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ScienceDirect

Cement & Concrete Composites 28 (2006) 716–721

Cement & Concrete Composites

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Steel protection capacity of polymeric based cement mortars against chloride and carbonation attacks studied using electrochemical polarization resistance

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Abstract

This work analyzes the protection capacity of modified Portland cement mortar with polymers: styrene butadiene, acrylic latex with reinforced plastic fibres and acrylic latex with silica fume, using the electrochemical polarization resistance (R_p) technique to monitor the behaviour of steel bars embedded in the specimens, when placed in environments with CO_2 and chloride. Results indicate that only chemical, physical and mechanical characterizations are not sufficient to classify these materials from the point of view of protection against aggressive agents. There is evidence that material performance depends on workability, chemical composition of squeezed pore solution in addition to the porosity and resistivity which have an important role in the protection against the corrosion of steel bars.

Keywords: Polymeric based cement mortar; Material repair; Corrosion; Carbonation; Chloride

1. Introduction

The alkaline nature of concrete pore solution renders steel reinforcement passive. However, the passive layer may be destroyed locally or generally by, respectively, the presence of chloride ions or the carbonation of the concrete cover. When steel is depassivated, the corrosion rate will depend, among other factors, on the concrete humidity content, the oxygen availability and the Cl^-/OH^- ratio [1,2].

Polymeric based cement mortars and concrete have been used in repairing damaged concrete structures. These kinds of products, besides restoring the alkaline medium, have also other complementary properties according to the manufacturers: compensated shrinkage, high bond to concrete mass, low permeability and high strength [3–5].

However, there are several interactions between the polymers and the hydration products, which depend on the type of polymers and cements. They can reduce the pH of pore solution or can release Cl^-. Due to these different behaviours a good performance of the polymers based cement mortars and concrete cannot to be assured when the structure is in CO_2 and chloride contaminated environment.

The tests, found in the literature, to check the suitability of theses materials aim, in general, to find out their physical characteristics, and only in few cases, results on their resistance against chloride penetration or carbonation progress and the steel bar performance [6,7] can be found in the literature.

The present work tries to explore a methodology to characterize the performance of polymer based cement mortars and concrete, using the polarization resistance electrochemical technique (R_p) that permits to detect depassivation and the evolution of the corrosion rate due to carbonation and Cl^-, O_2 and humidity changes [1]. This

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doi:10.1016/j.cemconcomp.2006.05.011

methodology is applicable to study the protection ability of the repair materials regarding the steel reinforcement, however in turn, it is not enough for a complete assessment of the performance of the repair material in the structure, because in situ there are many other factors, in addition to the corrosion aggressive, that may compromise the behaviour. Thus for instance, thermal effects or displacements due to cyclic loads may affect the bond between repair and concrete materials. Present tests serve to characterize the repair materials regarding the corrosion resistance and compare themselves. An integral methodology of evaluation should be used for a full characterization.

2. Experimental method

Table 1 shows the mortar types tested and their proportions in the mixes prepared. Mortar A is used as blank and Mortar B was prepared with the same high initial strength cement (I-45 in Spanish Code) and the same sand as the blank, but modified with the admixture (acrylic latex and silica fume) referred in Table 2, in order to obtain the same "flow table" results as the blank. Mortars E and G are commercially available, ready to be mixed with acrylic resin and styrene butadiene latex, respectively, and have different flows.

After being demoulded, the specimens were cured in a chamber of more than 95% at 20 ± 2 °C. Once cured, a set of specimens was carbonated on a chamber at RH between 60–70% and 20 ± 2 °C. The chamber was a drying glass recipient with an inlet and an outlet. The CO_2 flow was such that 100% of CO_2 filled the chamber. Although the proportion of CO_2 is too high, this procedure aims at a quick, full carbonation of the specimens that otherwise could take months to be carbonated in lower CO_2 ambient contents.

