Proposal of a digital image analysis method for determining the carbonated front in concretes

Proposta de método de análise digital de imagens para determinação da frente carbonatada em concretos

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Abstract

Carbonation is one of the most common pathologies in concretes and the correct determination of the depth reached by this process is essential to predict the lifespan of a structure. The most common method for measuring carbonation is to spray a phenolphthalein solution onto the concrete and then measure the colorless area of the solution. Traditionally, such measurement is done manually through visual assessment. However, as this is a subjective assessment, this process is subject to errors. In order to minimize these errors, researchers have used image editing processes and measurements obtained with computerized tools. Even using these programs, the process still depends on the operator's sensitivity and judgment to determine the areas affected by carbonation. This work proposes a digital analysis with the assignment of phenolphthalein turning pH values in order to obtain the carbonated front limit with greater precision and in a semi-quantitative way. For this, three admixtures of concrete with pozzolans (fly ash and rice husk ash) were analyzed in binary and ternary mixtures submitted to natural carbonation. The proposed method proved to be accurate and efficient as an aid in reading carbonated depths.

Keywords: Carbonation. Carbonation front. Durability. Digital imagens.

Resumo

A carbonatação é uma das patologias mais comuns em concretos e a correta determinação da profundidade atingida por este processo é fundamental para a previsão da vida útil de uma estrutura. O método mais comum para a medição da carbonatação é a aspersão de uma solução de fenolftaleína no concreto e posterior medição da área incolor da solução. Tradicionalmente tal medida é feita manualmente através de avaliação visual. Porém, por se tratar de uma avaliação subjetiva, este processo está sujeito a erros. A fim de minimizar estes erros, pesquisadores têm usado processos de edição de imagens e medidas obtidas com ferramentas computadorizadas. Mesmo utilizando estes programas, o processo ainda depende da sensibilidade e do julgamento do operador para determinar as áreas atingidas pela carbonatação. Este trabalho propõe uma análise digital com a atribuição de valores de pH de viragem da fenolftaleína para obter-se com maior precisão e de forma semi-quantitativa o limite da frente carbonatada. Para tanto, foram analisados três traços de concreto com pozolanas (cinza volante e cinza de casca de arroz) em misturas binárias e ternária submetidos à carbonatação natural. O método proposto mostrou-se preciso e eficiente como auxiliar na leitura das profundidades carbonatadas.

Palavras-chave*: Carbonatação. Frente de carbonatação. Durabilidade. Imagens digitais.*

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Introduction

When designing a concrete structure, Engineers and Architects must anticipate the functional requests of the structure to withstand stresses and loads. The long-term performance of the structure also depends on the interactions of the concrete with the environment where it is inserted. Among the possible interactions, carbonation is one of the most important ones. This process consumes the alkaline fractions of cement pastes and concrete hydrates, lowering their pH and, thus, providing conditions for the start of the corrosion process of reinforced concrete steel bars, after their depassivation. The concrete will carbonate with intensity depending on the aggressiveness of the environment and the quality of the material.

Chemically, the carbonation process occurs when the carbon dioxide that penetrates the concrete combines with the calcium hydroxide or with the hydrates (silicates, aluminates) of the paste, forming phases of calcium carbonate (calcite, vaterite and aragonite, mainly) and gradually reducing the pH of the cement paste from the surface.

The continuous carbonation process of the concrete generates the so-called carbonation front, which is the theoretical limit range of the material that goes from an approximate pH of 13 to values around 9.0. This limit is diffuse and irregular, since the carbonation front gradually lowers the pH of the concrete, through the dissociation of the calcium hydroxide crystals, from the outside to the inside. The rate of the front varies according to the physical-chemical characteristics of the concrete and the level of aggressiveness of the environment. Thus, being dependent on the variation of these factors, it can be said that the carbonation of the concrete is, in general, a slow process.

When using phenolphthalein to measure the pH of the concrete, the limit indicating the carbonation front threshold may not be well defined, due to the fact that the front of the phenolphthalein indicator does not depend on the exact degree of carbonation (KARI; PUTTONEN; SKANTZ, 2014). However, this method of measuring the carbonated layer of concrete is the most widely used in researches, because it is simple, cheap and fast. Determining the line that represents the carbonation front depends on the visual accuracy and experience of the person performing the analysis of the concrete sample, which may vary with the change of operator, which can cause distortions in the reading of the carbonated depth results. This way, a method that, jointly with the use of phenolphthalein, allows the researcher to have a better definition of the carbonation front limit becomes necessary, thus achieving greater accuracy in the measurements of carbonated depth in concrete, eliminating subjective decisions in conducting the readings.

The method presented in this work stipulates values for the non-carbonated and fully carbonated areas of the concrete, so that, using *Adobe Photoshop CC* software and with simple calculations, numerical estimates are obtained to determine the turning color of the phenolphthalein in the material. This way, it is possible to obtain the line that represents the carbonation front and the average carbonated depth of the concrete in a more reliable manner.

Background theory

The pH of the concrete pore solution changes according to its carbonation degree due to the transformation of $Ca(OH)_2$ into $CaCO_3$. For Portland cement concretes, Nepomuceno and Pessoa (2004) affirm that the pH of the concrete does not fall below 12.5 in normal conditions. Gjørv (2015) points out that even for cements with a high alkaline reserve, carbonation can reduce the pH of the concrete to about 8.5.

The amount of solid calcium hydroxide in the concrete helps to maintain the high pH of the material (KARI; PUTTONEN; SKANTZ, 2014). After the calcium hydroxide is consumed in carbonation, the C-S-H decalcifies and then decomposes, decreasing the pH value. This leads to the decomposition of other phases into new compounds, causing chemical changes in the cementitious matrix and in the microstructure of the concrete.

Chang and Chen (2006) report that the limit value of the concrete pH using the phenolphthalein method is generally 9, when the degree of carbonation is 50% and pH of 7.5 when the degree of carbonation has already reached 100%. This author identified in his research three distinct regions in the concrete, according to the degree of carbonation:

(a) fully carbonated zone: degree of carbonation greater than 50% ($pH < 9.0$);

(b) partially carbonated zone: degree of carbonation between 0 and 50% ($9.0 < pH < 11.5$); and

(c) non-carbonated zone: area with no sign of carbonation ($pH > 11.5$).

Houst and Wittmann (2002) also mention the existence of the three zones listed above, highlighting that the carbonation front is found in the partially carbonated area of the concrete, with its color diffused with the use of phenolphthalein.

Šavija and Lukovic (2016) and Lu *et al.* (2018) claim that the carbonation front can go beyond the limit visually defined by the spraying of phenolphthalein, considering that the turning of this substance occurs at a pH around 9.0 ~ 10.0 and the partially carbonated zone, with a diffuse limit and difficult to define visually, may be ahead of this line. However, Chinchón-Payá, Andrade and Chinchón (2016), Ashraf (2016) and Mobin Raj and Muthupriya (2016), among others, attest to the efficiency of the use of phenolphthalein. For Broomfield (1997) and Hussain, Bhunia and Singh (2017), phenolphthalein is the most used, reliable and convenient method of visual assessment of carbonation in cementitious materials, in addition to being simple to perform (CHOI *et al*., 2017; LIU *et al*., 2018; LU *et al*., 2018). Herrera, Kinrade and Catalan (2015) emphasize that, despite its deficiencies, the visual method is still the most practical and inexpensive for monitoring carbonation. Cui *et al.* (2019) compared results of carbonated depth in concretes with the use of X-ray tomography and tests with spraying of phenolphthalein solution and concluded that the two tests show similar results. However, the same authors point out that phenolphthalein has limitations in determining partially carbonated areas due to the diffuse coloring that the concrete presents in these areas, an opinion shared by Phung *et al.* (2015).

European standards, such as EN 14630 (BRITISH…, 2006) and CPC-18 (RILEM, 1988), establish the methodology to be used for the measurement of carbonated depth in concretes using the phenolphthalein solution (SILVA *et al*., 2009), which attests to the feasibility of this process.

There is no general consensus on the turning pH of phenolphthalein for studies on cementitious materials. Some authors define a fixed value, others cite intervals within which the turning occurs. Table 1 shows the pH values presented by some authors.

It can be inferred that at pH values below 10, phenolphthalein is colorless and at pH above this limit, it presents a color similar to purple or crimson. However, it is very difficult to check the pH of the concrete for the exact determination of the carbonation front limit. Traditionally, concrete carbonation research using phenolphthalein uses visual determination of the carbonated front limit and its measurement with a pachymeter. For Choi *et al.* (2017), manual measurements of carbonated depth using a pachymeter can result in measurements with low reproducibility, according to the person taking the measurements. According to Dilonardo *et al.* (2015), manual pachymeter measurement is a rough approximation that lacks accuracy.

The fact that manual measurements from the visual assessment of the carbonated zone bring implicit precision errors should not be under-rated in research in the area. Rigo, Oliveira and Possan (2018) states that the difficulty observed in certain models of prediction of carbonation in concretes is due to errors in measuring the carbonated depth that end up interfering in the results of the simulations. For Herrera, Kinrade and Catalan (2015), the difficulty in determining the carbonation front limit in the visual assessment method, leads to a significant underestimation of the carbonated depth.

Houst and Wittmann (2002) point out that mortars with water/binder (w/b) ratio of 0.4 to 0.5, for example, do not have a well-defined carbonation front, but a decreasing range of carbonate content, an opinion shared by Ruan and Pan (2012) and Bao *et al.* (2018). Thus, since the carbonation front has a diffuse threshold, mainly due to the heterogeneities of the material (BAO *et al*., 2018), the researcher can be induced to make a subjective decision regarding this limit (CHOI *et al*., 2017). It becomes useful and necessary, then, to adopt an image editing program for the correct assessment and separation of the carbonated area from the non-carbonated area.

Table 1 – **Phenolphthalein turning values**

Author	Phenolphthalein pH Turning Values
Chang and Chen (2006)	9.0 – 11.5
Chinchón-Payá, Andrade and Chinchón (2016)	9.0 – 10.5
Ashraf (2016)	9.0
Mobin Raj and Muthupriya (2016)	9.0 – 11.5
Rezagholilou, Papadakis and Nikraz (2017)	10
Liu *et al*. (2017)	10

The issue of sustainability has been present for many years in research on concrete technology, through the incorporation of agro-industrial residues in the lines, such as fly ash (FA) and rice husk ash (RHA). Such pozzolanic additions improve some characteristics of the concrete, such as the refinement of the microstructure, resistance to compression at advanced ages and resistance to chemical attacks. However, a factor to be considered when using pozzolanic additions to the concrete is the change in the color of the material. This color change leads to variation in the tonality of the concrete when sprayed with solutions such as phenolphthalein and thymolphthalein, visual markers that change color according to the pH of the material. Therefore, the visual assessment of the carbonation front limit with these markers may suffer distortions.

Dalla Lana (2005) developed the *COTA.LSP* routine that made it possible to use the *AutoCAD* program and the *Excel* spreadsheet to determine with high accuracy and greater number of readings at carbonated depth in concrete specimens with accuracy that would hardly be achieved with the traditional use of the pachymeter. However, the difficulty of determining the carbonation front limit persisted, considering that the verification of this threshold was still done visually and depended on the operator's perception.

