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Impact of Combined Action of Chloride and Carbonation on Cement-Based Materials with Fly Ash

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Abstract: Integrating waste and industrial by-products into concrete is an alternative way to reduce global cement consumption, enhancing its eco-friendliness. In this context, residues with fly ash have been increasingly utilised. Considering the vulnerability of concrete with fly ash to carbonation and, at the same time, its high resistance to chlorides, it is important to investigate the behaviour of these concretes under their combined actions. For this purpose, an experimental investigation was conducted, studying mortar and concrete specimens with 40% replacement of cement with fly ash. These specimens were subjected to a combination of actions (Cl^- and CO_2) in two phases: initially through immersion and drying tests, and subsequently through a combination of accelerated tests. Concerning the chloride impact study, free and total chloride profiles were studied. Concerning the impact of carbonation, colourimetric and chemical tests were used. The results demonstrate a significant influence of combined action not only on chloride penetration in cement-based materials with fly ash but also on the development of a carbonation front. Exposure of cement-based materials with fly ash to environments with high Cl^- and CO_2 content sequentially may lead, on the one hand, to an increase in carbonation resistance. However, on the other hand, it may result in a substantial reduction in chloride penetration resistance.

Keywords: concrete; fly ash; chloride; carbonation; combined action; durability

1. Introduction

The utilisation of fly ash (FA) in concrete holds significant importance in the context of current climate concerns and carbon emissions. FA, a byproduct of coal combustion, has been used as a sustainable alternative to traditional cement, contributing to a reduction in carbon dioxide emissions associated with concrete production. In 2022, more than 4100 million tonnes of cement were produced, emitting around 0.58 tonnes of CO_2 per tonne of cement [1]. In this context, FA residues have been increasingly utilised in countries where they are still available.

In addition to reducing the environmental impact of concrete, FA is also used in concrete to make it more resistant to the action of chloride ions. The silicon dioxide (SiO_2) in FA reacts with the calcium hydroxide ($Ca(OH)_2$) generated during cement hydration, forming calcium silicate hydrate (CSH) structures that significantly lower concrete porosity. Consequently, this inhibits the transportation of harmful agents like chloride ions. Moreover, the aluminates in FA undergo a chemical reaction with free chlorides, binding them and diminishing the quantity of free chlorides capable of infiltrating the concrete [2]. Moreover, with the inclusion of FA, the formation of $Ca(OH)_2$ is reduced, leading to a lowering of concrete pH. This reduction in $Ca(OH)_2$ content further decreases the production of

calcium carbonate ($CaCO_3$) during carbonation, thereby promoting the advancement of carbonation [3].

CO_2 and chloride ions are the most reported aggressive agents in concrete [4–6]. On the one hand, CO_2 can react with the alkaline components of cement, leading to the formation of soluble carbonates and compromising the material's integrity [7]. On the other hand, the penetration of chloride ions can accelerate the corrosion of steel reinforcements, contributing to concrete deterioration [8]. When it comes to concretes with FA, the interaction between aggressive agents and FA adds a layer of complexity. Understanding this interaction is essential to optimising the performance of these materials in challenging environments.

The impacts of CO_2 and chloride ions on concrete structures have traditionally been studied as separate phenomena. However, research into the combination of these aggressive agents gained more prominence from the year 2000 onwards. Important examples in this direction include studies conducted by AL-Ameeri et al. [9], Malheiro et al. [10], Zhang and Panesar [11], Wang et al. [12], Zhu et al. [13], and Hussain and Ishida [14]. However, even though the concurrent action of these mechanisms is acknowledged, a consensus regarding the combined effect of chlorides and carbonation on the durability of concrete, both with and without FA, remains elusive. According to Wang et al. [12], the exposure of Ordinary Portland Cement (OPC) concrete to a CO_2 environment increases chloride penetration. In their study, specimens underwent carbonation in a chamber (5% CO_2, 20 °C, and 65% RH) for 1, 2, and 3 months, followed by total immersion in a solution with 165 g/l NaCl. Conversely, Holthuizen [15] reported that for OPC mortar, carbonation decreases the chloride diffusion coefficient. Their specimens were subjected to a carbonation chamber (3% CO_2, 20 °C, and 65% RH) for 23 weeks, followed by a chloride migration test according to NT-Built 492.

This paper specifically focuses on studying the combined action of CO_2 and chloride ions in concretes with FA. Our research seeks to fill a significant gap in the literature because, as in the case of concretes without FA, most studies address these aggressors in isolation, neglecting the synergistic interactions that may occur in practice. Despite this, some studies using mortar and concrete with FA were found. Nagataki and Ohga (1992) [16] studied mortar with FA. Mortars were cured initially in distilled water or NaCl solution for 7, 28, 56, and 91 days and then exposed to accelerated carbonation. Their results show that the depth of carbonation of mortar cured initially in NaCl solution is smaller than of that in distilled water. Xie et al. (2019) [17] studied chloride profiles in carbonated concretes with FA (15% and 30%). Accelerated carbonation tests and rapid chloride permeability tests were performed to investigate the distribution and diffusion of chloride ions in concrete with FA after different carbonation degrees. The findings revealed that chloride binding capacity is enhanced in early carbonation but drops in late carbonation stages. Concerning carbonation resistance, it is improved for low water/binder ratios but reduced for high ones. The differences between the methodologies used by Nagataki and Ohga (1992) [16] and Xie et al. (2019) [17] make it difficult to compare results directly, but it is possible to identify some trends. Montemor et al. (2002) [3] wrote that the type of carbonation exposure is determinant. They studied mortar with 15% and 30% of FA under CO_2 (natural and 5%) and NaCl (15%) contamination. The chloride content in mortar exposed to accelerated carbonation (5%) increases with the amount of FA. However, under natural carbonation, it decreases with the addition of FA. Although the use of different methodologies can provide different dynamics in the laboratory, a convergence of results is clear concerning the decrease in chloride penetration resistance in carbonated FA concrete under high CO_2 levels.

This gap highlights the importance of the present study, which aims to fill this knowledge void by exploring the interaction between these two aggressive agents in FA concrete. Understanding this process is crucial for developing effective strategies to mitigate concrete degradation under adverse environmental conditions. The contribution of this study is significant as it will provide valuable insights for the construction industry, enabling the

development of more effective strategies to improve the durability and strength of concrete in challenging environments.