Other set of specimens was introduced in a salt spray chamber at 35 °C and with 3–7% of NaCl solution for spraying. The salt spray chamber was a Neutrek, model F that attends the ASTM B 117–64. In order to avoid the water saturation of specimens in this saturated ambient, that leads in an oxygen control, a cycling regime was imposed: the specimens were 6 days inside the chamber and for 1 day drying in a heater at 40 °C. This procedure enables the specimens to maintain active corrosion on the bars.

Corrosion potential, E_{corr}, and polarization resistance, R_p [1], were monitored continuously throughout the

Table 2
Results from squeezed pore solution

	Curing time (days)	OH^- (Mol/l)	Ca^{2+} (Mol/l) $\times 10^{-2}$	Na^+ (Mol/l)	K^+ (Mol/l)	Conduct. (mS/cm)
A	28	0.37	0.20	0.09	0.23	67.0
B	28	0.37	0.30	0.11	0.24	66.0
E	28	0.37	0.20	0.19	0.31	67.4
G	28	0.61	0.40	0.44	0.35	93.4

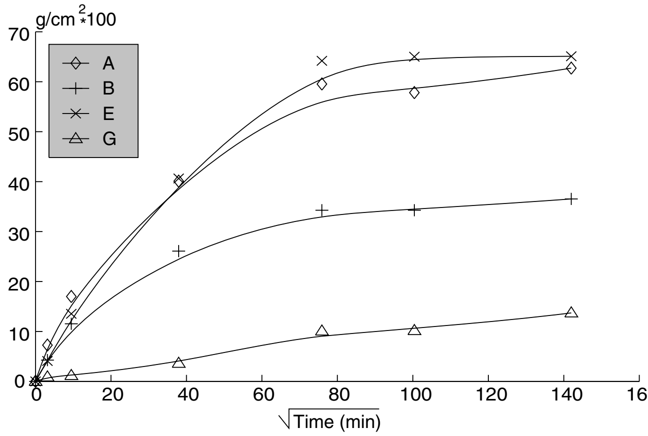

Fig. 1. Capillary absorption of specimens made with the four materials for 28 days.

Table 1
Characteristics of the mortars

Material	Components	Mix proportion	W/C	Flow table	Compression strength 28 days (MPa)	Flexural strength 28 days (MPa)
A	Cement I-45	1				
	Sand	3	0.5	12	59.50	8.36
	Water	0.5				
B	Cement I-45	1				
	Sand	3		12		
	Water	0.36			52.59	8.45
	Acrylic latex + silica fume	0.12	0.44 (1)			
E	Bind + aggreg + fibre	1				
	Acrylic resin	0.154	(2)	20	52.45	9.21
G	Bind + aggreg	1				
	Styrene butadiene latex	0.13	(3)	0	32	8.8

(1) The amount of water was determined summing up the water contained in the resin (after drying up in vacuum).
(2, 3) Ready mortars – no calculated W/C ratio.

experiment as well as resistivity between working and reference electrode, R_{ohm}. It was also measured the weight changes of the specimens before and after being embedded in the specimens, as was described in a previous paper [8]. The zone between 0.1 and 0.2 μmA/cm^2 marked with parallel dotted lines in the corresponding figures, was considered the frontier between a negligible corrosion and a significant one [1].

The chemical characteristics of the pore solution of these materials (see Table 2) were determined at 28 days of curing from the liquid squeezed at high mechanical pressures [9].

The water capillary absorption was determined in $5 \times 5 \times 5$ cm specimens also at 28 days of curing. The specimens were preconditioned in a laboratory environment during 60 days. After then, they were placed in water lamina of 5 mm up to the bottom. The water absorption (increase of weight) was monitored at 10 and 90 min, and then at time intervals as shown in Fig. 1.

3. Results

The capillary absorption results are given in Fig. 1. The higher values were obtained for materials A and E, and the lower for the material G. The modifications introduced in material B (the same cement of material A with acrylic latex) did not improve the mechanical strengths but reduced the capillary absorption ability.

