for many decades. Their use as admixtures to concrete, however, is more recent and

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more limited. There was a reluctance to their use in concrete because they could not be changed if found to be ineffective, replenished if found to be consumed, or removed if found to have deleterious effects [7]. The flexibility of corrosion inhibitors with regard to dosage and their compatibility with all aspects of construction and operation of structures makes them useful for protection against corrosion [8]. Any inhibitor should have good solubility characteristics and rapidly saturate the corroding surface. Also the physical and durability properties of concrete should not be adversely affected [9]. Many substances have been tested as inhibitors against the corrosion of reinforcing steel bars, e.g. calcium nitrite, sodium monofluorophosphate and alkanolamines [10]. Alkanolamine-based corrosion inhibitors can make use of the porosity of concrete, by moving through the pore structure of concrete to reach the surface of reinforcing steel, where they form a film. They also reduce chloride ion ingress into concrete [11]. They are classified as mixed inhibitors, because they influence both the cathodic and the anodic process of corrosion [12].

The strain gauge (SG) technique, used for fast monitoring of corrosion caused under impressed anodic potential, is based on the appearance of swelling strain near the steel rebars in the concrete. The cause of the swelling tension is the formation of corrosion products (iron oxides, Fe_3O_4, Fe_2O_3, $FeO(OH)$). For the measurement of the above-mentioned swelling tension, special SG sensors are embedded into the mortars specimens during their manufacture [13,14].

The purpose of this study is to compare the protective action against corrosion of an acrylic dispersion, an inorganic coating, an alkanolamine-based corrosion inhibitor and the combination of the inorganic coating with the corrosion inhibitor, in the presence of chlorides.

2. Experimental

2.1. Materials

The specimens were cast using a cement type II-35 (pozzolanic), sand (BS 4550:P6) for the SG technique specimens and pumice 0–5 mm maximum grain dimension from Yali Island in Southeastern Greece for the corrosion testing specimens. Chemical analysis of cement and pumice are shown in Table 1. Steel bars from steel type S400 and tap water were used. The mixture proportions are shown in Tables 2 and 3 (SG-test specimens w/c:0.5/1; corrosion-test specimens w/c:0.7/1). A solution of alkanolamine-based corrosion inhibitor was used as an admixture (1 wt.% of cement) in the concrete mass, according to the instructions given by the manufacturer.

Table 2
Categories of SG specimens—composition ratio (w/w)

Code name	Cement	Sand	Water	Inhibitor	Inorganic coating
SGC	1	3	0.50	–	–
SGI	1	3	0.49	0.01	–
SGW	1	3	0.50	–	+
SGB	1	3	0.49	0.01	+

The SG-test specimens were in the form of 80 × 80 × 100 mm prisms, as described in previous work [13], with one steel bar (diameter 12 mm, length 100 mm) machined on a lathe to a final diameter of 10 mm and prepared according to ISO/DIS 8407.3. The bar was embedded 85 mm into the mould. Thus, the exposed area equals to 2750 mm^2. The mortar specimens were stored in the curing room (20 °C, 100% humidity) for 24 h in the mould. The specimens, after being demoulded, were cured immersed in tap water at 20 °C for 7 days and then left dry for 24 h. A copper wire cable was connected to each steel bar and the specimens were covered with epoxy resin to protect the connection of steel with copper cable against corrosion.

Each corrosion-test specimen was cast to the form of 80 × 80 × 100 mm prisms with four steel bars (cylindrical diameter 12 mm, length 100 mm) embedded in it (Fig. 1). For the specimens' construction the surface of the steel bars was first cleaned from rust according to ISO/DIS 8407.3 and weighed. Subsequently, the bars were placed in moulds, as shown in Fig. 1, where the mortar was cast and stored to dry at ambient conditions for 24 h. Then the specimens, after being demoulded, were cured in tap water for 24 h. Finally they were stored for an additional 24 h at ambient conditions and thereafter the part shown in Fig. 1 was insulated with epoxy resin.

