

Effect of the addition of metakaolin on the carbonation of Portland cement concretes

Efeito da adição do metacaulim na carbonatação de concretos de cimento Portland



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Abstract

Carbonation has been a concern of constructors and researchers because, by lowering the pH of the interstitial solution of the concrete, it can favor the post-deposition and subsequent corrosion of reinforced concrete reinforcement. Among the factors that influence carbonation is the use of pozzolanic materials, such as metakaolin. However, there is no consensus as to the positive or negative contribution of these additions. This work evaluated the influence of metakaolin on the mechanical properties, porosity and in particular on the carbonation of concrete, from the addition of 0%, 5%, 10% and 15% of metakaolin, in relation to the cement mass. From the results, it was observed that the addition of metakaolin, while not significantly influencing the porosity, gave the concrete a greater resistance to axial compression, a decrease in the capillary absorption and delayed the advance of the carbonation front in the concrete.

Keywords: metacaulim, carbonatação, concreto.

Resumo

A carbonatação tem sido alvo de preocupação de construtores e pesquisadores, pois, ao diminuir o pH da solução intersticial do concreto, pode favorecer a despassivação e posterior corrosão das armaduras do concreto armado. Dentre os fatores que influenciam a carbonatação está a utilização de materiais pozolânicos, como o metacaulim. Entretanto, não há um consenso quanto à contribuição positiva ou negativa da presença destas adições. O presente trabalho avaliou a influência do metacaulim nas propriedades mecânicas, na porosidade e, principalmente, na carbonatação do concreto, a partir da adição de 0%, 5%, 10% e 15% de metacaulim, em relação à massa do cimento. De acordo com os resultados obtidos, observou-se que a adição de metacaulim, apesar de não ter influenciado significativamente na porosidade, conferiu ao concreto uma maior resistência à compressão axial, uma diminuição da absorção capilar e retardou o avanço da frente de carbonatação no concreto.

Palavras-chave: metakaolin, carbonation, concrete.

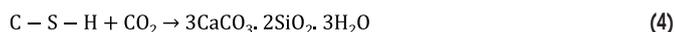
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1. Introduction

Carbonation is a complex physicochemical process of neutralization of the liquid phase present in the concrete pores. Calcium hydroxide ($\text{Ca}(\text{OH})_2$), a precipitated compound from the hydration of the cement, when dissolved in the aqueous phase of the pores, presents ions that react with the ionic constituents resulting from the dissolution of the carbon dioxide (CO_2), forming the carbonate of calcium and releasing water, according to equations 1, 2 and 3 [1].



Payá et al. [2] adds that carbonation does not occur only by the reaction of CO_2 with $\text{Ca}(\text{OH})_2$, but also with the hydrated calcium silicates (C-S-H), as presented in Equation 4.



With the formation of CaCO_3 , there is a reduction in the pH of the concrete due to the consumption of calcium hydroxide and a reduction in the hydroxyl concentration (OH^-), making the pH of the interstitial solution of the concrete fall from values above 12.5 to values lower than 9, favoring the depassivation of the reinforcing steel and a subsequent generalized corrosion of the same, according to the Pourbaix diagram (Figure 1) [3].

In the Pourbaix diagram of thermodynamic equilibrium, the domains of corrosion, passivation and immunity are delineated for the Fe-H₂O system at 25 °C. For the range of corrosion potential of the iron in the concrete, which is +0.1 a -0.4 V, a pH above 12 indicates that the iron is in the passivated state. However, with the carbonation reaction and therefore the pH decrease of the

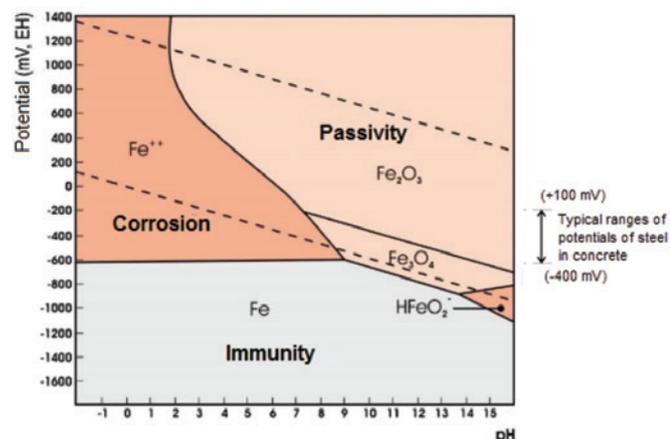


Figure 1
Diagram of Pourbaix. Thermodynamic equilibrium diagram for the Fe-H₂O system at 25°C, delimiting the likely domains of corrosion, passivation and immunity [5]

concrete to values around 8, the iron is in a thermodynamically corrosion-favoring region [4, 5].

