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Corrosion behaviour of rebars in fly ash mortar exposed to carbon dioxide and chlorides

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Abstract

Addition of fly ash has beneficial effects on some mechanical properties of concrete, as well as on the corrosion process induced by the chloride ion. The aim of this study was to investigate the effect of fly ash addition on the corrosion process occurring in reinforced concrete exposed simultaneously to carbon dioxide and chloride. The corrosion process of steel rebars embedded in mortar with 15% and 30% of fly ash was tested under carbon dioxide and sodium chloride contamination. Monitoring of open circuit potential and electrochemical impedance spectroscopy (EIS) were used to follow the corrosion process. Results have shown that under accelerated carbonation fly ash mortar shows higher corrosion rates. The chloride content in mortar exposed to accelerated carbonation increases with the amount of fly ash. However, under natural carbonation it decreases with the addition of fly ash.

Keywords: Concrete; Fly ash; Reinforcement; Carbonation; Corrosion; Impedance; Chlorides

1. Introduction

Corrosion of rebars in reinforced concrete is now recognized as a major problem in the maintenance of the structural integrity of structures. The concrete pH, usually in the range 12–13.5, provides chemical protection to the rebars due to steel passivation. However, with time, severe corrosion problems may occur in reinforced structures. The most important causes of corrosion initiation of reinforcing steel are the ingress of chloride ions and carbon dioxide to the steel surface. Chloride ion causes local destruction of the passive film leading to localised corrosion. Carbon dioxide, on the other hand, reacts with the hydrated cement matrix, leading to a pH decrease and subsequent loss of steel passivity and to corrosion initiation.

The need to extend concrete durability has led to the use of several admixtures and modifications to the concrete composition. Addition of fly ash as additive has become common practice in recent years. The fly ash particles react with calcium hydroxide, producing cementitious products that strongly decrease concrete porosity [1–3]. This effect leads to an increase of the concrete resistivity and consequently to a decrease on the diffusivity coefficients of some species, such as oxygen and chloride through the concrete [4–6]. In a previous work [6], a reduction of chloride diffusivity in immersed concrete to half its value was observed in concrete with 50% of fly ash addition. Consequently, the corrosion process in the presence of chlorides was delayed. This behaviour was shown in previous work for fly ash concrete under immersion in sodium chloride solutions [7–9]. The use of 30% fly ash as partial substitution of cement has lead to a significant increase of induction time and to a reduction of the corrosion rate by one order of magnitude [9].

Under carbonation, the presence of fly ash seems to have an opposite effect. It is well known that carbon dioxide reacts with calcium hydroxide (a main product of cement hydration) leading to the production of calcium carbonates ($CaCO_3$). This product is insoluble and precipitates, blocking the concrete pores and retarding the progress of the carbonation front [10]. In the presence of fly ash, the amount of CaO (one of the main components of cement) decreases and consequently less $Ca(OH)_2$ is formed, resulting in a decrease of the concrete pH. On the other hand, $Ca(OH)_2$ is partially consumed in the pozzolanic reactions. Since less $Ca(OH)_2$ is present, the amount of $CaCO_3$ produced during carbonation also decreases, facilitating the

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progress of the carbonation front. As soon as the carbonation front reaches the rebars, acidification leads to steel depassivation and the corrosion process is initiated. The acceleration of CO_2-induced corrosion in the presence of fly ash was confirmed in previous works [11,12].

As a consequence of the opposite effects of fly ash addition to concrete both in carbonation and chloride induced corrosion, one interesting point comes out: the behaviour of fly ash-containing concrete in the presence of simultaneous contamination by chlorides and carbon dioxide. The aim of this work is to study the effect of fly ash addition in concrete contaminated with chloride ions and exposed to carbon dioxide-rich atmospheres. Open circuit potential monitoring (OCP) and electrochemical impedance spectroscopy (EIS) were applied in order to evaluate the corrosion process.

2. Experimental

2.1. Preparation of the mortar samples

Ordinary Portland cement and Type-C fly ash (Table 1) were used in the preparation of the mortar blocks (Table 2).

