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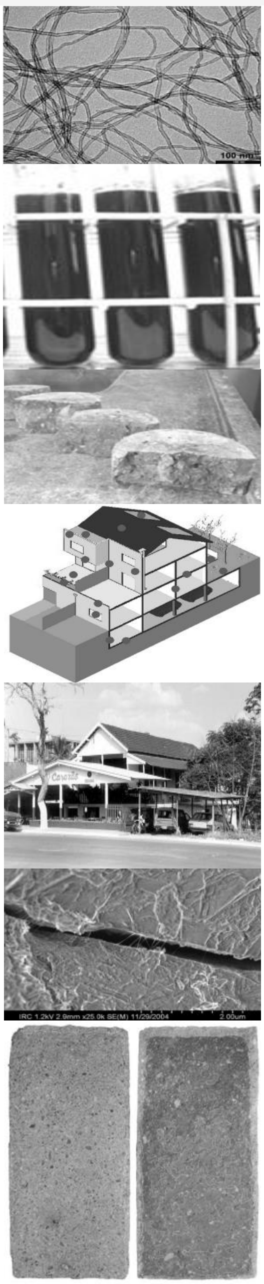

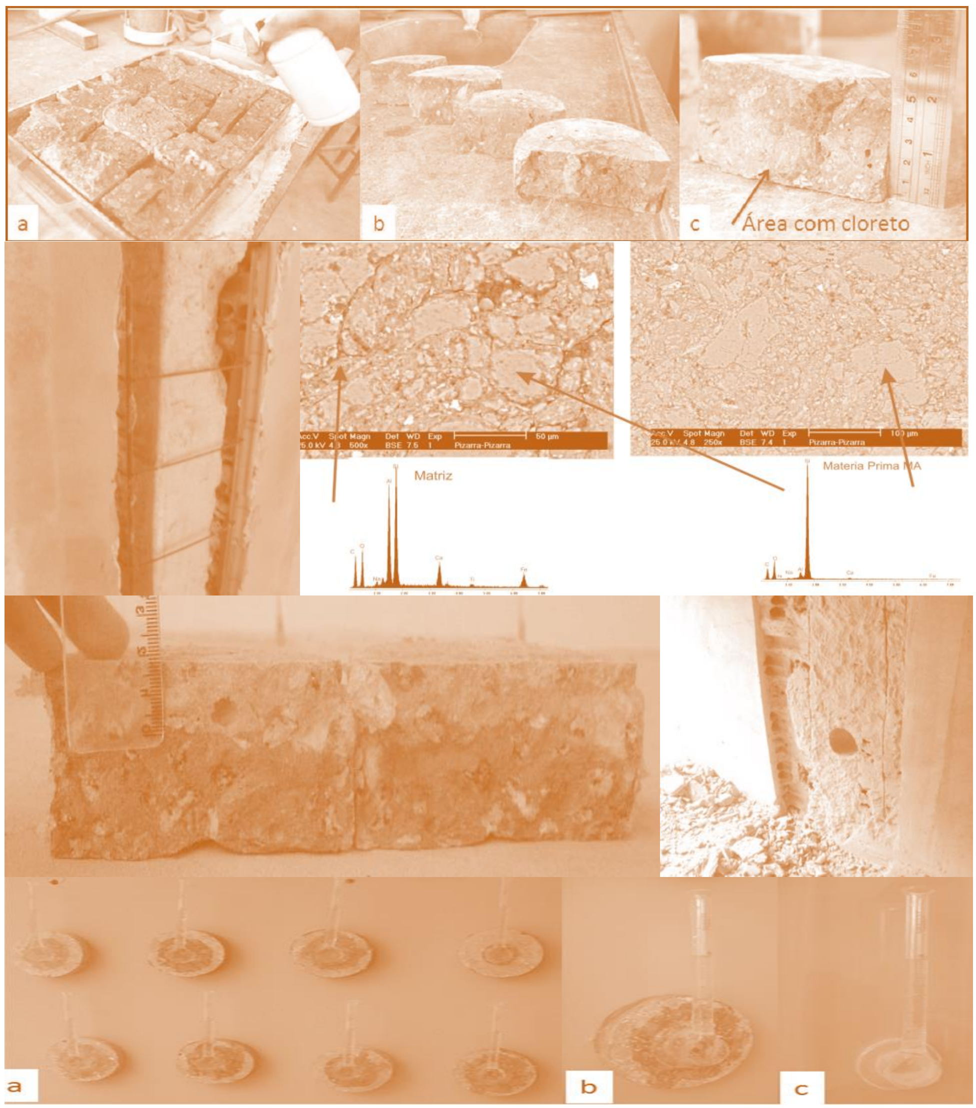

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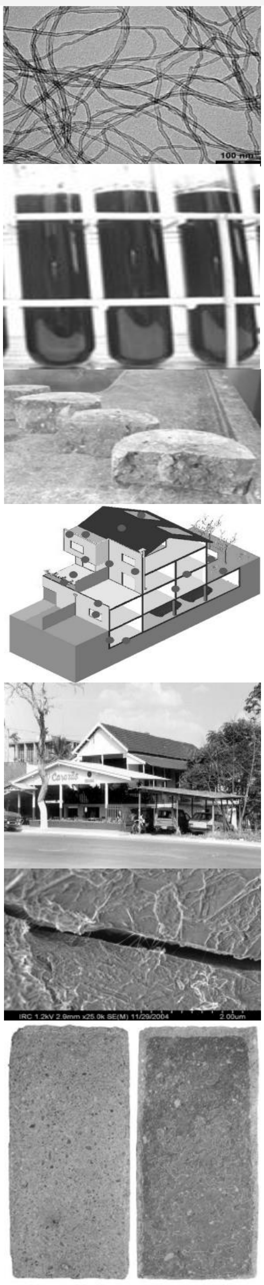

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RAV5N2, May-August 2015

Message from the Editor in Chief and Guest Editor

JOURNAL OF THE LATIN-AMERICAN ASSOCIATION OF QUALITY CONTROL, PATHOLOGY AND RECOVERY OF CONSTRUCTION.

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It is a proud and joyful moment for the Revista ALCONPAT team to see the third and last issue of our fifth year published.

The objective of the Revista ALCONPAT (RA) is the publication of case studies related to the topics of our association, quality control, pathology and construction recovery, motivating the presentation as well of basic or applied research that could be applied to case studies.

In this V5N2, we start with our special guest article from **Argentina**. Edgardo F. Irassar and colleagues discuss the hydration and properties of ternary cements with calcareous filler and slag. Their results showed a limitation of the filler content to obtain an adequate response of the mechanical resistance and durable to long ages, and of the slag content to obtain appropriate values at an early age.

In the second paper, C. G. N. Marcondes and his colleagues from **Brazil** discuss the influence of dispersion on the mechanical properties and water absorption of carbon nanotubes in Portland cement concrete. The ultrasonic technique was relevant to obtain the dispersion of the nanotubes and with it an improvement of the mechanical properties

The third article D. Martínez-Vásquez and colleagues from **Mexico** study the potential of the method of synthesis of ceramic-cement materials processed by alternative routes. Among their results they report that the proposed processing was promising to obtain high mechanical properties in short curing times.

Our fourth article comes from **Brazil**, where Denis Cley S. Amorim and Dênio Ramam C. Oliveira show a work of Structural Reinforcement of a Historic Building in the City of Río Blanco in Arce. It is to highlight and discuss the aspect of the encamisamiento of elements for the reinforcement

The fifth work of this issue is written by Goncalo T. Ferraz, Jorge de Brito and his colleagues from **Portugal**, who work on integrated management systems in buildings. His model draws much attention where they consider various pathology tables for building management

In the sixth article from **Brazil**, J. Ligia. V. Real and colleagues present the state of the art on the colorimetric method by pulverization of silver nitrate to evaluate the penetration of chlorides in concrete. Between their results they report the influence of the type of cement in the answer of the colorimetric method

Each RA issue aims to balance the participation of topics concerning the social objectives of the International ALCONPAT.

We are grateful for the authors' collaboration on this issue, their resolve and effort to comply with the established quality and deadlines.