Fig. 2 depicts the changes of I_{corr} values during the accelerated carbonation process. Material A depassivated after 4 h in the chamber while the rest of the materials started the corrosion process only after 24 h of contact to the CO$_2$ gas which indicates that material A has much smaller amount of carbonatable phases than the rest of the mortars.

The evolution of I_{corr} values all along the carbonation experiment is shown in Figs. 3–6 for materials A, B, G and E, respectively. From them it is possible to deduce that at the beginning, the corrosion rate I_{corr}, achieves in few days a perfect passivation (values below 0.1 μA/cm^2) in all mortars. The passive state is disrupted during the accelerated carbonation period because the I_{corr} values show an immediate increase until values above 1 μA/cm^2. The subsequent decrease in I_{corr} is due to the drying during the carbonation period which is performed at RH of 60–70% and, although water is produced due to carbonation, after some days this water evaporates from the mortar which progressively dries.

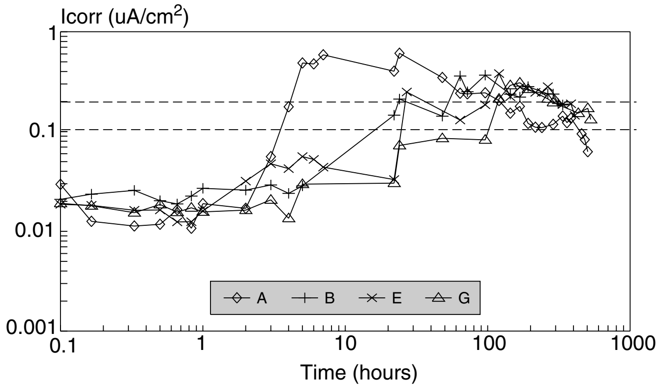

Fig. 2. I_{corr} during accelerated carbonation process of reinforced bar into mortar specimens of the four materials.

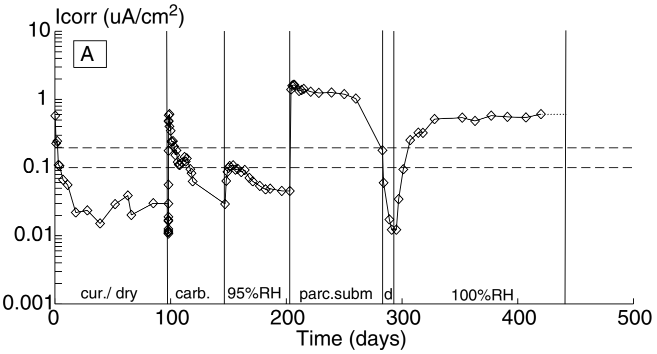

Fig. 3. Evolution of I_{corr} of the reinforcements bars into material A during the experiment of carbonation.

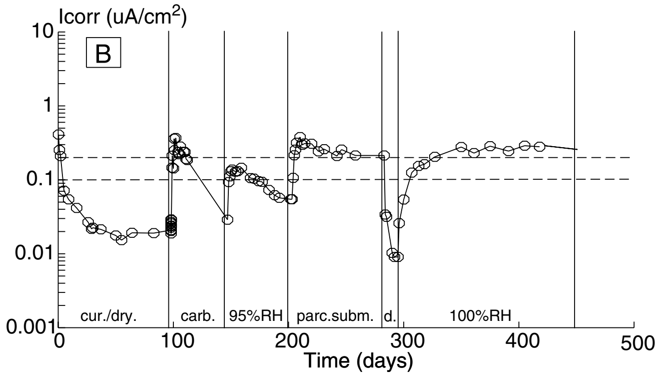

Fig. 4. Evolution of I_{corr} of the reinforcements bars into material B experiment of carbonation.