Two commercial steel rebars (type A-10) with 10 mm diameter, previously polished with a 600 silicon carbide (SiC) grit emery paper, were embedded in each block, with a cover thickness of 10 mm (Fig. 1). With this geometry, the distance between the inner surfaces of the steel rebars was 30 mm. At the interface mortar/air the rebars were isolated with epoxy glue in order to avoid crevice corrosion. The blocks were cured during 28 days in a saturated humidity chamber at room temperature.

Table 1
Chemical analysis of the Portland cement and the fly ash used in the concrete

Constituent (%)	Cement	Fly ash
Insoluble residue	1.10	
Ignition loss	3.88	3.27
SiO_2	19.23	53.62
Al_2O_3	6.89	28.15
CaO	60.69	1.97
MgO	3.15	1.06
SO_3	1.67	0.32
Na_2O	0.52	0.52
K_2O	0.74	2.51
Cl^-	<0.02	0.004
TiO_2	–	1.40
Fe_2O_3	–	6.64
P_2O_5	–	0.17

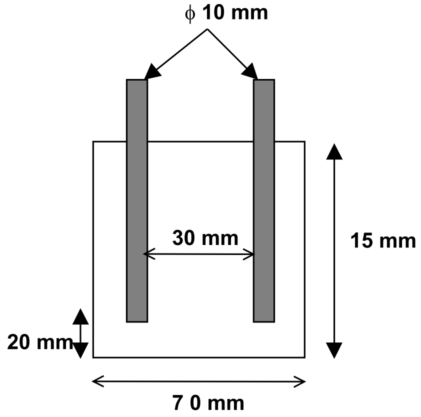

Fig. 1. Geometry of the mortar blocks.

2.2. Exposure conditions

Two types of exposure were applied. In one set of samples, simultaneous exposure to carbonation and chloride was achieved by keeping the blocks in a chamber with an atmosphere containing 5% CO_2 (room temperature and 60–70% relative humidity) and spraying the blocks weekly with a 15% NaCl aqueous solution. Blocks of each composition were also exposed in the same chamber, without application of NaCl solution. The use of very high concentrations of CO_2 and NaCl was decided in order to accelerate the tests.

The second set of samples was exposed to natural carbonation in the laboratory atmosphere (room temperature and 60–70% relative humidity) and weekly sprayed with the same 15% NaCl solution.

The carbonation depth was determined using the phenolphthalein test after 10 months of exposure. The chloride content of the contaminated mortar blocks was determined after 4 months at different depths according the British Standard BS 4550, part 2:1970 [13].

2.3. Electrochemical measurements

The open circuit potential of each steel bar was measured using a saturated calomel electrode (SCE) as

Table 2
Mortar mix composition

Mix designation (%)	Cement (kg)	Water (l)	Sand (kg)	Fly ash (kg)	Water/(cement + fly ash)
30	525	450	2250	225	0.6
15	637.5	450	2250	112.5	0.6
0	750	450	2250	0	0.6

reference. A sponge soaked with distilled water was placed between the tip of the reference electrode and the surface of the mortar, to provide ionic conduction. The measurements were made at sites on the surface, at a minimum distance from the rebars (≈10 mm), using a high impedance voltmeter (10 MΩ). Since the potential measurements were made across a concrete cover thickness of only 10 mm and the concrete was humid due to solution spraying, the potential values can be considered unaffected by the ohmic drop.

EIS measurements were made with a two-electrode system, between the identical steel bars of each mortar block. Measurements were made using a 1255 Solartron FRA (50 kHz down to 1 mHz) and a 1286 Solartron Electrochemical Interface. A 10 mV (r.m.s.) sine wave was applied. All the experiments were performed using the same arrangement in order to minimise errors induced by the geometry and thus, to allow the comparison of results. Numerical fitting of the impedance data was made using specific software. This allowed estimation of the low frequency resistance even when the corresponding semi-circle was not totally defined. At the end of the tests the blocks were broken for visual inspection and only those without signs of crevice corrosion were considered.