Each issue of the magazine will include the articles in the original language, and before the following issue the versions in other languages will be published. The official languages of the Revista ALCONPAT are English, Spanish and Portuguese

The Editorial Board

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Editor in Chief

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Hydration and properties of ternary cement with calcareous filler and slag

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ABSTRACT
The calcareous filler produces an increase in early hydration due to the physical effects (filler and heterogeneous nucleation). The dilution effect counteracts this benefit and limits its content. Slag reacts slowly, causes the refinement of grains and pores, and improves the mechanical and durable properties. This paper is a study on the hydration of cements with filler (0 to 20%) and slag (0 to 35%), utilizing the Powers model for slag expanded by Chen & Brouwers. The mechanical resistance of the concrete (a/mc = 0.50) and the segmentation of the pores in relation to the capillary absorption rate are analyzed from the hydration results. The results show a limit on the filler content to obtain an adequate response for the mechanical and durable resistances at a greater age, and a limit on the slag content to obtain appropriate values at an early age.
Keywords: calcareous filler; slag; resistance; capillary absorption; hydration.

RESUMEN
El filler calcáreo produce un incremento de la hidratación temprana debido al efecto físico (relleno y nucleación heterogénea). El efecto de dilución contrarresta este beneficio y limita su contenido. La escoria reacciona lentamente, provoca el refinamiento de granos y poros, y mejora las propiedades mecánicas y durables. En este trabajo se estudia la hidratación de cementos con filler (0 a 20 %) y Escoria (0 a 35%), empleando el modelo de Powers ampliado por Chen & Browers para escoria. A partir de los resultados de la hidratación, se analizan la resistencia mecánica del hormigón (a/mc = 0.50), y el proceso de segmentación de poros en relación con la tasa de absorción capilar. Los resultados muestran una limitación del contenido de filler para obtener una respuesta adecuada de la resistencia mecánica y durable a largas edades, y del contenido de escoria para obtener valores apropiados a temprana edad.
Palabras clave: filler calcáreo; escoria; resistencia; absorción capilar; hidratación.

RESUMO
Filler calcário produz uma aceleração da hidratação nas primeiras idades devido ao efeito físico (compactação e nucleação heterogênea). O efeito de diluição neutraliza os benefícios e limita o seu conteúdo. A escória reage lentamente, fazendo com que o refinamento dos grãos e poros, e melhora as propriedades mecânicas e duráveis. Neste trabalho a hidratação do cimento com filler (0-20%) e escória (0-35%) é estudada usando o modelo de Powers ampliado por Chen Browers para escória de alto forno. A partir dos resultados de hidratação, é analisada a resistência do concreto (com a /c = 0,50), e o processo de segmentação de poros é analisado com relação a taxa de absorção capilar. Os resultados mostram que o teor de filler deve ser limitado para obter uma resposta de resistência mecânica e de durabilidade. Também o conteúdo de escória deve ser limitado para obter propriedades adequadas nas primeiras idades.
Palavras chave: fíler calcário; escória; resistência; absorção capilar; hidratação.

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1. INTRODUCTION

The addition of minerals has taken vital importance in the formulation of cement mixtures due to the need to reduce energy consumption, protect natural mineral resources, and reduce gas emissions that contribute to the greenhouse effect. In order to meet sustainability objectives, it is also necessary for the formulated mixture to contribute to a longer working life for the concrete structures of which it will form part. Over the past few decades, there has been an increase in efforts to understand the behavior of concrete with the addition of natural minerals (pozzolans, calcareous filler), thermally activated additives (calcined clay), or industrial sub-products (fly ash, blast furnace slag, silica fume) (CEMBUREA, 2000 – 2010). In order to formulate binary cements, various mineral additions within the limits of the resources available in each region or country have been used. As of 1990, the use of ternary or cement compounds formulated with Portland clinkers and two mineral additions has increased given that it has various advantages over binary cements. The European (EN 197-1), Mexican (NMX C-414-0), and Argentinean (IRAM 5000) standards for cement have standardized cement compounds that contain up to 35% in weight a combination of two additives, and currently it is planned to increase this percentage up to 55%. In the United States, the ASTM C 1157 standard incorporated hydraulic cements based on performance that do not limit the type and quantity of the mineral additions that could be mixed with Portland cement.

Additives to be combined are chosen in such a manner that the deficiency of a mineral addition is compensated by virtue of the other, and the synergy produced improves the behavior of the ternary cement material. Finally, the mechanical and durable properties of the concrete will depend on the hydration process, which will determine the porosity and connectivity of the porous structure of the matrix, as well as the improvement of the paste-added interface (Soroka, 1979).

