

Rebar corrosion in mortars with high limestone filler content

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Abstract

Purpose – This research aims to study the influence of limestone filler on rebar corrosion.

Design/methodology/approach – Mortar samples containing 35% calcareous filler and with a rebar inserted in the axis, were cast. Specimens were cured at the open air and during 28 days in lime water. After curing, they were submerged in two electrolytes (tap water and 3% NaCl) and corrosion parameters (corrosion potential and corrosion current) were monitored over time by d.c. techniques. Simultaneously, electrochemical noise measurements were carried out. After corrosion tests, rebars were pulled out by lateral compression, and their surface observed by scanning electron microscopy.

Findings – In general, carbonate additions impaired mortar protective properties, especially in the presence of chloride and changed the nature of the protective layer on rebars. The curing process did not introduce significant differences except for mortars with a high water cement ratio cured in lime water for which the beneficial effects of the simultaneous presence of carbonate and lime in the pore solution could be appreciated. The role of carbonate additions is to provide carbonate anions to passivate rebars. This passivation process caused corrosion rates not to be so high. Carbonate anions also deposited on oxide spots which were rendered passive but this process was not uniform. Certain areas on the rebar underwent intense carbonation while others showed increased corrosion rates.

Originality/value – There are not many corrosion studies about the influence of limestone filler on rebars corrosion. Particularly, this paper deals with mortars containing high percentages of carbonate additions. Results showed that the presence of this type of admixture changes the structure of the passive layer and, sometimes, may increase corrosion rates.

Keywords Corrosion, Mortars, Mechanical behaviour of materials, Limestone filler, Rebars corrosion, Corrosion rates, Protective layer composition

Paper type Research paper

1. Introduction

Mineral admixtures can replace a definite percentage of cement without impairing the properties of concrete. The partial replacement of clinker by these mineral admixtures could result in important savings in the cement industry. The most common mineral admixtures are: puzzolans, granulated blast furnace slag, calcareous filler, flying ash with high or low lime content, condensed silica fumes and rice hush ash (Bonavetti *et al.*, 2000; Kumar Mehta, 1986; Malhotra, 1987; Xianming *et al.*, 2011). More recently, the employment of calcareous filler has gained increased acceptance.

The incorporation of mineral admixtures does modify the properties of concrete and influences rebar corrosion because the formation of passive layer on steel depends on the type and concentration of admixtures and the curing process (Kumar Mehta, 1986; Malhotra, 1987). Some of these properties improve due to the physical effects derived from the smaller particle size of mineral admixtures while others

are modified due to cementitious and pozzolanic reactions derived from the presence of these materials. Durability of concrete is also improved because of pore refinement and increased adhesion at the cement paste/aggregate interface together with reduced microcracking (Kumar Mehta, 1986; Malhotra, 1987; Beaudoin and Brown, 1992; Montemor *et al.*, 2000; Luo *et al.*, 2003). Researchers' opinions about the beneficial effects of mineral admixtures differ from each other (Kumar Mehta, 1986; Malhotra, 1987; Beaudoin and Brown, 1992; Montemor *et al.*, 1995; Andrade and González, 1981).

Rebar durability parameters such as capillary absorption, electrical resistivity, chloride diffusivity in concrete, among other properties, are modified by the presence of the mineral admixtures. Capillary absorption normally decreased by the incorporation of mineral admixtures while the electrical resistivity increases. Chloride migration coefficients diminish in the presence of mineral admixtures, being the ground blast furnace slag one of the most efficient ones (Villagrán Zaccardi, 2012). However, it was demonstrated that mineral admixture cause concrete to be more prone to carbonation (Andrassy Flores, 2010).

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More recently, calcareous filler was employed massively as a mineral admixture for Portland cement with contents ranging from 5 to 35 per cent (Benchour *et al.*, 2008; Kastis *et al.*, 2006; Poppe and De Schutter, 2005; Mayfield, 1990). There are strong arguments about the addition of limestone filler which lie on both sides of the question (Poppe and De Schutter, 2005; Mayfield, 1990). It seems that there is an optimal performance value which is achieved when 15-20 per cent of the cement content was replaced (Poppe and De Schutter, 2005; Mayfield, 1990). Calcareous filler has often been considered to be inert; however, experimental results show that it does influence the hydration processes (Poppe and De Schutter, 2005). It reacts with silicates, aluminates and it can modify the chemical structure of ettringite by replacing sulphate ions by carbonate ones. Calcareous filler accelerates the hydration of tricalcium silicate leading to concrete pore disconnection (Pèra *et al.*, 1999).

Ingram and co-workers suggested that limestone could replace gypsum because it may react in a similar way with C_3A and due to its effect on cement particle size distribution. However, it was demonstrated that only 25-50 per cent replacement would be possible without significant and deleterious effects (Ingram *et al.*, 1990; Campitelli and Florindo, 1990). As other mineral admixtures, calcareous filler modifies concrete properties showing, as a general rule, a beneficial effect (Neto and Campitelli, 1990; Adamas and Race, 1990; Bédard and Bergeron, 1990; Nehdi and Mindess, 1996; Tsvivilis *et al.*, 2000; Douglas Hooton, 1990; Matschei *et al.*, 2007a, b; González and Irassar, 1998; Lothenbach *et al.*, 2008). Some adverse consequences on the drying shrinkage of Portland cement were reported (Adamas and Race, 1990). With respect to the compressive strength, Weiss and co-workers (Bents *et al.*, 2009a, b) reported a decrease of 7 per cent for a replacement level of 10 per cent which increased to 20 per cent when 12 per cent of ordinary Portland cement (OPC) was replaced by limestone filler.

Tsvivilis *et al.* (2000) have found that carbonate filler did not affect negatively rebars corrosion. However, later research showed that the addition of limestone filler up to ~ 22 per cent may increase corrosion rate although passivation by carbonate was observed in many cases. The influence of limestone filler on rebar corrosion depended on the w/c ratio, the curing process and, of course, the presence of chloride (Batic *et al.*, 2010).

The diffusion of chloride ions in cement pastes and mortars containing limestone filler was investigated and the prevailing opinion is that this addition reduces the diffusion coefficient of chloride ions. This reduction was attributed to the effect of the limestone filler particles on the tortuosity of the system (Bonavetti *et al.*, 2000; Akrouit *et al.*, 2010; Hornain *et al.*, 1995). Other investigations led to the conclusion that the incorporation of filler has an adverse effect on concrete resistivity and the chloride experimental diffusion coefficient which, in turn, will make reinforced concrete more susceptible to corrosion (Villagrán Zaccardi, 2012; Boubitsas, 2004, 2005, 2007). In addition, it is expected that the carbonation process will be enhanced (Andrassy Flores, 2010).