Morandea *et al.* [6] point out that carbonation produces important changes in cement matrixes, such as a reduction in porosity and permeability, lower pore connectivity, higher specific surface area, among other properties. However, the effect of this impact on the microstructure is still an object of investigation and of divergence of opinion among researchers.

Metakaolin is usually obtained by calcining kaolinic clays or high purity kaolin. Due to its morphological characteristics, metakaolinite is responsible for the pozzolanic activity of metakaolin. The pozzolanic reaction of metakaolin occurs through the interaction of metakaolinite with the calcium hydroxide present in the cement paste, forming hydrated calcium silicates (C-S-H) and aluminates (C_2ASH_8 , C_4AH_{13} e C_3AH_6) [7, 8]. Its extremely fine particles, with a maximum dimension in the order of 10^{-6} m and high specific area, present reasonable chemical reactivity, enabling the metakaolin to act as a microfilm [7].

According to Barbhuiya *et al.* [9], metakaolin modifies the matrix due to the pozzolanic reaction, reducing porosity, creating nucleation points, and using changes in concentrations of C-S-H gel phases.

Several studies [10–12] the micromorphology by scanning electron microscopy (SEM) on the use of pozzolanic additions in cement matrixes have shown that they improve characteristics such as mechanical strength and porosity, increasing the durability of structures. However, there is as yet no consensus regarding the carbonation of concretes in which metakaolin is added. In his study, Ashish [13] observed that by replacing 10% of the Portland cement with metakaolin, a reduction in the carbonation depth of 32.1% was obtained after 56 days of accelerated carbonation, whereas Kim; Lee; Moon [14] reported a increase in the depth of carbonation of 70%, when replacing the same 10% content of cement with metakaolin.

The knowledge of this effect is important as there is a growing use of pozzolanic materials in concretes, even in large urban centers, where there are high emissions of carbon dioxide in the atmosphere due mainly to the burning of fossil fuels.

Despite the growing interest in the carbonation process in cementitious matrixes, this phenomenon is still poorly understood, and there is no established normative procedure for assessing its progress within the matrix. Thus, the present research aims to evaluate how the addition of metakaolin influences the carbonation process of cementitious matrixes.

2. Materials and methods

2.1 Materials

For the preparation of the concretes, natural quartz sand and crushed stone of basaltic origin, marketed in the city of Salvador, were used as aggregates. Due to the absence of pozzolans in their formula, Portland cement CP V ARI-RS was used. The water used comes from the public water supply system (Empresa Baiana de Água e Saneamento S.A – Embasa). The metakaolin used was HP Ultra, brand Metacaulim of Brazil, composed of aluminosilicates

Table 1

Proportion of materials used in the concretes produced

Mixture	Metakaolin content (%)	Water/cement ratio	Water/binder ratio
REF	0%	0.60	0.60
MK-5	5%	0.60	0.57
MK-10	10%	0.60	0.54
MK-15	15%	0.60	0.51

and obtained from the calcination of kaolinitic clays and kaolins at a temperature between 650°C and 800°C.

2.2 Methods

2.2.1 Characterization of materials

The particle size distribution and fineness modulus of the aggregates were determined according to NBR NM 248 [15], and the unit mass according to NBR NM 45 [16]. The specific gravity was defined according to NBR 9776 [17] for sand, and according to IPT-M9-76 [18] for the gravel.

The particle size distribution of metakaolin and cement was determined by laser granulometer (Horiba CAPA-700), the specific gravity by helium gas pycnometry (AccuPyc II 1340 Micromeritics) and the specific surface area by BET (Micromeritics Gemini 2370 V1.02) and Blaine automatic (only for cement), the samples used were dry and in powder form. The chemical compositions were determined by X-ray fluorescence (XRF) and the pozzolanic activity according to the European standard EN 196-5 [19].

2.2.2 Dosing and curing of specimens

For the preparation of the test specimens (CPs) the ratio by mass, 1:1.83:2.37:0.6 (cement: sand: gravel: water) with levels of 0%, 5%, 10% and 15% metakaolin, in addition to the mass of the cement were used. Table 1 shows the levels of metakaolin used, as well as the respective water /cement ratios (maintained at 0.60) and water/binder (cement + pozzolanic addition).