The hydration of Portland cement is a complex natural physicochemical process influenced by factors of the Portland cement itself (mineralogical composition, alkali, sulfates, finesse, etc.), the conditions of the mixture (a/c relation, unitary content of the cement), and the environment (temperature and relative humidity). When the mineral additions have been incorporated with the Portland cement, the effects produced on the hydration can be arbitrarily divided into three (Cyr et al., 2006):

- The **dilution effect** is the consequence of the partial replacement of a part of the cement by the mineral addition, which decreases the quantity of the cement and, consequently, creates an increase in the effective water/cement ratio. For an equal hydration grade of the cement material, this effect implies a lower volume of hydration products for the cement.
- The **physical effects** produced by the finely ground additions are: the filler effect and heterogeneous nucleation. The filler effect makes the fine particles of the additions fill the empty spaces between the cement grains, modifying its granular packaging, which implies a change in the initial porosity of the paste. This effect positively or negatively modifies the demand for water required to maintain the workability given the particle size and the ratio of the additions.
- The **chemical effect** is the pozzolanic reaction of the mineral addition in which the previously hydrated phases play a role at varying degrees, such as is the case for calcium hydroxide (CH). In the particular case of the calcareous filler, the reaction of calcium carbonate and tricalcium aluminate of Portland clinker produces the formation of hydrated calcium carboaluminate (general phase AFm: mono-substituted aluminoferrite) (Bonavetti et al., 2001); however, this addition does not generate hydrated calcium silicate (CSH) during its hydration (Sersale, 1992).

When inactive mineral additions are used, the influence of the first two effects is easy to quantify with the chemically combined water and the Powers and Brownyard model (Powers, 1948;

Brouwers, 2004, 2005), as is the case of the calcareous filler already mentioned (Bonavetti et al., 2003; Bentz et al., 2009; Bonavetti et al., 2013). Whereas when the addition presents a chemical effect, quantification becomes more complex and requires models that allow the determination of the contribution of the addition to the parameter.

The properties of concrete and its evolution with the passage of time depend in great measure on the advancement of the cement hydration which determines the evolution of the porosity of the matrix (Bentz et al., 2009). In ternary cements comprised of filler and slag, this process depends in great measure on the relative ratios of the components. The filler contributes to hydration in the initial stage and the slag contributes to hydration in the midterm, and the properties of the concrete they comprise vary in accordance to the evolution of this process.

The objective of this paper is to analyze the compression strength and the rate of capillary absorption in concrete elaborated with cement compounds that contain calcareous filler and blast furnace slag with regard to the hydration process of the cement material.

2. PROCEDURE

In the concretes studied, normal Portland cement (CPN, IRAM 50000), resistance class CP40 (f' c > 40 MPa at 28 days) with low C_3A (< 3%) content was utilized. The additions utilized were calcareous filler (F) and granular blast furnace slag (E). F originates from limestone with a high ground calcite content at a Blaine finesse of 522 m^2/kg. E is a cooled slag ground to a Blaine finesse of approximately 450 m2/kg. The slag has a high activity classification according to the index of determined cement in accordance with the standard ENV 196-1. The combinations of binary and ternary cements utilized can be found in Table 1.

The concretes were elaborated in two stages utilizing river silica sand as a fine aggregate and crushed granite stone as a thick aggregate (maximum size of 19 mm); the content of the cement material (CUMC) was 350 and 360 kg/m^3, and in all cases the a/mc (water/cement material) was 0.50. Full details of the first and second stage concretes have been previously published (Menéndez et al., 2006, 2007; Carrasco et al., 2003).

The resistance was determined in cylindrical test tubes (100 x 200 mm), cured 24 hours in molds and subsequently in water saturated with lime at 20±1 ºC until reaching the trial age. The informed values are the average of five test tubes. For the first stage concretes, the compression strength was determined at 3, 7, 28, 90, and 360 days, and for second stage concretes at 2, 7, and 28 days.

