

Monitoring the carbonation front progress in a cementitious composite having its pore structure analyzed through μ -CT imaging

Acompanhamento do avanço da frente de carbonatação em compósito cimentício com sua estrutura de poros analisada por microtomografia computadorizada de raios X (μ -CT)



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Abstract

The carbonation process is one among the primary factors that cause a reduction in the hydrogen ionic potential (pH) of cementitious composites that may lead to a depassivation of the reinforcement structures, thus furnishing conditions for corrosion processes to begin. In this paper, the research sought to monitor the advancement of the carbonation front in compliance with the European standard, EN 14630, whilst concurrently measuring the pH variation on the surface of the cementitious composite. Cylindrical mortar specimens of (2x4) cm were placed in a carbonation chamber, keeping up the humidity 65%, temperature 28° C and a CO₂ concentration of 5%. The structure of voids in the matrix was assessed with the μ -CT imaging technique. The pH reading enabled the monitoring of the carbonation front progress as a function of the loss of alkalinity, before the process established by standard EN 14630. The images obtained by μ -CT did not enable the visualization of the densification of the material found in the outer layer of the specimen.

Keywords: mortar, carbonation, pH, Xray microtomography.

Resumo

O processo de carbonatação é um dos causadores da redução do potencial hidrogeniônico (pH) em compósitos cimentícios, o qual pode levar a despassivação das armaduras, dando condições ao início de um processo de corrosão. Neste trabalho, buscou-se acompanhar o avanço da frente de carbonatação conforme a norma europeia EN 14630 paralelamente à medição da variação do pH na superfície do compósito cimentício. Foram utilizados corpos de prova cilíndricos (CP) de argamassa, com dimensão de (2x4) cm, acondicionados em câmara de carbonatação com condições controladas, mantendo-se a umidade em 65 %, a temperatura em 28° C e a concentração de CO₂ em 5 %. A estrutura de vazios da matriz foi avaliada por meio da técnica de microtomografia computadorizada de raios X (μ -CT). A leitura de pH permitiu um monitoramento do avanço da frente de carbonatação, em função da perda de alcalinidade, antes do processo estabelecido na norma EN 14630. As imagens obtidas por meio da μ -CT não permitiram visualizar a densificação do material presente na camada mais externa do CP.

Palavras-chave: argamassa, carbonatação, pH, microtomografia de raios X.

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1. Introduction

The carbonation phenomenon found in composites is a result of the diffusion of carbon dioxide (CO_2) in the pore structure of its matrix, where it is dissolved, forming carbonic acid (H_2CO_3). This then reacts with the alkalis content in the composite solution, mainly with calcium hydroxide to form calcium carbonate [1, 2, 3, 4].

The calcium carbonate (CaCO_3) will then contribute to filling the surface pores, thus reducing the material's diffusivity and, consequently, the carbonation front progress speed [5, 6]. Due to this process, the carbonation initially occurs quickly and progresses slower towards the maximum depth [1, 3]. The CaCO_3 produced does not, by itself, a deleterious action for cementitious composites. However, the alkalis consumption that takes place during the phenomenon described, leads to a reduction of hydrogenionic potential (pH) in the interstitial solutions of pores and capillaries, which under natural conditions, have a highly basic pH (usually between 12.6 and 13.5) [3]. In the case of reinforced structures, the loss of alkalinity can lead to depassivation of reinforcement, thus providing conditions for the beginning of a corrosion process, which may lead to a reduction of the lifetime constructions [4, 6, 7]. The utilization of a phenolphthalein solution sprinkled on the surface of cement based composites is the best known and most em-

ployed technique to estimate the depth of the carbonation front, as it is a simple and low cost method. It is also recommended by RILEM CPC-18 [8] and by CEN BS EN 14630 [9]. However, the test has some shortcomings, since the turning range of this solution is reached only when the pH values are between 8.0 and 10.0 [10, 11]. Consequently, the phenolphthalein solution has limitations with regards to monitoring the carbonation depth, as it is not able to detect within the range where the loss of alkalinity begins, which can lead to a depassivation of the reinforcement, as it can occur from pH values lower than 11.8 [3, 6, 12].

This study has sought to monitor the progress of carbonation front by utilizing the phenolphthalein indicator according to the standards of the European Standard BS EN 14630 [9], and by measuring the pH variation with specialized equipment for cementitious matrix composite surfaces. The use of this device allowed an efficient monitoring of the hydrogenionic potential variation induced by carbonation.