In a study by Villain, Thiery and Platret (2007), the authors note that, to determine the depth of carbonation, different methods are proposed, however most of them are only qualitative. In the analysis of the carbonated depth with the use of phenolphthalein, for example, the position of the carbonation front threshold is evaluated visually (qualitatively), without a numerical (quantitative) limitation of the carbonated edge in the areas where the color of the sprinkled concrete with the solution it is more diffuse.

Choi *et al.* (2017) mention that the adoption of an image processing technique to measure the carbonation of concrete can provide readings more efficiently and more accurately.

These authors developed an image processing technique to determine the carbonated regions of the concrete using the RGB[1] color standard in the process. However, since none of the three colors in the primary palette of this pattern resemble the color of non-carbonated concrete with phenolphthalein, green was used, which is complementary to purple in the RGB pattern to determine the boundary of the carbonation front. The process proposed by the authors automatically detects the intensity of the green color in the image, associating it to a value (zero or one) captured by an algorithm that analyzes the image on a gray scale. However, the authors do not mention the differences in lighting and shading that can occur from one image to another. It should be noted that the aforementioned method is qualitative and indirect, since the color of the non-carbonated area is given by the mixture of two primary and complementary colors, offering no numerical parameter for defining the carbonation front limit.

Dilonardo *et al.* (2015) propose a method of determining the carbonated area in mortars by editing images using the software *Photoshop CS 5.1* by *Adobe Systems*, in which, using the program tools, the carbonated area is separated from non-carbonated by the similarity of colors of adjacent pixels selected in each study zone. This method is easy to apply, presenting more reliable results in the delimitation of areas than the traditional visual method. However, this procedure also does not offer numerical values that can resolve any doubts regarding the accuracy of the selected area.

Matherials and methods

For the development of the image evaluation method and determination of the carbonation front in concrete, 10x20 cm cylindrical specimens of concrete mixtures molded by Vaghetti (1999) were used, which were sawn in half, resulting in in 10x10 cm cylindrical cylindrical specimens and subjected to natural indoor carbonation for 20 years. To evaluate the proposed method two mixtures with binary additions with 25% FA and 25% RHA were opted, replacing cement, respectively, and one mixture with a ternary admixture of 10% FA and 15% RHA replacing cement. Such mixtures were chosen to evaluate the method in concretes where the additions produce changes in the color of the material, which may hinder the visual assessment of the carbonation front limit with the spray of phenolphthalein. It should be noted that there was no more cylindrical specimens of the reference concrete (without mineral additions) to perform the tests.

Table 2 shows the chemical characteristics of the Portland cement (CP V ARI) and ashes used by Vaghetti (1999), obtained by X-Ray Fluorescence.

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[1] RGB is the abbreviation for an additive color system where Red, Green and Blue are combined in order to reproduce a wide chromatic spectrum (WIKIPEDIA, 2020).

Table 3 presents the physical properties of the cement and pozzolans used in the molding of the specimens.

Figure 1 shows the particle size distribution of the cementitious materials used.

Figure 2 shows the particle size curves of the natural aggregates used in the manufacture of the studied concretes.

The addition of the pozzolans in the concretes was carried out at replacement levels of equal mass of Portland Cement. The binary mixtures were identified as *FA* and *RHA* for mixtures with fly ash and rice husk ash, respectively, and the ternary feature was called *FA+RHA*. The w/b ratio was 0.45, with the necessary corrections in the water content of each mix to maintain the same workability between the mixtures. The proportioning of materials in the concretes was performed as shown in Table 4.

After the exposure period, the cylindrical specimens were ruptured diametrically, sprayed with a 1% solution of phenolphthalein, and the ruptured face was photographed. The digital images obtained were then analyzed by the methods described in this work. One specimen of each mix was analyzed in comparing methods.

Table 2 - **Chemical characterization of cement and ashes**

Compounds	CP V ARI (%)	FA (%)	RHA (%)
SiO_2	20.27	65.50	92.24
Al_2O_3	4.64	25.89	0.25
Fe_2O_3	3.36	3.15	0.59
CaO	60.86	0.34	0.78
MgO	3.66	1.53	0.48
SO_3	2.69	-	-
Na_2O	0.09	0.21	0.03
K_2O	0.85	1.98	2.12

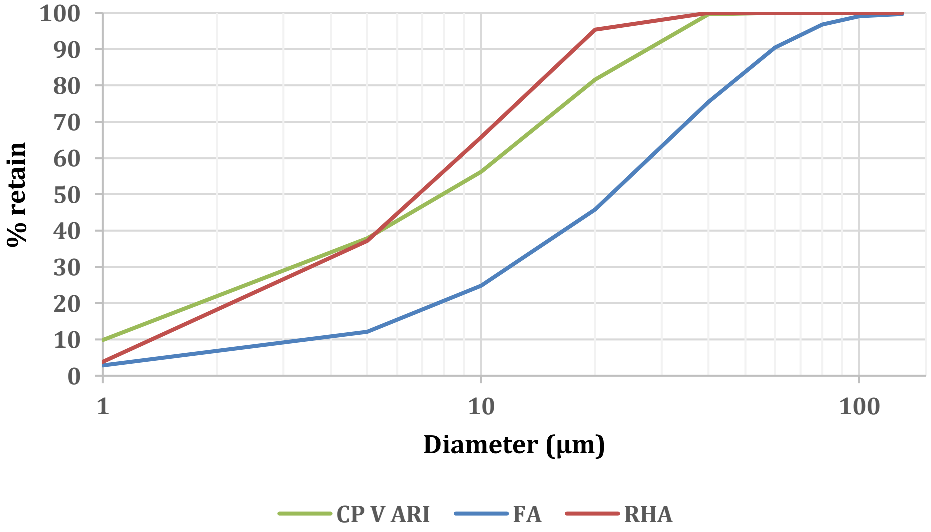
Source: adapted from Vaghetti (1999).

Table 3 - **Physical properties of the cement and pozzolans**

Physical properties	CP V	FA	RHA
Residue #0.075 (%)	0.28	2.11	3.00
Residue #0.045 (%)	1.80	13.20	0.20
Specific Surface (m^2/g)	0.463	3.91	18.90
Density (kg/dm^3)	3.14	2.19	2.16

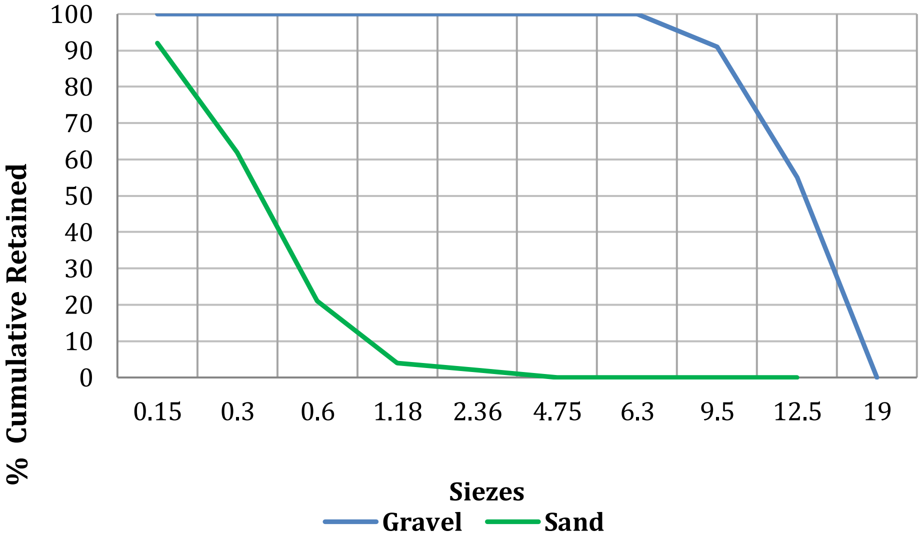
Source: adapted from Vaghetti (1999).

Figure 1 - **Particle size distribution of the cementitious materials**



Source: adapted from Vaghetti (1999).

Figure 2 - **Granulometry of the aggregates**



Source: adapted from Vaghetti (1999).

Table 4 - **Quantity of materials per m³ of concrete**

Mixture	Cement (kg/m³)	FA (kg/m³)	RHA (kg/m³)	Sand (kg/m³)	Coarse aggregate (kg/m³)	Water (kg/m³)
FA	290	97	-	683	1054	170
RHA	290	-	97	680	1058	166
FA+RHA	291	39	58	686	1058	165

Source: adapted from Vaghetti (1999).

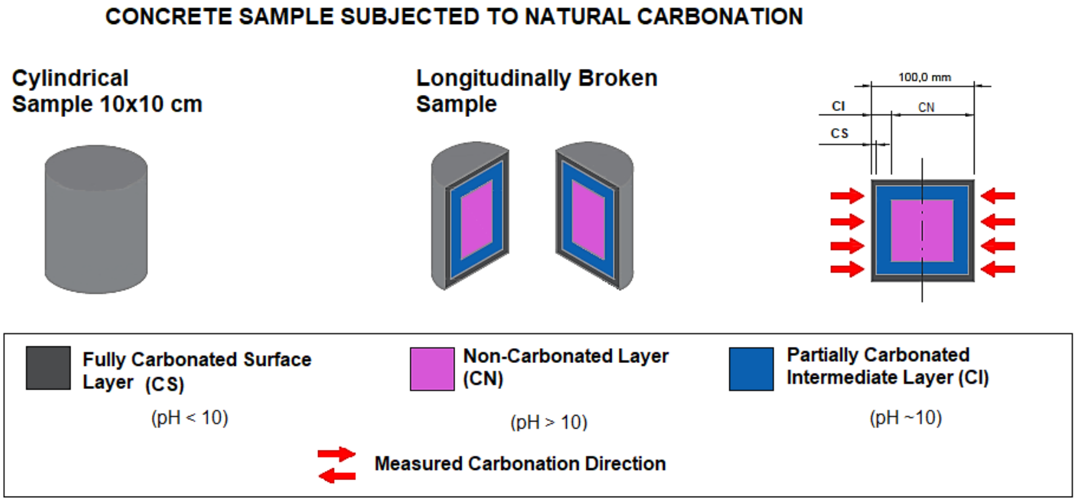
Due to the heterogeneities, the evaluation of the carbonation front in concrete is more complex than in mortars. For example, coarse aggregates of different sizes present in concrete should be disregarded. These aggregates, although they do not directly influence the advancement of the carbonation front, can interfere with the measurement of the carbonated depth, making the line that defines the carbonated limit more irregular and inducing evaluation errors.

Figure 3 shows schematically the areas observed with the phenolphthalein spray and the considered direction of the carbonated depth.

In the representation of Figure 3, the area defined as intermediate layer (CI) is partially carbonated, as defined by Chang and Chen (2006). This region, which has diffuse coloring after spraying the phenolphthalein solution, can have a thickness of a fraction of a millimeter, up to a few centimeters, depending on the characteristics of the concrete and the environment, as well as the exposure time. It is in this region that the carbonation front is located, that is, the threshold between carbonated and non-carbonated concrete. Using only visual acuity, the correct determination of this limit is subjective and can lead to different readings from one operator to another, either with the use of a pachymeter or with computerized measurement tools. The method proposed here aims to provide a routine with the aid of an image analysis program that minimizes the potential for error in these measurements and determines with the best possible approximation the true line that defines the carbonation front.

