

Durability Properties of Mortars Partially Substituted with Spent Catalytic Cracking Catalyst

E. Zornoza¹, P. Garcés², M.V. Borrachero³, J. Payá⁴

¹*Unidad de Investigación de Ciencia del Hormigón (UNICH). Dep. Ingeniería de la Construcción, Obras Públicas e Infraestructura Urbana. Universidad Alicante, Alicante, Spain. <emilio.zornoza@ua.es>. Carretera de San Vicente, s/n. San Vicente del Raspeig (Alicante, Spain)*

²*Unidad de Investigación de Ciencia del Hormigón (UNICH). Dep. Ingeniería de la Construcción, Obras Públicas e Infraestructura Urbana. Universidad Alicante, Alicante, Spain. <pedro.garces@ua.es>. Carretera de San Vicente, s/n. San Vicente del Raspeig (Alicante, Spain)*

³*Unidad de Investigación de Ciencia del Hormigón (UNICH). Dep. Ingeniería de la Construcción y Proyectos de Ingeniería Civil. Universidad Politécnica de Valencia, Valencia, Spain. <myborrachero@cst.upv.es>. Camino de Vera, s/n (Valencia, Spain)*

⁴*Unidad de Investigación de Ciencia del Hormigón (UNICH). Dep. Ingeniería de la Construcción y Proyectos de Ingeniería Civil. Universidad Politécnica de Valencia, Valencia, Spain. <jjpaya@cst.upv.es>. Camino de Vera, s/n (Valencia, Spain)*

ABSTRACT

Several durability properties of reinforced mortars of cement partially substituted with spent catalytic cracking catalyst (FC3R) in quantities up to 20% by cement mass are presented. Carbonation resistance of FC3R-OPC mortars under accelerated conditions mainly depends on the water/binder (w/b) ratio, but also the substitution level can affect this property when the w/b ratio is higher than 0.5, due to the reduction of alkaline reserve that is produced as a consequence of the pozzolanic reaction. Chloride ingress resistance is enhanced when cement is partially substituted by FC3R due to the high Al₂O₃ level of this material yielding higher chloride binding. In addition the porosity of substituted mortars is lower because of the formation of pozzolanic products that also reduces chloride ingress into the mortar. Corrosion rates of rebars embedded in FC3R-OPC mortars show that this substitution does not worsen under accelerated carbonation or chloride contamination conditions.

INTRODUCTION

It is generally admitted that the main problem affecting service life of reinforced concrete structures is the corrosion of steel reinforcement inside the concrete. Focusing on this aspect, one of the most important risks for the corrosion of steel rebars is the carbonation of the concrete cover, which produces a reduction of the pH in the pore solution and, consequently, the depassivation of the steel surface takes place increasing the corrosion rate of the reinforcement. The other process leading to an important risk of corrosion is the chloride ingress. When a sufficient amount of chlorides reaches the steel rebars, it is

produced a local break of the passive layer of the rebar, and corrosion pits appear in the surface of the steel which can cause a serious reduction in the steel cross section area. For these reasons, research on materials that could help in the enhancement of the corrosion problem of steel reinforcement is a matter of interest for civil engineers.

The fluid catalytic cracking catalyst (FC3R) is an aluminosilica-based powdered material used in petrol refineries. When this catalyst loses its catalytic properties, it must be replaced by a new catalyst. The wasted catalyst is then thrown out, and managed as an inert residue.

In recent years some authors have investigated the properties of this waste material as a pozzolan replacing cement in mortars or concrete [Su et al. 2000, Payá et al. 1999, Payá et al. 2001, Payá et al. 2002, Pacewska et al. 2002]. Some previous works have shown that FC3R is able to improve mechanical properties in mortars or concretes due to a densification of the cementitious matrix caused by pozzolanic reaction.

FC3R is characterized by a high initial reactivity and consumes a large quantity of calcium hydroxide which has been released by cement hydration [Payá et al. 2003]. Both phenomena (densification and calcium hydroxide consumption) produce opposite effects on the carbonation resistance of the mortar. On one hand, the precipitation of new hydration products as a consequence of the chemical reaction of portlandite and the aluminosilica framework of FC3R, diminishes the size of pores and the connectivity and tortuosity of pores and capillaries in the cemented matrix. On the other, the decrease of portlandite content due to its consumption in the pozzolanic reaction and the dilution effect by cement replacement diminishes the chemical capacity of the cement matrix for reacting with carbon dioxide.