Concurrently, we used the X-ray microtomography technique, to evaluate the void structure of one of the specimen tested. As it is a non-destructive technique that does not require any special preparation of the sample, the use of μ -CT enabled quantify the size, distribution and connectivity of the specimen's pores, without causing changes in the original structure of the specimen.

Table 1
Physical properties of the cement CPV utilized

Characteristics and properties		Unit	Cement utilized	NBR 5733
Fineness	Retained at sieve 75 μm Specific area	% m^2/kg	≤ 6 480.8	≤ 6 ≥ 300
Beginning of setting time		min	129	≥ 60
End of setting time		min	184	≤ 600
Soundness after boiling		mm	≤ 5	≤ 5
Compressive strength	1 day	MPa	28.5	≥ 14
	3 days	MPa	40.5	≥ 24
	7 days	MPa	44.3	≥ 34

Table 2
Chemical properties of the cement CPV utilized

Unit	Cement utilized	NBR 5733
Insoluble residue (IR)	0.79	≤ 1.0
Fire loss (FL)	3.75	≤ 4.5
Magnesium oxide (MgO)	0.69	≤ 6.5
Sulphur trioxide (SO_3)	2.98	≤ 4.5
- when C3A clinker - 8%	2.89	≤ 3.5
- when C3A clinker > 8%	-	≤ 4.5
Carbon dioxide (CO_2)	2.61	≤ 3.0
Aluminum oxide (Al_2O_3)	4.90	-
Iron oxide (Fe_2O_3)	3.05	-

Note: the percentage of C_3A contained in the clinker must be calculated with the following formula: $(\text{C}_3\text{A} \%) = 2.65 \times (\text{Al}_2\text{O}_3 \%) - 1.692 \times (\text{Fe}_2\text{O}_3 \%)$.

Table 3

Grain size fractions of regular sand

Matter retained on sieves of nominal size of	Size range	Denomination
2.4 mm and 1.2 mm	16	Coarse
1.2 mm and 0.6 mm	30	Medium coarse
0.6 mm and 0.3 mm	50	Medium fine
0.3 mm and 0.15 mm	100	Fine

2. Materials and experimental program

2.1 Cement

It was used the high early strength Portland cement (CP V – ARI), with chemical and physical properties in compliance with the standard NBR 5733 [13]. Tables 1 and 2 shows the results attained from the tests performed to characterize this material.

2.2 Sand

It was used the “Brazilian Regular Sand” produced and furnished by the Institute for Technological Research (IPT). Table 3 presents the grain size fractions of the standard sand, according to the standard NBR 7214 [14].

2.3 Dosage, molding and curing of specimens

The mortar was produced with a 1:3 (cement: sand) with a water/cement ratio (w/c) of 0.60. The amounts used in the dosages are shown in Table 4.

The tests were made on cylindrical mortar specimens, measuring (2 x 4) cm. Specimens with reduced sizes were used in order to make the sample compatible with the reading capacity of the X-ray microtomography equipment used in this research [15].

The molding of the test specimens was done according to the procedures established by standard NBR 7215 [16] and was carried

Table 4

Quantity of materials per dosage mix

Material	Mortar mix (g)
Portland Cement	624.0 ± 0.4
Water	374.4 ± 0.2
Standard sand	–
Coarse fraction	468.0 ± 0.2
Medium coarse fraction	468.0 ± 0.2
Medium fine fraction	468.0 ± 0.2
Fine fraction	468.0 ± 0.2

out in an environment with relative humidity of (65 ± 2) %, and temperature of (26 ± 1.0) °C.

Twelve (2 x 4) cm specimens were molded, of which 11 specimens were placed in the carbonation chamber and 1 specimen was used to determine the initial pH of the material (reference).

Out of the 11 specimens that underwent the accelerated carbonation process, 10 were used in the pH measurement and phenolphthalein tests, and 1 specimen was utilized for μ -CT test.

The process of mortar consolidation was carried out on a vibrating table. The metallic molds were fully filled with the mortar and vibrated for 10 seconds. The time for consolidation was previously adjusted, taking into account the consistency of the mortar produced. Following the molding stage, the specimens were kept in a humid chamber with a controlled temperature of (23 ± 2) °C and relative humidity (RH) greater than 95% for a period of 24 hours. After the initial cure, specimens were demolded and left for more than 48 hours submerged in a tank filled with potable water, until the moment of the first pH measurements, prior to being placed in the carbonation chamber.