It was decided to adopt the carbonation direction perpendicular to the cast for reading the depths, as this was the one used in the research by Vaghetti (1999), for which the cylindrical specimens studied here were molded, so the values can be compared in future works. It should be noted that the carbonation direction considered in this work is unidimensional, that is, carbonate depth measurements were taken from two opposite sides of the cylindrical specimens. In order to avoid the interference of carbonation on adjacent perpendicular sides, the measurement of depths on the considered sides was always initiated with a spacing of the top and bottom of the cylindrical specimens equal to the greatest carbonated depth observed on the adjacent face.

Figure 3 - **Representation of the carbonated depth measurement direction in the broken specimens**



Description of the image analysis method

In order to develop an easy-to-apply methodology, without the need for technical deepening in the area of digital design and image editing, the method described here was based on basic precepts and simple routines, applicable to any research that uses chemical markers with color change to determine the depth of a phenomenon in concrete, such as carbonation.

It should be noted that in this work, the Portuguese version of the *Photoshop CC* software was used, so that in the description of the method, the nomenclature of the tools used was maintained in this language, in order to avoid erroneous translations of the aforementioned routines.

Color pattern used

In this research, the *Photoshop CC* program by *Adobe Systems* was used. In this software there is a tool for analyzing the pixel color of the image that works by decomposing the colors according to two patterns: RGB (Red, Green, Blue), which decomposes any color tone according to the red, green and blue tones present in the studied pixel of the figure; and CMYK (Cyan, Magenta, Yellow, Black), which decomposes the color of the studied pixel into cyan, magenta, yellow and black, according to the percentage of each color in the color composition of the target pixel.

The RGB and CMYK color systems are called, respectively, the *additive system* and the *subtractive system*, according to their interactions with light (Figure 4).

Thus, it is possible to analyze a certain pixel and decompose its color into the two patterns mentioned, according to the “quantity” of the colors of the chosen pattern that form the color of the pixel.

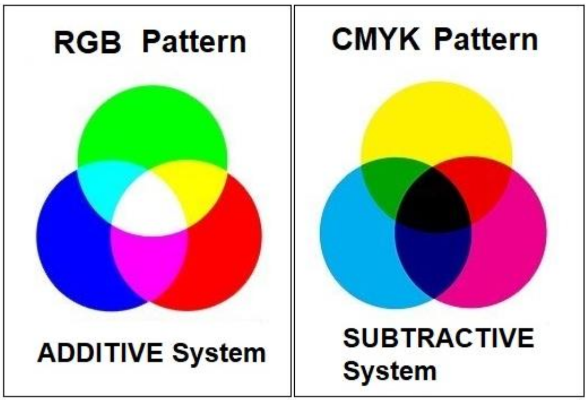
In this work, the basic parameters described by Dilonardo *et al*. (2015) were used, adding to these the assignment of percentage values of *magenta* in the CMYK color standard, taking as a basis a phenolphthalein turning value with pH = 10 and reference values for the same color taken from the analyzed image itself. Thus, in addition to the qualitative data referring to the color tone of the figure, semi-quantitative reference values for the more precise delimitation of the carbonation front limit were taken. According to Houst and Wittmann (2002), there is no simple correlation between measures of carbonated depth determined with phenolphthalein and data of carbonate contents in a studied concrete range. However, with the values attributed by the method described here, it is possible to achieve not only more accurate measures of carbonation, but the achievement of carbonated bands that are beyond the carbonation front determined by the color of the concrete after the spraying of the phenolphthalein solution.

In the CMYK system, it is observed that the magenta color is the closest to the color of the non-carbonated concrete sprinkled with phenolphthalein. The magenta staining of phenolphthalein at pH above 10 is the result of the optical absorption of the molecular indicator at a wavelength of approximately 550 nm (LIU *et* *al*., 2017). This way, the percentage of the magenta color in any pixel can be obtained directly in *Photoshop*, through the window "*Seletor de Cores (Cor do Primeiro Plano)*". Strictly speaking, any color of a pattern can be used as a reference for the intensity of the coloring of non-carbonated concrete. The magenta color was chosen due to its similarity in tone to purple or crimson, obtaining a direct visual relationship in the perception of non-carbonated areas.

It is important to mention that the concrete itself may have different shades of color, depending on the nature and type or content of its compounds and the presence or not of mineral additions. Broomfield (1997) affirms that some aggregates may confuse readings with phenolphthalein: some concrete mixtures are dark colored, making it difficult to visually check the carbonated zone. Herrera, Kinrade and Catalan (2015) point out that the carbonated mortar has slightly lighter shades of gray than the non-carbonated mortar.

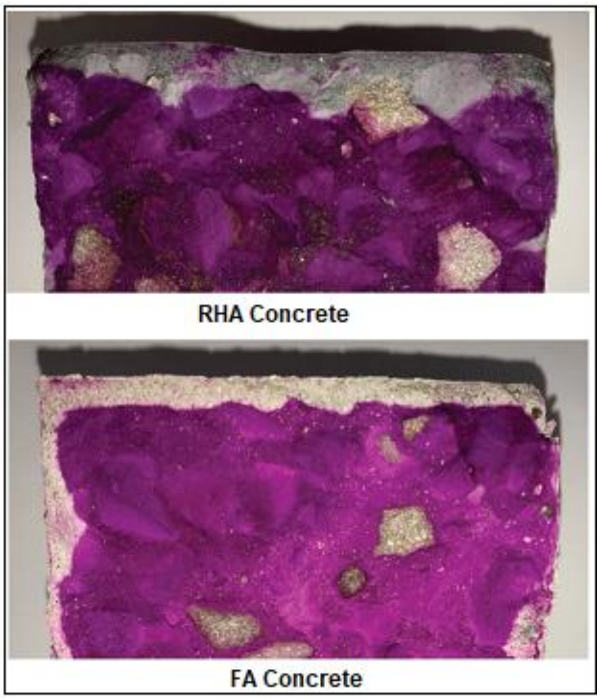
A concrete with the addition of RHA, for example, has a darker color than a concrete without additions or with the addition of FA. This characteristic color of each concrete ends up influencing the final shade of the non-carbonated material sprinkled with phenolphthalein. Thus, it can be said that a non-carbonated concrete with the addition of RHA sprinkled with phenolphthalein will present a different purple color than a concrete in the same conditions without additions or with FA, for example (Figure 5).

Figure 4 – **RGB and CMYK color standards**



Source: adapted from Sala7design (2016).

Figure 5 – **Comparison of the color of concrete sprayed with phenolphthalein**



Thus, in order to evaluate the percentage of magenta of the pixels of a given area in the concrete photograph, before everything, this value from fully carbonated and totally non-carbonated reference points within the same image must be taken. This way, the operator avoids having to work with a single standard percentage, as each photograph has its color tone differences compared to other images. This difference is due to changes in the lighting of each photograph (HERRERA; KINRADE; CATALAN, 2015) and because of the change in the natural tone of the concrete from one sample to another. It should be noted, then, that for each photograph analyzed, it is necessary to take these references. This idea is reinforced by Choi *et al.* (2017) when stating that there is no method for determining a limit value for the turning of phenolphthalein that can be applied generically to any image, due to the differences from one image to another.

Description of the procedure for using the *Photoshop CC* software

After opening the photograph of the broken face of the cylindrical specimens in *Photoshop CC*, using the "*Seleção Rápida*" tool, the edges of the cylindrical specimens in order to increase the contrast between the background and the concrete boundary (Figures 6 to 8) were cut.

The area to be studied was enlarged, carbonated or not, and with the "*Conta Gotas*" tool and the "*Seletor de Cores (Cor do Primeiro Plano)*" window open, the chosen pixel was clicked on, noting the *magenta* percentage value (Figures 9 to 11).

Figure 6 – **Original photograph of the cylindrical specimens opened in *Photoshop CC***