3. Results

3.1. Electrochemical measurements

Fig. 2 depicts the evolution of the OCP of the steel rebars in the mortar blocks exposed to 5% of CO_2 and periodically sprayed with 15% NaCl solution. For each composition, the results of two samples from different blocks are presented. Immediately after exposure the potential readings were in the range 0 to −250 mV, revealing a passive state. After a period that was dependent on the fly ash content, all the samples showed a potential decay towards more negative values, revealing the initiation of the corrosion process. Samples with 30% remained passive for about 1 week, whereas samples with 15% remained passive during the first 3–4 weeks. Samples without fly ash revealed loss of passivity after 1 month of exposure. The time for activation significantly decreased in the presence of 30% of fly ash addition. During the active state, the corrosion potential was dependent on the fly ash content. Samples with higher fly ash amount showed more negative potentials than the samples without fly ash (Table 3).

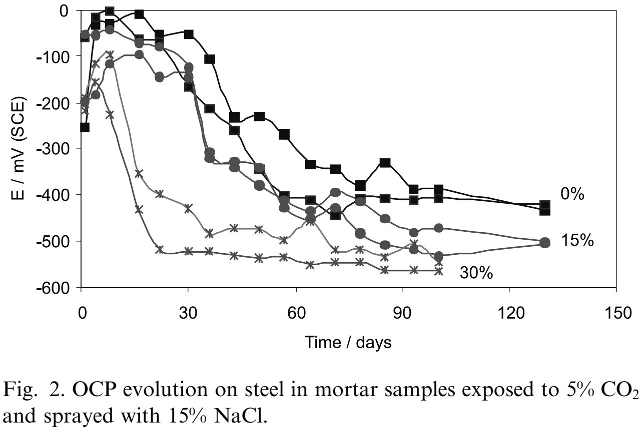

Fig. 2. OCP evolution on steel in mortar samples exposed to 5% CO_2 and sprayed with 15% NaCl.

Table 3
OCP values in the active range as function of the fly ash content

Fly ash content (%)	OCP/mV (SCE)
30	−450 to −550
15	−350 to −450
0	−300 to −400

The condition of the rebars was evaluated by EIS. The shape of the EIS spectra can be described by using the RC network depicted in Fig. 3. The series resistance (R_s) accounts for the ionic conduction in the electrolyte filling the pores, whereas the other elements refer to the double layer capacitance at the steel/concrete interface (C_{dl}) and the charge transfer resistance (R_{ct}). R_{HF} and C_{HF}, were introduced to simulate high frequency loops that may be associated with the dielectric properties of concrete [14,15].

Fig. 4 depicts the impedance spectra after 1 week of exposure to the aggressive environment. The electrical resistivity of concrete can be measured above 100 rad/s. At this stage (1 week) it was practically independent of the composition. At lower frequencies a capacitive behaviour was observed, characterised by a slope close to −1 in the Bode magnitude plot. In this situation the charge transfer resistance, obtained from numerical fitting, was higher than $1 \times 10^6\ \Omega\ cm^2$. The capacitive response reveals a situation of passivity for all the samples. After 3 weeks of exposure (Fig. 5), the samples with 15% and without fly ash still revealed a passive

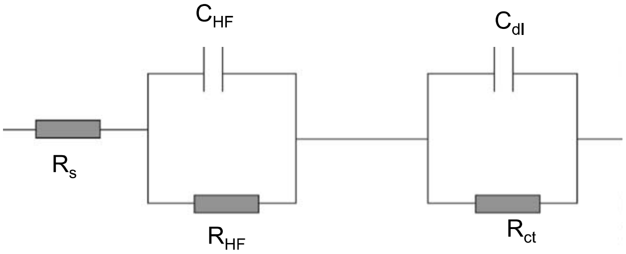

Fig. 3. Equivalent circuit used in numerical fitting of the impedance data.

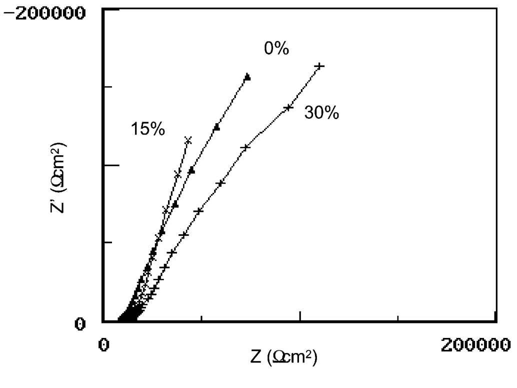

Fig. 4. Impedance spectra for samples with different fly ash contents after 1 week of exposure to 5% CO_2 and sprayed with 15% NaCl.