Table 2 presents the consumption of material for the production of one cubic meter of concrete, for all the mix design used in the research.

The prismatic CPs, (4x4x16) cm³ were immersed in a water tank saturated with calcium hydroxide and the mechanical resistance was

determined at the ages of 3, 7 and 28 days. After 28 days of curing, the CPs were exposed to the microprocessed CO₂ chamber (Quimis, model Q316C1), at a temperature of 29 ± 1°C, relative humidity of 65 ± 5% and concentration of carbon dioxide 5 ± 0.5 %, as shown in Figure 2. For the carbonation analysis, two batches of samples were used: In the first batch, the samples were dried in an oven (100° C) for 24 hours and then inserted into the carbonation chamber, while the second batch the samples were placed in the chamber still saturated, as soon as they were removed from the cure.

2.2.3 Concrete performance analysis

A) PHYSICAL-MECHANICAL PROPERTIES

In order to analyze the performance of the test specimens, they were tested after 21, 42 and 63 days of exposure to the carbon dioxide chamber, that is, at the ages of 49, 70 and 91 days (after molding). The specimens were characterized for resistance to axial compression (NBR 13279 [20]), water absorption by capillarity (ABNT NBR 9779 [21]) and bulk density (NBR 9778 [22]).

B) CARBONATION DEPTH

As previously stated, after 28 days of curing, CPs were exposed to the microprocessed CO₂ chamber at a temperature of 29 ± 1°C, , relative humidity of 65 ± 5% and carbon dioxide concentration of 5 ±



Figure 2
Microprocessed of carbon dioxide chamber

Table 2

Consumption of materials in a cubic meter of concrete produced

	REF	MK-5	MK-10	MK-15
Cement (kg/m ³)	411.66	408.52	405.43	402.39
Sand (kg/m ³)	753.33	747.59	741.93	736.36
Gravel (kg/m ³)	975.63	968.19	960.87	953.65
Water (kg/m ³)	246.99	245.11	243.26	241.43
Metakaolin (kg/m ³)	0.00	20.43	40.54	60.36

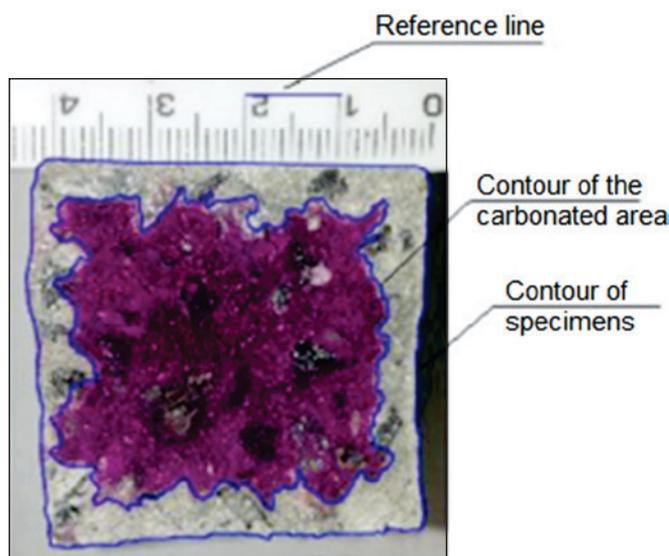


Figure 3
Representation of the carbonated area of the test specimens obtained using Autocad software

0.5%. At each age, 8 CPs of each sample, 4 CPs of the initially dried batch and 4 CPs of the initially saturated batch were measured. The visualization of the carbonated area was possible thanks to the sprinkling of an aqueous-alcoholic solution containing 1% of the phenolphthalein pH indicator. The samples were fractured by bending and the solution was sprayed on the fracture surface of the samples, which was photographed for a later comparison of the carbonated area. The pH difference between the carbonated region (pH around 8) and the turning range of the phenolphthalein solution (pH between 8.3 and 10) causes a measurement error in the carbonation depth. According to recommendations of RILEM [10], this imprecision is 0.5 mm when the carbonation front exceeds 3 mm and must be corrected.

The carbonate area of the test specimens was calculated with the aid of the Autocad program, in a procedure illustrated in Figure 3. First, the non-carbonated area and the test body were delineated with the software’s “polyline” function, in addition to creating a reference line of a known dimension, with the aid of a ruler. Afterwards, the “scale” function was used to resize the photograph so that its dimensions corresponded to the actual dimensions of the specimen. The carbonate area (colorless) was calculated by

subtracting the non-carbonated area (pink-carmine, represented by the dark color in the figure) of the total area of the section of the specimen. The correlation between carbonated area and carbonation depth was calculated.