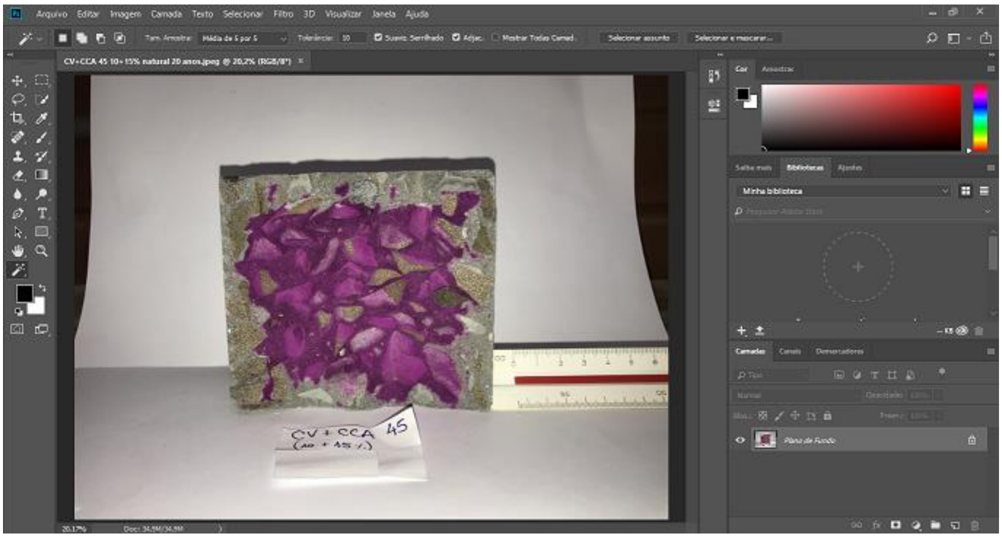


Figure 7 – **Definition of the edges of the cylindrical specimens limit**

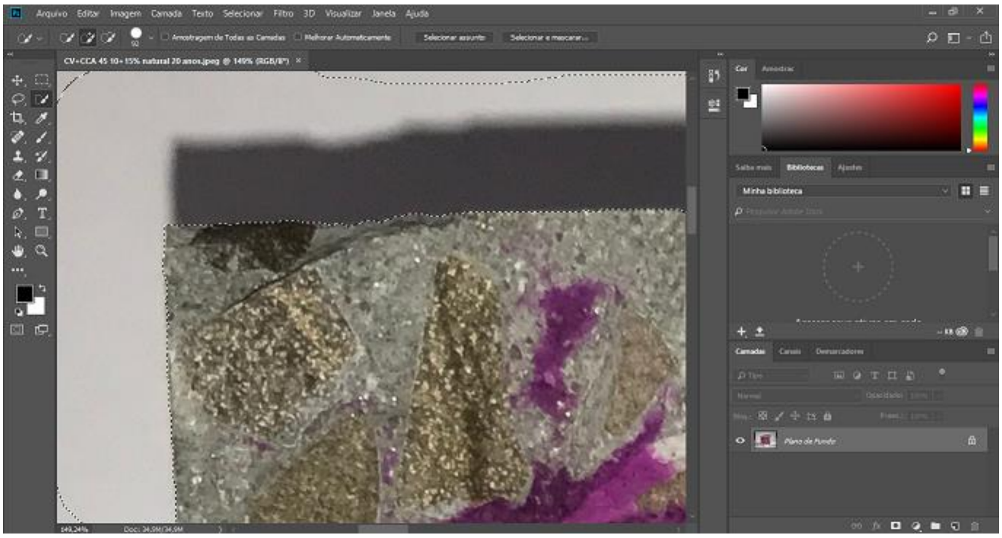


Figure 8 – **Photograph of the cylindrical specimens with the cut-out edges**

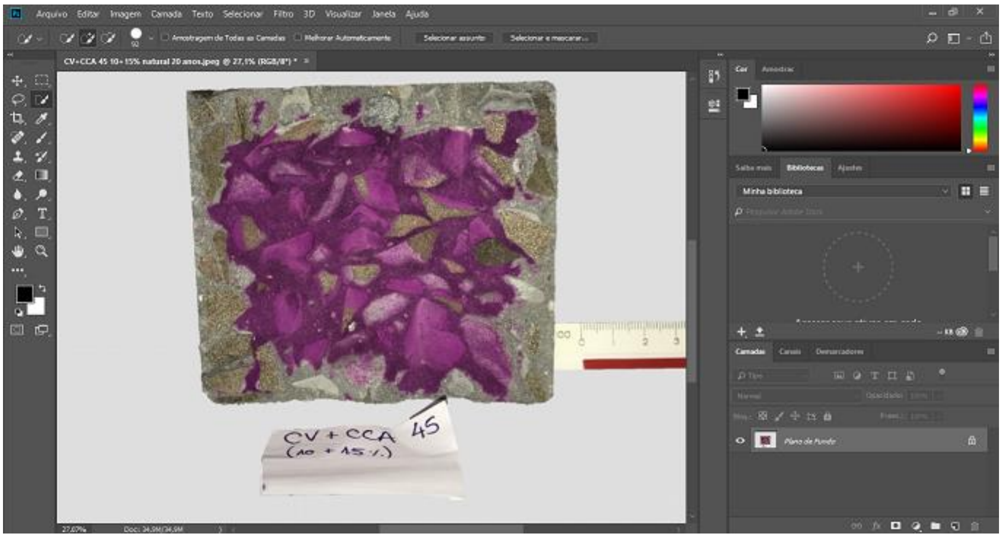


Figure 9 – **Part of the cylindrical specimens where there is a completely carbonated area and another completely non-carbonated area**

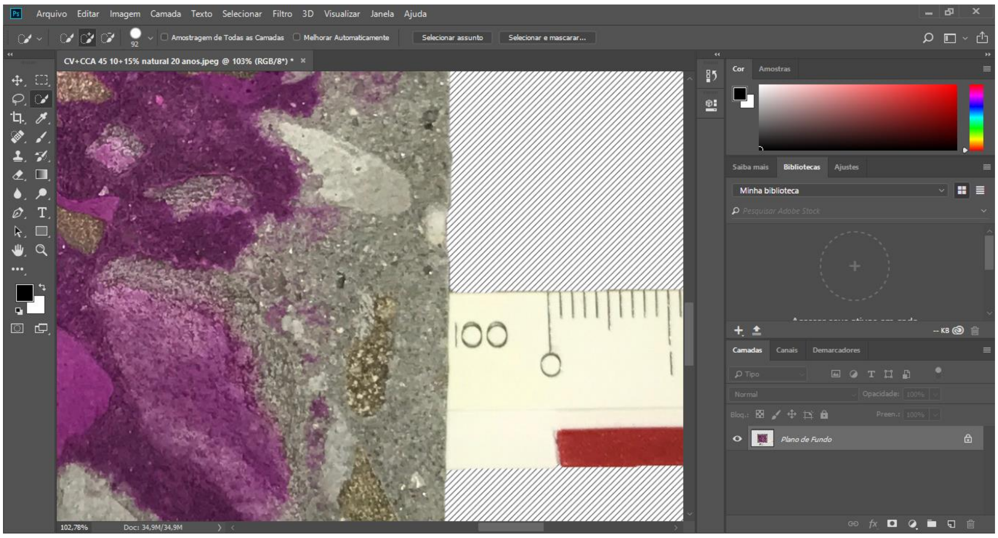
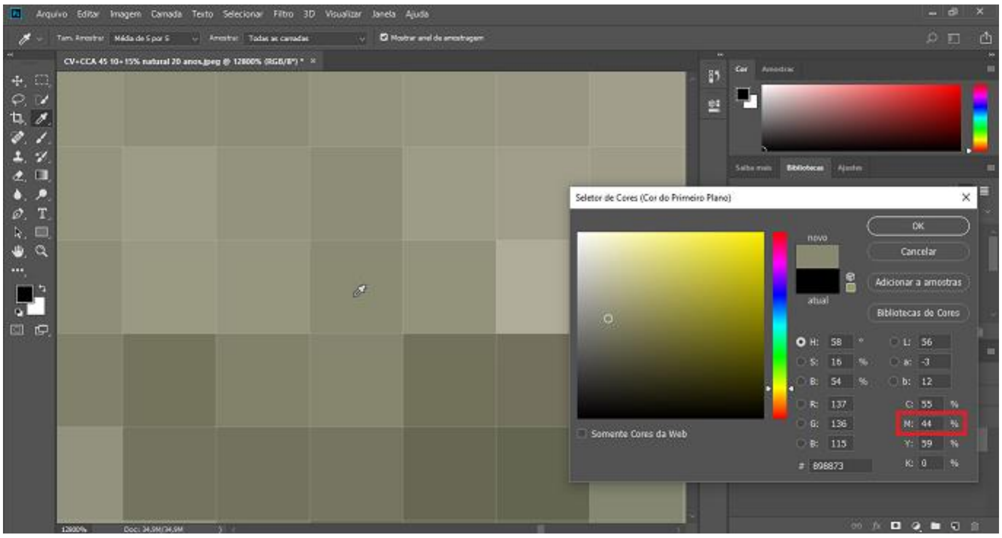


Figure 10 – **Magenta percentage (highlighted) of a pixel in a fully carbonated area**



Tam. Amostra: Média de 5 por 5

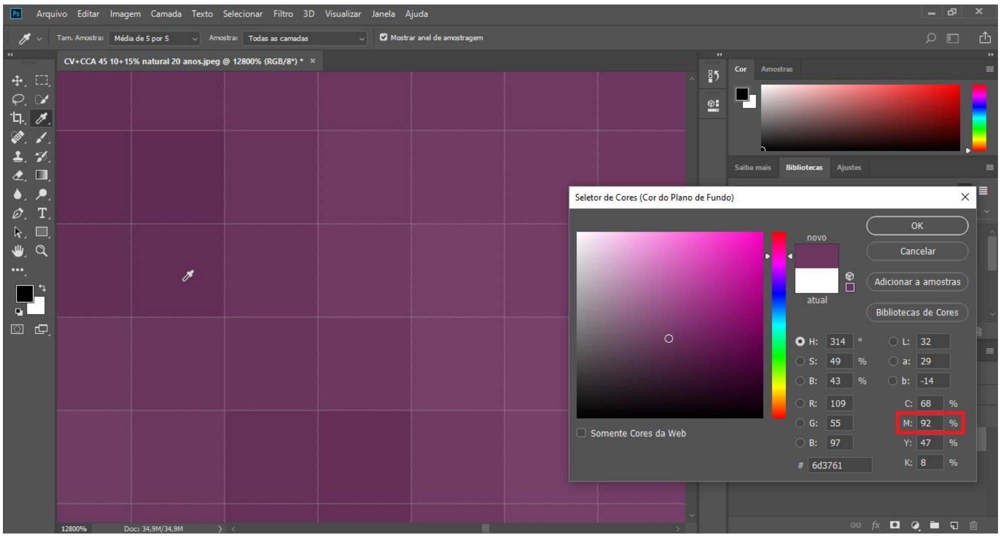
Amostra: Todas as camadas

☑ Mostrar anel de amostragem

● H: 58 °
○ S: 16 %
○ B: 54 %
○ R: 137
○ G: 136
○ B: 115
898873

○ L: 56
○ a: -3
○ b: 12
C: 55 %
M: 44 %
Y: 59 %
K: 0 %

Figure 11 – **Magenta percentage (highlighted) of a pixel in a totally non-carbonated area**



Tam. Amostra: Média de 5 por 5

Amostra: Todas as camadas

☑ Mostrar anel de amostragem

CV+CCA 45 10+15% natural 20 anos.jpeg @ 12800% (RGB/8*) *

Seletor de Cores (Cor do Plano de Fundo)

● H: 314 °
○ S: 49 %
○ B: 43 %
○ R: 109
○ G: 55
○ B: 97
○ L: 32
○ a: 29
○ b: -14
C: 68 %
M: 92 %
Y: 47 %
K: 8 %
6d3761

☐ Somente Cores da Web

In this research, at least five points were taken for areas that were visually totally carbonated and another five points for areas that were not completely carbonated in different parts of the cylindrical specimens. Points always close to the visual limit of the carbonation front were tried to be captured, to average the magenta values for each situation in the cylindrical specimens under study. Here, it is worth mentioning the statement by Broomfield (1997), that the advance of the carbonation front reduces the pH of the concrete in a transition area of 6 to 8 mm between the *fully carbonated* zone and the *non-carbonated* zone. Within this range, according to the author, the pH varies and the color of phenolphthalein change.

It was assumed, then, that the *fully carbonated* area should have a pH of 8.0 and the *fully non-carbonated* area should have a pH of 12, for simplification purposes. Therefore, the midpoint between the average values of magenta for the carbonated and non-carbonated areas was found. Thus, the midpoint of these values indicated the magenta value for the phenolphthalein turning color, that is, *a pH around 10*. With this magenta value and using the "*Conta Gotas*" tool with the "*Seletor de Cores (Cor do Primeiro Plano)*" activated, it was possible to find the concrete changing color area (phenolphthalein turning color) in the image to find the magenta values that corresponded to the midpoint found. Supposing, for example, that for carbonated pixels, the values of 38%, 39%, 40% and 53% of magenta (mean of 42.2%, pH = 8) were found, and, for non-carbonated pixels, values of 92%, 91%, 91%, 93%, 96% of magenta (average of 92.6%, pH = 12), were found that the midpoint between these values shows 67.4% of magenta, which corresponded, in this cylindrical specimens, to the turning point of phenolphthalein (pH = 10).

This way, for each cylindrical specimens studied, a specific color gradation for the concrete was obtained, whose percentages of magenta were linked to a theoretical pH of the material (Figure 12). Figure 13 shows the phenolphthalein turning area in the concrete and the magenta percentage of one pixel in this region.

Assuming this value of magenta as being that which represents pixels with an approximate pH of 10, it can be said that there is the limit of the carbonation front. In this work, a tolerance of 5% more or less in the magenta value of the midpoint was considered when selecting the studied areas.

With the magenta value for the phenolphthalein turning defined, using the "*Varinha Mágica*" tool, pixels with a magenta value close to the average value are selected, automatically selecting an area around this pixel (Figure 14).