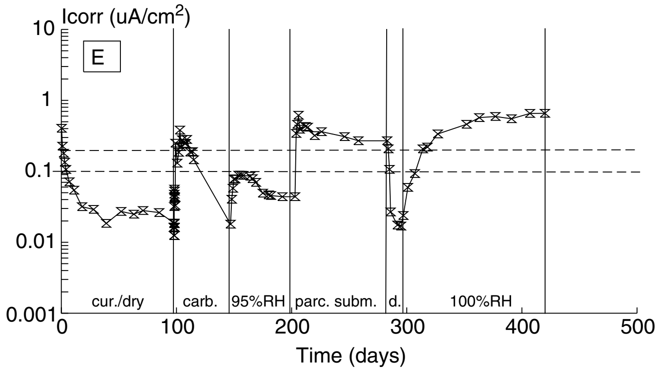

Fig. 5. Evolution of I_{corr} of the reinforcements bars into material E during the experiment of carbonation.

After being carbonated, the mortars are introduced in a chamber at 95% RH where the I_{corr} again increases until a certain value, which depends on the resistivity of each

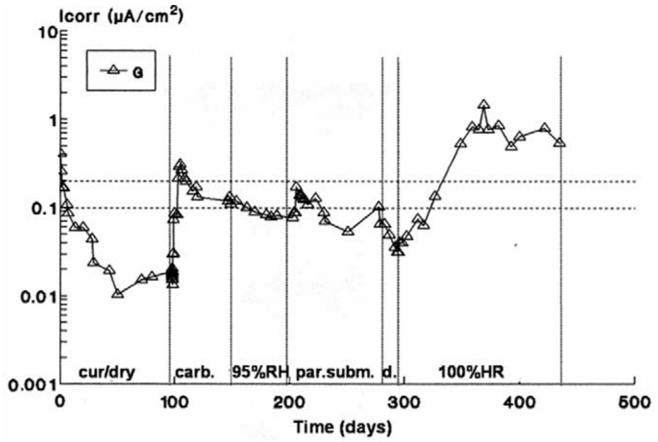

Fig. 6. Evolution of I_{corr} the reinforcements bars into material G during the experiment of carbonation.

mortar. Then they are transferred to partial immersion conditions which raises I_{corr} values to their maxima, which are again noticed at 100% RH in a further period. Not lowering of I_{corr}, due to oxygen control has been found during the testing period. In between both wet periods, a short drying one was tried and the I_{corr} values are lower following the increase in resistivity.

Regarding the performance of the different mortars during carbonation, in material A were present the highest I_{corr} values in the very wet periods while materials B and E do not enable so high values of the corrosion in any of the wet conditions. Finally, material G only induces high I_{corr} values in the 100% RH environment.

Results of salt spray chamber experiment are given for the same materials A, B, E and G in Figs. 7–10 in which the evolution of I_{corr} and R_{ohm} values are represented. The cycling regime of several days in the spray chamber and some hours of drying at higher temperatures are well monitored through the R_{ohm} and I_{corr} values which show more or less pronounced cycling values. The I_{corr} values also evolve by a continuous increase while R_{ohm} values remain rather stable along the experiment. The increase in I_{corr} value is attributed to the incremental arrival of chlorides to the bar which indicates that the drying periods are short enough to not enable a drying significant enough to induce a lowering of the I_{corr}, but at the same time avoiding an oxygen control of the corrosion by saturation of the pore network.

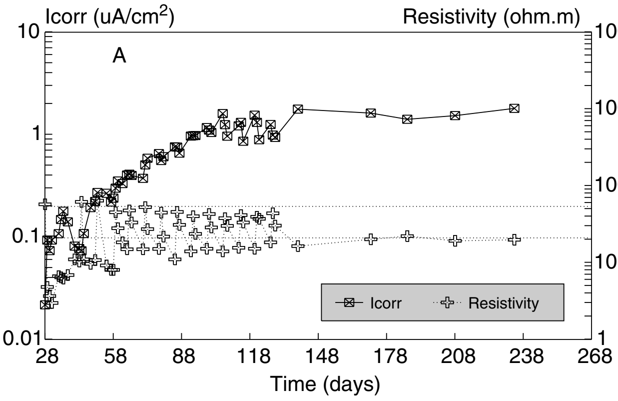

Fig. 7. Evolution of I_{corr} and R_{ohm} of material A in salt spray chamber.