For the carbonation analysis, reference cement pastes (REF) and with MK addition were also produced, which were maintained in immersed curing for 28 days and then dried in an oven for 24 hours at 100°C and exposed to CO₂ for 63 days. The crystalline phases of cement pastes were identified at 28 days of curing and after exposure to CO₂ using the X-ray diffraction (XRD) technique using a D2 Phaser diffractometer, Bruker; with copper tube, the diffraction spectra were obtained in the scanning range 2θ from 5° to 80°, and increase of 0.3°/min, with 10mA current and 30kV voltage. The phases was identified using the DIFFRAC plus-EVA software, with a database centered on the COD system (Crystallography Open Database).

2.3 Results and discussion

2.3.1 Characterization of materials

The physical properties and granulometric distribution of the materials used are shown in Table 3 and in Figure 4 respectively. It can be observed that the metakaolin was the finest among the materials, followed by cement, sand and gravel, respectively. From the Particle size distribution shown in Figure 4, the sand was classified, according to NBR 7211[23], as very fine sand, characteristic of the sands of the Salvador region, and the gravel belongs to the 4.75/12.5 granulometric zone, with a maximum dimension of 9.5 mm.

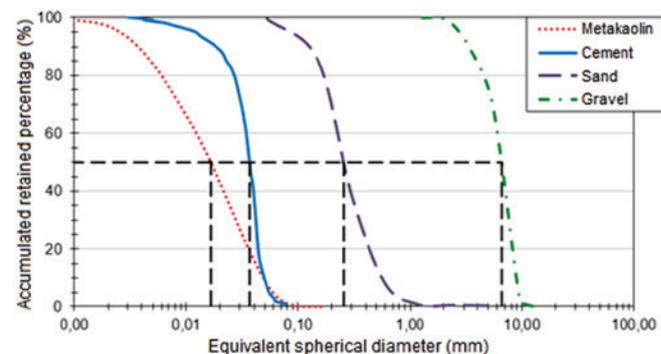


Figure 4
Particle size distribution of raw materials

Table 3
Physical characterization of the materials used

Feature	MK	Cement	Sand	Gravel
D50 (mm)	0.017	0.037	0.254	6.604
Specific Gravity (g/cm ³)	2.68	3.17	2.66	2.87
Specific Surface Area - BET (m ² /g)	16.85	8.92	—	—
Specific Surface Area - Blaine (cm ² /g)	—	4466	—	—
Unitary mass (g/cm ³)	—	—	1.46	1.40
Compact Unitary Mass (g/cm ³)	—	—	—	1.52
Fineness Modulus	—	—	1.32	5.72

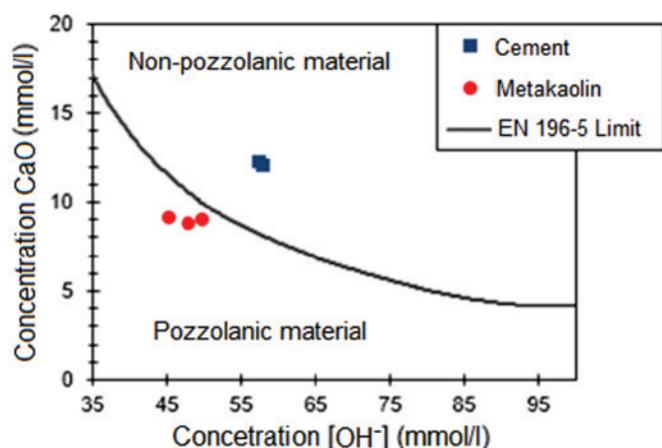


Figure 5
Concentration of calcium oxide as a function of the hydroxyl ions concentration, with a concentration line of saturation of CaO in the solution, characterizing metakaolin as a pozzolanic material

The evaluation of pozzolanic activity by chemical titration, which result is shown in Figure 5, characterized the metakaolin used as pozzolanic material.

The chemical compositions of metakaolin (MK) and cement (CP) are presented in Table 4, showing the high content of SiO_2 and Al_2O_3 in MK and CaO in the cement.

2.4 Concrete performance analysis

The axial compressive strength results for the MK-containing concretes, shown in Figure 6A, show that there was an increase in the mechanical strength as a function of the increase in the added MK content. This is because when MK is added to the cement, the ratio water/binder decreased. In addition, the increase in resistance occurred due to the pozzolanic reactions and the reduction in the porosity of these materials caused by the presence of more nucleation points and the products resulting from the carbonation reaction [6].