2.4 pH and carbonation measurements

The specimens were taken out from the curing tank on the third day of age for pH measurement stage of its top and bottom. For this test, the PH150-C ExStik® equipment, specifically designed

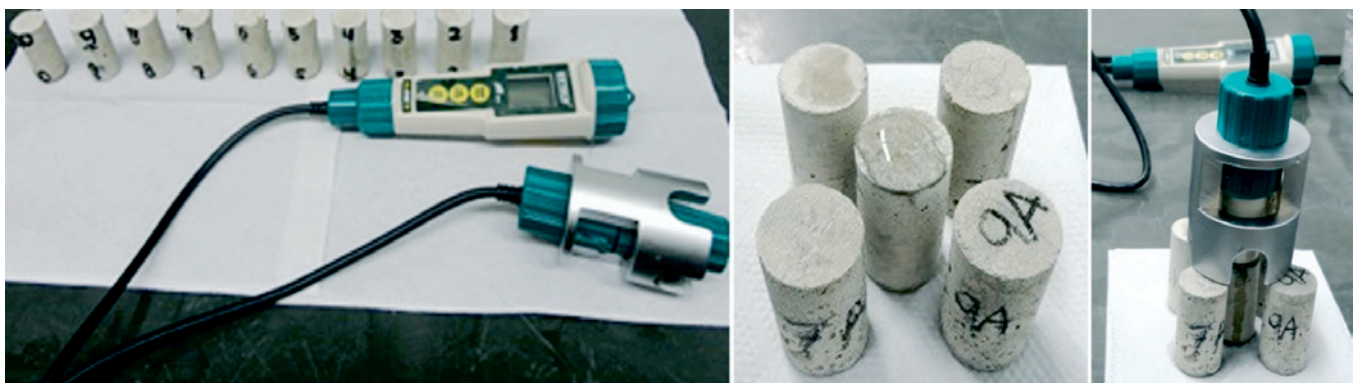


Figure 1
pH measurement of one (2 x 4) cm specimen



Figure 2
Carbonation chamber – exposure conditions of the specimens

for making quantitative pH measurements (measure the hydrogen ions in the solution) on the surface of cementitious materials was used.

The measurements were performed on samples with dried surfaces, and deionized water was sprinkled over the region in contact with the probe, as shown in Figure 1 [17]. The equipment was calibrated with standard solutions of pH 7, 4, and 10, before each utilization.

After the initial pH measurement, 11 specimens were put into a carbonation chamber, model Thermo Scientific Steri-Cult® CO₂, where they were exposed to a relative humidity of $(65 \pm 1) \%$, temperature at $(28,0 \pm 0,5) ^\circ\text{C}$ and carbon dioxide concentration (CO₂) of $(5,0 \pm 0,1) \%$, as shown in Figure 2, until the day scheduled for the tests. The conditions herein established were based on other studies on carbonation [3, 4, 18]. The remaining specimen was used as a pH reference at 3 days of age.

On the 2nd, 5th, 7th, 12th, 14th, 16th, 18th, 21st, 23rd and 25th day, one specimen was taken out of the carbonation chamber in order to measure the pH and perform the phenolphthalein test.

The pH was measured at the mid-height of the specimen's side surface. Next, they were perpendicularly sawed in half with a disc saw. The two resulting surfaces were cleaned with a brush to re-

move powdery material resulting from the cutting. On one of the surfaces, a pH measurement was taken. Next, a phenolphthalein solution was sprinkled on the sawed surface of the second half of the specimen, so as to verify the average depth of carbonation front in line with the specifications of standard CEN 14630 [9].

In order to determine the average carbonation depth, a calculation was done based on 16 measurements, made with a caliper, from the outer surface of the section up to the boundary edge of the red-purple color region. An evaluation of the average carbonation depth was also performed using an image analysis software system.

The specimens' surfaces, which were sprinkled with phenolphthalein, were photographed with a digital camera to enable the quantification of the carbonation front using the ImageJ software.

The same procedure adopted for measuring the pH was performed in the reference specimen (age of 3 days). This specimen was not placed in the carbonation chamber.

2.5 X-ray microtomography (μ -CT)

X-ray microtomography (μ -CT) is a non-destructive test that can produce 3D informations based on the piling of 2D sections while the specimen is rotated, thus generating data on the inner microstructure of the material analyzed, such as density and pore structure [19].

The μ -CT test was performed with the SkyScan 1172 high resolution microtomography equipment that operates with a voltage up to 100 kV and 10 W of power. The equipment is controlled by a set of four networked computers that increase the processing capacity and production of 3D models. This set is shown in Figure 3.

One specimen was removed from the chamber after 14 days of exposure for a microtomography scan and was immediately wrapped into a PVC film, to avoid interaction with the CO₂ present in the air. The film was removed at the moment of testing.