In first stage concretes, the capillary absorption coefficient was determined in prismatic test tubes whose lateral faces were painted with epoxy paint, except for the face corresponding to the mold where a 100 cm^2 area was left unpainted. The prisms were consecutively submerged at a constant depth of 1 cm. The quantity of water absorbed was measured as the weight gain at 1, 5, 10, 15, 30, 60, 120, 240, 360, 720, 1440, and 2880 minutes, and the capillary absorption rate (S) of the concretes was measured as the slope of the graph between the water quantity absorbed per unit area versus the square root of time in the zone comprised between 1 hour as long as linearity was maintained (Menéndez et al., 2002).

The quantity of non-evaporable water (Wn) was determined from the fragments obtained from the tested samples in accordance with the procedure proposed by Powers (Powers, 1949; Escalante-Garcia, 2005). For the average mineralogical composition of the Portland cements utilized, the quantity of non-evaporable water of the cement used to achieve total hydration was 0.195 g of water per g of cement. Assuming the hypothesis of the hydration model proposed by Chen & Brouwers (2007a), for the total hydration of the slag utilized, 0.20 g of water per g of slag is required. For this particular case, due to the small difference between the total Wn for the hydration of the type of cement utilized (low C_3A), there is an assumed value of 0.20 g/g for the cement and slag. By having the total Wn values coincide, it is possible to calculate the degree of hydration for the combined cement material. With the degree of hydration calculated using the Powers model (Powers, 1948: Brouwers, 2004, 2005) and the Chen & Brouwers model (2007b) for the cements with slag, it is possible to estimate the volumes of the hydrated phases assuming that the calcareous filler is hydraulically inactive and that the total of the incorporated slag reacts. Calculating the volume of hydrated products and knowing the free space created by the effective water/cement ratio, the gel-space (X) ratio and the capillary porosity (ϕ) of the cement matrix of the concrete can be calculated following the expressions described previously (Bonavetti et al., 2013).

3. RESULTS AND DISCUSSION

Table 1 shows the results obtained for the combined water (Wn), compression strength (*f'c*) and rate of capillary absorption (*S*) for the various concretes and the ages included in this study. As was expected, the course of time for curing increases the content of combined water and compression strength, and decreases the capillary absorption rate.

In relation to the reference concrete (CP or CPN), it can be observed that the calcareous filler contributes to the content of Wn at an early age, and that the contribution of slag is appreciable after seven days of hydration. For concretes with binary cement with calcareous filler, the quantity of Wn relative to the content of reactive material increases when the level of early age replacement is increased (Figure 1a), and then the progress of the hydration of the Portland phase tends to minimize this advantage. For binary cements with slag (Figure 1b), the incorporation of slag produces a relative decrease of the Wn at an early age. At 7 days, the slag reacts slowly and the relative Wn increases reaching a similar value to that of the Portland cement reference at 28 days.

Table 1. Composition of the cement material, combined water (Wn), compression strength (*f'c*), capillary absorption rate (*S*); degree of hydration (α), gel/space ratio (*X*), and capillary porosity (ϕ) of the studied concretes.

Concrete	**CUMC,** kg/m^3	**F,** %	**E,** %	**Age** days	**Wn**	**f'_c** MPa	**S,** $g/cm^2\ h^{1/2}$	**a/c** effect	**α**	***X***	**ϕ,** %
CP	350	0	0	3	10.04	18.3	0.222	0.50	0.515	0.536	30.9
				7	11.77	25.5	0.181		0.604	0.603	27.7
				28	13.29	36.0	0.100		0.682	0.657	24.8
				90	16.76	39.0	0.081		0.859	0.768	18.2
				360	17.71	41.3	0.081		0.908	0.796	16.4
CPN	360	0	0	2	10.66	15.9	-.-	0.50	0.547	0.561	29.8
				7	11.74	27.4	-.-		0.602	0.602	27.7
				28	14.91	34.0	-.-		0.764	0.711	21.7
CP12F	350	12	0	3	10.96	20.6	0.214	0.57	0.562	0.520	36.0
				7	14.21	28.3	0.126		0.729	0.630	29.9
				28	15.41	34.5	0.093		0.790	0.667	27.6
				90	17.85	38.4	0.063		0.915	0.736	22.9
				360	18.28	39.6	0.065		0.937	0.748	22.1
CP18F	350	18	0	3	11.36	20.9	0.288	0.61	0.583	0.506	39.5
				7	15.32	27.2	0.214		0.786	0.631	32.0
				28	16.50	35.2	0.097		0.846	0.665	29.7
				90	18.20	37.7	0.068		0.933	0.711	26.5
				360	18.91	38.0	0.062		0.970	0.730	25.2
CPN15F	360	15	0	2	11.66	18.0	-.-	0.59	0.598	0.531	36.7
				7	12.70	27.0	-.-		0.651	0.566	34.7
				28	16.10	32.7	-.-		0.826	0.671	28.3
CP20E	350	0	20	3	9.18	16.6	0.288	0.50	0.471	0.501	32.6
				7	11.72	25.0	0.214		0.601	0.601	27.8
				28	13.72	34.7	0.097		0.704	0.672	24.0
				90	16.95	41.5	0.068		0.869	0.774	17.8
				360	18.46	43.5	0.062		0.947	0.817	15.0
CPN35E	360	0	35	2	8.31	11.1	-.-	0.50	0.426	0.464	34.2
				7	10.78	21.4	-.-		0.553	0.566	29.5
				28	13.81	29.0	-.-		0.708	0.675	23.8