The objective of this research was to study rebar corrosion in mortars with OPC containing high percentages (35 per cent) of calcareous filler and two different w/c ratios (0.50 and 0.65, respectively). The study was conducted in parallel with mortars without the admixture. The behaviour of rebars was evaluated by electrochemical techniques: the measurement of corrosion potential, linear polarization tests and the electrochemical noise technique, in tap water and 3 per cent sodium chloride.

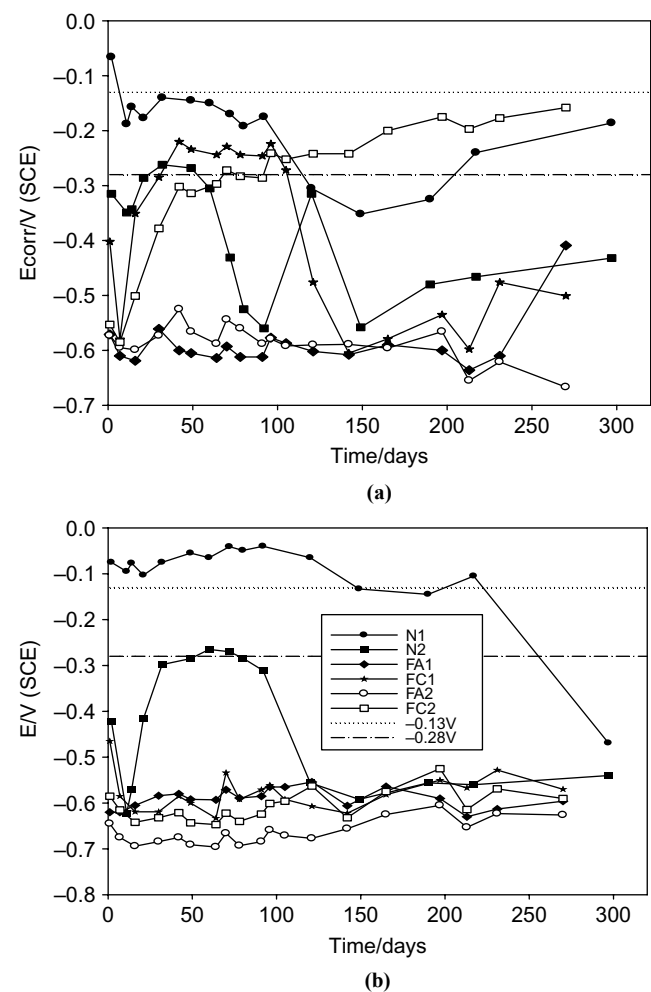
The nature of the protective layer formed on rebars was observed by scanning electron microscopy (SEM) and its composition obtained by X-rays energy dispersive analysis (EDX).

2. Experimental section

Cylindrical mortar specimens were cast. A grooved rebar of ordinary hardness (6 mm diameter, 25 cm long) was inserted along the axis of each specimen. The rebar had a deformation pattern similar to that shown in Figure 1 of ASTM C 234-91a. Its chemical composition was similar to AISI 1040 steel but with a high Mn content (C: 0.40; Mn: 1.00 per cent; Si: 0.40-0.50 per cent; P and S < 0.02 per cent). The mortar was manufactured with a 1:3 cement/sand ratio by weight and two w/c ratios: 0.50 and 0.65. OPC (ASTM C 150 Type I), the same cement modified by the addition of calcareous filler and ordinary graduated siliceous river sand (similar to ASTM C 778) were employed.

Mortar cylinders (5×10 cm in size) were obtained filling the moulds in three layers, pressing each layer with a tamper. In the first 24 h, specimens were in the humid chamber (95 per cent

Figure 1 Rebar corrosion potential as a function of time in different electrolytes



Notes: (a) Tap water; (b) 3 per cent sodium chloride

RH and $23 \pm 2^\circ\text{C}$) and, finally, they were removed from their moulds and cured in different ways:

- in air, to reproduce the conditions under which most mortars cure in practice; and
- under lime water to complete the 28-day curing period.

Previously to testing, the emerging part of the rebars was coated with an anticorrosive paint formulated with zinc phosphate and chlorinated rubber plus a top coat. The upper and lower surface of the mortar specimens were coated with the same topcoat and sealed with a paraffinic compound. Electrical leads were soldered on the extreme of the emerging rebar. After the curing period, the specimens were immersed in containers filled either with tap water or with a 3 per cent sodium chloride solution, for almost one year. The level of the liquid was maintained 0.5 cm below the upper surface of the mortar specimen.

Electrochemical measurements (corrosion potential, linear polarization and electrochemical noise measurements (ENM)) were performed during the test period, in stationary normally aerated solutions. The corrosion potential was monitored as a function of time against a saturated calomel electrode (SCE). Linear polarization measurements were carried out employing a three electrodes cell where the working electrode was the rebar and a SCE and a platinum grid were used as reference and counter electrodes, respectively. The swept amplitude was $\pm 0.150\text{V}$ from the open circuit potential and the scan rate $0.250\text{mV}\cdot\text{s}^{-1}$. Measurements were carried out with a Potentiostat/Galvanostat EG&G PAR Model 273A plus SOFTCORR 352 software. Steel corrosion rates were obtained, in both electrolytes, from apparent polarisation resistance measurements, employing the above mentioned software.

The cell for ENM was constituted by two nominally identical electrodes (joined together during measurement via a zero resistance ammeter) and a reference electrode. The three electrodes were in the same container which made it easier to control the effect of temperature fluctuations. The experimental arrangement for ENM was a computer-controlled, automated digital system for the simultaneous measurement of electrochemical voltage and current. Data was recorded according to a prefixed schedule (Kearns *et al.*, 1996; Gabrielli and Keddah, 1992; Mansfeld and Xiao, 2005). Adequate filtering was provided just to eliminate line and aliased signals (Cottis, 2001; Huet, 2005). The sensitivity of the measuring device in the E-scale was $100\mu\text{V}$ and 1nA in the current measurements. Spectra were taken more frequently at the beginning of the test. The sampling frequency was 1 Hz, which is commonly used to study corroding systems (Kearns *et al.*, 1996; Cottis, 2001; Huet, 2005) and each time series contained 1,000 points. Each set of data was controlled to verify they distribute normally (Mabbutt *et al.*, 2007; Tan *et al.*, 1996). Statistical analysis of each time series was performed. Mean values from noise potential spectra and from coupling current ones were obtained. The noise resistance (R_n) was calculated as quotient between the noise potential standard deviation and coupling current standard deviation. The localization index (LI) for each coupling current spectrum was calculated with the following equation:

$$LI = \sqrt{\frac{\sum_{i=1}^n (x_i - \bar{x})^2}{\sum_{i=1}^n (x_i)^2}}$$

It has been suggested in the literature that the LI can be used to determine the nature of the prevailing corrosion mechanism

with values of 1 characteristics of localized corrosion. However, Mansfeld and Sun (1999) and Eden (1998) suggested that it may be used with care and the LI must be considered as a measure of the deviation from the assumed identical behaviour of the two test electrodes.