3. Results and discussions

3.1 Carbonation and pH

Figure 4 shows the average values of the pHs measured on the top and base surfaces of each of the eleven specimens tested. These measurements were performed immediately before the specimens were placed in the carbonation chamber, and after three days of submerged curing. It was verified that all specimens featured good

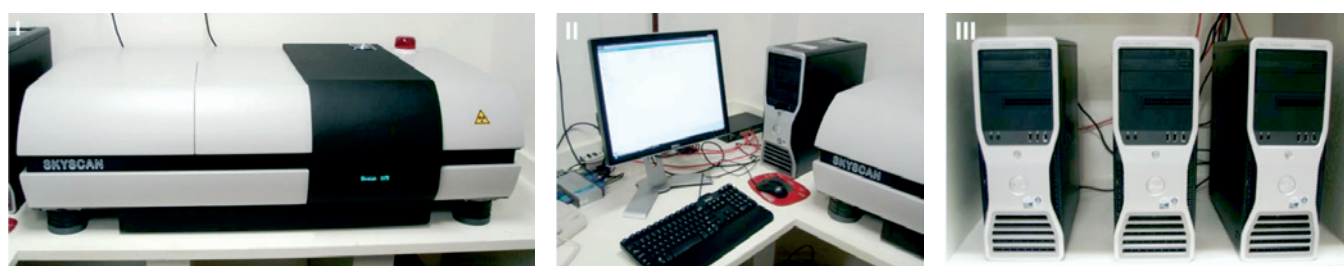


Figure 3
X-ray microtomography equipment, I – SkyScan 1172 Microtomography, II and III – Control and data acquisition computers

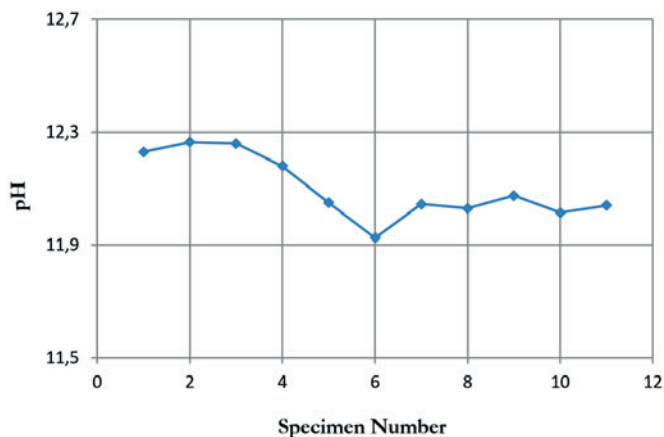


Figure 4
Average initial pH of non-carbonated specimens

alkalinity with an average global value of 12.10.

Figure 5 shows the pH averages attained from the mid height of the outer side surface of the transversal and from the central section of the transversal cut of each one of the specimens, tested after staying for a pre-established time in the carbonation chamber. A more intense trend of alkalinity loss was verified on the first days, thus confirming data presented in other studies that demonstrate that carbonation occurs with high speed in the beginning, progressing more slowly towards the maximum depth [1]. It was also noted that the central region of the specimens underwent a reduction in alkalinity even before it was detected by the phenolphthalein solution test.

At the age of 14 days, the pH on the outer regions of the specimen reached a value of 9.07, which led the phenolphthalein indicator to clearly mark a deeper region, indicating the advancement of the

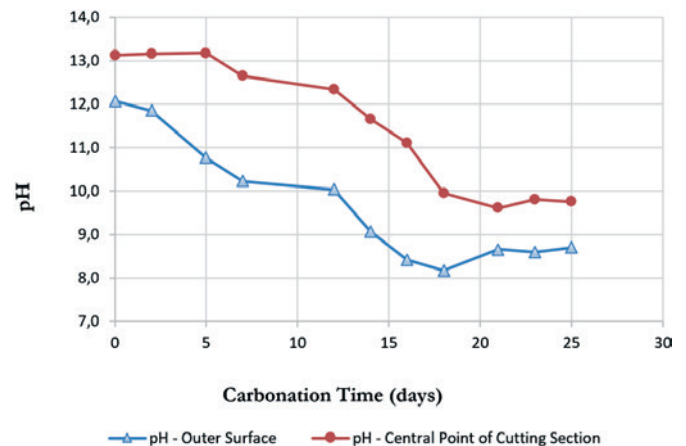


Figure 5
Average initial pH of carbonated specimens

carbonation front, as shown in Figure 6. On the 5th day, it was noted that a slight loss in alkalinity could already be seen, as the pH of 10.77 was still out of the best turning range of phenolphthalein solution, which usually occurs when the pH reaches values between 8 and 10.