The capillary coefficients, shown in Figure 6B, show that CM contributes to the decrease in capillary absorption and this is also decreased with the increase in time of exposure to CO_2 . It is noteworthy that at 63 days, the MK10 samples showed an increase in capillary water absorption when compared to the previous age (42 days); however, the capillary coefficients were lower than those at the control age (28 days of cure) and after 21 days of exposure. The inversely proportional relationship between the amount and

interconnectivity of capillary pores and the content of pozzolans in the composites has been observed in several recent works [11, 12]. This phenomenon can be explained by the fact that the reaction of pozzolan with Ca(OH)_2 produces a larger volume of C-S-H, leading to a further reduction in the capillary porosity during hydration [8]. Barbhuiya et al. [5] explain that the MK can cause a pore refinement and make them discontinuous, thus reducing the absorption of water by capillarity.

In addition, the volume of CaCO_3 , resulting from carbonation, is higher than that occupied by Ca(OH)_2 , which may cause pore buffering, reducing capillary absorption. Arandigoyen [24] states that carbonates formed have between 2.9 and 11.2% more volume than portlandite (11.2% for calcite, 2.9% for aragonite and 2.54% for vaterite). However, some researchers have observed an increase in capillary absorption due to carbonation [6].

Regarding the results of apparent porosity (Figure 6C), no significant difference was observed until the control age. With the exposure to carbon dioxide, the apparent porosity decreased for all samples, due to the filling of the pores caused by the products of the carbonation reaction and the continuity of the pozzolanic and hydration reactions. Since the results of apparent porosity and capillary absorption are concordant, it can be concluded that the decrease in porosity is mainly related to the reduction of capillary pores.

2.5 Determination of carbonation depth

For the carbonation analysis, two batches of samples were used. For the first batch, the results of which are shown in Figure 7A, the samples were oven dried prior to being inserted into the carbonation chamber. Samples from the second batch were placed in the oven as soon as they were removed from the cure, in other words, water saturated, and the results are shown in Figure 7B.

According to Fig. 7A, up to 21 days of exposure no considerable carbonation was observed in the samples. This is due to the fact that the samples were inserted into the chamber in the dry state, i.e. extremely low humidity, hampering the occurrence of the carbonation reaction which requires water. At 42 days, the carbonated area increased significantly. Because the pores, mainly the capillaries, had no water, the diffusion of the CO_2 became easier and with the subsequent absorption of moisture present in the chamber, the environment became favorable to the occurrence of carbonation [25].

In Figure 7B it is possible to observe that the reference samples (REF) and MK5 presented carbonation already at 21 days, and that samples MK10 and MK15 presented carbonation at 42 days and 63 days, respectively. Thus, until the end of the test, the reference samples presented a larger carbonated area, followed by samples MK5, MK10 and MK15, showing that the rate of the carbonation reaction decreases with the increase in the added MK content.

Table 4
Physical characterization of the materials used

Material	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	Na_2O	MgO	CaO	SO_3	K_2O
MK(%)	57.0	34.0	2.0	1.5	<1.5	<0.1	<0.1	<0.1	—
CP(%)	19.1	4.8	3.2	—	0.2	2.7	61.1	3.4	0.7