Once the testing period ended, the rebars were pulled out from the mortars and their surface morphology was studied by SEM employing a PHILLIPS SEM 505 coupled with an EDAX OX PRIME 10 (energy dispersed form) to determine the surface composition which was expressed as oxides percentages. The EDX device was calibrated with a Zn (30 per cent) – Cu (70 per cent) alloy for both gain and peak position.

3. Results

The analysis of the OPC employed to carry out this research is shown in Table I. Ground calcareous filler (average particle size $10\text{--}20\mu\text{m}$) was added to OPC up to 35 per cent. In order to facilitate the analysis of results, each slab was identified with a letter to denote the cement type; N was employed for OPC and F for the cement with calcareous filler. The w/c ratio was named with a number; “1” for w/c ratio 0.50 and “2” for w/c ratio 0.65. Curing procedure was also identified with a letter: “A” for slabs cured in air and “C” for slabs stored in lime water.

3.1 Corrosion potential

According to the project DURAR (de Rincón *et al.*, 1997) only rebars in mortars with OPC and the lowest w/c ratio exhibited corrosion potentials close to that indicating the absence of corrosion, in tap water, during the first period of immersion (Figure 1(a)). The ASTM C 86 standard specifications were summarized in Table II. The rest of the slabs showed more negative values, particularly those with the highest w/c ratio which exhibited values corresponding to corroding steel. The tendency to repassivation was observed in both slabs made with OPC; this process was particularly effective for specimens with the lowest w/c ratio. It was also observed that slabs cured in lime water had more positive potentials maybe due to the passivation of rebars by carbonate from the addition and calcium ions coming from the curing medium. This effect was more noticeable in specimens with the highest w/c ratio (FC2) whose behaviour could be compared with that of mortars with OPC and w/c ratio 0.50.

As it could be expected, rebars potentials in 3% NaCl were displaced to negative values, from the beginning of the test period, except in the case of specimens containing OPC and w/c ratio equal to 0.50. However, corrosion potential of these specimens evolved to negative values as time went on.

3.2 Corrosion rate as a function of time

The analysis of the variation of the corrosion rate as a function of time is of great interest. In tap water, most values were lower than $0.5\mu\text{Acm}^{-2}$ (Figure 2(a)). Within the first three months of immersion, most specimens exhibited corrosion rates close to $0.10\mu\text{Acm}^{-2}$. The exceptions were slabs N2 and FA2. After this period, corrosion rate of specimens with OPC oscillated indicating the presence of a passivation process which was only effective when the w/c ratio was 0.50. In the case of specimens N2 rather high corrosion rates were measured. The abrupt changes in corrosion rate, as time elapsed, were attributed to changes in the structure of the passive film to finally generate an improved protective layer.

Table I Chemical analysis of cements employed in this research

	Loss at (1,000°C)	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	SO ₃	Insoluble residue
Ordinary portland cement	1.81	23.90	4.35	2.85	62.90	0.59	0.13	0.94	2.10	0.43

Table II Criteria for predicting corrosion in concrete structures

Corrosion potential (V)	Risk of corrosion	Corrosion rate ^a (i/μA cm ⁻²)	Corrosion level
E > -0.20 V vs CSE	Absence of corrosion	< 0.1	Despreciable
E > -0.13 V vs SCE			
-0.28 V < E < -0.13 V vs SCE	90 per cent probability corrosion is absent	0.1-0.5	Moderate
E < -0.28 V vs SCE			
E _{corr} < -0.28 V vs SCE	90 per cent probability of corrosion	0.5-1	High
-	-	> 1	Very high

Notes: ^aData taken from de Rincón *et al.* (1997); CSE – copper/copper sulphate electrode; SCE – saturated calomel electrode

Slabs with calcareous filler did not show active – passive transitions but corrosion rate was rather low and found to lie between 0.06 and 0.19 μAcm⁻² except for slabs FA2 whose corrosion rate increased as time elapsed, but always exhibiting a moderate attack (de Rincón *et al.*, 1997).

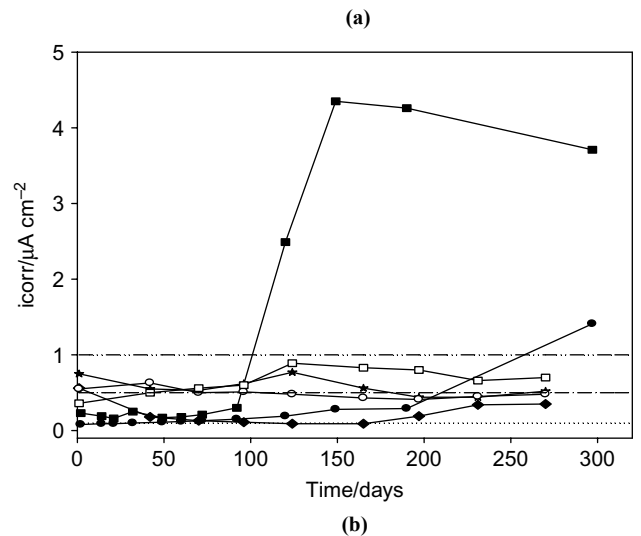
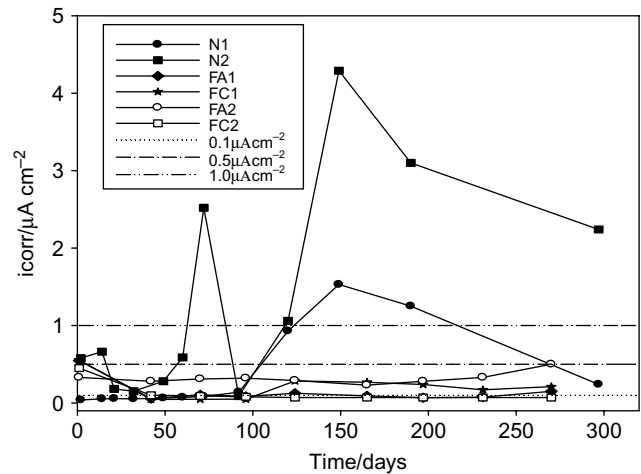
In general, none of the specimens immersed in 3% NaCl was in the passive state except slabs N1 at the very beginning of the test period and F1 during three to six months of immersion (Figure 2(b)). As a general rule, corrosion rate was moderate or high and the lowest w/c ratio corresponded to the lowest corrosion rate. Curing in lime water did not lead, necessarily, to lower corrosion rates.