FC3R has high level of Al_2O_3 (47.47%) so it is possible that this could enhance the chloride ingress resistance of mortars containing the spent catalyst due to an expected higher formation of Friedel's salt. This fact, along with the reduction in porosity that takes place due to the pozzolanic reaction of FC3R can help to diminish the corrosion risk of steel reinforcement in concrete or mortars.

The aim of this research is to assess the role of this pozzolanic material in carbonation resistance and the chloride ingress resistance of mortars, as well as its effect on the corrosion rate of steel rebars when they are subjected to carbonation and chloride exposure.

EXPERIMENTAL

All mixtures have been prepared using portland cement type I 52.5 R, siliceous aggregate, FC3R (supplied by BP España) and tap water. Table 1 shows chemical composition of FC3R. In some mixtures Sika Viscocrete plasticizer has been used.

Table 1. Chemical composition of FC3R in percentages. *LOI: loss on ignition at 950° C, 1 h.

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	LOI*
46.04	47.47	0.58	0.11	0.17	0.02	0.49

In the carbonation experiments, samples consisted of 4x4x16 cm mortar specimens. The samples were made changing two parameters: the level of replacement of cement by FC3R,

0 and 15%; and the water/binder ratio (w/b ratio, b being the sum of cement and FC3R), ranging from 0.3 to 0.7. The aggregate used was normalized sand [EN 196-1] and the aggregate/cement ratio was 3/1. In mortars prepared containing w/b ratio lower than 0.5, superplasticizer was added.

After demoulding, the specimens were cured under water for a 28-day period. After curing, the specimens were maintained in the laboratory environment for a 15-day period in order to favour the evaporation of water present in the pores of the specimens. After this conditioning step, the samples were placed in a carbonation chamber containing an atmosphere consisting of 100% CO₂ and 65±5% relative humidity, for a three week period. During this period, two parameters were monitored: the mass of the samples by weighing and the depth of the carbonation front by spraying phenolphthalein solution and measuring the carbonation front, according to UNE/112011:1994. When the carbonation period finished, porosimetry analysis was performed in order to analyze the changes in the porous structure of the material. The mercury intrusion porosimeter used was an Autopore IV 9500 V1.05 supplied by Micromeritics Instrument Corporation. The analyses were performed from a pressure of 3.5 Pa to 230 MPa.

Mortars have been prepared with a w/b ratio of 0.5 for specimens used in the migration tests. Sand/binder ratio has been 3/1. The migration test specimens were cylindrical (Ø100 mm) and a cylindrical sample (Ø100 mm, 15 mm thick) was extracted from each mortar specimen after 28 days of curing time in a 100% RH chamber. Several cement replacements by FC3R has been used in mortars: 0, 5, 10, 15, 20% of cement mass.

To perform the migration tests, a two compartment cell [Castellote et al. 2001], as shown schematically in Fig. 1, was used. Graphite electrodes were used to apply 12 V potential between both sides of the sample, although the real voltage drop across the specimen was measured as indicated in [Castellote et al. 2001]. The anolyte chamber was filled with distilled water and the catholyte chamber was filled with NaCl 1 M. Periodically along the experiments, conductivity of the anodic solution was measured by introducing an electrode of conductivity in the compartment, while the power supply was switched off. Conductivity values (*C*) were translated into chloride concentration by using the relation [Castellote et al. 2001]:

$$\left[Cl^{-}\right] \text{ (mM)} = -1.71 + 11.45 \cdot C \text{ (mS / cm)} \quad (1)$$

and steady and non-steady state diffusion coefficients were calculated for each specimen. The corrosion rate test specimens were prismatic 20x55x80 mm and contained, embedded, two identical bars of carbon steel (Ø8 mm, 15.07 cm² exposed area). A graphite bar was also embedded as counter-electrode in these specimens. For the corrosion rate study under carbonation attack three w/b ratios were used: 0.3 with plasticizer, 0.5 and 0.7 without plasticizer. Additionally two types of binder were used: control mortars without FC3R and mortars with a 15% of cement replacement by FC3R. These corrosion rate test specimens were demoulded 24 hours after the preparation and were stored in a humid chamber (100% RH) until steady values of corrosion rate was obtained. Then specimens were stored in a carbonation chamber with 5% of CO₂ and 65% of relative humidity for 70 days. After this period specimens were stored in a more aggressive environment with an atmosphere that consisted of 100% CO₂ and 65% of relative humidity for 40 days.