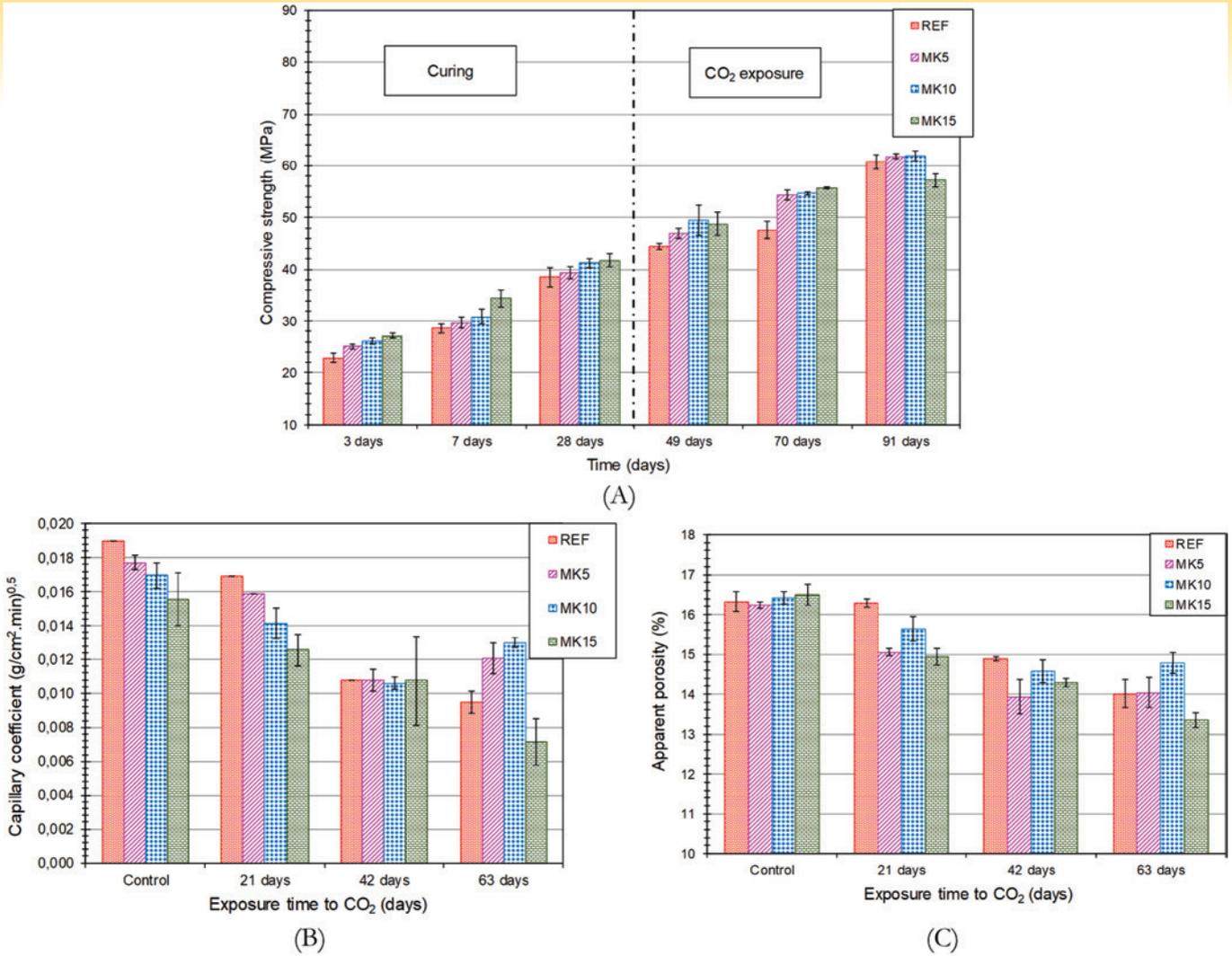


Figure 6 (A) Compressive strength, (B) Capillary absorption coefficients and (C) Apparent porosity of specimens containing different levels of metakaolin and at different ages of exposure in a CO₂ chamber