Coatings examined were an aqueous acrylic dispersion and an inorganic coating on silicate basis, both with main pigment TiO_2. They were applied by brush on the dried surface of the concrete specimen at two layers, the second layer 24 h after the first one. The acrylic dis-

Table 1
Chemical analysis (%) of cement and pumice

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	Na_2O	SO_3	cor LOI	CaO_f	Sb (cm^2/g)
II-35	27.38	9.10	5.65	45.39	2.73	0.94	0.56	2.71	5.04	2.67	4275
Pumice	70.55	12.24	0.89	2.36	0.10	4.21	3.49	0.03	–	–	–

Table 3
Categories of corrosion testing specimens

Code name	Cement	Pumice	Water	Inhibitor	Acrylic dispersion	Inorganic coating
C	1	3	0.70	–	–	–
I	1	3	0.69	0.01	–	–
A	1	3	0.70	–	+	–
W	1	3	0.70	–	–	+
B	1	3	0.69	0.01	–	+

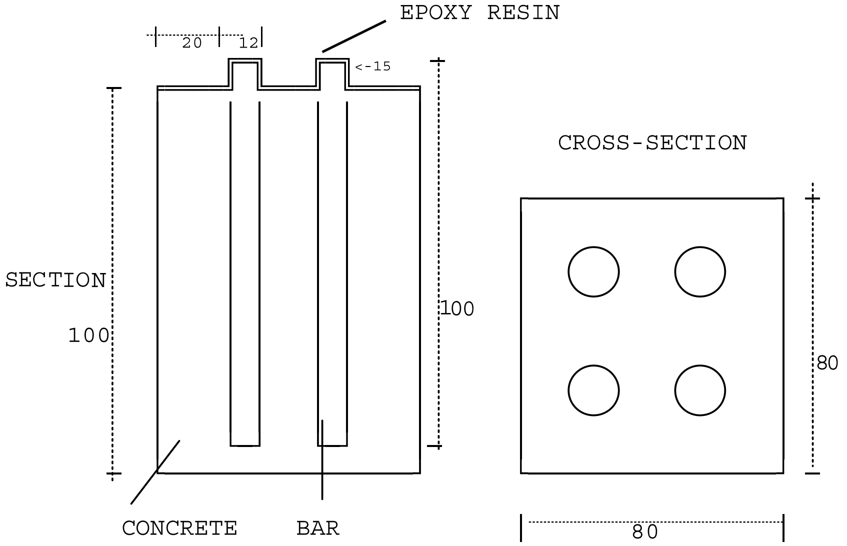

Fig. 1. Shape and dimensions of specimens (mm).

persion creates a film on the surface of the mortar, whereas the inorganic coating reacts chemically with the surface. The total consumption of the acrylic dispersion is given by the producer equal to 0.44 kg/m^2 and that of the inorganic coating equal to 0.36 kg/m^2.

Finally all specimens were partially immersed in 3.5 wt.% NaCl solution, the SG specimens up to 50 mm and the corrosion testing specimens up to 20 mm from their bottom, in order to simulate aggressive conditions and impose an accelerated rate of corrosion.

2.2. Methods

2.2.1. SG technique

The SG technique is based on the stresses appearance caused by steel corrosion products monitored by SG extensiometers embedded in mortar specimens. The SG sensors used were KM-30-120 type KYOWA.

Two SG sensors were embedded in each specimen. The first one was measuring the swelling of the specimen due to cumulative action of corrosion and other parameters that change the specimen's volume. This sensor was placed near the rebar. The second one was compensating the parameters of specimen volume variation, except corrosion, and it was placed far from the rebar [13,15].

For the acceleration of the corrosion process of the reinforced specimens, which were partially immersed in 3.5 wt.% NaCl solution, stable anodic corrosion potential of 1, 1.5, 2.5, 3, 4.5 and 6 V was applied for several days. The test set-up, including a potentiostat (EG&G PAR Model 173) for applying the anodic potential, a SG 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

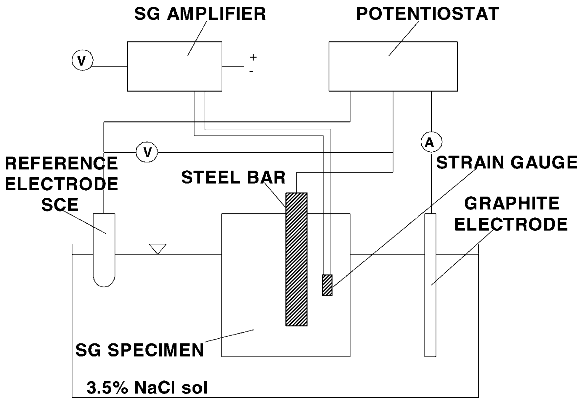

Fig. 2. Test setup diagram.