Figure 7 shows an image ready to be analyzed by ImageJ. Figure 8 shows the monitoring of the carbonation front progress, likely to be detected with the use of phenolphthalein solution, as established by the standards of the European standard CEN 14630 [9], and the results attained with the help of the software.

In order to assess whether there is a significant difference in the average of measurements obtained by the two methods, the hypothesis test was applied, based on the Student's t-Distribution (or Student's t-test) for independent samples. The null hypothesis is that the average is equal between the two groups. The alternative

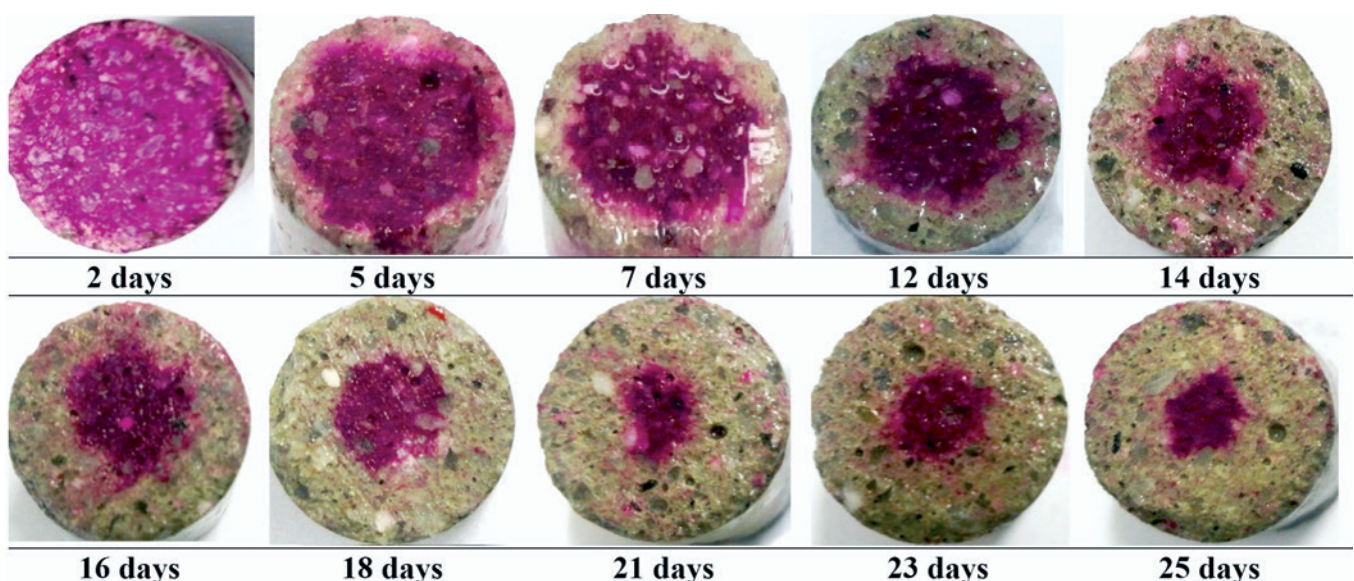


Figure 6
Carbonation front progress by phenolphthalein indicator

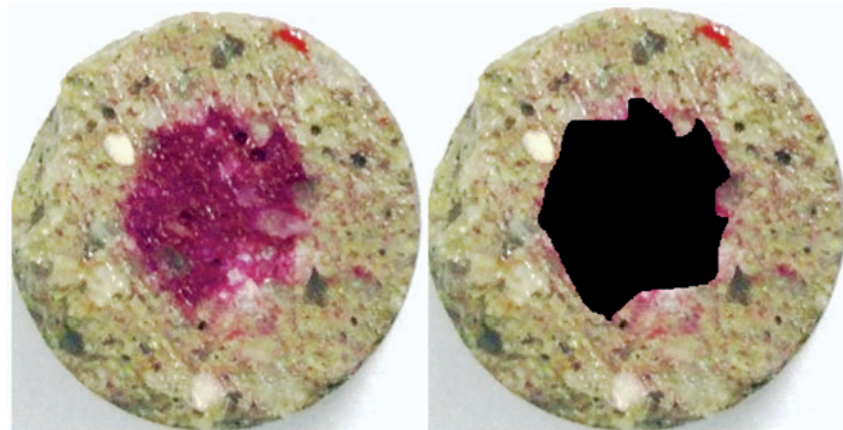


Figure 7
Image of a specimen after sprayed phenolphthalein and prepared to be analyzed by ImageJ

hypothesis is that the average is different. If the p-value (probability to err by rejecting the null hypothesis) is less than 5%, reject the null hypothesis. That is, it is assumed that the average is different between the two groups.