Table 1. (Continued)

Concrete	**CUMC,** kg/m³	**F,** %	**E,** %	**Age** days	**Wn l**	***f´c*** MPa	***S,*** g/cm² h$^{1/2}$	**a/c** effect	**α**	***X***	**ϕ,** %
CP12F10E	350	12	10	3	10.39	19.4	0.208	0.57	0.533	0.500	37.1
				7	13.27	28.4	0.147		0.681	0.600	31.6
				28	14.33	36.6	0.111		0.735	0.634	29.6
				90	17.97	39.4	0.069		0.922	0.740	22.7
				360	18.55	40.0	0.063		0.951	0.755	21.6
CP12F20E	350	12	20	3	9.18	15.6	0.236	0.57	0.471	0.453	39.4
				7	11.72	28.2	0.194		0.601	0.547	34.6
				28	13.72	36.9	0.113		0.704	0.614	30.8
				90	16.95	39.3	0.050		0.869	0.711	24.7
				360	18.46	39.7	0.047		0.947	0.753	21.8
CP18F10E	350	18	10	3	11.14	19.1	0.238	0.61	0.571	0.499	39.9
				7	14.55	26.1	0.196		0.746	0.609	33.4
				28	15.68	35.4	0.137		0.804	0.642	31.3
				90	18.27	38.3	0.105		0.937	0.713	26.4
				360	19.13	38.8	0.086		0.981	0.735	24.8
CP18F20E	350	18	20	3	10.92	15.3	0.249	0.61	0.560	0.491	40.3
				7	14.15	24.4	0.199		0.726	0.596	34.2
				28	15.50	34.6	0.126		0.795	0.637	31.6
				90	17.62	37.7	0.061		0.904	0.696	27.6
				360	18.65	38.2	0.062		0.956	0.723	25.7
CPN6F22E	360	6	22	2	9.05	16.3	-.-	0.53	0.464	0.472	36.0
				7	13.25	27.1	-.-		0.680	0.628	28.0
				28	14.16	36.9	-.-		0.726	0.658	26.3
CPN11F11E	360	11	11	2	10.46	18.7	-.-	0.56	0.536	0.506	36.3
				7	12.89	27.8	-.-		0.661	0.592	31.7
				28	16.21	34.4	-.-		0.831	0.696	25.4
CPN22F6E	360	22	6	2	9.84	14.2	-.-	0.64	0.504	0.435	45.4
				7	14.53	24.6	-.-		0.745	0.587	36.5
				28	15.42	29.6	-.-		0.791	0.613	34.8

The contribution of slag to the Wn corresponds to the pozzolanic reaction of the slag, whose main hydration products are the calcium aluminium silicate (C-A-S-H) with a lower C/S reaction than that which corresponds to C-S-H, hydrotalcite (M_5AH_{13}) and ettringite ($C_3A.3CS.H_{32}$) (Chen & Brouwers, 2004). This reaction is initially stimulated by the alkaline solution that contains the CH provided by the hydration of the Portland cement.

For concretes with ternary cements of low (Figure 1c) and high filler content (Figure 1d) and variable slag content, it can be observed that the Wn is slightly greater than the reference concrete for the first case and much greater at an early age for the second case, tending to converge at 90 days.