3.3 Electrochemical noise measurements

Mean noise potential values measured on specimens N1, in tap water, were more positive than the other cases, thus indicating a higher protection degree of rebars. This behaviour was observed till 200 days of immersion (Figure 3(a)) and, at the end of the test period, all measured values indicated 90 per cent probability of rebar corrosion. The displacement of noise potential to more negative values and, then, to more positive values suggested that some kind of passivity was achieved. This displacement coincided with a decrease in the coupling current after 100 days of immersion (Figure 3(b)). The variation of the coupling current during the test period confirmed the existence of a protective film on rebars. Mean noise potential measurements in 3% NaCl pointed out that only specimens with OPC and w/c ratio 0.50 exhibited the best anticorrosive behaviour (Figure 4(a)). Differences between the behaviour of the other specimens are not significant and coupling current measurements confirmed this statement (Figure 4(b)).

The analysis of the variation of the Rn as time elapsed revealed that the best protective behaviour in tap water was obtained with OPC and for the lowest w/c ratio, as it was also deduced from mean noise potential determinations (Figure 5(a)). As it could be expected, Rn was lower in chloride medium (Figure 5(b)) and, as a general rule, it increased slightly when specimens containing calcareous filler were cured in lime water.

Figure 2 Rebar corrosion rate as a function of time in different electrolytes



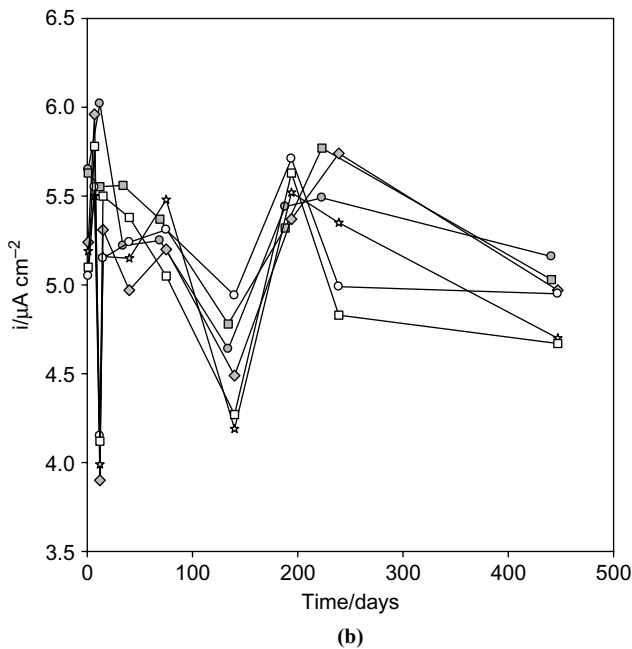
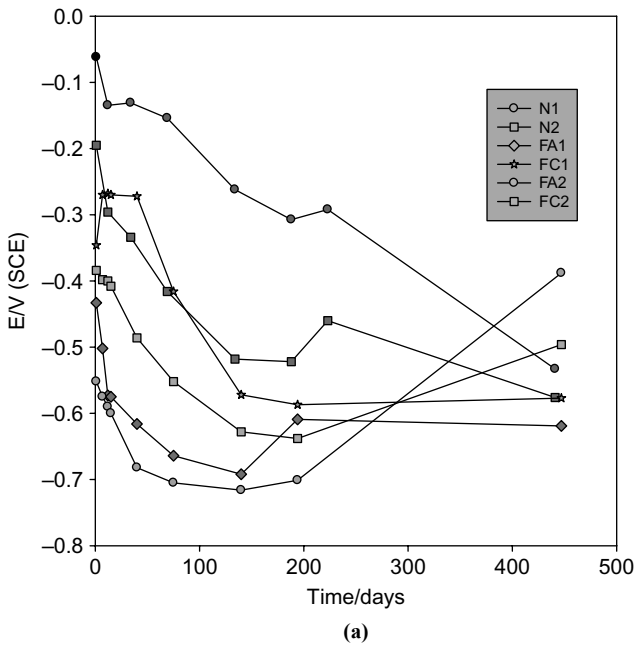
Notes: (a) Tap water; (b) 3 per cent sodium chloride

In most cases, LI values were comprised between 0.50 and 0.60; almost just half way between 0 (uniform corrosion) and 1 (localized corrosion). Actually, both types of corrosion were detected on rebars, independently of the w/c ratio, the addition of filler and the curing procedure.

3.4 Visual and SEM analysis of rebar corrosion

Once electrochemical tests were finished, rebars were pulled out by lateral compression and observed, in first instance, with the unaided eye. N type specimens, in tap water, both w/c ratios, only developed small corrosion spots randomly distributed over the entire rebar surface. In change, rebars in 3% NaCl, w/c ratio 0.65, presented 20-30 per cent of the surface covered with corrosion products. This percentage increased to ~75 per cent when calcareous filler was incorporated to the mortar.

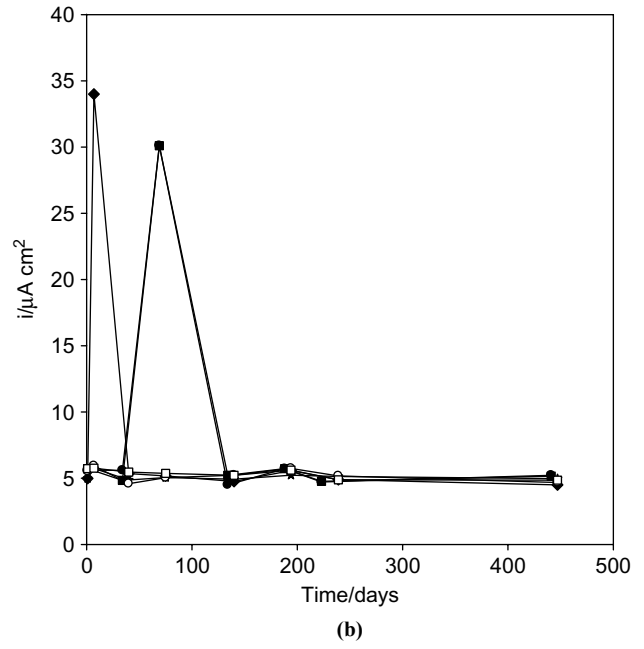
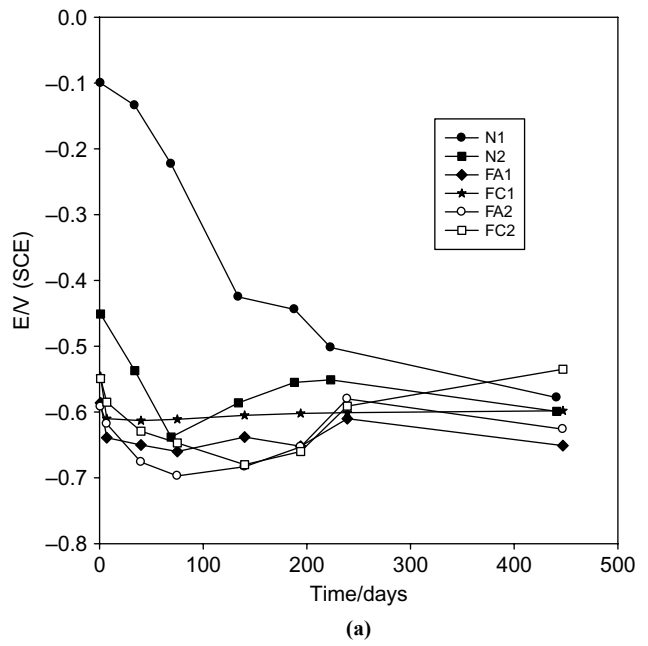
Figure 3 Mean noise parameters for rebars in mortars immersed in tap water