In the case of this study, the p-value found was 90.2%, indicating that there isn't a significant difference between the measures of the depth of carbonation front advance from both groups [21].

On the 25th day of exposing the specimens to the pre-established conditions in the carbonation chamber, it was noted that the phenolphthalein solution showed the carbonation front had progressed 6.4 mm. It is important to note that only the region where the pH of the cementitious material was reduced to levels enabling detection by this pH indicator are being measured, and not the presence of the carbonic acid (H_2CO_3) reactions with the mortar's alkalis.

It can also be seen in Figure 5 that with only 14 days in the chamber, the central point of the transversal section of the specimen cut, 10 mm from the edge, had already reached a pH value of

11.6. This value would be enough to allow the depassivation of the reinforcement, which, according to Neville [3], can occur when the pH reaches values between 11.4 and 11.8. It was also verified that, even on the 18th day of exposure and with the pH in the central region equal to 10.03, the loss of alkalinity would still not be detected by the use of the solution.

3.2 X-ray microtomography

Figure 9 shows the images attained from the scans performed on the specimen after 14 days of exposure in the carbonation chamber. Through these images a qualitative evaluation of the difference in the density of the material was performed.

When the binarized images are compared to the grayscale images, it is concluded that the material present in the outer region (green) of the specimen has a lower density, since in the gray scale, this region has become darkest. Similar results have been found in other studies [15].

Specifically in this analysis, it was not possible to detect the densification of the outer layer of the specimen, due to formation of $CaCO_3$. In the study conducted by Lydzba *et al.* [20], it was also not possible to see the carbonation front progress by X-ray microtomography images. However, Jiande *et al.* [19], who used equipment with higher voltage, were able to visualize this densification. Table 5 shows several microstructural parameters of the specimen. When observing the Fragmentation Index (FI), it can be seen that the connectivity in the outer region is greater than the central region. The fragmentation is characterized by the rupture of connectivity. The more negative the fragmentation index, the greater the connectivity of the pores, which favors the system's permeability.

The open porosity of $(14.3 \pm 0.2) \%$ attained for the global region proves to be much higher than the $(1.8 \pm 0.1) \%$ in the central region bearing diameter equal to 1 cm. These results are in accordance with the fragmentation ratios presented.

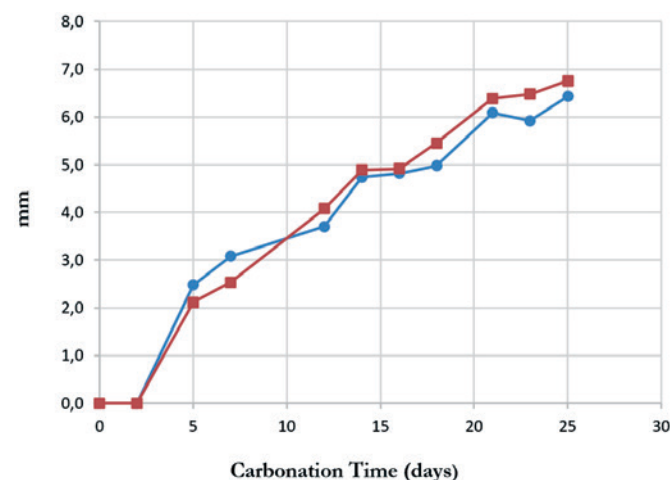


Figure 8
Carbonation front depth detected by phenolphthalein solution and caliper