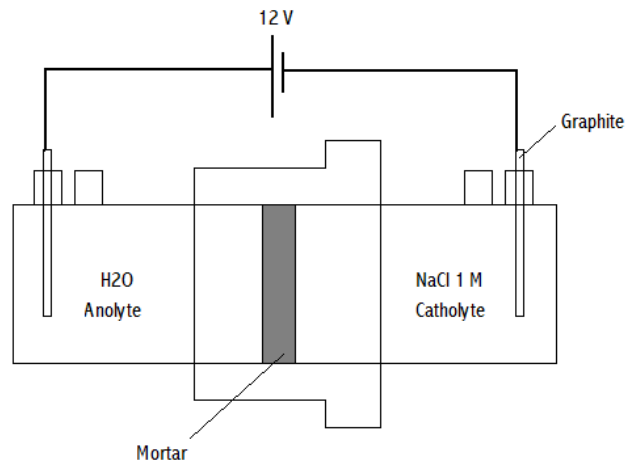


Fig. 1. Scheme of migration cell used.

In the case of the chloride ingress attack specimens, w/b ratio was 0.5 for all the samples and several cement substitution levels were used: 0, 5, 10, 15, 20% by cement mass. These corrosion rate test specimens were demoulded 24 hours after the preparation and were stored in a humid chamber (100% RH) until steady values of corrosion rate was obtained. Then specimens were partially submerged in a 0.5 M NaCl solution.

Corrosion potential (E_{corr}) and corrosion rate (I_{corr}) was monitored along the duration of the experiments. The electrochemical technique used to measure the instantaneous corrosion rates, I_{corr} , was the polarization resistance technique, through the well known Stern-Geary formula [Stern & Geary 1957, Andrade & González 1978] $I_{corr} = B/R_p$. I_{corr} was calculated assuming values of $B = 26$ mV. R_p and corrosion potential (E_{corr}) were periodically measured during the time of the experiment, and also the weight loss was measured, for each electrode, at the end of the test in order to check that electrochemical measurements were right. All potentials are referred to saturated calomel electrode (SCE). Potentiostat-Galvanostat 362 EG&G was used. I_{corr} given data were calculated as average values of two measurements. (one specimen, two electrodes). The electrochemical loss estimated from the integration of the I_{corr} -time curves has been compared with the corresponding gravimetric loss (obtained by direct weighing). The good agreement obtained between the two weight loss values validates the B values employed.

RESULTS AND DISCUSSION

It has been described by other authors that porosity with diameters between 0.05 and 3 μm is the most affected by changes in the w/b ratio and has the bigger effect on the permeability of mortars [Parrot 1987]. Fig. 2 shows the porosity within this range for the cement/FCC mortars. In this Fig., it can be observed that the higher the w/b ratio, the bigger the volume of porosity in this range. It can also be observed that the presence in the mortar of FC3R produces a significant decrease in this type of porosity due to the additional formation of binder products from the pozzolanic reaction. This reduction was more evident for pastes with lower w/b ratio (0.3 and 0.4).

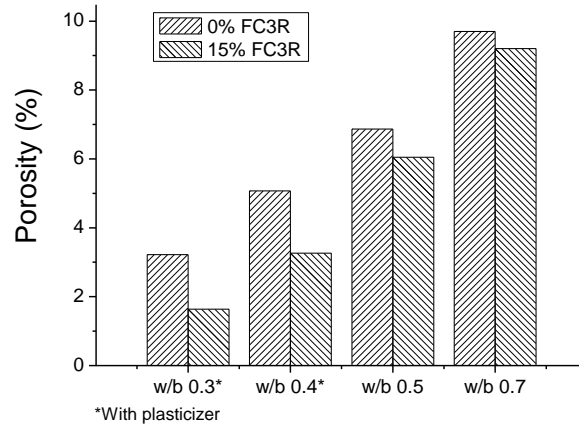


Fig. 2. Cumulative intrusion in the pore range of 0.05-3 μm for studied mortars before carbonation.