potentiostat is performed by means of the working electrode, an 80 × 100 × 20 mm graphite auxiliary electrode and a reference saturated calomel electrode (SCE). The position of the auxiliary electrode results in corrosion of the steel bar, mainly on the side facing the SG, in order to achieve faster measurements response.

2.2.2. Half-cell potential versus time

During the exposure of the specimens in the corrosive environment the half-cell potential of steel bars was periodically measured versus a SCE.

2.2.3. Carbonation depth

The carbonation depth of concrete was measured on a vertical section of the specimen by the phenolphthalein indicator method recommended by RILEM CPC-18.

2.2.4. Reinforcing bars mass loss

The corrosion rate of reinforcing steel was determined by measuring their mass loss. The steel bars were cleaned from any corrosion products with the same above-mentioned procedure and were weighted. The average mass loss was calculated from the difference between the initial and the final mass of each steel bar.

2.2.5. Chloride diffusion rate

The concentration of chlorides versus time through the cement was measured using a special device, in which a cylindrical concrete slice was placed in contact with a glass tube filled with a 3.5 wt.% NaCl solution at one end and a glass tube filled with distilled water at the other end (Taywood Engineering Limited, “In-House Test Method A9: Measurement of ionic diffusion coefficient”). A specimen without coating was prepared for reference along with concrete slices that were coated with the two categories of coatings. The amount of chlorides diffused through the mortars was calculated by titration.

2.2.6. Impedance measurements

Specimens with alkanolamine-based inhibitor, with both categories of coatings and without coating were immersed in 3.5 wt.% NaCl solution and their impedance spectrum was examined in order to obtain information about the mechanism of corrosion, using the Solartron 1260 Impedance Gain-Phase Analyzer.

3. Measurements and results

The test results obtained for the given categories of specimens by the SG technique under fixed anodic potential are illustrated in Fig. 3 as a function of time. The initial time is the moment of application of anodic potential to the specimen.

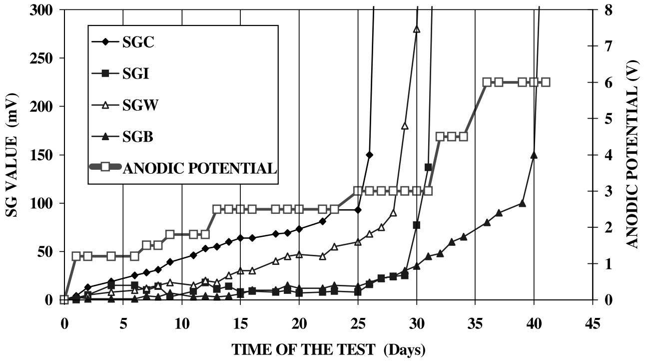

Fig. 3. SG values versus time for specimens SGC, SGI, SGW, SGB.

During the first 20 days of the anodic potential application a low rate of expansion of the specimen SGC is observed, which turns out in rapid expansion (25th day) due to mortar cracking caused by rebar corrosion.

Regarding the specimens SGI containing corrosion inhibitor, a lower expansion caused by corrosion is observed, excluding the one appearing at the final stage of anodic potential application. The most probable explanation for this very low corrosion rate is the fact that the corrosion process is controlled by the inhibitor presence, forming a corrosion protective film in the rebar surface. The time of corrosion appearance for the specimen SGI is the 29th day and the specimen’s cracking follows on the 31st. Specimen SGW protected with the inorganic coating shows a slightly better corrosion protection character compared to SGI specimen. The time of corrosion appearance for the specimen SGW is the 28th day and the specimen’s cracking follows on the 31st. The presence of the inorganic coating improves the corrosion resistance compared to reference ones. Finally, for specimen SGB containing corrosion inhibitor and coated with the inorganic coating, corrosion appears on the 39th day and cracking follows on the 41st day, presenting the best corrosion protection improvement.