4. Conclusions

It should be noted that, using the phenolphthalein solution is a very

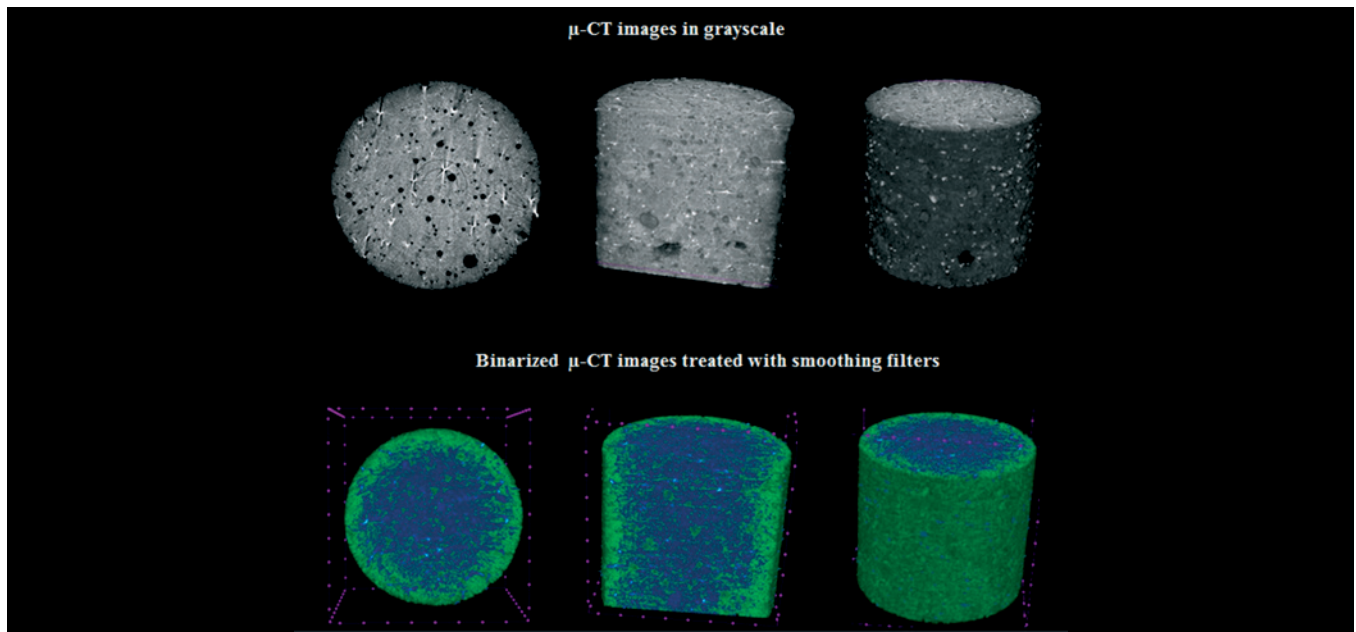


Figure 9
μ-CT images of a specimen after 14 days of exposure in the carbonation chamber

Table 5
Quantity of materials per dosage mix

Specimen region	Total porosity (%)	Open porosity (%)	Fragmentation index (μm^{-1})	Mean diameter of pores (μm)
Global	30.9 ± 0.2	14.3 ± 0.2	-0.0012 ± 0.0002	37.8 ± 0.1
Central region ($\varnothing = 1 \text{ cm}$)	19.4 ± 0.2	1.8 ± 0.1	0.0146 ± 0.0003	36.5 ± 0.1

useful method to visualize the presence of a carbonation front, as it is simple and inexpensive. However, it has not been able to provide information on the innermost regions of the specimen, where reactions of the carbonic acid (H_2CO_3) with the mortar's alkalis causing the reduction of hydrogenionic potential of the cementitious material. The results of this paper suggest that the carbonation reached depths greater than the line indicated by phenolphthalein. Additionally, the monitoring of pH variations on the cementitious composite surface proved to be a simple and efficient technique to monitor not only the carbonation front progress, but also to provide a good quantitative reference of the pH value at a certain point of the analysis.

Considering that some studies point out the possibility of depassivation occurring to reinforcements in cementitious environments, when the pH reaches values lower than 11.8, precisely determining quantitatively the pH measurements in the regions where its values are found to be above the phenolphthalein transition range, bring advantages when it seeks to guarantee the expected useful life time of structures.

The use of X-ray microtomography enabled the quantification of several microstructural parameters that are relevant to studies re-

garding the diffusion of CO_2 in the cementitious composite. The μ-CT equipment used in this study did not provide images that could visualize the densification of the outer layers of the specimen.

It is important to point out that, both methods used to monitor the pH are not able to indicate the reason why the loss of alkalinity occurred, be it by carbonation or other causes, such as the exposure to acids, for example. Thus, in cases where the factor causing the reduction of the pH is unknown, laboratory tests are required [9].

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6. References

- [1] HELENE, P. R. L., Contribuição ao estudo da corrosão em armaduras de concreto armado. Tese de Livre Docência, EPUSP, São Paulo, 1993, 231 p.
- [2] HEWLETT, P. C., Lea's Chemistry of Cement and Concrete, 5th edition, ed. Elsevier, Oxford, p. 324-334, 1998.