Fig. 3 depicts total porosity of mortars with and without FC3R, before and after the accelerated carbonation process. It is observed that the carbonation process produces a reduction in the total porosity for both FCC and non-FCC mortars. This behaviour is due to the formation of calcium carbonate from the calcium hydroxide, making a denser final structure. It is also interesting to observe that total porosity values for substituted mortars are always lower than those obtained for non-substituted mortars, except for w/b ratio of 0.3. In this case minor difference is observed.

Fig. 4 shows the evolution of the carbonation depth in 4x4x16cm mortar specimens during the carbonation process. Those mortars with low w/b ratio (0.3 and 0.4) showed a very low carbonation depth after the 21-day carbonation period. These mortars do not show differences between those that are not substituted and those that have a 15% cement replacement by FC3R. As the w/b ratio is raised, the carbonated layer becomes larger. Mortars with 15% of FC3R, and w/b ratio of 0.5 and 0.7 showed faster carbonation than plain cement mortars (without FC3R).

Experimental data from Fig. 4 can be fitted to the equation that correlates the carbonation depth, X , with the exposure time, t :

$$X = V_{CO_2} \sqrt{t} \quad (2)$$

where V_{CO_2} is the constant that relates the carbonation depth with the exposure time and is usually named as the carbonation rate ($\text{mm}/\text{year}^{0.5}$).

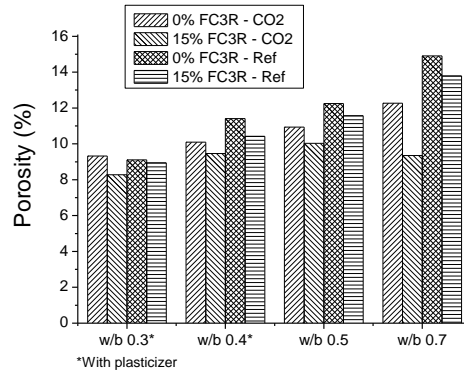


Fig. 3. Total porosity of cement/FC3R mortars before and after the accelerated carbonation process.

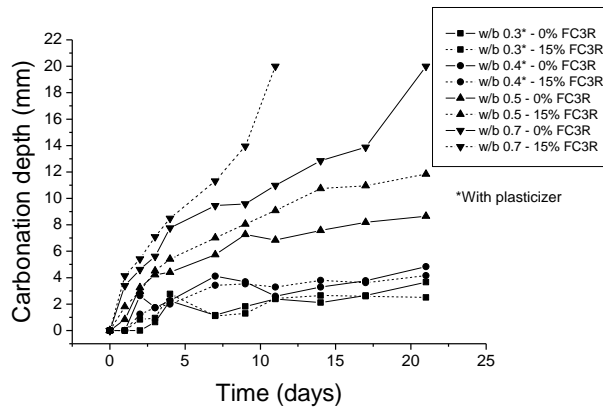


Fig. 4. Evolution of the carbonation depth for cement/FC3R mortars in the carbonation chamber. Atmosphere: 100 CO₂, 65% relative humidity.

In Fig. 5, the carbonation rate obtained in 100% CO₂ atmosphere tests for cement/FC3R mortars are represented. The lowest w/b ratio mortars showed very low carbonation rates. The replacement of cement by FC3R, diminishing the portlandite content of the cementing matrix by pozzolanic reaction and by dilution effect, did not negatively affect behaviour in carbonation tests. Apparently, the refinement in pore size due to the pozzolanic reaction in cement/FC3R mortars compensates the partial loss of the chemical portlandite barrier. However, for the highest w/b ratio, mortars containing FC3R displayed the fastest rate of carbonation, suggesting that the pozzolanic role of FC3R in these mixtures was not enough to compensate for the decrease in portlandite.