2. Experimental Procedures

Accelerated tests were used to simulate the combined action of chloride and carbonation. The experimental work was divided into two important parts (Figure 1). In Part I, an exploratory study was carried out using mortar specimens to study the influence of chloride presence on carbonation development. Mortar was used because its high porosity and absence of coarse aggregate help to reach results faster than concrete. Immersion and dry cycles were used to accelerate damage.
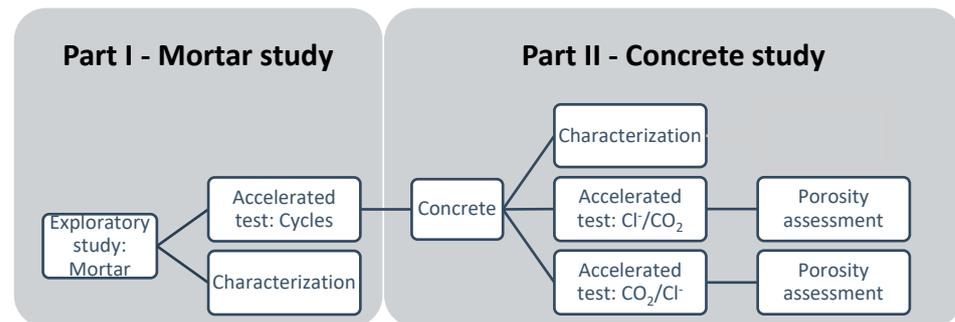

Figure 1. Outline of the testing process.

The results reached in Part I helped to define the methodology used in Part II. In Part II, concrete specimens were used to study two situations: the influence of chloride presence on carbonation development and the influence of carbonation on chloride transport. In this case, a combination of accelerated tests (chloride penetration by immersion and carbonation chamber) was used instead of immersion and dry cycles.

2.1. Mortar and Concrete Specimens Production

Ordinary Portland Cement, CEM I 42.5R, and FA were used as binder materials in the mortar and concrete specimens. Their chemical compositions are presented in Table 1. The chemical composition of FA was determined using X-ray fluorescence spectroscopy. These FA were obtained from burning South African and Colombian coal in Portuguese thermoelectric power plants. In specimens with FA, 40% of cement was replaced by FA. A superplasticiser based on polycarboxylic ether was used in the composition of concrete without FA to help reach values near the predefined slump, 100 mm ± 5 mm. Compositions with FA have greater workability than compositions without FA and, therefore, it was not necessary to use a superplasticiser. Concerning mortar, flow spread was fixed at 190 mm. Granitic crushed sand with a fineness modulus of 2.96 and two types of granitic crushed coarse aggregate, one with a fineness modulus of 6.07 and the other with 6.94, were used as aggregates. Tap water with a maximum value of 10 mg of chlorides per litre of water was used for all the produced mixtures. The mortar and concrete mixtures are shown in Table 2. It is important to clarify that the compressive strength of the specimens studied is not a central parameter of this study. The focus of this study is on the interaction between carbonation and chloride ions. Therefore, the compositions were designed to produce concrete facilitating access for attacking agents.

Table 1. Chemical composition of OPC and FA.

	SiO_2 [%]	Al_2O_3 [%]	Fe_2O_3 [%]	CaO [%]	MgO [%]	SO_3 [%]	K_2O [%]	Na_2O [%]	TiO_2 [%]	Cl^- [%]	LI* [%]	IR* [%]	RE [%]
OPC	20.33	4.59	3.06	62.30	2.12	3.10	0.76	0.19	-	0.07	1.78	1.21	0.49
FA	55.10	26.60	5.70	2.58	1.30	-	1.41	0.26	1.33	-	3.07	-	2.65

Table 2. Mortar and concrete mixtures.

Materials	Mortar		Concrete	
	M0FA	M40FA	C0FA	C40FA
Cement [kg]	380	228	380	228
Fly ash [kg]	-	152	-	152
Water [L]	209	198	190	192
Superplasticiser [%]	-	-	0.45	-
Sand 0/4 [kg]	1140	1140	989.83	926.18
Coarse aggregate 4/8 [kg]	-	-	261.30	281.18
Coarse aggregate 6/12 [kg]	-	-	492.64	483.10

When the mortar and concrete specimens were cast, they were covered with plastic film and stored in a humid chamber (18 ± 2 °C and $93 \pm 2\%$ RH) for 24 h. Afterwards, they were removed from the moulds and stored in a box with tap water saturated with lime. Since the specimens with FA (M40FA and C40FA) are at the centre of this study, the curing period was fixed at 90 days due to pozzolanic reactions related to FA.

2.2. Accelerated Tests

2.2.1. Immersion and Dry Cycle Test

Cubic mortar specimens, $50 \times 50 \times 50$ mm^3, were used for this test in Part I of the methodology. Since there are no standards to define the methodology of immersion and dry cycle tests, these dimensions were chosen based on previous laboratory experience and ease of handling samples during the test. The specimens were waterproofed (with epoxy resin) on five out of six faces to allow for a unidimensional penetration of aggressive agents. Immersion and dry cycles were chosen to promote combination of a severe environment with fast penetration of aggressive agents (Cl^- and CO_2). Regardless of its large utilisation, there are no standards to fix the variables involved in the procedure (time to immersion, temperature and humidity of the dry stage…). Thus, the variables used here were decided based on previous studies [18,19]. Figure 2 summarises the test. A complete cycle comprised seven days. The cycles were carried out for two and six months in order to evaluate sample behaviour over time.
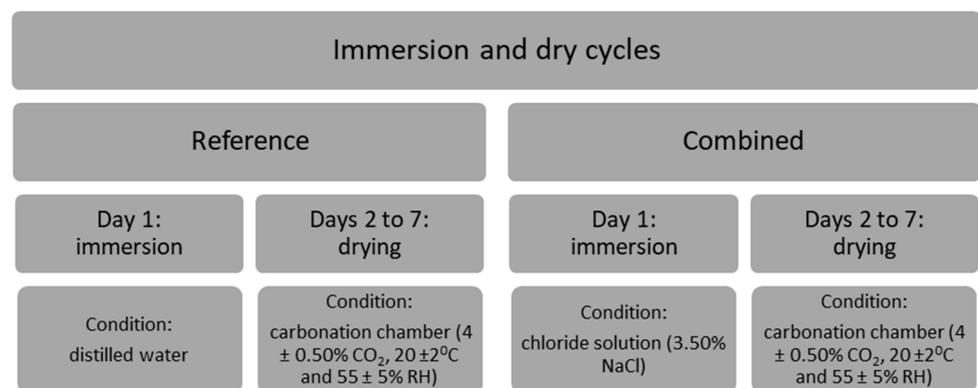
Figure 2. Immersion and dry cycle variables for mortar specimens studied.