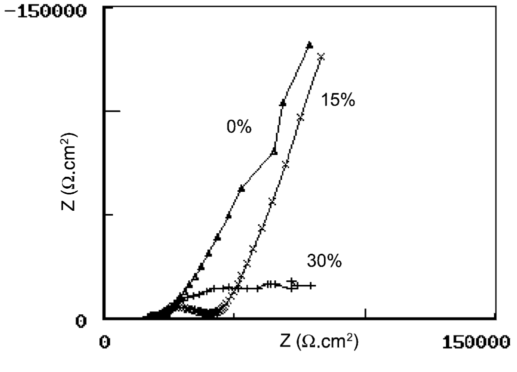

Fig. 5. Impedance spectra for samples with different fly ash contents after 3 weeks of exposure to 5% CO_2 and sprayed with 15% NaCl.

state. Their charge transfer resistance was higher than 1×10^6 Ω cm². In contrast, the sample with 30% of fly ash showed a time constant in the low frequency range that revealed a corrosion process with a charge transfer resistance around 2×10^4 Ω cm². After 3 months of exposure all the samples were active – Fig. 6. The highest charge transfer resistance was measured on the sample without fly ash, being above 1×10^5 Ω cm².

The evolution of the charge transfer resistance, which is inversely proportional to the corrosion rate, was dependent on the fly ash content – Fig. 7. Samples with 30% of fly ash show corrosion rates about one order of magnitude higher than the samples without fly ash, in which the charge transfer resistance was always above 10^5 Ω cm².

The evolution of the concrete resistance with time is an important parameter in understanding the behaviour of the system. This resistance was calculated from the simulation of the high frequency response of the spectra. Its evolution was compared for samples that were exposed to 5% CO_2 only and samples exposed to 5% CO_2 plus chloride. In the absence of chloride (Fig. 8(a)) the resistance is characterised by a strong rise during the first month of immersion followed by a stabilisation period. This can be explained by a slowdown of the hydration reactions and the carbonation process. Under chloride contamination (Fig. 8(b)), the resistance evolution is very similar to that observed in the absence of chloride, except for the sample with 30% of fly ash, which revealed much lower concrete resistances.

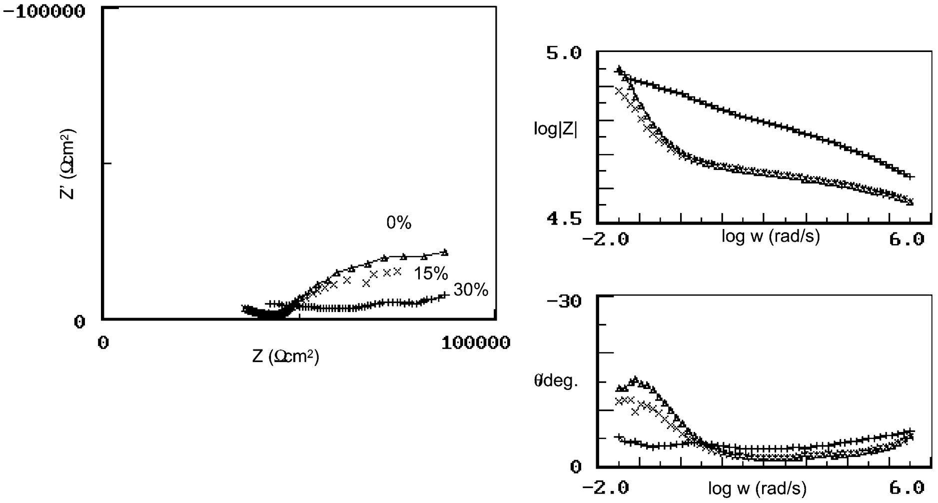

Fig. 6. Impedance spectra for samples with different fly ash contents after 3 months of exposure to 5% CO_2 and sprayed with 15% NaCl.