Notes: (a) Mean noise potential; (b) mean coupling current

After visual examination, representative samples cut from the exposed rebar were observed by SEM. Cut pieces were obtained in such a way that all formations were represented on them; if necessary several pieces were cut. The presence of carbon dioxide in cut samples was due to calcareous filler because samples were stored in an air tight container from the very moment they were obtained. Results from EDX analysis were expressed as percentage of oxides. It must be beared in mind that the surface analysis by the EDAX sound is subjected to certain error, not higher than 20 per cent, and results must be regarded as semiquantitative. Errors are higher in the case of elements of lower molecular weight. As rebar analysis was comparative,

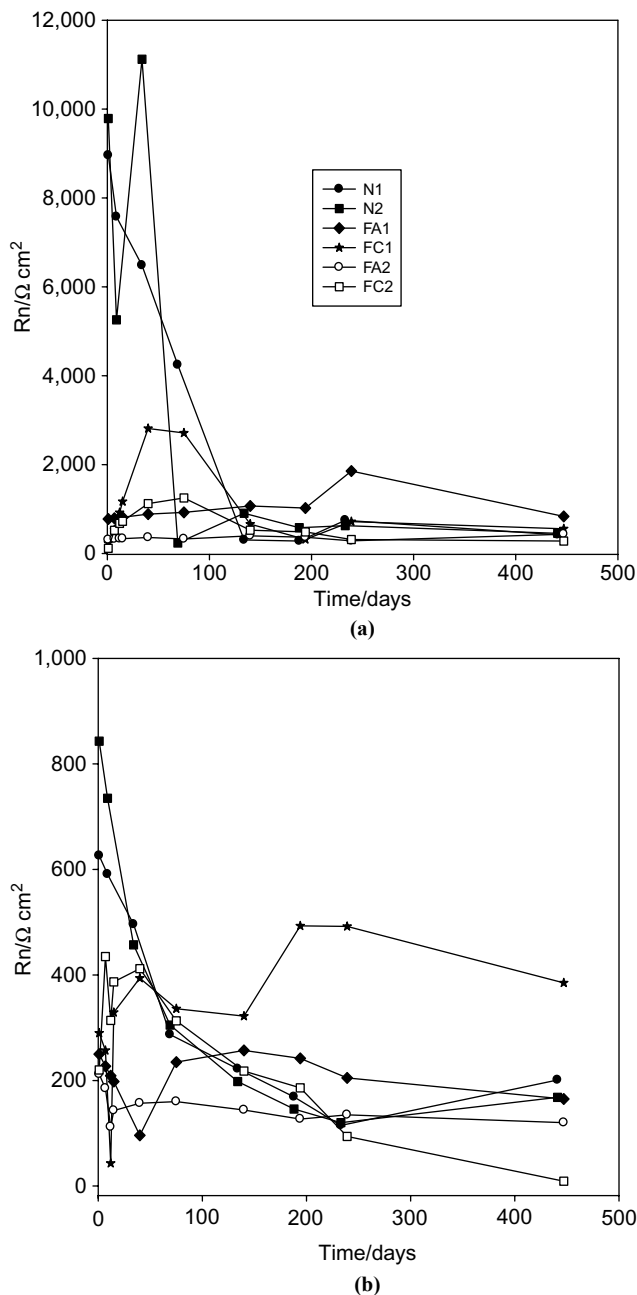
Figure 4 Mean noise parameters for rebars in mortars immersed in 3 per cent sodium chloride



Notes: (a) Mean noise potential; (b) mean coupling current

clear tendencies were observed and reported in this section. Iron oxide content in protective rebars was rather high and, sometimes, it may be due to the detection of iron from the substrate because of the low thickness of the protective layer.

Rebars extracted from N1 specimens, stored in tap water, presented two well differentiated regions after SEM examination. The most widespread morphology was constituted by gels with filament like formations (Figure 6(a)) and was similar to others reported in the literature (Romagnoli *et al.*, 2002). Spectral data showed that these formations were rich in hydraulic compounds (SiO_2 : 20-25 per cent; CaO : 32-40 per cent) with lower amounts of iron oxides (Fe_2O_3 : 11-19 per cent) and carbon

Figure 5 Rn value as a function of the exposure time

Notes: (a) Tap water; (b) 3 per cent sodium chloride

dioxide (CO₂: 8–10 per cent). The other morphology contained gels constituted by non-expansive iron oxyhydroxides (Figures 6(b)). Expansive iron oxides usually exhibit a globular morphology. Although the iron oxide content may be influenced by the base metal, high values (Fe₂O₃: ~83 per cent) were detected in certain regions of the rebar. When the w/c ratio increased to 0.65 the surface configuration was similar but with higher amount of these iron oxyhydroxides formations (~33 per cent).