Figure 12 – **Color grading that relates the percentage of magenta to the pH of the FA + RHA concrete**

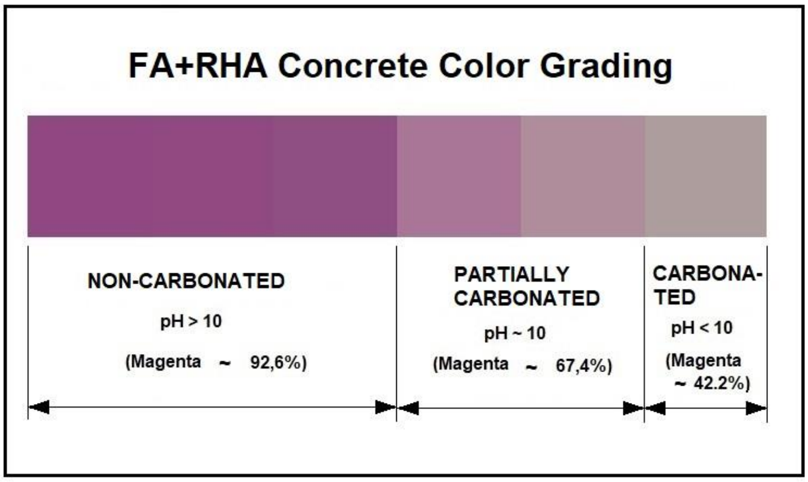
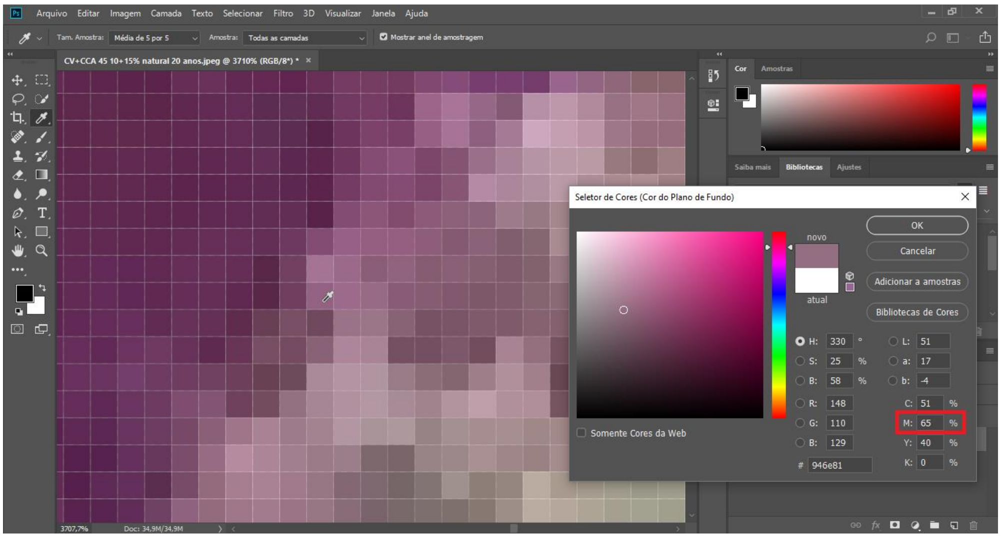


Figure 13 – **Magnification of the phenolphthalein turning area, with the magenta percentage of one pixel (highlighted)**



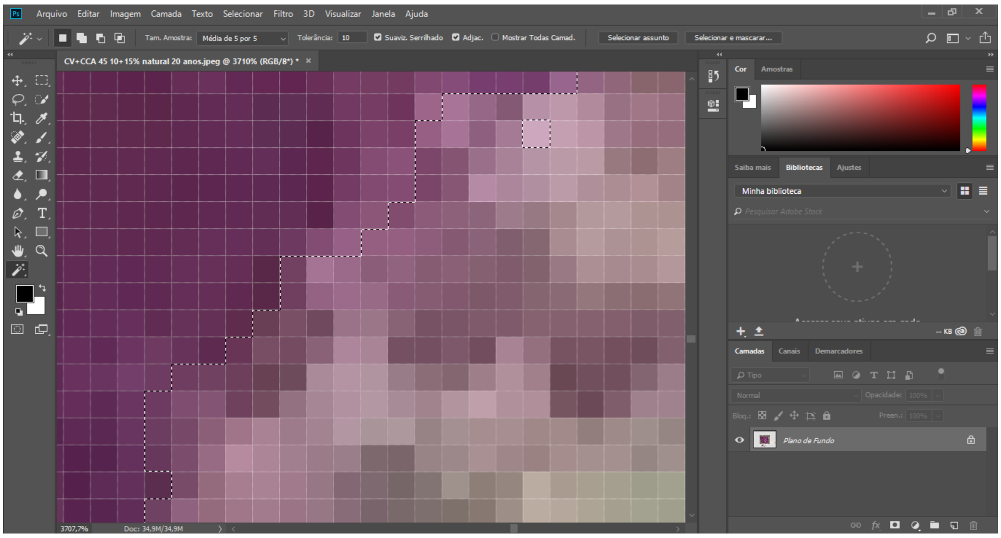
Tam. Amostra: Média de 5 por 5
Amostra: Todas as camadas
☑ Mostrar anel de amostragem

Seletor de Cores (Cor do Plano de Fundo)

☐ Somente Cores da Web

● H: 330 °
○ S: 25 %
○ B: 58 %
○ R: 148
○ G: 110
○ B: 129
○ L: 51
○ a: 17
○ b: -4
C: 51 %
M: 65 %
Y: 40 %
K: 0 %
\# 946e81

Figure 14 – **Limit of the selected area taking as a reference a pixel with a value close to the average found**



Tam. Amostra: Média de 5 por 5
Tolerância: 10
☑ Suaviz. Serrilhado
☑ Adjac.
☐ Mostrar Todas Camad.

Then, with the "*Conta Gotas*" tool and the color selection window open, it was verified whether the limit of the selected area was within the range of magenta values stipulated for the phenolphthalein turning (Figure 15).

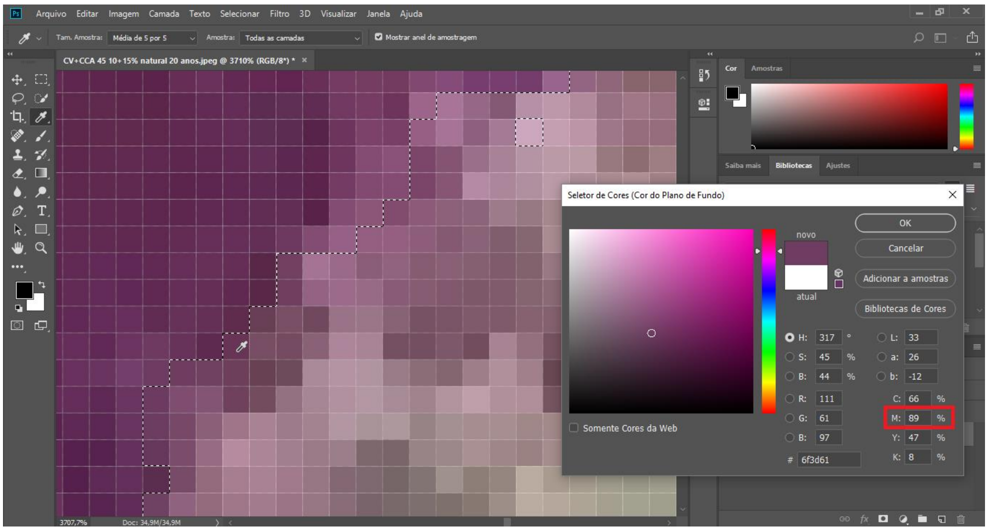
If the pixels of the selected limit line were outside the stipulated range, above or below, the selection was undone and the procedure was repeated, selecting a reference pixel closer to the defined value and/or decreasing or increasing the "*Tamanho da Amostra*" in the screen top menu (Figure 16).

With the command "*Adicionar à Seleção*" or "*Subtrair da Seleção*", the entire selected area was adjusted according to the limit value stipulated for magenta at the carbonation front threshold (Figure 17).

This way, having adjusted the magenta percentage limits corresponding to the phenolphthalein turning, the software would automatically delimit in the image the line that defined the carbonation front in the cylindrical specimens.

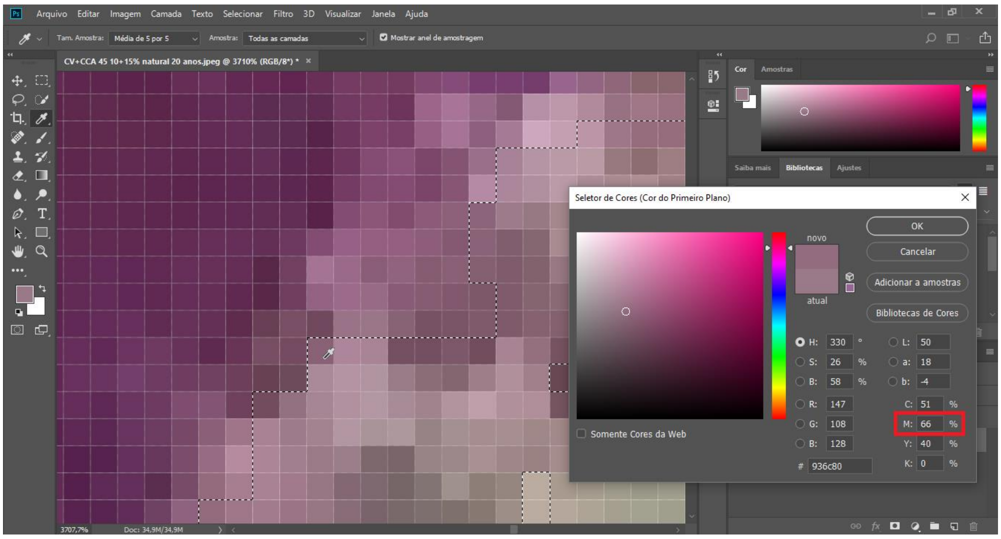
After selecting the entire carbonated area to be studied, the selection was inverted ("*Selecionar Inverso*" command, right-clicking on the selected area) and the non-carbonated area was deleted. The resulting figure shows only the carbonated area of the cylindrical specimens, where the concrete had a pH value above 10 (Figure 18).