Once the test periods were finished, i.e., after two and six months, the specimens were broken up and carbonation depth was determined using a colourimetric test (phenolphthalein) based on RILEM specification [20].

2.2.2. Combined Test

Considering the difficulty experienced in the dry stage of immersion and dry cycles, combined tests were the option chosen for Part II. Other researchers have also used this methodology [21,22]. We used the chloride diffusion by immersion test based on Portuguese Specification LNEC E390 [23] and the accelerated carbonation test based on EN 12390-12 [24].

Regarding the immersion test, first, the specimens underwent immersion in lime-saturated distilled water until achieving a consistent mass. Subsequently, these specimens were placed in a container with a mixture of lime-saturated distilled water and 15% NaCl for three months. A solution-volume-to-specimen-volume ratio of two was employed. Throughout the test, the container remained sealed, and the chloride solution was renewed on a weekly basis. Upon the completion of the immersion period, the specimens underwent a consistent grinding process, gradually transforming into a fine powder. This grinding occurred in two consecutive layers, each with a thickness of 5 mm, extending from the surface to a depth of 30 mm. The powdered samples resulting from grinding were used to determine chloride and pH profiles. Water-soluble chloride profiles (Figure 3a) and total chloride profiles (Figure 3b) were determined using RILEM TC 178-TMC [25] and RILEM TC 178-TMC [26], respectively.

(a)   (b)

Figure 3. The main steps of chloride content determination: (**a**) free chloride and (**b**) total chloride.

Regarding carbonation, the samples underwent preconditioning before being exposed to this accelerated test. The preconditioning involved procedures aimed at achieving an internal humidity equilibrium, aligning it with the environmental humidity of approximately 60%. This approach ensured a more uniform carbonation process and optimised its efficiency. The process comprised two stages. Initially, the specimens were placed in a chamber with controlled temperature and relative humidity (20 °C and 60% RH) until reaching a constant mass (about one month). In the subsequent stage, multiple layers of plastic film shielded the specimens, which were then positioned in a ventilated oven (40 °C) for 20 days to evenly distribute humidity within. The specimens were weighed before and after oven storage, with water loss limited to 0.10%. Following preconditioning, the specimens underwent carbonation in a designated chamber ($4 \pm 0.50\%$ CO_2, 20 ± 2 °C, and $55 \pm 5\%$ RH) for three or seven months. After the carbonation period, carbonation depth was determined using a colourimetric test (phenolphthalein) based on RILEM specification [20]. pH profiles were also determined using McPolin's method [27]. Each sample, with a solid-to-liquid ratio of 1:20, was immersed in distilled water, and the container was sealed to prevent evaporation. The samples were stored in a laboratory environment (18.5 ± 2 °C and $58 \pm 2\%$ RH) for 24 h to allow the solution to reach equilibrium. Subsequently, the alkalinity of the solution was measured by assessing its pH.

The scheme for combining these tests is shown in Figures 4 and 5. Figure 4 refers to the study of the impact of the presence of chlorides on carbonation. The reference test used

for this case is only carbonation. Figure 5 refers to the opposite situation, the study of the impact of carbonation on the penetration of chlorides. The reference test used for this case is only chloride diffusion by immersion.

Figure 4. Scheme for combining tests to study the effect of the presence of chlorides on carbonation.
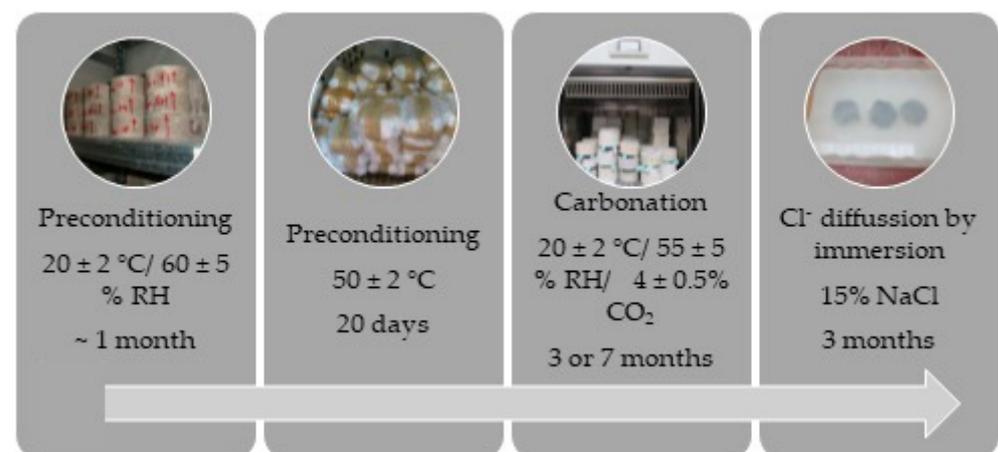

Figure 5. Scheme for combining tests to study the effect of carbonation on the penetration of chlorides.

3. Influence of Chloride Presence on Carbonation in Matrixes with FA

3.1. Exploratory Tests: Mortar Specimens

3.1.1. Mortar Characterisation

Figure 6 shows the compressive strength evolution of mortars studied before they were submitted to accelerated tests. M0FA shows better performance than M40FA in early ages. This behaviour is expected, and it is related to the necessary period to develop the pozzolanic reactions in the M40FA specimens. Despite the higher water/binder ratio of M40FA (0.56) when compared to M0FA (0.52), the compressive strengths of M0FA (39.07 MPa) and M40FA (44.44 MPa) are very similar. A reduction in connectivity between pores produced using FA is the most frequently reported cause [28].
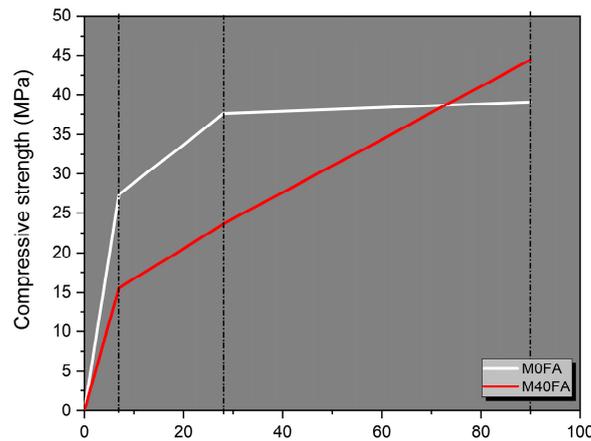
Figure 6. Compressive strength evolution of mortars (7, 28, and 90 days).