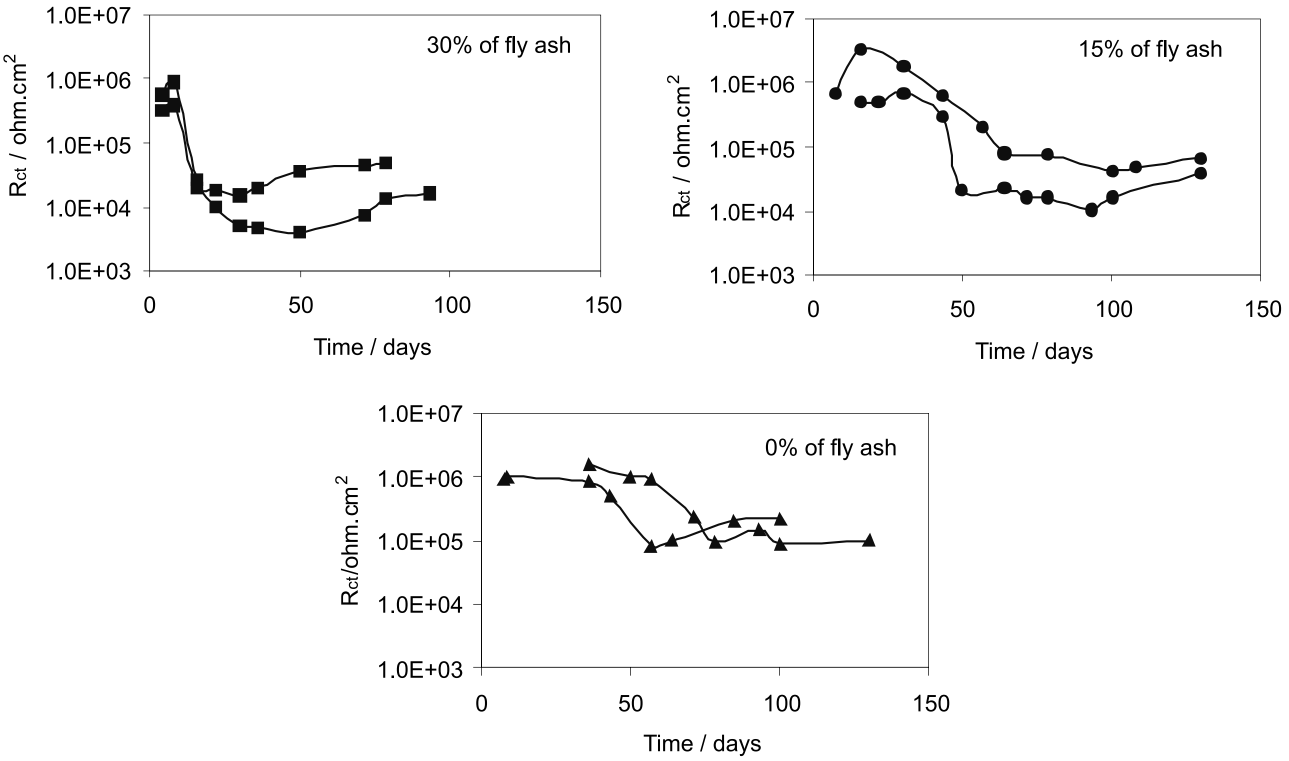

Fig. 7. Charge transfer resistance for samples exposed to 5% CO_2 plus chlorides.

3.2. Carbonation depth

The carbonation depth was determined at the end of the exposure tests. Samples that were exposed to 5% of CO_2 without chloride contamination were completely carbonated after the exposure period (10 months). However, samples exposed to natural carbonation for the same period showed penetration depths that increased with the fly ash content, as follows:

- 30% of fly ash 0.6 cm,
- 15% of fly ash 0.4 cm,
- 0% of fly ash 0.3 cm.

The same trend was observed in previous works [11,12] for accelerated carbonation in 5% CO_2 atmosphere.