In line with the previous results on the mortars regarding the hydration of the binary and ternary cement systems with calcareous filler and slag (Menéndez et al., 2003; Carrasco et al., 2007), it can be observed that the effects of the additions (dilution, physical and chemical effects) cause variations in the Wn.

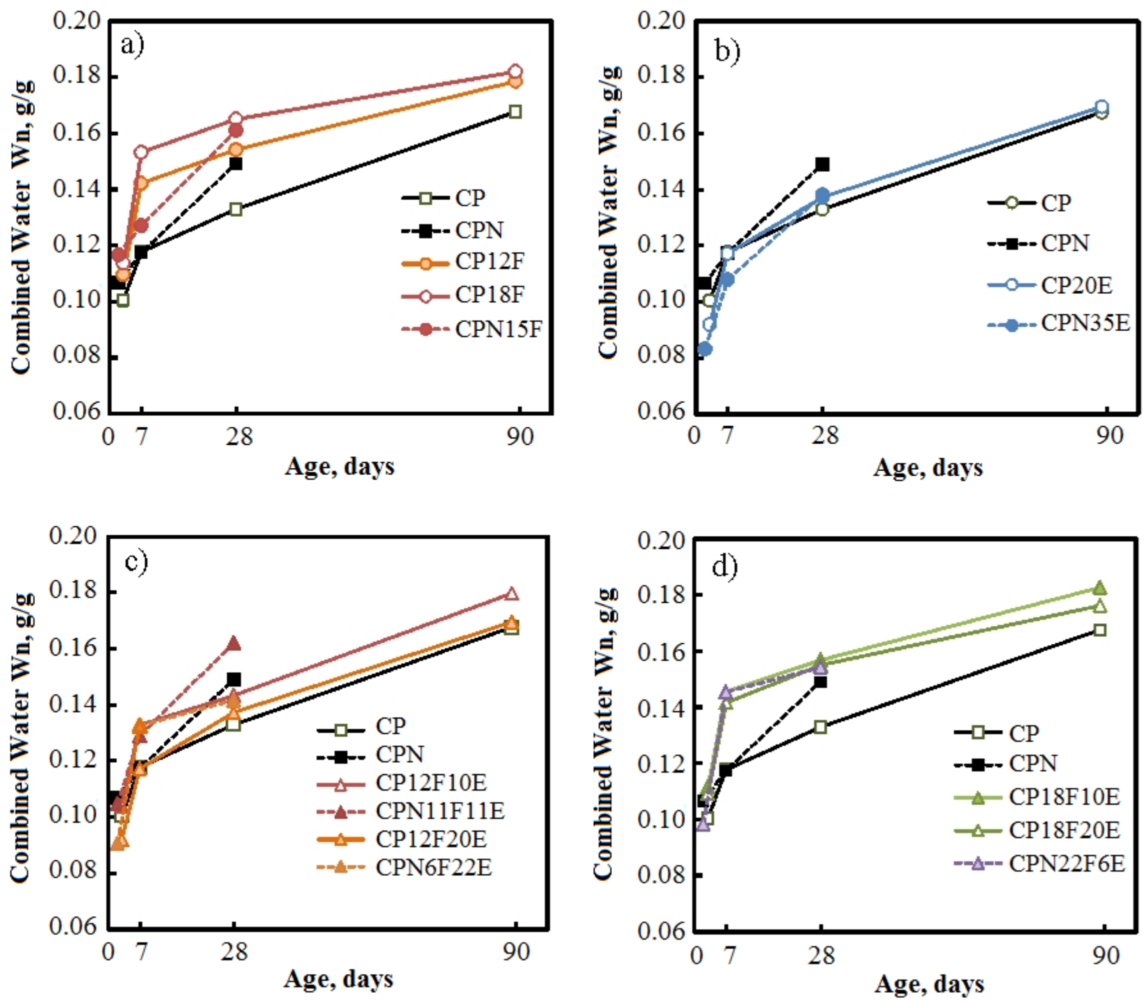

Figure 1: Evolution of the non-evaporable water (Wn) in the concrete matrix in function of time. a) Binary cements with calcareous filler; b) Binary cements with slag; c) Ternary cements with low filler ratio; d) Ternary cements with high filler ratio.