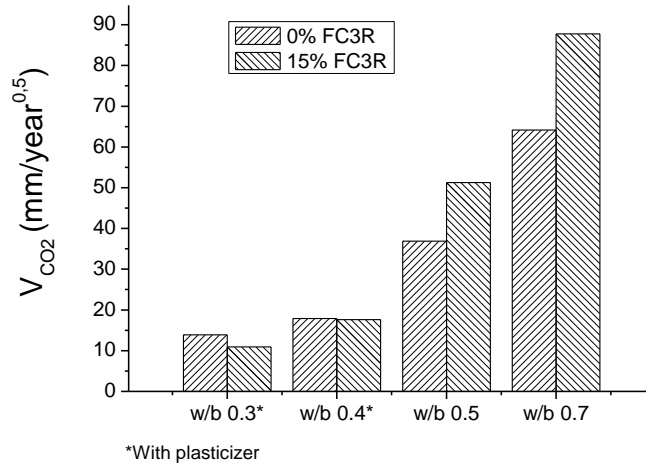


Fig. 5. Carbonation rate in cement/FC3R mortars from the carbonation chamber test. Atmosphere: 100% CO₂, 65% relative humidity.

Fig. 6 shows the evolution of the chloride concentration in the anolyte chamber during chloride migration tests performed on cement/FC3R mortars. In Fig. 6 there are two important parameters: *time lag* is the time needed for chlorides to appear in the anolyte chamber and it is related to non-steady state chloride diffusion coefficient (D_{ns}) through Equation 3; and *slope* after the *time lag* that is related to steady state chloride diffusion coefficient (D_s) through Equation 4 (both equations according to [Castellote et al. 2001]):

$$D_{NS} = \frac{2x^2}{\tau\nu^2} \left[\nu \coth \frac{\nu}{2} - 2 \right] ; \quad \nu = \frac{zF\Delta\phi}{RT} \quad (3)$$

where x is the sample thickness (cm), F is Faraday's constant (96485 C/mol), $\Delta\Phi$ is the effective voltage applied (V), R is 8.31 J/mol·K, T is the temperature (K) and τ is time lag in migration test (h).

$$D_s = \frac{JRTx}{zFC_1\gamma\Delta\phi} \quad (4)$$

where J is flux of chlorides (mol/cm²·s), C_1 is the chloride concentration in the catholyte (mol/cm³), z is the electrical charge of the considered ion and γ is the activity coefficient of the catholyte solution.

D_{ns} is mainly influenced by chloride binding capability, the concentration and the mobility of charge carriers at the start of the test (e.g. alkali ions) and porosity of mortars, while D_s is only affected by the porosity and its connectivity since the chloride binding capacity has been exhausted in the previous stage of the experiment.

In Fig. 6 it can be observed that for control mortar (0% FC3R) the time lag is the shortest, as well as increasing the substitution level of cement by FC3R produces an increase in the time needed for the chloride to pass through the mortar. In addition, when the substitution level is increased the slope slightly decreases, so the fluxes of chlorides through the substituted mortars are lower than for control mortar.

Fig. 7 depicts the calculated non-steady state and steady state chloride diffusion coefficients for cement/FC3R mortars. It is clearly noticed the benefits of increasing cement replacement by FC3R in these two parameters.

Fig. 8 shows the corrosion rate (I_{corr}) and corrosion potential (E_{corr}) of steels embedded in cement/FC3R mortars with various W/Cm ratios under carbonation attack. In a first stage specimens were subjected to an atmosphere of 5% of CO_2 and then the CO_2 concentration was raised to 100% of CO_2 .

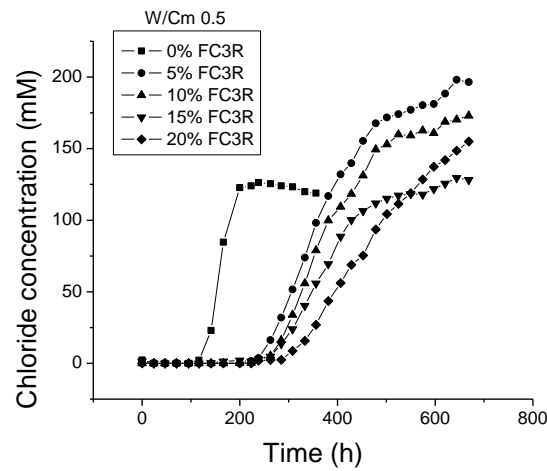


Fig. 6. Evolution of chloride concentration in the anolyte chamber during the migration test for cement/FC3R mortars.