Figure 15 – **Magenta percentage (highlighted) of a pixel at the limit of the selected area, with a value well above the stipulated for the turning**



Tam. Amostra: Média de 5 por 5
Amostra: Todas as camadas
☑ Mostrar anel de amostragem
CV+CCA 45 10+15% natural 20 anos.jpeg @ 3710% (RGB/8*) *
Seletor de Cores (Cor do Plano de Fundo)
H: 317 °
S: 45 %
B: 44 %
R: 111
G: 61
B: 97
\# 6f3d61
L: 33
a: 26
b: -12
C: 66 %
M: 89 %
Y: 47 %
K: 8 %
☐ Somente Cores da Web
3707,7% Doc: 34,9M/34,9M

Figure 16 – **New limit selected, with magenta value (highlighted) within the range stipulated for the phenolphthalein turning**



Tam. Amostra: Média de 5 por 5
Amostra: Todas as camadas
☑ Mostrar anel de amostragem
CV+CCA 45 10+15% natural 20 anos.jpeg @ 3710% (RGB/8*) *
Seletor de Cores (Cor do Primeiro Plano)
H: 330 °
S: 26 %
B: 58 %
R: 147
G: 108
B: 128
\# 936c80
L: 50
a: 18
b: -4
C: 51 %
M: 66 %
Y: 40 %
K: 0 %
☐ Somente Cores da Web
3707,7% Doc: 34,9M/34,9M

Figure 17 – **Selection of the entire carbonated area of the cylindrical specimens**

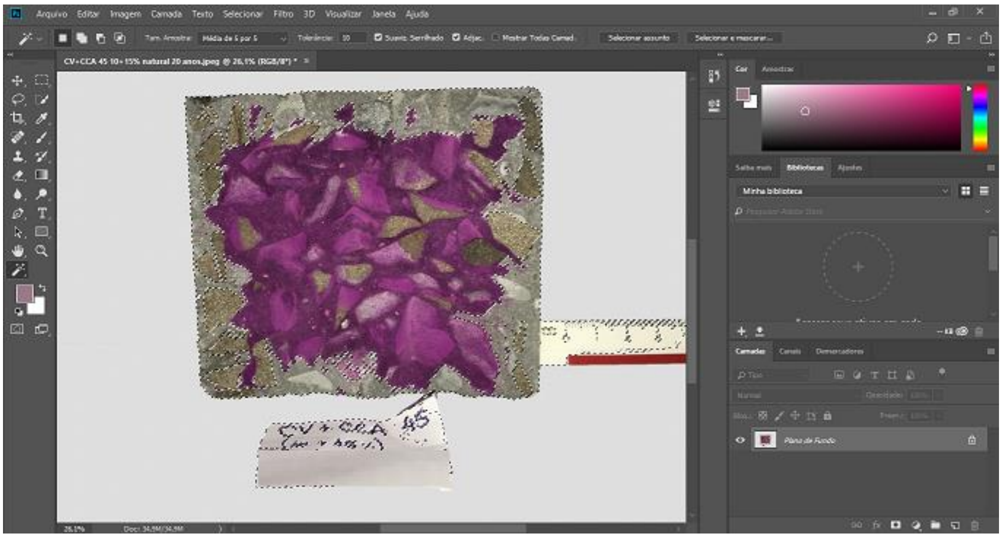
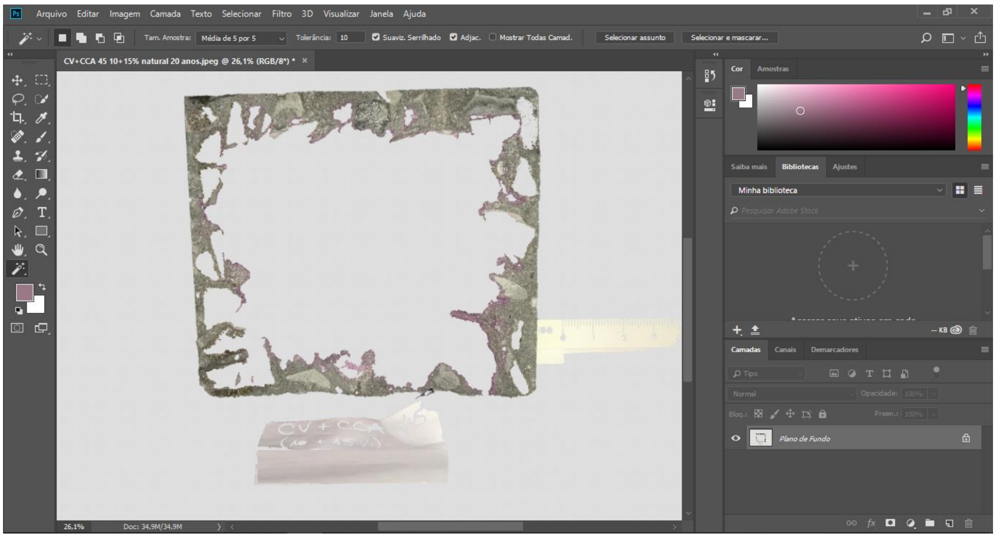


Figure 18 – **Final photograph of the cylindrical specimens, where there was only the carbonated area of the concrete, the sample identification and the scale**



With this procedure, the objective was to select, in a semi-quantitative way, only the carbonated area of the concrete, with pH below the theoretical turning value of phenolphthalein. It was verified, enlarging the image of the cylindrical specimens after the treatment with *Photoshop*, that the limit of the carbonation front was well defined (Figure 19), facilitating the determination of the carbonated depth in *AutoCAD*.

In Figure 19, the diagonal lines on the white background indicate that that part of the figure, corresponding to the area with a pH above 10, were deleted.

After the application of the procedure, the final edited photo, showing only the *carbonated mask* of the cylindrical specimens, was opened in the *AutoCAD* software for application of the *COTA.LSP* routine, developed and described by Dalla Lana (2005) (Figure 20). The *COTA.LSP* routine could provide carbonated depth readings every 1 mm, for example, for each side of the studied face of the cylindrical specimens. The readings collected generated a chart that was opened through a *Microsoft Excel* spreadsheet to calculate the average carbonated depth.

Thus, in summary, the specimens' image treatment follows the sequence:

(a) with the photograph opened in *Photoshop CC*, the edges of the specimen (command "*Seleção Rápida*") was cut;

(b) verification of the percentage of *magenta* in non-carbonated and fully carbonated areas of the specimen ("*Conta Gotas*" and "*Seletor de Cores (Cor do Primeiro Plano)*" commands);

(c) assigning pH values: 12.0 for non-carbonated area and 8.0 for fully carbonated area;

(d) calculating the percentage of *magenta* in pixels with a pH value of 10.0 (phenolphthalein turning),

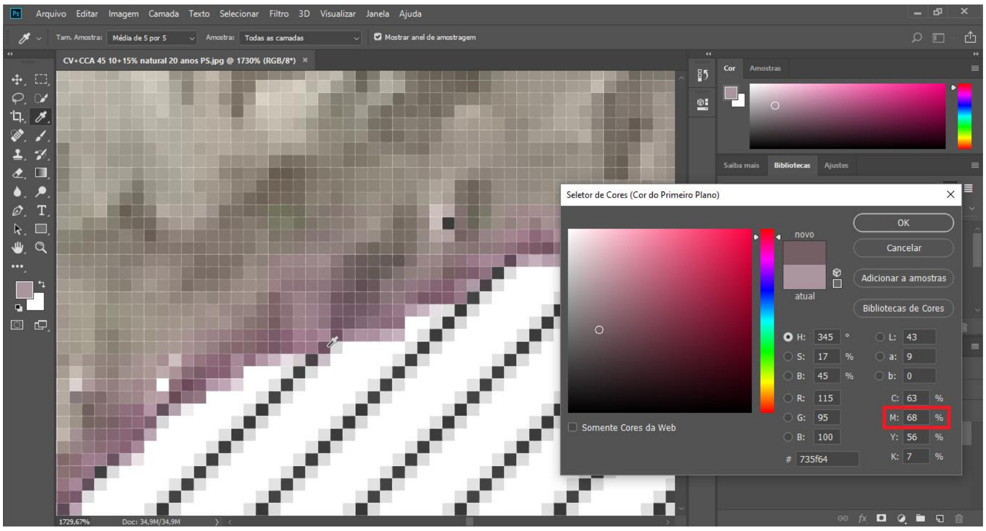
(e) selecting areas with pixels in the image that have magenta percentages close to the phenolphthalein turning ("*Conta Gotas*" and "*Seletor de Cores (Cor do Primeiro Plano)*" and "*Varinha Mágica*" commands);

(f) selecting the entire carbonated area of the concrete (command "*Adicionar à Seleção*" or "*Subtrair da Seleção*");

(g) deleting the non-carbonated area of the concrete (command "*Selecionar Inverso*"); and

(h) opening the photograph in *AutoCAD* software and apply the *COTA.LSP* routine, as described by Dalla Lana (2005).

Figure 19 - **Magnification of the limit of the carbonated zone of the cylindrical specimens, with the percentage of magenta (in the highlight) of a pixel at the cut threshold**



Tam. Amostra: Média de 5 por 5
Amostra: Todas as camadas
☑ Mostrar anel de amostragem

CV+CCA 45 10+15% natural 20 anos PS.jpg @ 1730% (RGB/8*)

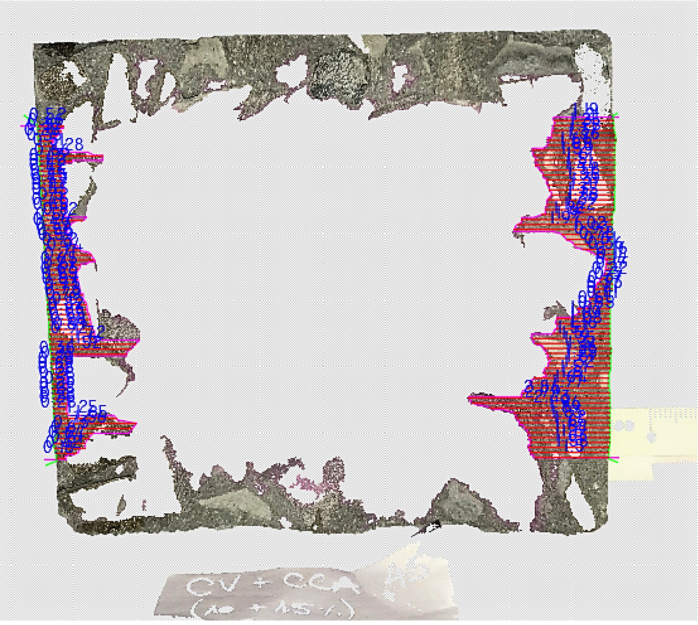
Seletor de Cores (Cor do Primeiro Plano)

☐ Somente Cores da Web

● H:	345	°	○ L:	43	
○ S:	17	%	○ a:	9	
○ B:	45	%	○ b:	0	
○ R:	115		C:	63	%
○ G:	95		M:	68	%
○ B:	100		Y:	56	%
#	735f64		K:	7	%

1729,67% Doc: 34,9M/34,9M

Figure 20 - **Digital photograph containing the carbonated mask after treatment in *AutoCAD* and *COTA.LSP* routine**



Experimental results and discussion

Figures 21, 22 and 23 show the edited images of the cylindrical specimens, where only the carbonated areas of the concrete appear. These images were opened in the *AutoCAD* software to apply the *COTA.LSP* routine and obtain readings. Afterwards, the generated spreadsheet was imported into *Excel* for statistical treatment and to obtain the average value of the carbonated depth of each concrete, with calculation of the standard deviation and variation coefficient, taking as a maximum limit 30%, calculated with a minimum number of 30 measurements per specimen.

Figure 21 – **Edited face of the FA concrete**

Figure 22 – **Edited face of the RHA concrete**

Figure 23 – **Edited face of the FA+RHA concrete**

In all concretes, it was noticed that in some parts of the carbonation front line there was an area where the concrete had a slightly pink color, reminiscent of the crimson color of the phenolphthalein solution in partially carbonated areas. Since the images were treated with the described method, the operator can be sure that these areas, although slightly colored, had a pH below 10, thus being considered carbonated. If the measurement method was purely visual, that is, with a certain degree of subjectivity in the judgment, the operator could disregard these areas, which would result in underrated carbonated depth readings. It should be noted that, in image editing softwares, the non-use of a numerical criterion for the selection of areas with different shades of colors can also result in the under- or over-dimensioning of the carbonated area, depending on the previous calibration of the tool used.