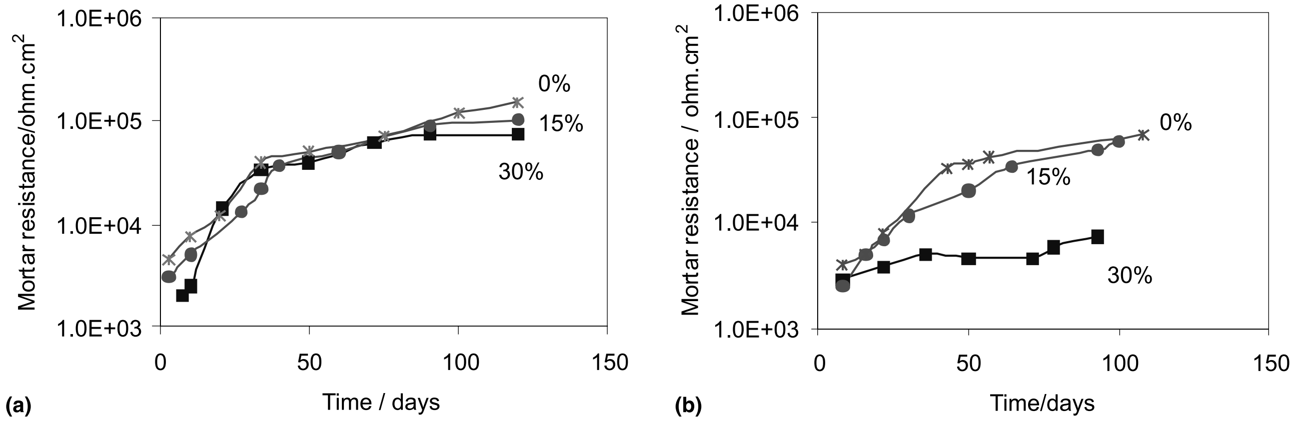

Fig. 8. Mortar resistance: (a) 5% CO_2; (b) 5% CO_2 plus chloride.

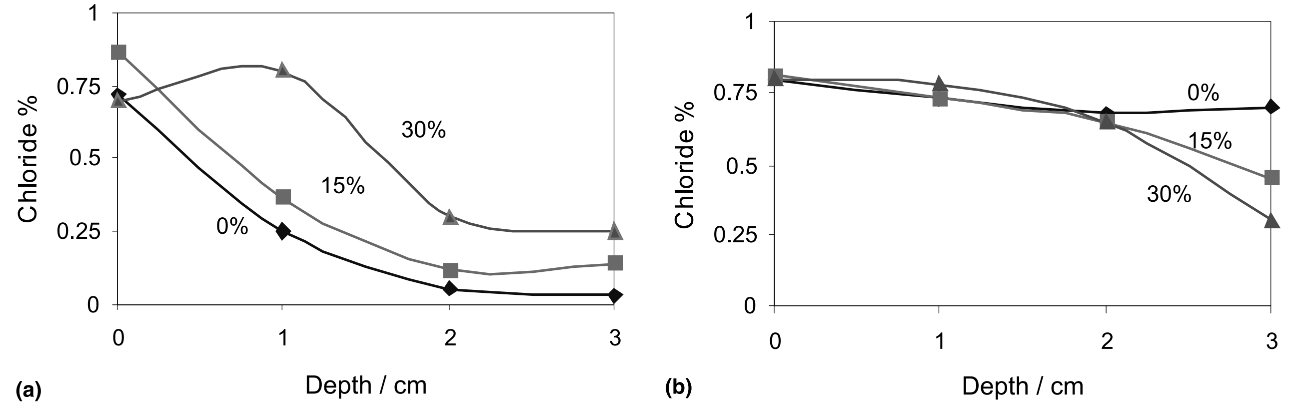

Fig. 9. Chloride content in mortar samples exposed to 5% CO_2 (a) and to natural carbonation (b).

3.3. The chloride profile

After 4 months the chloride content at different depths was determined on the samples periodically contaminated with NaCl under accelerated carbonation or under natural carbonation – Fig. 9. The chloride content at different depths increased with the amount of fly ash when the samples were exposed to accelerated carbonation. On the other hand, the chloride content on the naturally carbonated samples decreased in the presence of fly ash. The chloride contents in the samples exposed to accelerated carbonation were lower than the ones measured in the naturally carbonated samples. This effect became more pronounced when the fly ash content decreased. For the sample without fly ash, at a depth of 3 cm, the chloride content was approximately 20 times lower than in the sample exposed to natural carbonation. However, the chloride content was about the same order of magnitude on the sample with 30% of addition. The evolution of the chloride profile is thus, affected by the carbonation process. Moreover, the evolution of the chloride content with fly ash shows an opposite evolution, depending on the carbonation rate.