For a further explanation of the results, the relationship between SG measurements and corrosion of

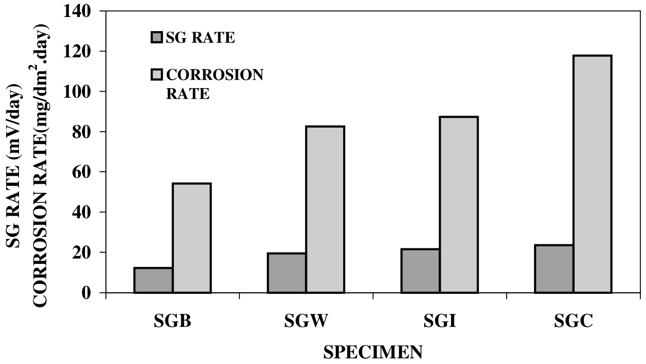

Fig. 4. Mass loss—SG values comparison.

Table 4
Comparison of SG values—mass loss of rebars

Code name	Mass loss (mg)	SG value (mV)	Corrosion time (days)	SG rate (mV/day)	Corrosion rate (mg/dm^2 day)
SGC	810	590	25	23.6	117.8
SGI	744	670	31	21.6	87.3
SGW	732	600	31	19.4	82.5
SGB	610	500	41	12.2	54.2

steel bars was investigated via gravimetric mass loss determination of each specimen bar. The correlation between SG measurements and the rebars mass loss caused by corrosion for the tested specimens is shown in the diagram of Fig. 4 and in Table 4. A sufficient correlation provided between SG rates in mV/day and rebars mass loss rates in mg/dm^2 day for all specimens demonstrates that the SG sensor elongation is affected by the formation of the corrosion products and consequently SG measurements correspond to the real corrosion caused in steel rebars.

The corrosion rate in specimen SGC (without corrosion inhibitor) under anodic potential application was 117.8 mg/dm^2 day. The inorganic coating acts protectively against corrosion (corrosion rate 82.5 mg/dm^2 day) with similar efficiency in comparison with the inhibitor, which retarded the rate to 87.3 mg/dm^2 day. The combined use of inorganic coating and corrosion inhibitor has effectively decreased the corrosion rate to 54.2 mg/dm^2 day.

The SG technique is performed under accelerated conditions and so the rest of the measurements should verify its results.

Half-cell potentials of the reinforcing bars for all types of specimens are given in Fig. 5 as an average of four values measured on each specimen. The position of the reference electrode was at the bottom of the specimens. In all cases, at the beginning of the exposure, steel bars show corrosion potentials in the region of −100 to −300 mV and subsequently there is decay to more negative values. After five months of exposure, an almost steady state condition is reached in the region of −500 to −600 mV. These values are typical when there is a greater than 90% probability that corrosion of reinforcing steel bars is occurring at the time of measurement (ASTM C876). All specimens exhibit similar behavior of half-cell potentials versus time, but the specimen coated with the acrylic dispersion shows a slightly lesser corrosion tendency.

The carbonation depth of uncoated and coated specimens, without the presence of corrosion inhibitor, was measured. The corresponding results are given in Fig. 6. The high carbonation depths measured are due to the high porosity of mortars. Specimens with corrosion inhibitor and these with the combined action of the corrosion inhibitor and inorganic coating are not examined, since the inhibitor does not affect porosity [16]. It is obvious that both coatings reduce the carbonation depth. The reduction offered by the acrylic dispersion is higher than that offered by the inorganic coating. This difference could be attributed to the fact that despite both coatings offer a barrier effect against the carbon dioxide access, the acrylic dispersion forms a continuous film over the mortar surface, whereas the inorganic coating reacts chemically with the surface and reduces the diameter of the surface pores.