Throughout this research it was observed that the percentage of magenta in the carbonated areas of the studied cylindrical specimens varied from a minimum value of 15.5% in the binary FA mixture, to a maximum value of 67.3% in the binary RHA admixture. The great variation in the coloring of the concretes justifies the use of an image editing software in the process, as well as the taking of the reference color in each image under study.

In the figures presented, it can be seen that some elements of the image, such as the concrete's identification label, the scale, and some gravels on the broken face appear sometimes whole or cut out. This is due to the lighting changes of each photograph, as well as the different shades of the concrete portions taken as a reference for the magenta percentage of the carbonated and non-carbonated areas to be cut. According to these references, the software automatically cuts out elements with a hue outside the determined limit. However, it is important to note that such differences do not change in obtaining the carbonated depth in the mortar. Indeed, such differences emphasize the need, as already mentioned, to take the reference percentages of magenta within the studied image itself, with no single value for all photographs.

The carbonated depth values obtained in this study with the proposed method (*Photoshop + AutoCAD/COTA.LSP*) are shown in Table 5.

Although the specimens of this research were exposed to carbonation for a long period, it was observed that all concretes presented carbonation below 10.0 mm. Among the studied mixtures, the binary admixture with FA showed the smallest carbonate depth. It is known that the carbonation of concrete is closely linked to the calcium hydroxide content of the paste, that is, the smaller the amount of CH, the greater the carbonated depth. Considering that pozzolans are added to concrete to consume free CH from the paste, forming new phases of hydrated calcium silicate in the pozzolanic reaction, it can be inferred that concretes with more reactive pozzolans will result in greater carbonation depths. As RHA is thinner and therefore more reactive than FA, the binary mix with RHA provides greater carbonated depth than the binary mix with FA.

The ternary mix presented a carbonated depth 0.63 mm greater than the binary mix with RHA. Although the difference is small, these results are explained by the synergistic effect provided by the two pozzolans used in FA+RHA. According to Isaia, Gastaldini and Moraes (2003), Mala *et al*. (2013) and De Schutter (2016), ternary admixtures tend to provide more intense pozzolanic reactions, which leads to a higher consumption of CH in the paste and, therefore, greater susceptibility to carbonation.

The observation of the images after the process shows great irregularity in the path of the line that represents the carbonation front. The tortuosity of this line is influenced by the heterogeneity of the concrete (presence of coarse aggregates), microstructural characteristics of the material, type and content of additions, calcium hydroxide content and environmental factors where the cylindrical specimens were stored (carbon dioxide content, relative humidity). It was then possible to visualize how irregular the carbonation front in the concrete can be and the consequent difficulty in determining this line and its depth with the naked eye with the simple use of a pachymeter.

In order to compare the method proposed in this work (*Photoshop+AutoCAD/COTA.LSP*) with two other methods for obtaining the carbonated depth in concrete (*manual measurement with a pachymeter* and *measurement using AutoCAD/COTA.LSP*), consider the points A, B, C and D, as presented in a generic way in Figure 24.

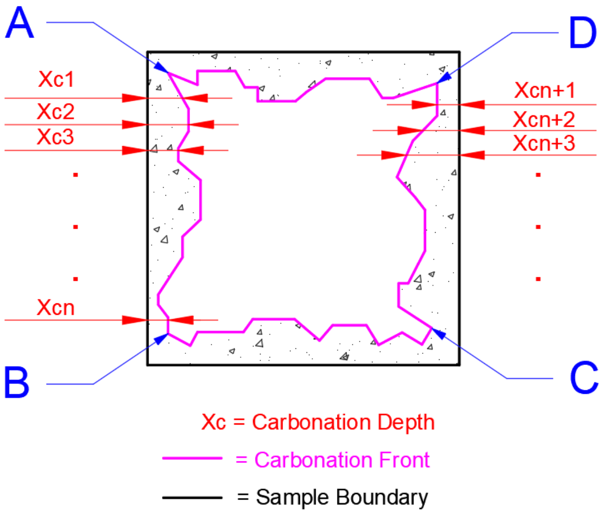
In Figure 24, the sinuous lines AB and CD, in magenta, represent the limits of the carbonation front on the left and right sides of a specimen, so that the carbonated depths (Xc) are measured perpendicular to the concrete molding way. According to Bao *et al*. (2018), the tracing of the line that represents the carbonation limit in concrete is irregular, presenting maximums and minimums, characterized by the random distribution of depths throughout the sample.

In manual measurement with a pachymeter, values are taken with readings obtained every 10.0 mm, where the carbonated front limit is determined by the operator's visual accuracy. The measurement of carbonation depth with the *AutoCAD* software associated with the *COTA.LSP* routine, as described by Dalla Lana (2005), is characterized by obtaining measures 1.0 mm apart from each other, after the delimitation, through the drawing of a line, from the front carbonated in a photograph of the broken specimen. In this method, the line that defines the carbonation front boundary also depends on the operator's visual analysis.

Table 5 - **Average carbonated depth obtained in each studied concrete with the proposed image evaluation method**

Mixture	**Natural carbonation**
	Carbonation Depth (mm)
FA	7.89
RHA	9.05
FA+RHA	9.68

Figure 24 - **Schematic representation of the points that define the AB and CD delineations of the carbonation front in a specimen**



Figures 25, 26 and 27 show, respectively, the application of each of the three methods in the admixtures FA, RHA and FA+RHA. In the comparisons presented here, the sinuous lines AB and CD, which represent the limit of the carbonation front, were folded over a two-axis system, and the average carbonate depth of each sample was calculated from the measurements obtained with each method under study.

Figure 25 - **Representation of carbonation front contours and carbonation depth measurements with the methods under study for the FA mix**

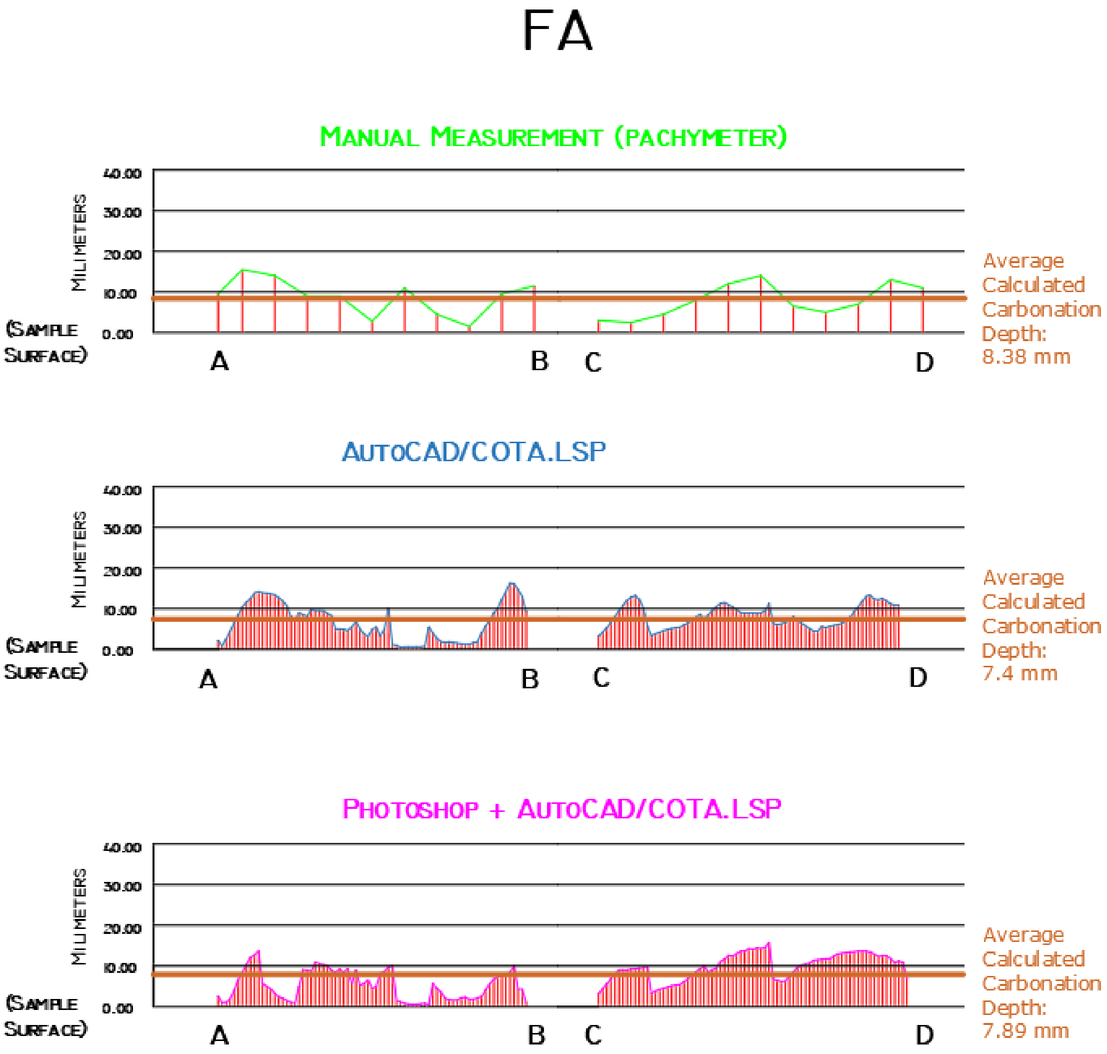


Figure 26 - **Representation of carbonation front contours and carbonation depth measurements with the methods under study for the RHA mix**