4. Discussion

4.1. The carbonation process

Carbon dioxide present in the atmosphere reacts with some constituents of the concrete leading to strong changes in the chemical and physical properties of the system. The carbonation of concrete is dependent upon a number of factors, namely: type and content of cement, composition and porosity of concrete, concentration of CO_2 in the environment and relative humidity [10,16,17].

The most simple carbonation model [10] considers four steps.

1. CO_2 diffusion through the concrete.
2. CO_2 dissolution in the pore solution item Reaction with calcium hydroxide

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \qquad (1)$$

3. Reaction with silicates and aluminates:

$$2SiO_2 \cdot 3CaO \cdot 3H_2O + 3CO_2 \rightarrow 2SiO_2 + 3CaCO_3 + 3H_2O \quad (2)$$

$$4CaO \cdot Al_2O_3 \cdot 13H_2O + 4CO_2 \rightarrow 2Al(OH)_3 + 4CaCO_3 + 10H_2O \quad (3)$$

The final step of the carbonation process always produces calcium carbonate and water. Calcium carbonate, however, has a very low solubility and precipitates inside the concrete pores, reducing the porosity and forming a barrier to the progress of the carbonation front. The precipitation of carbonates consequently tends to increases the resistance of the concrete and therefore the corrosion rate can be affected, as reported in literature [18].

The carbonation of concrete follows according to reactions (1)–(3) leading to a pH decrease to values lower than 9. Under these conditions, and according to the *Pourbaix* diagram, the steel rebars become active. As soon as this happens, the corrosion process is initiated and the chemistry of the interface steel/concrete suffers dramatic changes that affect the reinforced concrete properties, such as the interfacial adhesion as reported by Cleven et al. [19]. However, in the presence of water and excess of CO_2 another reaction (4) may precede, leading to bicarbonate formation, which due to its acid behaviour lowers the pH to nearly neutral values. In these conditions, the steel corrosion can be catastrophic [20].

$$CaCO_3 + H_2O + 2CO_2 \rightarrow Ca(HCO_3)_2 \quad (4)$$

4.2. The effect of fly ash in carbonated concrete

As mentioned before, the addition of fly ash in partial substitution of cement decreases the initial content of CaO in the fresh mix and consequently the amount of $Ca(OH)_2$ to be formed. On the other hand, the presence of fly ash retards the setting process [21]. Thus, in the first stages of exposure to CO_2-rich environments, the carbonation reactions are facilitated and the expected fly ash reactions are hindered. As a consequence, the porosity of concrete with fly ash addition tends to increase, resulting in a decrease of the concrete resistance. The effect becomes more pronounced when chlorides are added to carbonated concrete. The diffusion of chlorides is thus facilitated and the concrete resistance strongly decreases, facilitating the corrosion process. On the other hand, the excess of CO_2 increases the extension of reaction (4) and the interstitial solution in samples with fly ash become more acidic, leading to faster corrosion of rebars. This was supported by both the OCP monitoring and the impedance measurements. The highest corrosion rates were observed in the samples with 30% of fly ash addition. Thus, it seems that the differences in the initial amount of CaO (that reacts further to produce $Ca(OH)_2$) are a determinant factor in controlling the corrosion rate when the samples are exposed to CO_2-rich environments.

The effect of fly ash addition in carbonated concrete thus results in a decrease of the concrete resistance and in an increase of the corrosion rate. This behaviour contrasts with the results observed under immersion in sodium chloride [9], where fly ash revealed a beneficial effect.