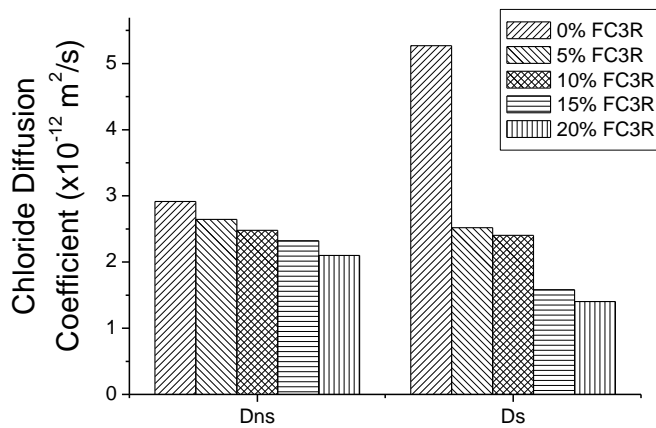


Fig. 7. Steady state and non-steady state chloride diffusion coefficients for cement/FC3R mortars.

In the first part of the experiment (5% CO₂), only the mortar with the highest porosity and the lowest alkaline reserve (W/Cm ratio of 0.7 and 15% of FC3R) suffered an increase in I_{corr} values due to the carbonation front reached the surface of steels. This increase in I_{corr} was accompanied by a decrease in E_{corr} values due to the depassivation of steels. It is clear that in this case the reduction of the alkaline reserve produced by the cement replacement was high enough to produce a decrease in the carbonation resistance of mortars.

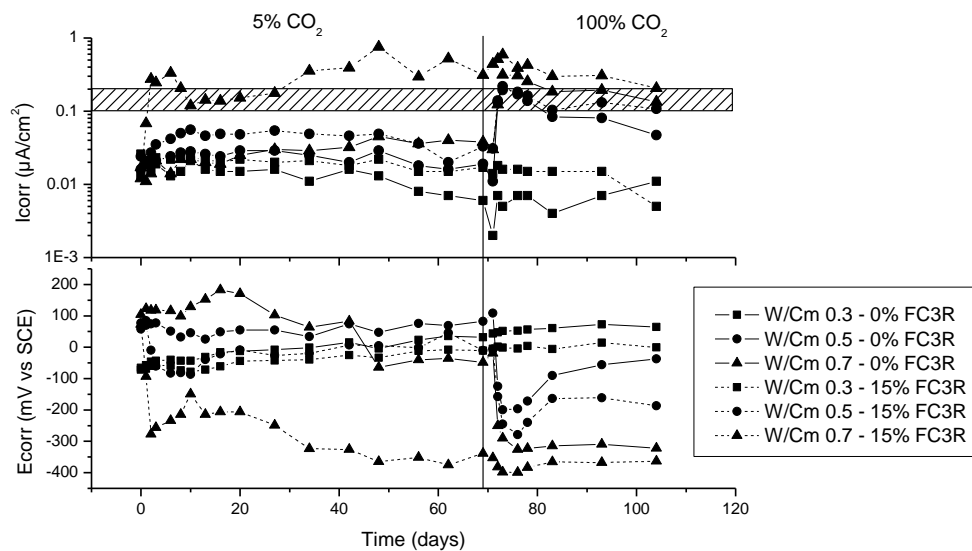


Fig. 8. Corrosion rate and corrosion potential of steels embedded in cement/FC3R mortars under carbonation attack.

In the second stage (100% CO₂), steels embedded in mortar with W/Cm ratio of 0.7 and 0% of FC3R, as well as substituted and non-substituted mortars with W/Cm of 0.5 increased their I_{corr} values as a result of the carbonation of the mortar cover. However, mortars with W/Cm ratio of 0.3 with plasticizer did not suffered any change in their corrosion rate values.

The reduction in the alkaline reserve in mortars due to the presence of FC3R has only affected the corrosion behaviour the steels when the W/Cm ratio is very high. Additionally it can be seen that the use of a very low W/Cm ratio protects efficiently steels against the carbonation process, even if the FC3R has reduced the portlandite content of the mortar.