3.1.2. Accelerated Test: Immersion and Dry Cycles

The carbonation depths reached after accelerated tests are shown in Figure 7. As expected, the specimens with FA have a greater carbonation depth than those without FA, regardless of the test period. There is a reduction in the $Ca(OH)_2$ content and pH level of the liquid phase of mortars with FA, which facilitates the advancement of carbonation [29]. The evolution of the carbonation depth of the studied specimens over time is residual, regardless of the presence of FA. For the specimens without FA (M0FA), considering the reference situation, there is even a slight reduction (around 2 mm) in the depth of carbonation from 2 to 6 months. This reduction is not significant, being within the acceptable error range for the colourimetric test. This residual evolution over time may be related to the low efficiency of the drying period during the cycles. The drying period and/or conditions (temperature and relative humidity) may not have been sufficient to reduce humidity and create favourable conditions for the development of the carbonation process inside the specimen. Therefore, carbonation was limited to the surface, never reaching 20 mm. Thus, it is important to evaluate the limitations of this type of test for situations involving a combination of chlorides and CO_2, regardless of FA presence. Malheiro et al. (2021) [10] studied the combined action of chlorides and CO_2 using three types of tests: immersion and dry cycles, chloride diffusion by migration, and chloride diffusion by immersion. They concluded that the immersion test is more indicated for this combined action studied.
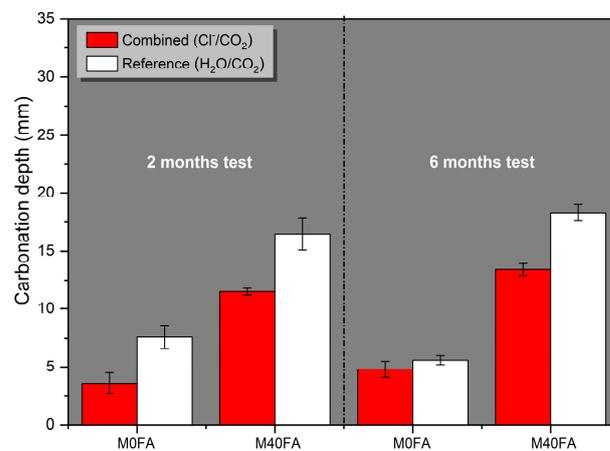
Figure 7. Carbonation depths in mortars after immersion and dry cycles: 2 months' test (left); and 6 months' test (right).

Regarding the influence of chlorides on carbonation, it is observed that regardless of the test period and FA presence, chloride influences carbonation depth, decreasing it. This

reduction in carbonation depth was attenuated over time. In specimens without FA, this reduction trend was more noticeable, with values that went from 53.00% at two months of testing to 14.00% at six months of testing, while in specimens with FA, these values were, respectively, 30.00 and 27.00%.

3.2. Concrete Specimens

Since preliminary tests showed that chloride influences carbonation depth in mortar with and without FA, concrete specimens were produced to evaluate this phenomenon. Considering the limitations of combined cycles, at this stage, were used combined tests as previously explained in Section 2.2.2.

3.2.1. Concrete Characterisation

Figure 8 shows the compressive strength evolution of concretes studied before they were submitted to accelerated tests. Similar to the mortars studied, C0FA shows better performance than C40FA at early ages. However, at later ages (after 90 days), C40FA shows a more pronounced growth than C0FA, presenting very similar compressive strength values at 360 days. Despite different values of compressive strength at 90 days, the capillary absorption coefficient presented similar values. C0FA ($0.104 \, kg/m^2/min$) presents a slightly lower value when compared to C40FA ($0.116 \, kg/m^2/min$). This behaviour may be related to the reduction in connectivity between pores provided using FA, as previously explained in the mortar case.
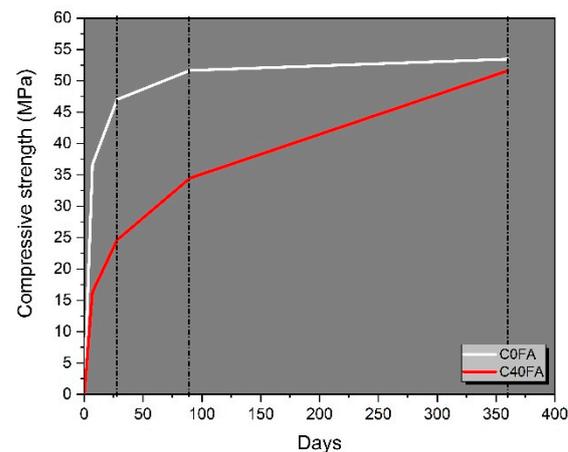

Figure 8. Compressive strength evolution of concrete (7, 28, 90, and 360 days).

3.2.2. Accelerated Test: Chloride Diffusion by Immersion Followed by Carbonation

The effect of chloride presence on the development of carbonation in concretes subjected to a combination of tests, chloride diffusion by immersion (three months) followed by carbonation (seven months), can be assessed in Figure 9.

As expected, specimens with FA have a greater carbonation depth than those without FA. Furthermore, the analysis of Figure 9 corroborates the mortar results (Figure 7) and makes it clear that chloride presence in the matrix, under the conditions studied, strongly influences the development of a carbonation front, regardless of FA. However, this influence is more pronounced in concrete without FA. The reduction in carbonation front is 87% for C0FA, while in C40FA, it is only 25%. This same trend was verified by mortar results. Nagataki and Ohga (1992) [16] studied mortars with and without FA cured initially in distilled water or NaCl solution for 7, 28, 56, and 91 days and then exposed to accelerated carbonation. They also found that FA mortar shows a higher depth of carbonation than the reference mortar.
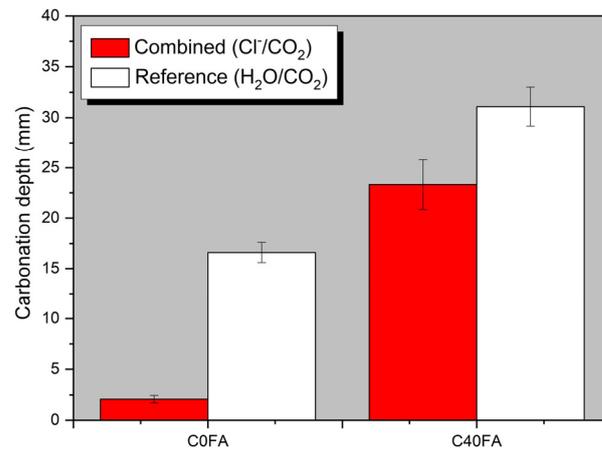
Figure 9. Carbonation depth of concrete.