4.3. The effect of fly ash and carbonation on the chloride profile

The presence of fly ash and the carbonation process strongly affects the chloride profile. Usually chlorides penetrate in concrete by diffusion along water paths or open pores. Part of these chlorides can react with the cement hydration products, mainly tricalciumaluminates (C_3A), forming stable chlorocomplexes. The excess of chloride is free and leads to the initiation of the corrosion process. The presence of fly ash leads to an increase of the amount of C_3A due to the higher amount of alumina present in the mix and to an increase of the content of calcium silicate hydrate that is formed in the pozzolanic reactions. Thus, the binding capacity of the concrete to chloride tends to increase and consequently less free chloride will be available to initiate the corrosion process as observed by Koulombi et al. [22]. On the other hand, the porosity decrease caused by fly ash also hinders the diffusion across the concrete. Consequently, it is expected that samples with fly ash present lower free chloride contents. This evolution was observed on the samples exposed to natural carbonation. Under these conditions, the carbonation rate is very slow, the consumption of $Ca(OH)_2$ is not significant and the setting mechanism proceeds in the usual way with fly ash producing reaction products that are able to bind chlorides and to block pores, decreasing porosity and consequently hindering the penetration of chlorides. The same trend was observed in samples immersed in chloride-containing environments [7–9]. Under immersion the carbonation process is practically negligible since it is hindered in high humidity environments and the presence of fly ash leads to a strong increase of concrete resistivity and consequently to lower corrosion rates.

Under excess of CO_2, during the initial setting period that is retarded in the presence of fly ash, the consumption of $Ca(OH)_2$ is accelerated as well as the production of carbonates and bicarbonates. Since bicarbonates are soluble, their formation can lead to increased porosity. On the other hand, CO_2 also reacts with the chloroaluminates destructing the ability of the concrete to bind with chlorides. Thus, it is expected a decrease on the amount of bound chloride and consequently an increase on the content of free chloride.

Comparison of the chloride profiles have shown that for the same fly ash addition, the accelerated carbonation has lead to a lower free chloride content, when compared to the naturally carbonated blocks. This behaviour was more evident for samples without and with 15% of fly ash, being very small in the presence of 30% of addition. Under natural exposure the carbonated depth after 10 months was very small (below 0.6 cm), which means that when the chlorides were determined (after 4 months) the carbonated depth was even lower, being practically negligible for samples without fly ash and with 15% of addition. Thus, in this situation the chloride profile was practically unaffected by carbonation, being mainly dependent on the porosity evolution due to the hydration and pozzolanic reactions.

However, in the presence of excess of CO_2 since the carbonation rate is much higher the chloride content tends to decrease with depth as observed in Fig. 9(a). This behaviour was marked for the samples without and with 15% of fly ash. However, the samples with the highest amount (30%) did not follow this trend. For these samples the carbonation process led to a strong decrease of resistivity and to higher porosities, facilitating the conversion of carbonates into bicarbonates. Consequently, no beneficial effects of the carbonated depth were observed in the chloride profile with these samples, showing chloride contents very close to those of the naturally carbonated samples.

Although the testing conditions used in this work were extremely aggressive the results obtained suggest that the amount of fly ash plays an important role when the concrete is exposed to a CO_2-rich environments. Thus, in the presence of fly ash the corrosion rate increases. On the other hand, the chloride profile is strongly influenced by the carbonation products. The results show that a competition effect between carbonation rate, pozzolanic reactions and chloride diffusion determines the final chloride content in mortar. This competition leads to chloride profiles that change in opposite ways with the amount of fly ash, when the concrete is fully carbonated or only partially carbonated. This result suggests that care must be taken when extrapolating results from accelerated tests to natural conditions.

For the mortar composition under test, the present results, together with previous ones [7–9] reveal that the amount of fly ash added to concrete should be chosen according to the environments where the structure will be exposed. Thus, in aggressive chloride environment, such as seacoast or structures where de-icing salts are used, the addition of fly is beneficial. However, in strongly polluted environments, with very high concentrations of CO_2 and other aggressive species such as chlorides and sulphates, fly ash may accelerate the corrosion process and its use should therefore be considered with care.

5. Conclusions

Under accelerated carbonation and chloride contamination, the addition to concrete of 30% of fly ash increases the corrosion rate by about one order of magnitude, when compared with samples without any fly ash.

The content of chloride in mortar decreases with fly ash addition under natural carbonation but increases with fly ash addition under accelerated carbonation. This opposite trend can be explained by a competition effect between carbonation, pozzolanic reactions and chloride diffusion during exposure.

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