Rebars from slabs FA1, submerged in tap water, presented a rather uniform surface covered by gels (Figure 7(a)) which were composed by high amounts of iron oxyhydroxides (Fe₂O₃: ~45 per cent) and carbon dioxide (CO₂: ~38 per cent)

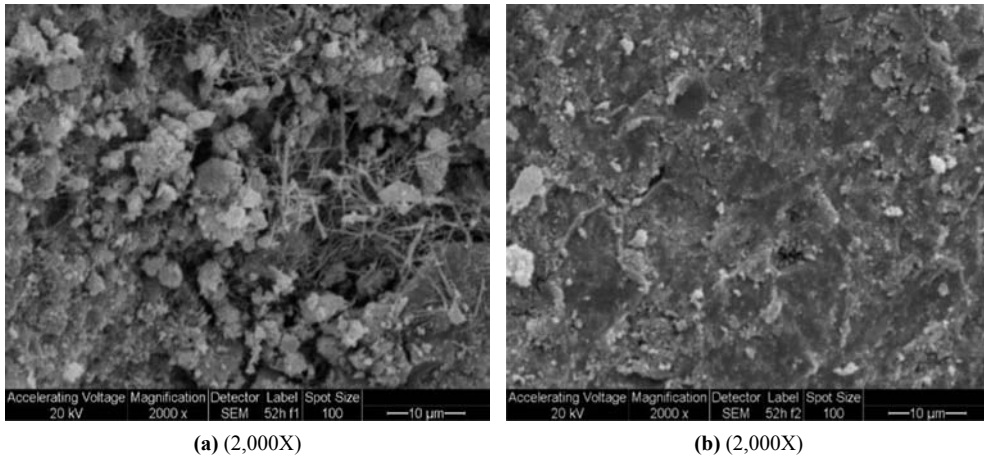
and lower contents of calcium oxide (CaO 9 per cent) and silica (SiO₂: ~4 per cent). These gels alternated with some distinctive formations which may be appreciated in Figure 7(b). Plate like formations contained higher amounts of silica and calcium hydroxide than the sticks which seemed to be carbonated iron oxyhydroxides. Specimens cured in lime water (FC1) were covered with a porous protective layer which was also constituted by a high percentage of carbonated iron oxyhydroxides (Fe₂O₃: ~60 per cent; CO₂: ~30 per cent). Differential morphologies like those shown in Figure 7(c) appeared on different regions of the scanned surface. Plates had higher calcium hydroxide content (~25 per cent) and a reduced level of iron compounds (~18 per cent). Carbon dioxide (~41 per cent) and the aluminium oxide (Al₂O₃: 9 per cent) contents, both of them were also high. The presence of SCH (CaO: 51 per cent and SiO₂: 15 per cent), with lower carbon dioxide content, was detected on other regions on the scanned rebar (Figure 7(d)). It seemed that specimens cured in lime water generated more hydraulic compounds on the rebar surface.

Rebar surface of slabs FA2 was similar to that of specimens with lower w/c ratio; a more or less uniform film covered it. The iron oxide content was rather high (~65 per cent) and partially carbonated. An iron oxide spot, perceivable at the unaided eye, appeared to be constituted by sticks and plates after SEM examination (Figure 8(a)) which had slightly different compositions. The iron oxide content ranged between 20 and 40 per cent and the carbonation degree was high (CO₂: ~35 per cent). Calcium oxide content increased in this iron oxide spots (~20 per cent) as well as the aluminium content (Al₂O₃ 7–12 per cent). It was thought that they were passivated by the carbonation process although they appeared as corroding spots at the unaided eye. Rebars surface of similar slabs (w/c ratio 0.65) cured in lime water was quite uniform and presented many crystalline formations (Figure 8(b)) with lower oxyhydroxide content (Fe₂O₃: ~28 per cent) and increased calcium oxide content (CaO: ~21 per cent). Hexagonal formations as well as sticks like ones appeared to be carbonated. Gels contained higher amounts of iron oxyhydroxides (~60 per cent). The good anticorrosive behaviour of these specimens may be attributed to the higher carbonation degree (CO₂: ~36–45 per cent) and to the presence of compounds enriched in calcium oxide, probably generated by the curing medium filling the mortar pores.

Rebars in mortars N1, submerged in 3% NaCl, were covered by gels and, in certain zones, a fine particulated material deposited on it, as it occurred in tap water with specimens N1 and F1. The iron content increased as the w/c ratio increased.

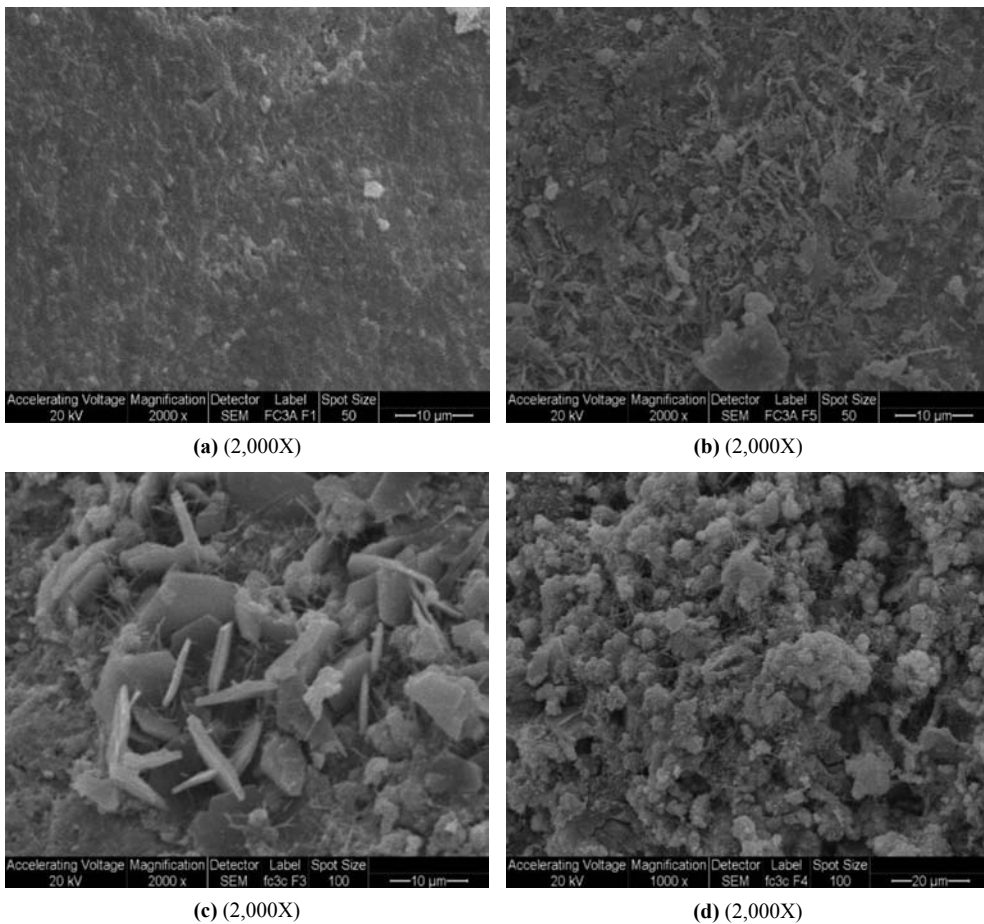
The surface of rebars embedded in specimens FA, immersed in 3% NaCl, was covered by a cracked gel whose surface composition was characterized by a high iron oxide content (>75 per cent) and lower carbon dioxide contents (CO₂: 8–14 per cent). The lower content of calcium carbonate was attributed to the solubilization of calcium by chloride, so the amount of CO₂ fixed by the rebar was lower. Curing in lime water produced formations enriched in silica and calcium oxide and, consequently, with lower amounts of iron oxide. The carbon dioxide content was a little higher than in samples cured in the air (CO₂: ~23–33 per cent). Three different morphologies were observed in FC specimens: a cracked surface constituted by amorphous plates (Figure 9(a)), formations similar to those reported for OCP hydration products (Romagnoli *et al.*, 2002) in certain zones of the rebars (Figure 9(b)) and, finally, the third one with high calcium oxide content and low levels of iron oxide (Figure 9(c)).