In the results in Figure 9, unlike in the case of mortars, internal humidity was not high because there was a preconditioning process before carbonation. Preconditioning sought to provide a favourable internal humidity for carbonation (around 60%). Therefore, it is very likely that this reduction in the depth of carbonation is related to the blocking of the pores caused by the NaCl (crystallised) remaining from the immersion test. The chloride's capacity to physically obstruct the concrete pores results in a reduction in pore size. This, in turn, impedes the infiltration of CO_2, effectively serving as a "barrier". While it was not possible to verify this hypothesis through microstructural analyses within the context of the present work, results from other authors support it. Leivo et al. [30] suggested in their findings that salt crystallisation within the pore network could lead to pore blockage. Malheiro et al. [31] identified a crystalline structure associated with the precipitation of sodium chloride (NaCl solubility in H_2O at 25 °C is 36.9 g/100 mL), a process occurring during the drying phase of cycles as water evaporates from the solution.

Since chlorides penetrate more easily into C0FA than into C40FA, the blocking effect has a greater impact on specimens without FA. In the combined situation, the chloride penetration depths were 32.76 mm ($\pm$0.50) for C0FA and 23.00 mm ($\pm$0.15) for C40FA. The capillary absorption curves presented in Figure 10 corroborate the hypothesis of the blocking effect as they show a lower capillary water absorption coefficient for C0FA (0.089) instead of C40FA (0.141). It is important to highlight that this test was performed after the combined tests (chloride diffusion by immersion followed by carbonation).
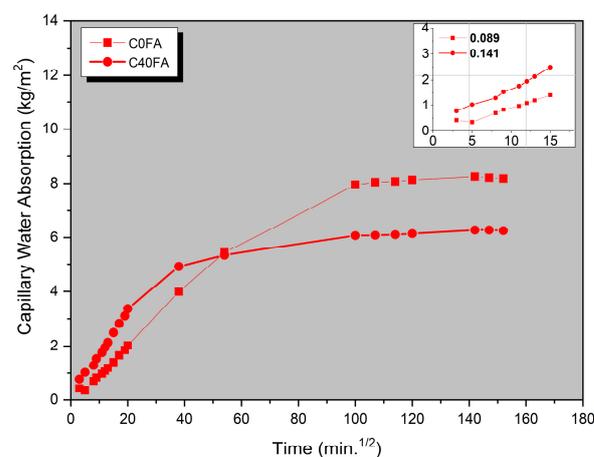
Figure 10. Capillary water absorption after combined tests and capillary water absorption coefficient (detail in right).

Despite the effect of chloride action on carbonation development not being given due attention, some results have been published on this topic, considering concretes without FA. In this case, a reduction in carbonation depth or consumption of hydroxyls (OH^-) in concrete previously contaminated by chlorides has been found [12,22]. Despite the lack of results for concrete with FA, the results reached in this study corroborate the results found for concrete without FA. However, the impact on concrete with FA is lower than the impact on concrete with FA.

Considering the results, it is possible to say that, under the conditions studied, the vulnerability of concrete with FA to the action of carbonation is reduced in environments where concrete is simultaneously exposed to Cl^- and CO_2. Pore blockage is probably the main cause of this effect.

4. Influence of Carbonation on Chloride Transport in Matrices with FA

The specimens studied at this stage of our work were produced using only concrete. Concrete characterisation is shown in Section 3.2.1.

4.1. Accelerated Test: Carbonation Chamber Followed by Chloride Immersion

Figures 11 and 12 present the results obtained for concrete with FA (C40FA) subjected only to a chloride immersion test (reference) (Figures 11 and 12a) and subjected to carbonation followed by a chloride immersion test (combined) (Figures 11 and 12b). The carbonation depth shown for the combined situation was determined using a colourimetric test (phenolphthalein). The evolution of behaviour over time was evaluated; Figure 11 refers to three months of carbonation, while Figure 12 refers to seven months of carbonation.

After three months of the carbonation test, the data indicate a change in the behaviour of the chloride profiles and the pH profile related to carbonation. Regarding pH profiles, the reference profile (Figure 11a) shows a generally stable behaviour, with only one visible disturbance at around 15 mm, which is most likely associated with deviations occurring during the experimental determination. In the case of the combined profile (Figure 11b), a continuous reduction in pH value is observed, starting at a depth of 20 mm and remaining so until the superficial zone, where the value reached is close to 9.
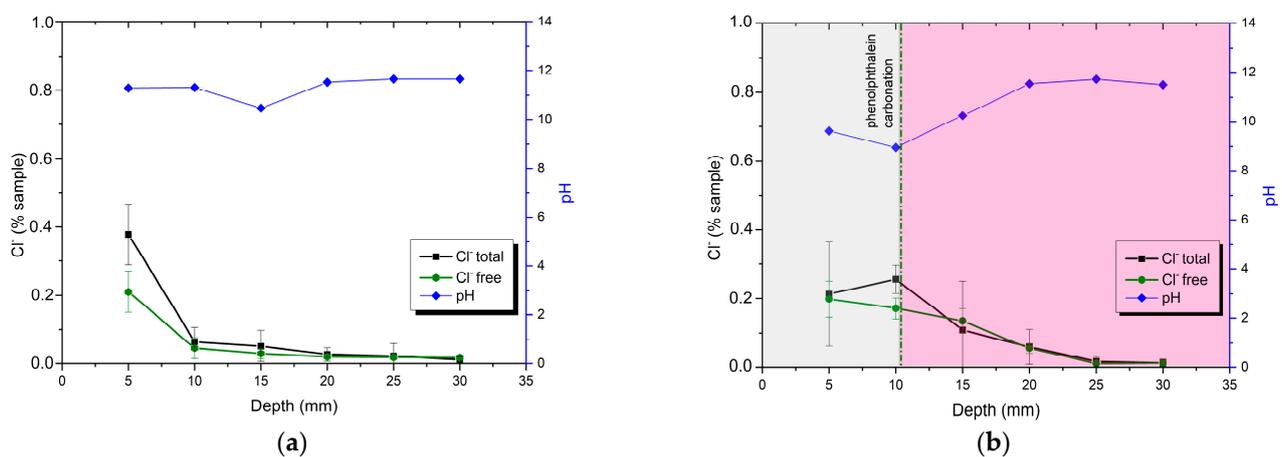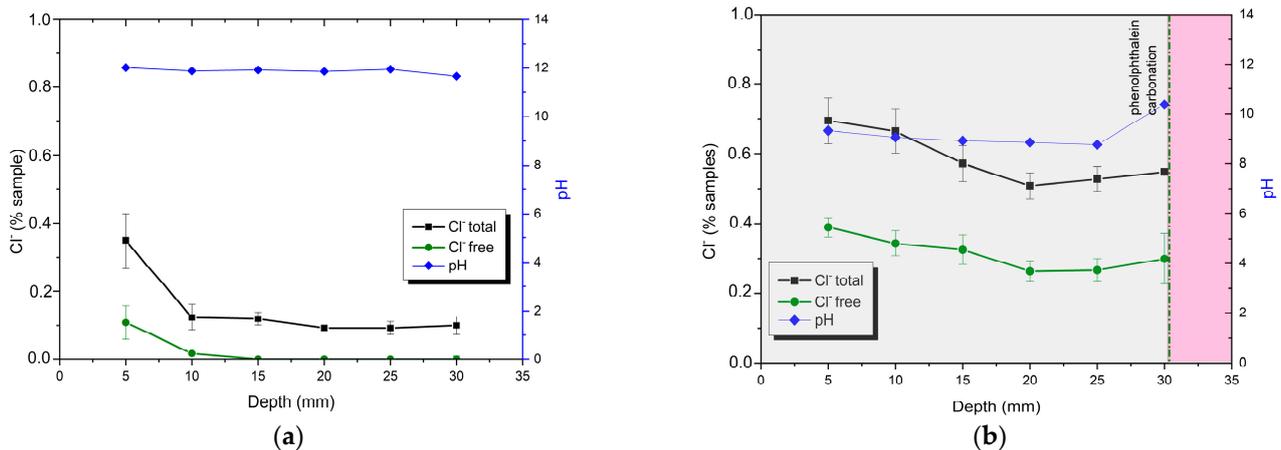