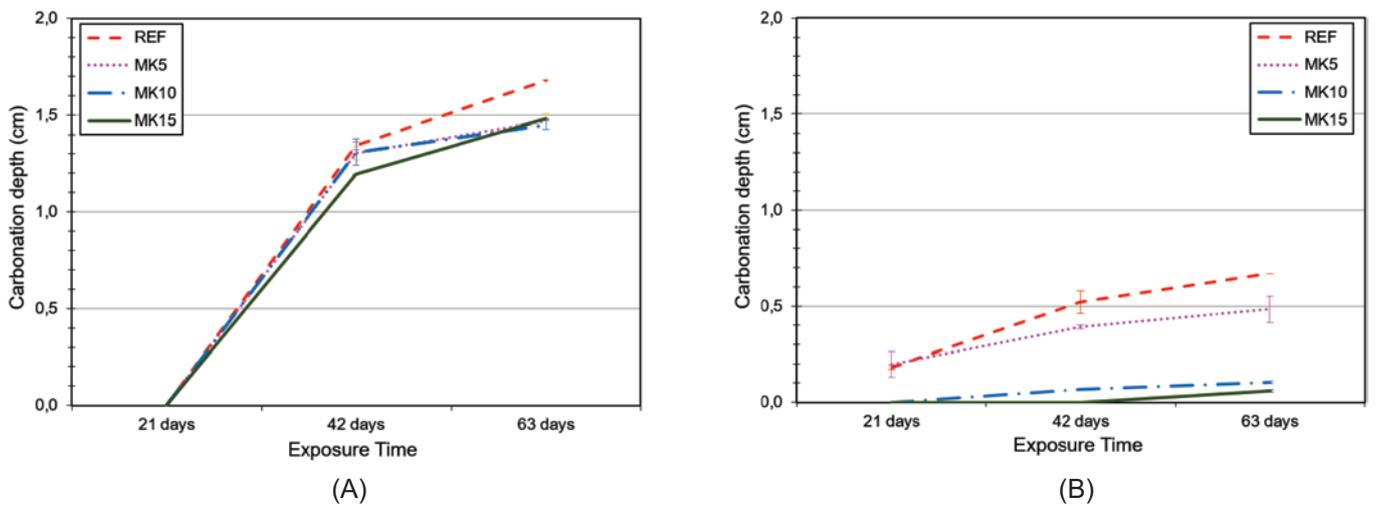


Figure 7 Verification of the carbonate region of dried (B) and saturated (A) concrete samples in water, after exposure in a carbonation chamber