Figure 6 SEM micrographs of rebars from mortars elaborated with OPC



Notes: Water/cement ratio: 0.50; electrolyte: tap water

Figure 7 SEM micrographs of rebars from mortars elaborated with Portland cement with limestone filler



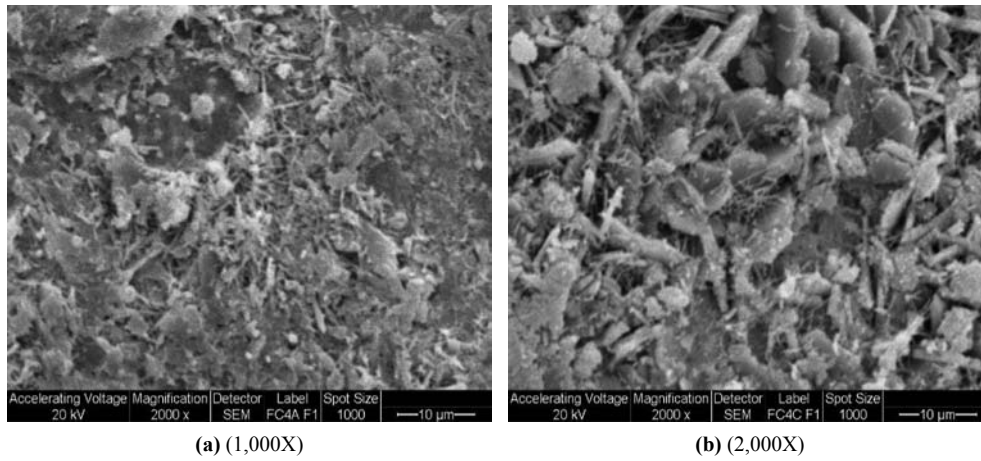
Notes: Water/cement ratio 0.50; (a) and (b) cured at open air; (c) and (d) cured in lime water; electrolyte: tap water

All the formations were enriched in hydraulic compounds as it was revealed by the higher contents of SiO_2 and CaO .

The rebars surface of specimens FA2, exposed to 3% NaCl , was similar to those with the lowest w/c ratio in the sense that a highly cracked surface was observed together with high iron

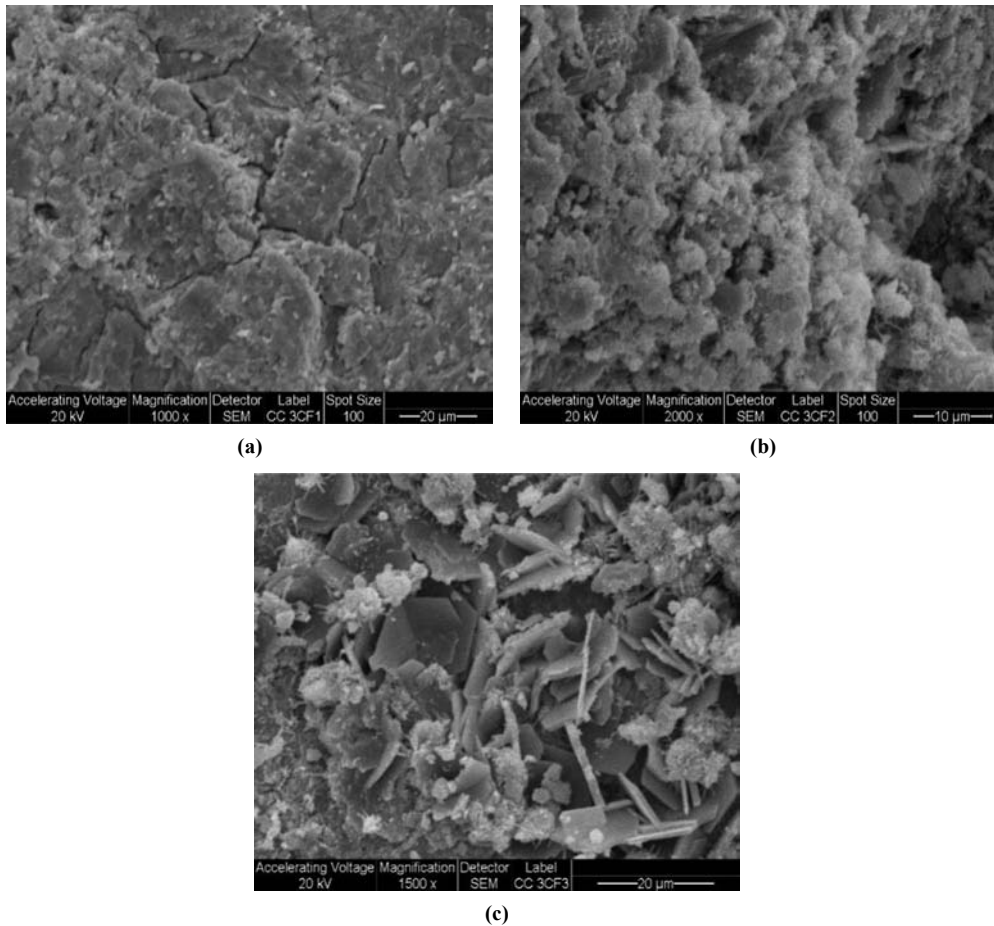
oxyhydroxide content (~ 94 per cent; Figure 10(a)). The rebars surface of specimens cured in lime water presented two different morphologies which covered the most part of the rebars. The first one (Figure 10(b)) was a plate-like morphology constituted by hydraulic compounds (SiO_2 : ~ 11 per cent and

Figure 8 SEM micrographs of rebars from mortars elaborated with Portland cement with limestone filler



Notes: Water/cement ratio 0.65; (a) cured at open air; (b) cured in lime water; electrolyte: tap water