- [3] NEVILLE, A. M., Properties of Concrete. 5th edition. Pearson Education Limited, Harlow, England, 2012. 872 p.
- [4] BOUNY, V. B.; CAPRA, B.; LAURENS, S., A durabilidade das armaduras e do concreto de cobrimento In: OLLIVIER, J. P.; VICHOT, A. Durabilidade do Concreto: Bases Científicas para a formulação de concretos duráveis de acordo com o ambiente. Tradução OSWALDO CASCUDO e HELENA CARASEK. 1o ed. São Paulo: IBRACON, 2014. 615 p.
- [5] TAYLOR, H. F. W., Cement Chemistry. 2o edition. London: Thomas Telford Publishing, 488 p. 1997.
- [6] RIBEIRO, D. V.; SALES, A.; SOUSA, C. A. C.; CUNHA, M. P. T.; LOURENÇO, M. Z.; HELENE, P., Corrosão em Estruturas de Concreto Armado: Teoria, Controle e Métodos de Análise. 1o ed. Rio de Janeiro, Elsevier Ed. 2014; p. 272.
- [7] KROPP, J., Relations between transport characteristics and durability In: Performance Criteria for Concrete Durability. KROPP, J.; HILSDORF, H. K., RILEM Report 12. London and New York, 1995, p. 97-102.
- [8] RILEM CPC-18. Measurement of hardened concrete carbonation depth. Materials and Structures, 1988, p. 453-455.
- [9] CEN - COMITÉ EUROPÉEN DE NORMALISATION: Products and systems for the protection and repair of concrete structures - Test methods - Determination of carbonation depth in hardened concrete by the phenolphthalein method. (BS EN 14630:2006).Brussels, Belgium, 2006.
- [10] YU, M. Y.; LEE, J. Y.; CHUNG, C. W., The Application of Various Indicators for the Estimation of Carbonation and pH of Cement Based Materials. Journal of Testing and Evaluation, 2010: vol. 38, No. 5.
- [11] MCPOLIN, D. O.; BASHEER, P. A. M.; LONG, A. E., Carbonation and pH in concretes manufactured with supplementary cementitious materials. J Mater Civil Eng. 2009: 21, p.217–225.
- [12] FIGUEIREDO, E. P.; MEIRA, G. R., Corrosão das armaduras das estruturas de concreto. México: Boletim técnico ALCONPAT Internacional. v. 6. 2013.
- [13] ABNT - ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS - NBR 5733 /EB-2: Cimento Portland de alta resistência inicial. Rio de Janeiro, 1991.
- [14] ABNT - ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS - NBR 7214: Areia normal para ensaio de cimento – Especificação. Rio de Janeiro, 2012.
- [15] BERNARDES, E. E.; MAGALHÃES, A.G.; VASCONCELOS, W.L.; NUNES, E.H.M., Evaluating of the effect of varying the workability in the concrete pore structure by using X-ray microtomography. RIEM, 6 (4), August (2013), 582-597.
- [16] ABNT - ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS - NBR 7215 (Incorpora a Errata nº 1 de 1997): Cimento Portland – Determinação da resistência à compressão. Rio de Janeiro, 1996.
- [17] PU, Q.; JIANG, L.; XU, J.; XU, Y.; ZHANG, Y., Evolution of pH and chemical composition of pore solution in carbonated concrete. Construction and Building Materials, 2012: v.28, p.519–524.
- [18] PAULETTI, C.; DAL MOLIN, D. C. C.; KASMIERCZAK, C. S.; BREZEZINSKI, D. Profundidade de carbonatação em ensaios acelerados com diferentes percentuais de CO₂ In: 47^a Congresso Brasileiro do Concreto. Anais em CD. Pernambuco, 2005.
- [19] JIANDE, H.; WEI, S.; GANGHUA, P., X-ray Microtomography of the Carbonation Front Shape Evolution of Cement Mortar and Modeling of Accelerated Carbonation Reaction. Journal of Wuhan University of Technology-Mater. Sci. Ed. Apr.2013: p.303-308.
- [20] LYDZBA, D.; RAJCZAKOWSKA, M.; STEFANIUK, D., Identification of the Carbonation Zone in Concrete Using X-Ray Microtomography. Studia Geotechnica et Mechanica, Vol. XXXVI, No. 1, 2014.
- [21] DILONARDO, I.; VARHEN, C.; LEE, C.; FIGUEIREDO, A., Avaliação Metodológica da Medida de Carbonatação em Microconcretos. In: 57^o CONGRESSO BRASILEIRO DO CONCRETO, 2015, Bonito – MS. Anais... Bonito: CBC, 2015.