Mass loss measurements versus exposure time are given in Fig. 7. The improvement of the corrosion resistance of the bars when the corrosion inhibitor is combined with the inorganic coating is evident. The performance of these specimens is slightly worse than that of specimens with the acrylic dispersion, but better

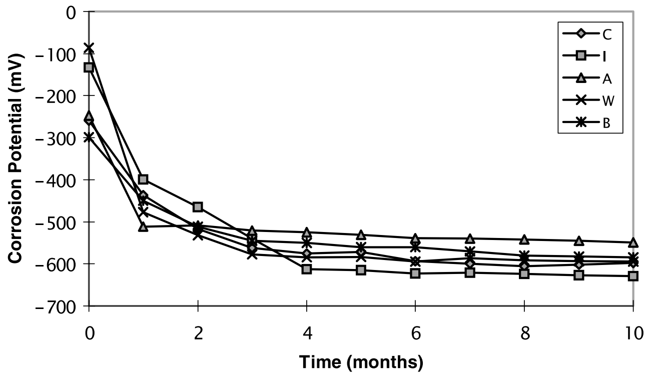

Fig. 5. Half-cell potentials versus time.

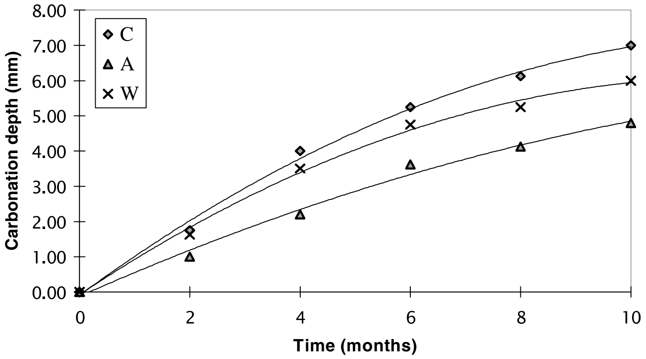

Fig. 6. Carbonation depth versus time.

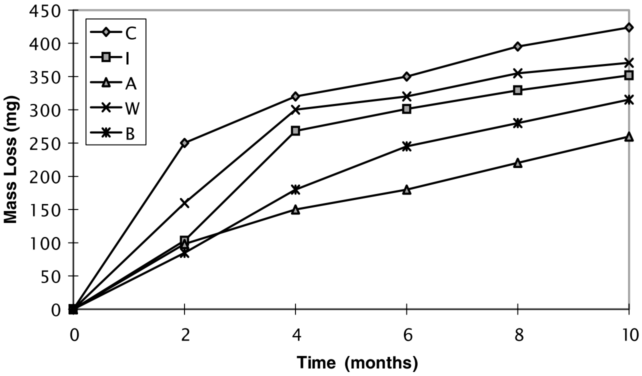

Fig. 7. Mass loss of reinforcing steel bars.

than the specimens with the alkanolamine-based corrosion inhibitor. The better protective effect of organic coatings compared to inorganic ones is also referred elsewhere [17]. In all cases the unprotected specimens behave the worst.

The results of the measurement of the chlorides concentration into the above mentioned three types of specimens are shown in Fig. 8. There is a regular increase in chloride diffusion during the first hours followed by a slower process. This could be attributed to the high porosity (total porosity 32%) of the mortar, which allows fast chloride intrusion. Both coatings inhibit the chloride diffusion, but the inorganic one permits greater amount of chlorides to be diffused, due to the partial coverage of the surface pores it provokes.

The impedance measurements of uncoated specimens, the ones with the inorganic coating and those with the combination of inorganic coating and corrosion inhibitor are shown in Fig. 9, after 10 days and after 10 months of immersion in the corrosive environment of 3.5 wt.% NaCl solution, where the imaginary part of resistance (Z'') is drawn versus the real part of resistance (Z'). The polarization resistance of the steel bars in the specimens with the alkanolamine-based corrosion inhibitor is greater than the polarization resistance of the acrylic dispersion and the inorganic coating, either in the beginning or at the end of the immersion time. These results are not in accordance with the mass loss measurements. This kind of differences has been reported by other investigators too [18], fact that is not reducing the importance of impedance measurements, which are very useful in the investigation of the corrosion mechanism. The 10-months polarization resistance values are smaller than those of the 10 days, as it is normally expected, since specimens after 10 months are more corroded.