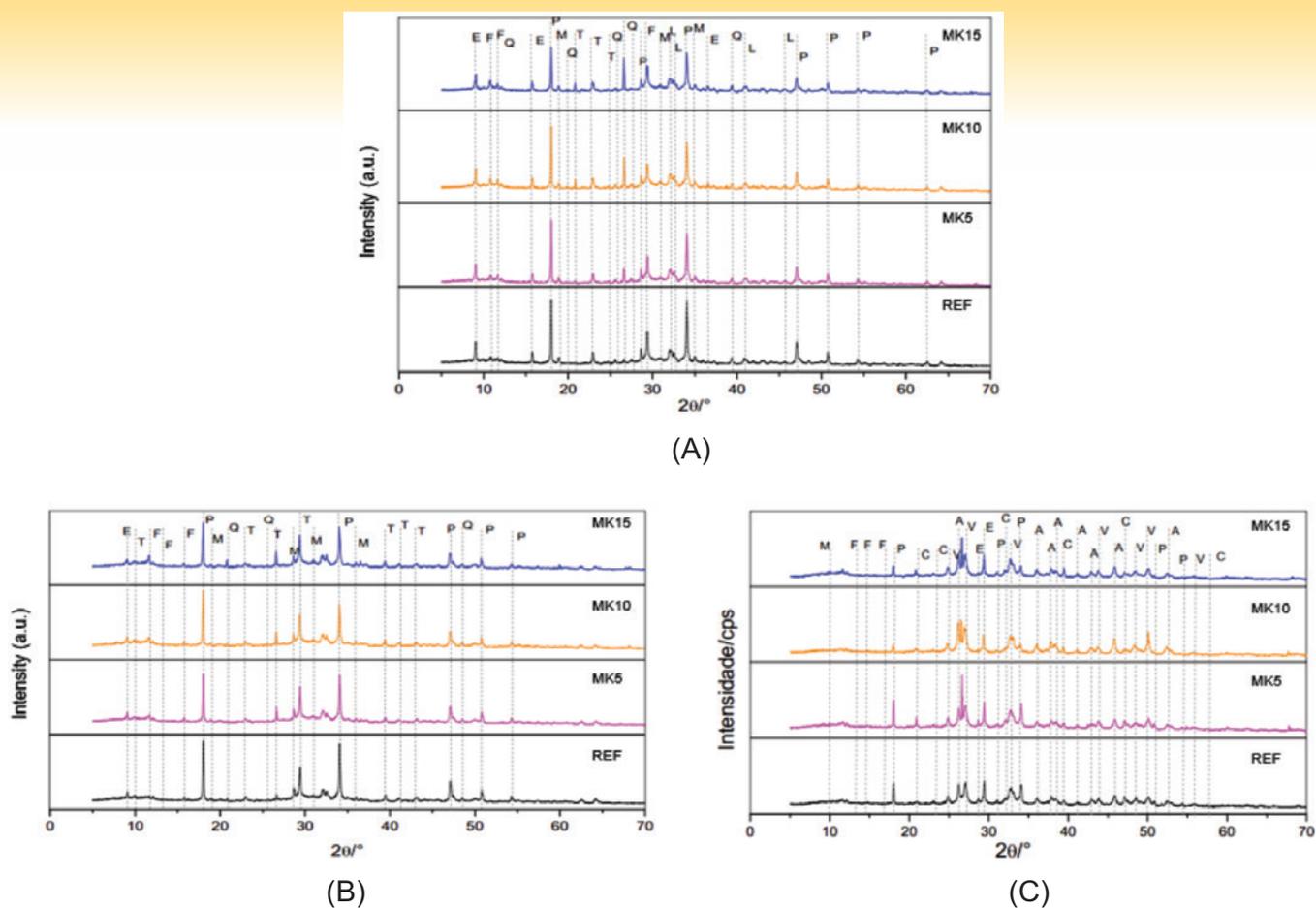


Figure 8

Diffraction patterns of cement pastes containing different levels of metakaolin, (A) in the control age (after 28 days of wet treatment) and at 91 days, (B) without exposure to CO_2 and (C) with exposure to the carbonation chamber for 63 days. E-ettringite, T-tobermorite, F-Fluorarrjadite, L-Larnite, P-Portlandite, Q-Quartz, M-Muscovite, C-Calcite, V-Vaterite, A-aragonite

Although the initially dry samples presented a more pronounced evolution of the carbonation reaction in comparison to the initially wet samples, in both the presence of metakaolin resulted in a reduction in the carbonated area.

Barbhuiya *et al.* [9] showed that a 10% mass replacement of cement with metakaolin did not negatively affect the carbonation resistance, even though it had a lower concentration of Portlandite ($\text{Ca}(\text{OH})_2$) after 28 days of cure.

2.6 Mineral analysis

Figure 10 shows the x-ray diffraction of the pastes after 28 days of wet curing (Figure 10A) and at 91 days of age without exposure in the carbonation chamber (Figure 10B) and pastes after 63 days of exposure in the carbonation chamber (91 days of age).

After 28 days of hydration (Figure 8A), all samples show intense peaks of Portlandite (P) showing that there is a high alkaline reserve concentration in the pastes. These results show that there was no significant reduction of Portlandite due to the addition of metakaolin to the mixture, which contributes to the fact that there is no increase in the rate of carbonation. In previous studies [9, 12, 25], researchers have shown that, by replacing the cement with metakaolin, the representative peaks of Portlandite are reduced, showing a higher consumption of this mineralogical phase, and thus explaining the accelerated advance of the carbonation front.

Differently from what occurs in the present study, where metakaolin was added to the cement mass and the $\text{Ca}(\text{OH})_2$ reserve was not impaired.

After 91 days (Figure 8B), the samples showed an increase in the concentration of Portlandite and Tobermorite, providing evidence that the pozzolanic and hydration reactions continued to occur, probably favored by the residual moisture in the specimens [27]. In addition, samples containing metakaolin showed higher C-S-H peaks (tobermorite, T).

In the carbonate samples (Figure 8C), a decrease in the concentration of Portlandite was more pronounced for the samples containing metakaolin, because of the formation of the calcium carbonate products (aragonite, A, calcite, C and vaterite, V). However, it should be noted that Portlandite consumption is also caused by the Pozzolanic reaction, forming the C-S-H gel; thus, not all the Portlandite becomes CaCO_3 . Similarly, the carbonation reaction also occurs in the C-S-H and other hydrated cement phases; Thus, not all the CaCO_3 formed originated from Portlandite [2], however, C-S-H products have a higher resistance to carbonation [6].

The samples containing MK presented an alkaline reserve similar to those observed in the reference samples at the beginning of the exposure to CO_2 and a higher concentration of CSH, which, together with a reduction in the capillary coefficients for the MK containing samples, contributed to the samples containing metakaolin to have a higher resistance to carbonation.

3. Conclusions

From the obtained results, it can be concluded that:

- The addition of metakaolin to the concrete provided an increase in the mechanical resistance and decrease in the capillary pores, the main means of entry of aggressive agents.
- The addition of metakaolin caused a decrease in the apparent porosity of the blends, contributing to a reduction in the intensity of the carbonation reactions and consequently a delay in the advance of the carbonation front.
- Samples exposed on the carbonation chamber, in the dry state, is more susceptible to CO₂ ingress, but the carbonation reactions did not occur because there was no water available in the pores. However, these samples, when acquiring ambient humidity (about 65%), carbonated faster than completely saturated samples, in which CO₂ presented difficulties in diffusing.
- The X-ray diffraction technique proved to be efficient in evaluating the products from carbonation and the pozzolanic reaction.
- As regards the evaluation of the influence of metakaolin in the carbonation reaction, it is possible to predict its behavior due to the different influential variables such as initial alkaline reserve, formed microstructure, simultaneous reactions of hydration and carbonation, porous macrostructure, humidity, among others. Thus, a specific study of the concrete specified in the project regarding carbonation is necessary in order to assure better technological control of it before use.

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