Figure 11. Chloride and pH profiles for C40FA subjected to (**a**) reference test (only chloride) and (**b**) combined tests (3 months of carbonation followed by chloride).

Figure 12. Chloride and pH profiles for C40FA subjected to (**a**) reference test (only chloride) and (**b**) combined tests (7 months of carbonation followed by chloride).

Regarding chloride profiles, a reduction in the surface concentration of the combined profiles (Figure 11b) is observed when compared to the reference profiles (Figure 11a). This reduction is followed by a significant increase in chloride penetration that remains up to 20 mm depth. This happens because when not subjected to carbonation (reference situation), C40FA exhibits high resistance to chlorides. In this way, chlorides are retained on the surface (weakest zone), and penetration into the interior of the concrete is reduced. In situations where C40FA is carbonated, resistance to chlorides decreases in the carbonated zone, and the superficial concrete is no longer able to retain a large portion of these chlorides. Chlorides that are not retained on the surface penetrate the interior of the concrete, increasing the chloride content.

Thus, at three months of carbonation testing, carbonation increases the penetration of chlorides in concrete with FA. The increase in the amount of free chlorides resulting from the reduction in chloride-binding capacity verified for the specimens subject to combined action is the most likely cause for the increase in carbonation depth (superficial in the reference situation and increasing to 11 mm in the combined situation).

With the increase in the carbonation test period (from three to seven months) and the consequent increase in carbonation depth, the increase in the penetration of chlorides is more evident. It happens throughout the entire depth of the specimens subject to the combined action (Figure 12).

Regarding pH profiles, the values of the reference profile (Figure 12a) remain stable when compared to the situation at three months of testing (Figure 11a). However, they present slightly higher values. For the combined profile (Figure 12b), there is a sudden reduction in pH values (close to 8) throughout the entire carbonated region which coincides with the carbonation depth determined by phenolphthalein.

Regarding chloride profiles, an enormous increase in chloride content in the combined profiles (Figure 12b), throughout the entire depth, when compared to the reference profiles (Figure 12a) is clear. It is observed that, for the reference situation (Figure 12a), free chlorides are almost non-existent. For the combined situation, free chloride content is quite high throughout the depth (Figure 12b). The increase in the amount of free chlorides could be the cause of this significant increase in the penetration of chlorides in C40FA when subjected to combined action for seven months. To highlight the increase in free chlorides, Figure 13 shows the subtraction of the free chlorides present in the combined profile from those present in the reference profile.
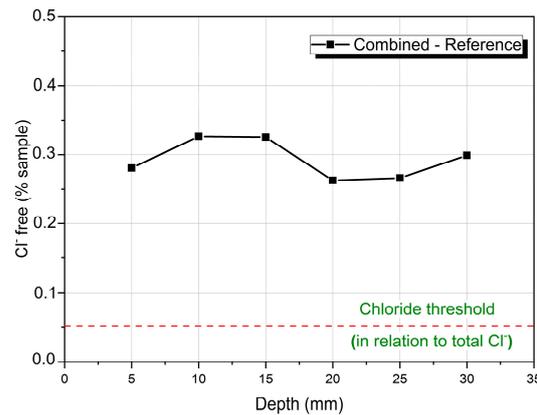
Figure 13. Free chlorides resulting from the subtraction of the reference situation from the combined situation.

The result of the subtraction between free chloride profiles is a profile with values so high that they far exceed the chloride threshold (0.5% of the mass of concrete) recommended by Comité Européen du Béton (CEB) for total chlorides in reinforced concrete.

This enormous increase in chloride content can be related to the difficulty of binding chlorides in a low pH environment. The chemical binding of chloride ions can occur through Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) [32]. Friedel's salt results from reactions with tricalcium aluminate (C_3A), prevalent in concretes with high FA content, and free chlorides. Nevertheless, Friedel's salt remains stable at a relatively elevated pH [32], a condition not met in carbonated concrete. Some researchers investigated the combined effect of chloride presence and carbonation in concrete without FA [13,33,34]. However, the combined effect of chloride presence and carbonation in concrete with FA has been scarcely explored to date.

4.2. Accelerated Test: Comparation between Concretes with and without FA

The performance of concrete with and without FA concerning combined action is compared in Figure 14. This figure shows the total chloride profiles achieved for the combined situation at three months of carbonation (Figure 14a) and seven months of carbonation (Figure 14b).