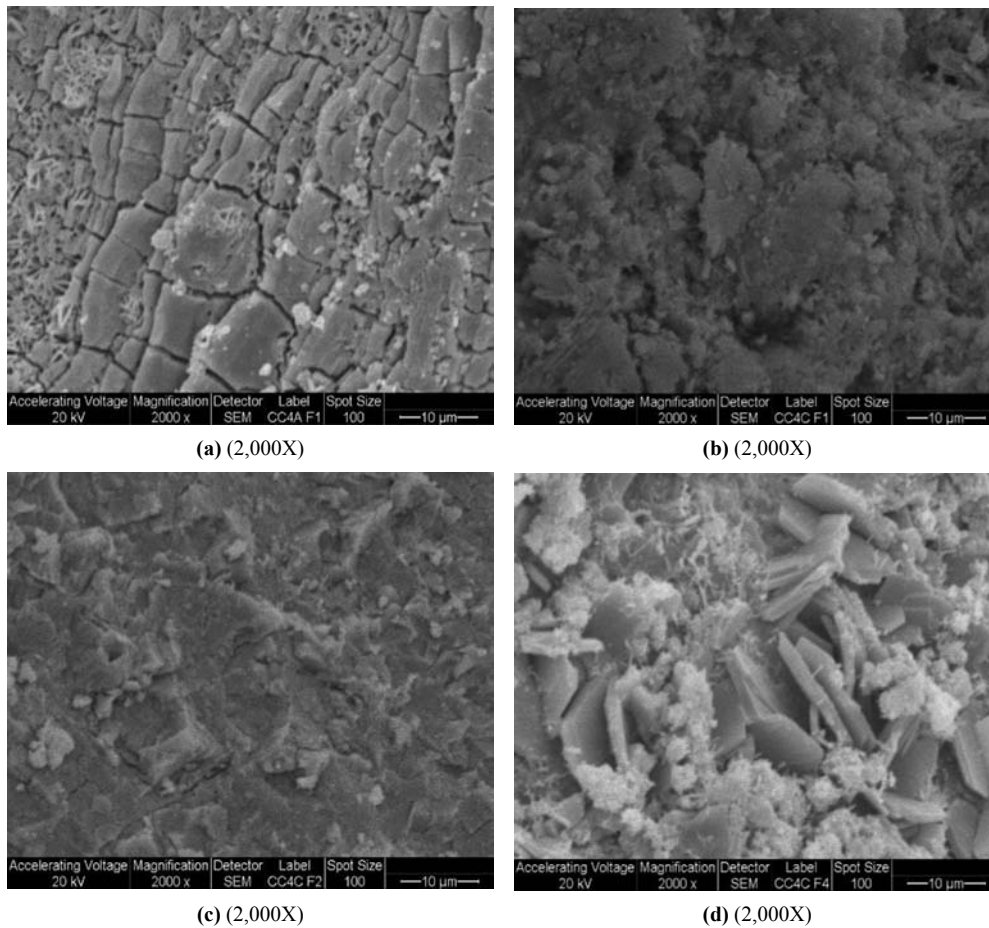
Figure 9 SEM micrographs of rebars from mortars elaborated with Portland cement with limestone filler



Notes: Water/cement ratio 0.50, cured in lime water; electrolyte: 3 per cent sodium chloride

CaO: ~39 per cent) and the other (Figure 10(c)) contained high percentages of iron oxides (Fe_2O_3 : 63 per cent). Crystalline compounds were also observed (Figure 9(d)) with rather high CaO (25 per cent) and Al_2O_3 (15 per cent) contents.

In the case of samples stored in 3% NaCl variable amounts of chloride were detected on the rebar surface; typically 0.7-2.0 per cent but, in certain cases, it increased up to ~7 per cent, particularly associated with high Al_2O_3 contents.

Figure 10 SEM micrographs of rebars from mortars elaborated with Portland cement with limestone filler

Notes: Water/cement ratio 0.65; (a) cured at open air, (b-d) cured in lime water electrolyte: 3 per cent sodium chloride

4. Discussion

According to corrosion potential measurements, the best protective behaviour as well as the possibility of repassivation, both were observed in mortars with OCP. The curing medium had an important role in the case of specimens with limestone filler because it improved rebar passivation, modifying the protective layer. The influence of the curing medium was also more important as the w/c ratio increased as it was observed with slabs FC2. Corrosion current measurements confirmed that the addition of calcareous filler did not impair rebars corrosion significantly.

Only slabs with OCP and a w/c ratio equal to 0.50 underwent the action of chloride successfully. In this sense, the addition of limestone to the mortars made them more susceptible to chloride attack.

The electrochemical noise technique resulted useful to differentiate mortars and the curing processes employed in this research. In general, noise measurement also revealed that the behaviour of specimens made with OPC and those with limestone additions did not differ significantly.

It seemed that carbonate anion passivated corroding rebars, as it could be deduced from visual examination. Carbonate anions also deposited on oxide spots which were rendered passive but this process could not be uniform. At the unaided

eye, it appeared that the rebar surface was covered with oxide spots and the rusted area was increased in the presence of limestone filler. However, these areas were passivated as it could be deduced from corrosion rate measurements and after SEM examination.

Rebars surfaces appearance changed by the presence of carbonate addition. Hydraulic compounds tended to be replaced by carbonated iron oxyhydroxide and the CO_2 content increased when limestone was incorporated to the mortar. When the curing medium was limestone water, the growth of hydrated calcium silicate and crystalline calcium hydroxide was favoured. In 3% NaCl, the protective layer cracked and calcium carbonate was solubilised by chloride, thus facilitating the corrosion process.

As reported in the literature, carbonate additions could affect the hydration of Portland cement in a certain degree and they have the beneficial effect of reducing chloride diffusivity. At the same time they lower the pH of the cement paste. However, it is thought that the determining factor in rebars protection is the higher amounts of carbonate which changed rebars passivation as it was revealed after SEM examination of rebars. The other important factor, the diminution in the pH of the medium, seemed to be counterbalanced by the presence of carbonate anion which passivated the rebar surface. Finally, it must be said that there was a change in the mechanism of rebars passivation in the sense

that the formation of calcium silicate hydrates and calcium hydroxide was replaced by an important carbonation process.

5. Conclusions

In general, carbonate additions to OPC impaired mortar protective properties, in the presence of chloride and changed the nature of the protective layer on rebars. This mineral addition caused rebars to be more susceptible to corrosive chloride attack. The increase in the w/c ratio minimizes the differences between both types of mortars. The curing process did not introduce significant differences except for mortars with a high water cement ratio cured in lime water for which the beneficial effects of the simultaneous presence of carbonate and lime in the pore solution could be appreciated. The role of carbonate additions is to provide carbonate anions to passivate rebars. This passivation process caused corrosion rates not to be so high. It is advisable to employ limestone filler controlling the w/c ratio and employing the adequate curing medium.

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