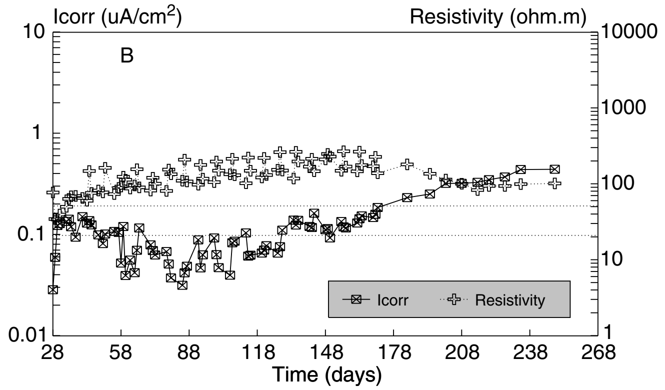

Fig. 8. Evolution of I_{corr} and R_{ohm} of material B in salt spray chamber.

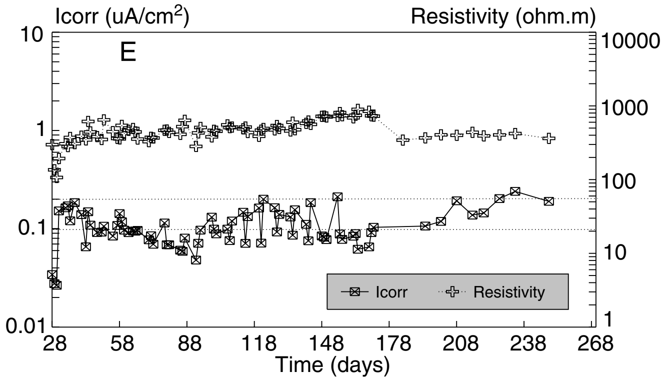

Fig. 9. Evolution of I_{corr} and R_{ohm} of material E in salt spray chamber.

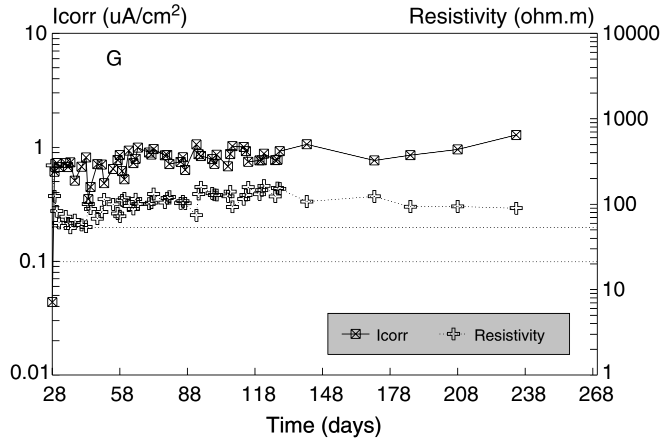

Fig. 10. Evolution of I_{corr} and R_{ohm} of material G in salt spray chamber.

Regarding the corrosion performance of the different mortars in the salt conditions, surprisingly, the bars of material G started to corrode immediately after being placed in salt spray chamber. It was the unique material that presented rust in the surface of specimens at the end of the experiment. Material A (blank) allows an increase of I_{corr} values after depassivation in spite of the R_{ohm} values remaining unchanged as mentioned, during the whole testing period. This fact is attributed as said, to the progressive increase of chloride ions near the steel surface which is transformed in an increase of the I_{corr} values but not influencing the R_{ohm} ones.