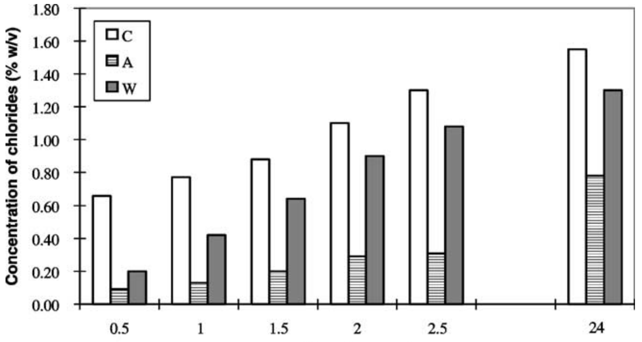

Fig. 8. Concentration of chlorides versus time.

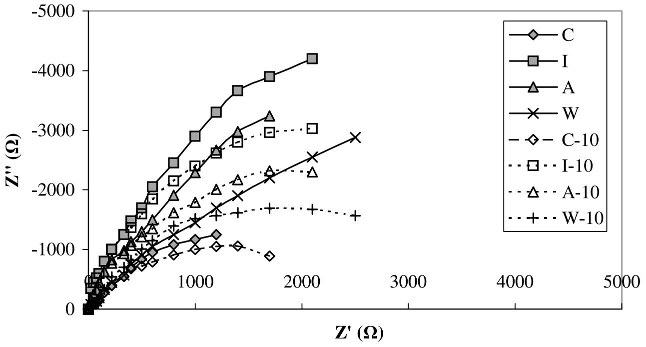

Fig. 9. Nyquist plot for impedance results. Specimens C, I, A, W after 10 days and C-10, I-10, A-10, W-10 after 10 months in 3.5 % NaCl solution.

4. Discussion

It is well known that the acrylic dispersion coatings provide the best protection against concrete carbonation [19,20]. In the case of chloride-induced corrosion the acrylic dispersion coatings exhibit an adequate protection. The reinforcement mass loss determined is less than the half than that of the reference specimens [3,4].

On the other hand inorganic coatings on silicate basis are also suitable for use on the surface of reinforced concrete. They present microcrystalline texture with admirably aesthetic appearance and lower absorption of sun radiation, they do not flake off, their coloration does not change by the UV-radiation, they do not build up algae or micro-organisms, they do not have organic solvents and they do not bring out pollution. Also in the case of repainting, it is difficult to detect the change of coloration between old and new coating [17]. In this investigation, it was observed that the use of inorganic coating provides a relatively lower protection, which has as consequence greater mass loss of the reinforcement, due to greater carbonation depths and higher chloride diffusion rates, than the acrylic dispersion. Therefore, in the case where concrete is exposed to an aggressive environment the use of inorganic coatings alone is not recommended [17].

Furthermore, alkanolamine-based corrosion inhibitors protect effectively the reinforcement against corrosion [9]. They influence both the cathodic and the anodic process by the formation of a protective layer at the surface of steel, as they diffuse from the surface through the concrete mass surrounding the steel bars. After 10 months of exposure in the corrosive environment, the use of the acrylic dispersion gives a protection level of 39% based on mass loss measurements, the corrosion inhibitor 21% and finally the combined use of inorganic coating with the inhibitor 26%. It should be pointed out that the presence of the inorganic coating leads the protection level from 21% to 26%, so the predominant contribution is due to the inhibitor. It is evident that the protection offered by the acrylic dispersion is superior to that of this combination. However, the simultaneous use of the corrosion inhibitor with the inorganic coating, offers the possibility of exploiting the advantages of the inorganic coating, along with a sufficient level of corrosion protection.

Given that corrosion protection offered by inhibitors is depended by the ratio inhibitor/chlorides [21], the above-mentioned relative low protection is due to the insufficient amount of inhibitor used in the chloride corrosive environment. Furthermore, this could be attributed to the increased porosity of concrete specimens, which does not allow the corrosion inhibitor to offer its maximum capability of protection.

5. Conclusions

From the measurements performed in this study, the following conclusions can be drawn:

- Uncoated specimens exhibit the worst properties having the higher corrosion rate of the reinforcing steel bars.
- The acrylic dispersion coating provides adequate protection of reinforced concrete under aggressive corrosion environment.
- The inorganic coating alone results in poor protection.
- The simultaneous use of alkanolamine-based corrosion inhibitor and inorganic coating almost equals the protection offered by the acrylic dispersion.

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