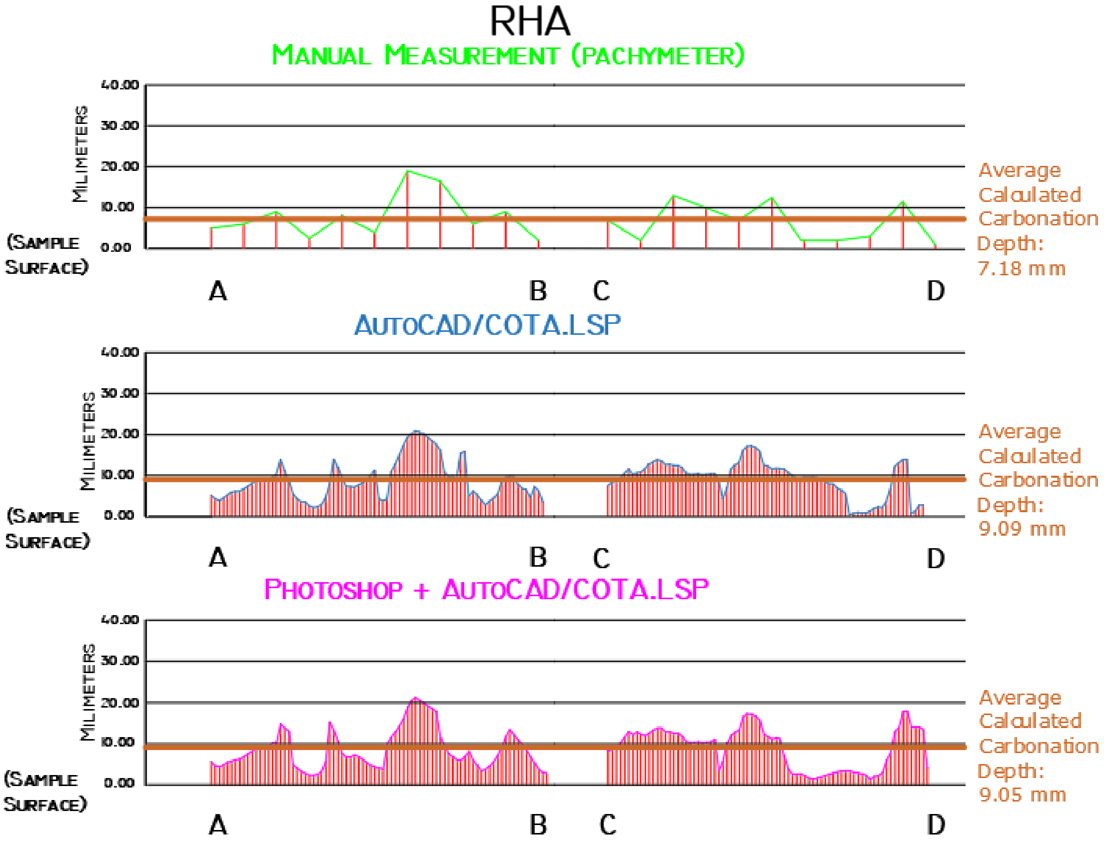
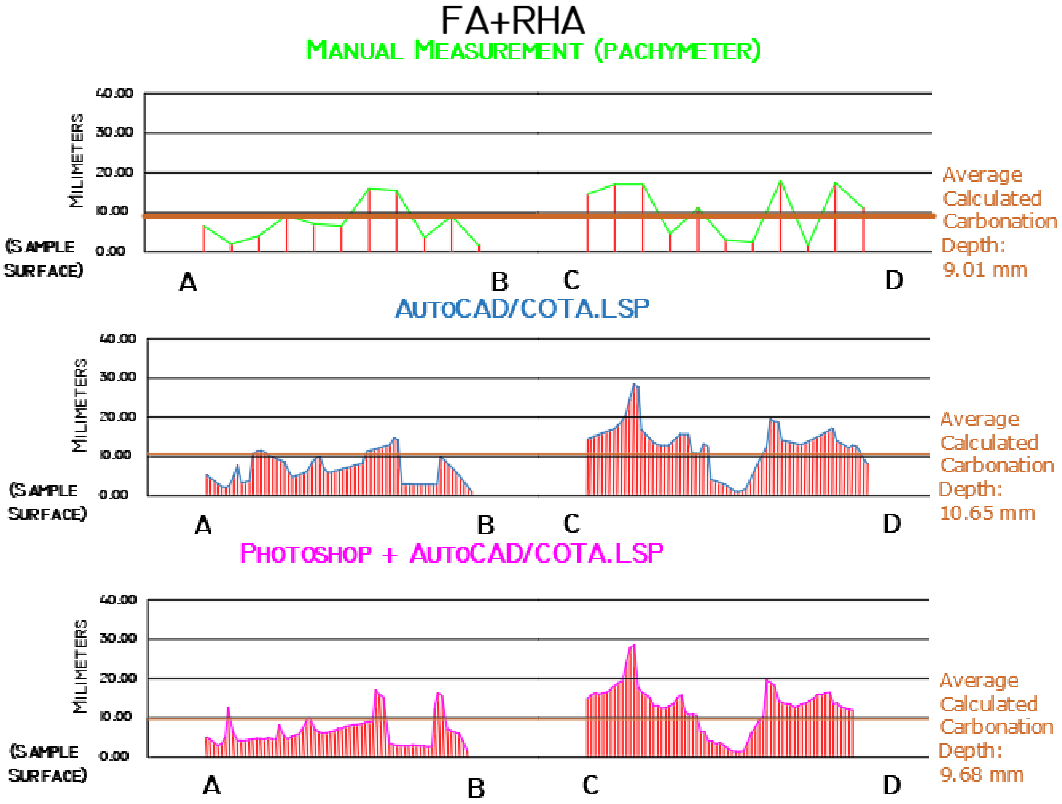


Figure 27 - **Representation of carbonation front contours and carbonation depth measurements with the methods under study for the FA+RHA mix**

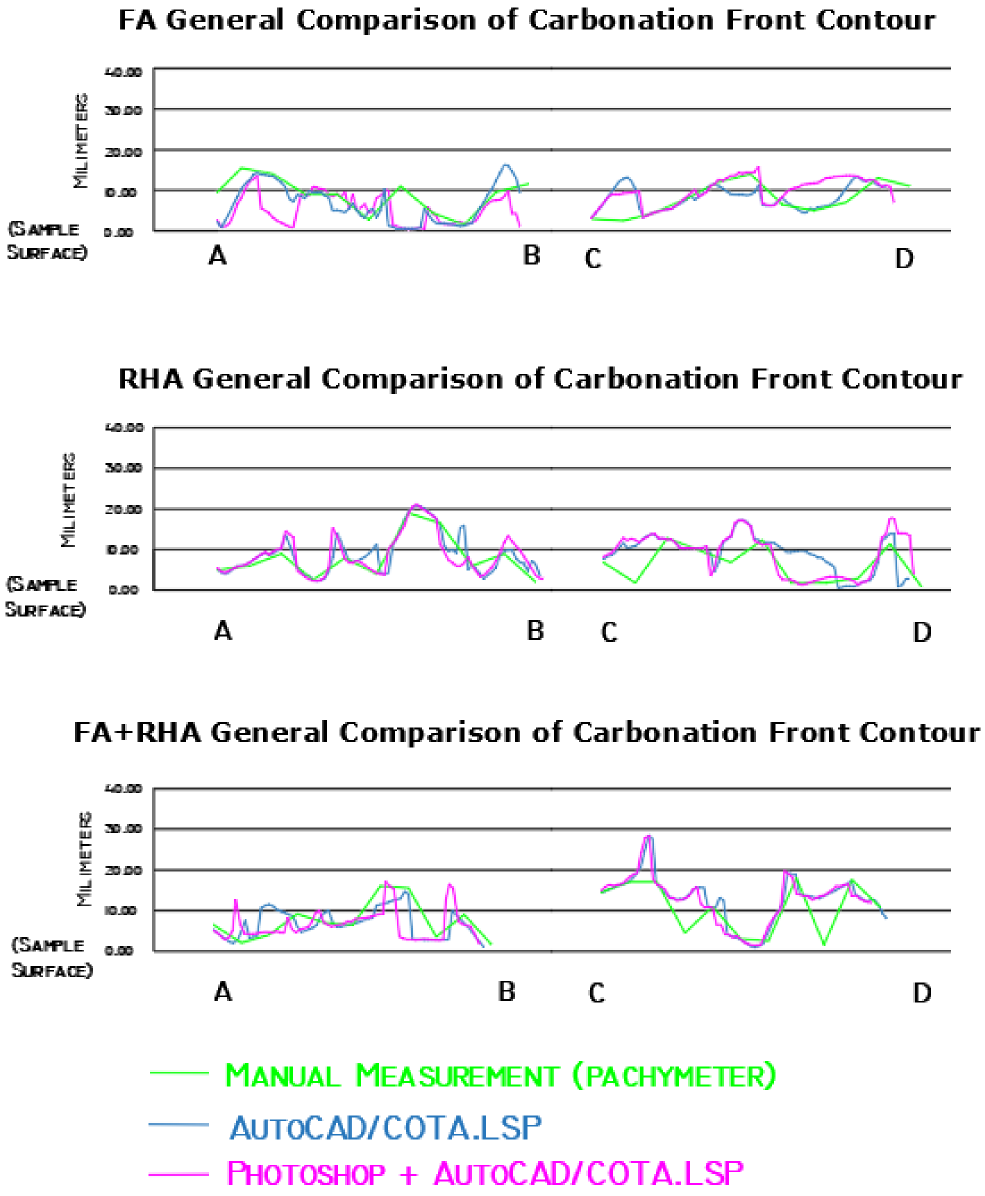


By observing Figures 25, 26 and 27, it is possible to notice that the methods that use *AutoCAD* associated with the *COTA.LSP* routine provide more detailed contours of the phenolphthalein turn tracing on the carbonation front, as well as a greater number of readings to obtain the average carbonated depth of each mix. The average carbonation values for each mixture presented in the figures differ, mainly between the *manual method with a pachymeter* and the two methods that use the *AutoCAD/COTA.LSP* tools. Between the *AutoCAD/COTA.LSP* and *Photoshop + Autocad/COTA.LSP* methods, the average carbonated depths differences were small in the three mixtures, ranging from 0.04 mm in RHA to 0.97 mm in FA+RHA.

For better visualization of the differences in the carbonation front tracing obtained with each method, Figure 28 presents the three profiles of each studied mixtures.

In concretes with low permeability and, consequently, small carbonated depths, the more efficient determination of the carbonation front can make a very small difference, in the order of fractions of a millimeter, which does not affect the durability of the material with any significance, but it can make a big difference in the measured absolute value. In conventional concretes, with w/b above 0.45, the carbonated depths tend to be more accentuated and the exact determination of the carbonation front limit can result in a difference of a few millimeters, strongly influencing the carbonation forecast calculation in long term.

Figure 28 - **Plot of the carbonation front for each mix with the compared methods**



Conclusions

The carbonation front in concrete is diffuse and, in some cases, difficult to assess visually, even with the use of markers such as phenolphthalein. Such difficulty can compromise the correct determination of the carbonated depth in concrete. An attempt was made to develop a method for analyzing images of carbonated concrete samples that would help in the exact determination of the line that represents the carbonation front, providing more reliable results of the material's carbonation depth.

The method presented is complementary for the determination of the carbonation front in concretes and mortars, presenting a routine that takes into account the theoretical pH of the material, promoting greater precision in the identification of the carbonated threshold. This methodology allows the visualization of the carbonation limit line, based on the percentage of a reference color (magenta) in the pixels located in the zone of diffuse coloring of the carbonation front.

The proposed process allows areas of concrete where there is a slightly pink color, indicating partial carbonation of the material, to be analyzed through the numerical pH value assigned to the phenolphthalein turning, so that they are considered or discarded in the final calculation, releasing the operator to make subjective decisions based on some particular visual perception.

With the image treatment suggested, the discrepancies observed in carbonated depth measurements read by different operators in the same sample can be reduced, giving more reliability to the values obtained in the researches.

The observed carbonate depths are small, considering the 20-year exposure period. Such results can be attributed to the densification of the concrete microstructure provided by the pozzolanic additions. Among the studied admixtures, carbonation was higher in mixtures with RHA, as this, being thinner, is more reactive than FA, consuming the alkaline reserve of the paste with greater intensity in the pozzolanic reaction. It can be observed that the ternary and binary admixtures with RHA presented values very close to carbonate depth. The synergistic effect of FA with RHA provided the ternary mix with the greatest depth of carbonation read in the research.

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