Material B presented a similar behaviour to material A except that it took more cycles to reach the onset of corrosion (0.1–0.2 $\mu A/cm^2$) and depassivation, and the I_{corr} value at the end of the experiment was smaller. This fact is attributed to the higher resistivity of material B (around one order of magnitude with respect to material A) which perhaps enables lower chloride content at the steel surface.

Material E reaches the corrosion threshold for depassivation only after 208 days and its R_{ohm} is 4–5 times higher than that of material B and more than one order of magnitude than material A. The I_{corr} values in this material never reach values above 0.2 $\mu A/cm^2$.

4. Discussion

The polymer based cement mortars and concrete are considered more protective than the plain cement one, due to the pore obstruction induced by resins and latexes [10]. Present results confirm that trend.

The modifications of material A (I-45, Spanish Code) by the acrylic latex and silica fume to form material B are important mainly from the microstructural point of view because its pore solution composition has practically the same characteristics, at least regarding the analyzed ions. Bentur et al. [10] have found that Portland cement mortar modified with vinyl sulphonate and silica fume is more effective against Cl^- penetration than vinyl sulphonate only. This shows that silica fume plays an important role in the microstructure changes, with respect to ion penetration.

Regarding the carbonation rate of materials A and B, the beneficial effect of the acrylic latex plus silica fume (Figs. 2–4) is also clear because carbonation is much delayed and the maximum corrosion currents, I_{corr}, reached in material B are insignificantly smaller.

However, the high resistivity of material E given by the acrylic resin employed is not enough to assure smaller corrosion rate after carbonation. This behaviour appears to be due to the plastic fibres used in its composition, not mentioned in the catalogue of the manufacturer, because in the analyses of interface mortar-fibre there was observed a capillary canal due to the lack of adherence [9]. However it is very effective in stopping Cl^- penetration which suggests that acrylic resin may work as a semi-negative membrane, as was stated by Ohama et al. [11].

The surprising performance of material G, Portland cement mortar modified with styrene butadiene latex, either after carbonation or in salt spray chamber, reflects that other variables were decisive to its weak final protection capacity. This material was the only one that presented rust in the exterior surface [9] at the end of the experiment in the chloride chamber. It was observed during the casting that the material presents a very short pot life and high thixotropy that enables only hand application. This could have produced an interface between the placed layers generating a preferential path to the aggressive agents, in spite of the fact that the material has good physical and chemical characteristics to protect against aggressive agents, small capillary sorptivity, high pH, despite its not very high resistivity. Another hypothesis could be the increase in water uptake with time. This explanation has been deduced from the observation of Fig. 6, where the I_{corr} presents a significant increase only after one year, in spite that 100% RH storage was less corrosive than the previous condition of total immersion.

Regarding the test methodology it has enabled the study of the performance of the materials in a variety of environments. It has been particularly useful to understand the processes to monitor the I_{corr} and resistivity simultaneously during the experiment.

5. Conclusions

The main conclusions that can be drawn up are

- With respect to the methodology:
  - The physical and chemical characterisation of the repair materials alone is not enough to enable prediction of corrosion performance of the steel bars embedded in polymer based cement mortars.
  - The testing methodology used in the present work has allowed the characterisation of polymer based cement mortars performance in the two main aggressive environments for corrosion of steel bars: carbonation and chloride attack. This alone is as well not enough and an integral set of tests seems to be the most informative.
- Regarding the materials studied:
  - (a) Modification (silica fume and acrylic latex) introduced in the blank material A based in OPC, leading to mortar B improved its performance against both types of aggressive conditions.
  - (b) Material E (Portland cement modified with acrylic latex and plastic fibres) has proved very resistant to chloride penetration but showed no improvement with respect to the blank in the case of carbonation.
  - (c) Material G (Portland cement modified with styrene butadiene latex) has a very poor performance in the two types of aggressive conditions, perhaps due to its poor workability or its deterioration when submitted to high humidity contents.

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