(a)

(b)
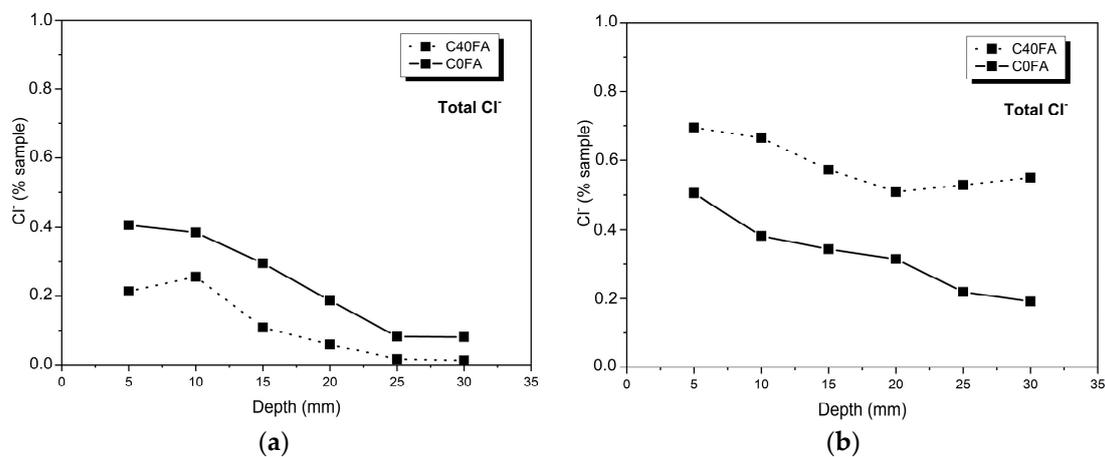
Figure 14. Total chloride profiles achieved for C0FA and C40FA after the combined situation: (**a**) 3 months of carbonation followed by chloride; and (**b**) 7 months of carbonation followed by chloride.

According to Figure 14, for a short period of carbonation, C40FA can maintain its efficiency against the penetration of chlorides when compared to C0FA. However, when

evaluating the results obtained for the combination of tests after seven months of carbonation, an important increase in the chloride content of C40FA is observed, throughout the entire depth, when comparing its values with those obtained for C0FA. Thus, under the conditions studied, FA's resistance to chloride ion penetration is reduced when concrete structures are in environments which are also subject to high concentrations of CO_2.

5. Conclusions

The impact of the combined action of chloride and carbonation on cement-based materials with fly ash was evaluated for specimens with a 40% replacement of cement with fly ash. Accelerated tests were conducted to simulate the synergistic effect of Cl^- and CO_2 in mortar and concrete specimens. The influence of the carbonation period was also evaluated. Conclusions are possible based on the results of this study.

Concerning the methodology for combining Cl^- and CO_2 actions, the combination of accelerated tests reached better results than immersion and drying cycles in specimens with fly ash. Since humidity is a crucial factor in carbonation development, the preconditioning stage before accelerated carbonation was very important to promote representative carbonation depths for this study. This is an important contribution of this study since there is no consolidated methodology or standards for studying this type of combined action.

The impact of chloride presence on carbonation depth in specimens with fly ash was verified. There was a reduction in carbonation depth in specimens with and without fly ash. Although this reduction was significant in specimens with fly ash, it was more pronounced in specimens without fly ash. The main cause may be related to the hypothesis of reduction in pores blocked by crystallisation. In this context, the amount of NaCl was greater in specimens without FA than in specimens with FA because the latter fixed more Cl^- and, therefore, contained less absorbed Cl^-. It is important to highlight that cementitious materials with fly ash have low resistance to carbonation; however, in environments strongly affected by CO_2 and Cl^- simultaneously, this resistance is increased.

The impact of carbonation on chloride penetration in concrete with fly ash was more evident. There was a strong reduction in chloride resistance for carbonated specimens. This reduction was clearer with greater carbonation depth. The increased aluminates from substitution of cement with fly ash contributed to lowering free Cl^- content in concrete with fly ash through chemical reactions that bind with Cl^-. The enormous increase in chloride content in the profiles studied can be related to the difficulty of binding chlorides in a low pH environment. Comparing concretes with and without fly ash in the reference (chloride presence only) and combined (carbonation followed by chloride presence) situations, under the conditions studied, it is possible to say that fly ash concrete's resistance to chloride ion penetration was reduced when the concrete structure was in an environment that was also subject to high concentrations of CO_2. Considering the real dynamics of the phenomenon, in the future, it is also important to study the impact of variables such as the concentration of CO_2 and Cl^- on these results.