Fig. 9 presents I_{corr} and E_{corr} results of steels embedded in cement/FC3R mortars for various levels of cement replacement by FC3R and W/Cm ratio of 0.5 under chloride ingress attack. In this case only steels embedded in mortar with 20% of replacement presented a high corrosion rate value during the chloride attack. The explanation for this result is that such a high level of substitution can drastically reduce the amount of portlandite in pores. As a result the [Cl⁻]/[OH⁻] ratio is increased. Some authors have demonstrated the relation

between this ratio and the corrosion rate [Garcés et al. 2005], so probably mortars with 20% FC3R can be more sensitive to the chloride content.

Regarding the chloride ingress attack, it seems that a substitution of 15% of FC3R is the maximum admitted in order to avoid a significant reduction in the service life of steel reinforced structures.

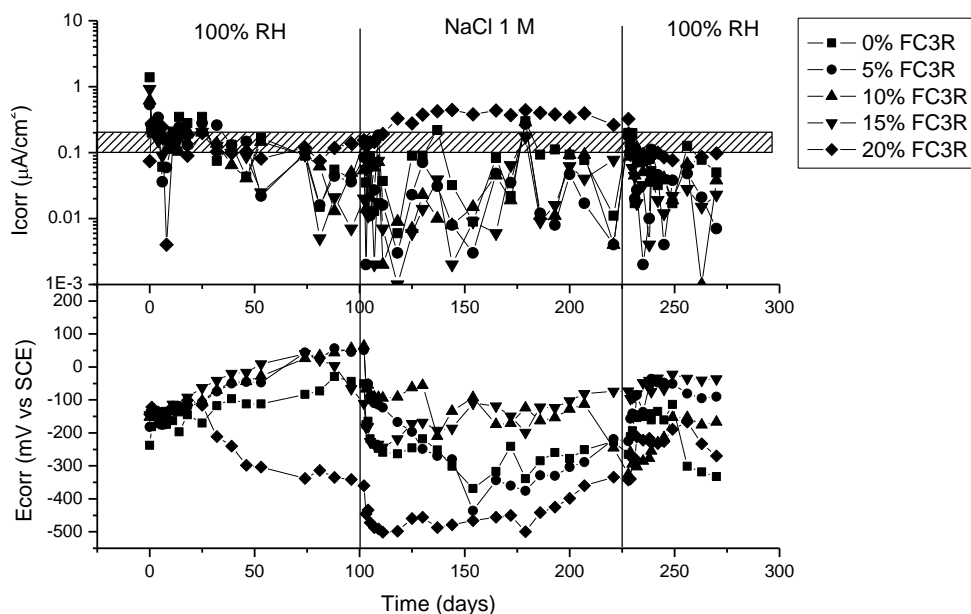


Fig. 9. Corrosion rate and corrosion potential of steels embedded in cement/FC3R mortars under chloride ingress attack. W/Cm ratio of 0.5.

The enhanced chloride binding capacity and porosity of mortars with FC3R are due to the higher aluminate phase content and the pozzolanic reaction, respectively. As it was previously mentioned FC3R consists of 47.47% of Al_2O_3 , so higher amounts of Friedel's salt is formed during the chloride ingress and higher level of chloride binding is obtained. In addition, the pozzolanic reaction of FC3R with portlandite makes a denser microstructure as it was previously shown in Fig. 2. Both facts makes a significant improvement in the chloride ingress resistance of mortars containing FC3R in quantities up to 20%, according to these results.

CONCLUSIONS

The following conclusions can be drawn from the results obtained in this study:

- Cement substitution for FC3R reduces the porosity of mortars as a result of the pozzolanic activity of FC3R.
- The incorporation of FC3R reduces the carbonation resistance of mortars but this reduction is only significant when the W/Cm ratio is 0.5 or higher.
- The chloride ingress resistance of mortars, in terms of chloride diffusion coefficients, is improved when the cement substitution by FC3R is increased.

- Corrosion rate studies of steel reinforcements under carbonation and chloride attack has shown that substitution levels up to 15% does not worsen the corrosion behaviour of steels if the W/Cm ratio does not exceed 0.5.

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