References

1. Cement—Analysis—IEA. Available online: https://www.iea.org/reports/cement (accessed on 8 March 2022).
2. Alonso Alonso, M.C.; Acha, M.; Andrade, P. Incidencia de La Adición de Cenizas Volantes En La Durabilidad de Las Estructuras de Hormigón Armado. *Hormigón Acero* **1994**, *45*, 194.
3. Montemor, M.F.; Cunha, M.P.; Ferreira, M.G.; Simões, A.M. Corrosion Behaviour of Rebars in Fly Ash Mortar Exposed to Carbon Dioxide and Chlorides. *Cem. Concr. Compos.* **2002**, *24*, 45–53. [CrossRef]
4. Brenna, A.; Bolzoni, F.; Beretta, S.; Ormellese, M. Long-Term Chloride-Induced Corrosion Monitoring of Reinforced Concrete Coated with Commercial Polymer-Modified Mortar and Polymeric Coatings. *Constr. Build. Mater.* **2013**, *48*, 734–744. [CrossRef]
5. Kuziak, J.; Woyciechowski, P.; Kobyłka, R.; Wcisło, A. The Content of Chlorides in Blast-Furnace Slag Cement as a Factor Affecting the Diffusion of Chloride Ions in Concrete. *MATEC Web Conf.* **2018**, *163*, 05007. [CrossRef]
6. Sulapha, P.; Wong, S.F.; Wee, T.H.; Swaddiwudhipong, S. Carbonation Test of Concrete Containing Mineral Admixtures. *J. Mater. Civ. Eng.* **2003**, *15*, 134–143. [CrossRef]
7. Parrott, L.J. A Review of Carbonation in Reinforced Concrete. In *Corrosion of Steel in Concrete*; Shciessl, P., Ed.; Cement and Concrete Association: Wexham Spring, Buckinghamshire, UK, 1987; p. 69.
8. Bars, S.; Mohammed, U.; Hamada, H.; Yamaji, T. Concrete after 30 Years Exposure—Part II: Chloride Ingress and Corrosion of Steel Bars. *ACI Mater. J.* **2004**, *101*, 13–18.
9. AL-Ameeri, A.S.; Rafiq, M.I.; Tsioulou, O. Combined Impact of Carbonation and Crack Width on the Chloride Penetration and Corrosion Resistance of Concrete Structures. *Cem. Concr. Compos.* **2021**, *115*, 103819. [CrossRef]
10. Malheiro, R.; Camões, A.; Meira, G.; Amorim, M.T. Influence of Chloride Contamination on Carbonation of Cement-Based Materials. *Constr. Build. Mater.* **2021**, *296*, 123756. [CrossRef]
11. Zhang, R.; Panesar, D.K. Mechanical Properties and Rapid Chloride Permeability of Carbonated Concrete Containing Reactive MgO. *Constr. Build. Mater.* **2018**, *172*, 77–85. [CrossRef]
12. Wang, Y.; Nanukuttan, S.; Bai, Y.; Basheer, P.A.M. Influence of Combined Carbonation and Chloride Ingress Regimes on Rate of Ingress and Redistribution of Chlorides in Concretes. *Constr. Build. Mater.* **2017**, *140*, 173–183. [CrossRef]
13. Zhu, X.; Zi, G.; Cao, Z.; Cheng, X. Combined Effect of Carbonation and Chloride Ingress in Concrete. *Constr. Build. Mater.* **2016**, *110*, 369–380. [CrossRef]
14. Hussain, R.R.; Ishida, T. Critical Carbonation Depth for Initiation of Steel Corrosion in Fully Carbonated Concrete and Development of Electrochemical Carbonation Induced Corrosion Model. *Int. J. Electrochem. Sci.* **2009**, *4*, 1178–1195. [CrossRef]
15. Holthuizen, P.E. Chloride Ingress of Carbonated Blast Furnace Slag Cement Mortars. Master's Thesis, Delft University of Technology, Delft, The Netherlands, 2016.
16. Nagataki, S.; Ohga, H. Combined Effect of Carbonation and Chloride on Corrosion of Reinforcement in Fly Ash Concrete. In *Fly Ash, Silica Fume, Slag, and Natural Pozzolans in Concrete, Proceedings of the Fourth International Conference, Istanbul, Turkey, 3–8 May 1992*; American Concrete Institute: Farmington Hills, MI, USA; pp. 227–244.
17. Xie, X.; Feng, Q.; Chen, Z.; Jiang, L.; Lu, W. Diffusion and Distribution of Chloride Ions in Carbonated Concrete with Fly Ash. *Constr. Build. Mater.* **2019**, *218*, 119–125. [CrossRef]
18. Malheiro, R.; Camões, A.; Ferreira, R.M.; Meira, G.; Amorim, T. Effect of Carbonation on the Chloride Diffusion of Motar Specimens Exposed to Cycle Wetting and Drying. In Proceedings of the XIII International Conference on Durability of Building Materials and Components, São Paulo, Brazil, 2–5 September 2014.
19. Backus, J.; McPolin, D.; Holmes, N.; Long, A. Combined Chloride and Carbon Dioxide Ingression in Concrete Exposed to Cyclic Wetting and Drying. In Proceedings of the Civil Engineering Research Association of Ireland, Belfast, UK, 28–29 August 2014.
20. Rilem, T.C.; CPC-18 RILEM RECOMMENDATION. CPC-18 Measurement of Hardened Concrete Carbonation Depth. *Mater. Struct.* **1988**, *21*, 453–455.
21. Li, K.; Zhang, Y.; Wang, S.; Zeng, J. Impact of Carbonation on the Chloride Diffusivity in Concrete: Experiment, Analysis and Application. *Mater. Struct./Mater. Constr.* **2018**, *51*, 164. [CrossRef]
22. Kuosa, H.; Ferreira, R.M.; Holt, E.; Leivo, M.; Vesikaria, E. Effect of Coupled Deterioration by Freeze–Thaw, Carbonation and Chlorides on Concrete Service Life. *Cem. Concr. Compos.* **2014**, *47*, 32–40. [CrossRef]
23. *LNEC E 390*; Determination of the Resistence to Chloride Penetration. Immersion Test. LNEC: Lisbon, Portugal, 1993.
24. *EN 12390-12*; Testing Hardened Concrete—Part 12: Determination of the Carbonation Resistance of Concrete—Accelerated Carbonation Method. European Committee for Standardization: Brussels, Belgium, 2020.
25. Andrade, C. RILEM TC 178-TMC: "Testing and Modelling Chloride Penetration in Concrete" Analysis of Water Soluble Chloride Content in Concrete. *Mater. Struct.* **2002**, *35*, 586–588. [CrossRef]
26. Andrade, C. RILEM TC 178-TMC: "Testing and Modelling Chloride Penetration in Concrete" Analysis of Total Chloride Content in Concrete. *Mater. Struct.* **2002**, *35*, 583–585. [CrossRef]
27. McPolin, D.O. New Test Method to Obtain PH Profiles Due to Carbonation of Concretes Con-Taining Supplementary Cementitious Materials. *J. Mater. Civ. Eng.* **2007**, *19*, 936–946. [CrossRef]
28. Aires, C. High Performance Concrete with Fly Ash Incorporation. Ph.D. Thesis, University of Minho, Braga, Portugal, 2002. (In Portuguese)
29. Reis, R.; Malheiro, R.; Camões, A.; Ribeiro, M. Carbonation Resistance of High Volume Fly Ash Concrete. *Key Eng. Mater.* **2015**, *634*, 288–299. [CrossRef]

30. Leivo, M.; Sistonen, E.; Al-Neshawy, F.; Piironen, J.; Kuosa, H.; Holt, E.; Koskinen, P.; Nordqvist, C. *Effect of Interacted Deterioration Parameters on Service Life of Concrete Structures in Cold Environments: Laboratory Test Results 2009–2011*; Aalto University: Espoo, Finland, 2011.

31. Malheiro, R.; Camões, A.; Meira, G.; Amorim, M.T.; Castro-gomes, J.; Ferreira, R.M. Behaviour of Cementitious Matrices Subjected to the Combined Action of Chloride Ions and Carbonation. *Rev. Mater.* **2018**, *23*. [CrossRef]

32. Lannegrand, R.; Ramos, G.; Talero, R. Condition of Knowledge about the Friedel's Salt. *Mater. Constr.* **2001**, *3*, 63–71. [CrossRef]

33. Narde, A.R.; Gajbhiye, A.R. Durability Studies on Concrete with Fly Ash, Rice Husk Ash and Quarry Sand. *Int. J. Civ. Eng. Technol.* **2018**, *9*, 587–595.

34. Ramezanianpour, A.; Ghahari, S.; Esmaeili, M. Effect of Combined Carbonation and Chloride Ion Ingress by an Accelerated Test Method on Microscopic and Mechanical Properties of Concrete. *Constr. Build. Mater.* **2014**, *58*, 138–146. [CrossRef]