The physical effects fundamentally appear during the first days of hydration and the chemical contribution of the slag is appreciable after the first seven days of hydration. Dilution is an effect present at all times.
The increase in the percentage of mineral added to the Portland cement causes the dilution effect, which decreases the quantity of Portland cement and consequently produces a change in the effective water/cement ratio. In the case of the calcareous filler-slag system, the same can be calculated as indicated by the equation below (1).

$$a/c_{\text{effective}} = A / (C + \chi_f F + \chi_E E) \qquad (1)$$

Where A, C, F, and E are the quantity in weight of water, Portland cement, calcareous filler, and slag utilized in the mixture. χ_f and χ_E are the efficiency factor of the calcareous filler and of the slag utilized, respectively. This factor represents a measurement of the relative behavior of each addition compared to Portland cement, and this factor also depends on the type of Portland cement utilized, its age, type, and the quantity of the addition utilized in the mixture and the initial a/c ratio (Cyr et al., 2000).
When considering that the calcareous filler is an inactive mineral addition, the efficiency factor χ_f tends to 0 and therefore produces an increment in the effective a/c ratio proportional to the content of the addition in the cement. For slag, the value of χ_E varies with time, the level of replacement, and the cement used. At longer ages (>90 days), the value of $\chi_E > 1$ increases the resistance and decreases the permeability. At 28 days, the value of χ_E varies from 0.79 to 1.5 for a 50% replacement making it necessary to increase the CUMC and decrease the a/mc to reach a similar resistance to that of Portland cement (Boukhatem et al., 2011). In order to simplify the calculations, this study assumes that χ_f is null and that $\chi_E = 1$ for all ages.
For the same degree of hydration as Portland cement, the dilution effect caused by the filler ($\chi_f = 0$) produces a lower volume of hydrated products and therefore a lesser quantity of combined water with regard to the total cement material incorporated. The reduction in volume of the hydrated products at the first ages for elevated percentages of additions leads to a lower compression strength. For low addition percentages (Menéndez et al., 2003), the heterogeneous nucleation increases the degree of reaction of the cement material and can, in part, compensate for the dilution. The filler effect makes the fine particles of the additions fill the empty spaces between the cement grains, modifying its granular packaging, which implies a change in the initial porosity of the paste and consequently the resistance could slightly increase.
In this study a constant a/mc ratio has been used in the concrete mixture, therefore the space to be occupied by part of the hydration products shall be the same. The difference will be given by the quantity of material that has reacted at each age that determines the gel/space ratio of the system. Consequently, in order to know the influence of the content of the addition on any resistant or durable property, it is necessary to study the volume of the hydration products produced in accordance with the degree of hydration (α) of the cement material.
Table 1 shows the effective values of the a/c ratio calculated for each of the concretes studied assuming the stated hypothesis. Starting from the Wn, the degree of hydration of the Portland cement can be estimated, dividing this value by the total necessary water to hydrate the entirety of the Portland cement. Whereas for slag, the degree of hydration was calculated from the difference between the total combined water minus the combined water of the fraction of Portland cement in the mixture, dividing the total necessary water to hydrate the entirety of the slag. Subsequently, the

volume of the hydration products was calculated according to the Chen & Brouwers model (2007b) and finally the gel/space ratio (X) whose values are shown in Table 1.
The compression strength of a material of a cement base (f'_c) can be calculated as the intrinsic resistance (f_0) of the material affected by the gel/space ratio (X) raised to the n (2).

$$f'_c = f_0 X^n \tag{2}$$

Figure 2 shows the relation between the compression strength and the gel/space ratio obtained utilizing this simplified model. The coefficients of the equation (2) obtained through the best approximation by least squares for each type of cement are shown in Table 2. For every group, it can be observed that the intrinsic resistance value of this material of cement base (concrete) is approximately 75 MPa and coefficient n varies from 2.0 to 2.3, whose values are found within reported literature.
This good correlation between the experimental results of the compression strength of the concretes elaborated with different cement materials, with variable ratios of calcareous filler and slag, in binary and ternary mixtures, confirm that those postulated by the simplified hydration models of Powers, which were later revised and expanded on by Chen & Brouwers, are acceptable for the studied system. This observation is important for the design of concretes with multicomponent cements that allow the design of the replacements from the wanted resistance or durability objective.

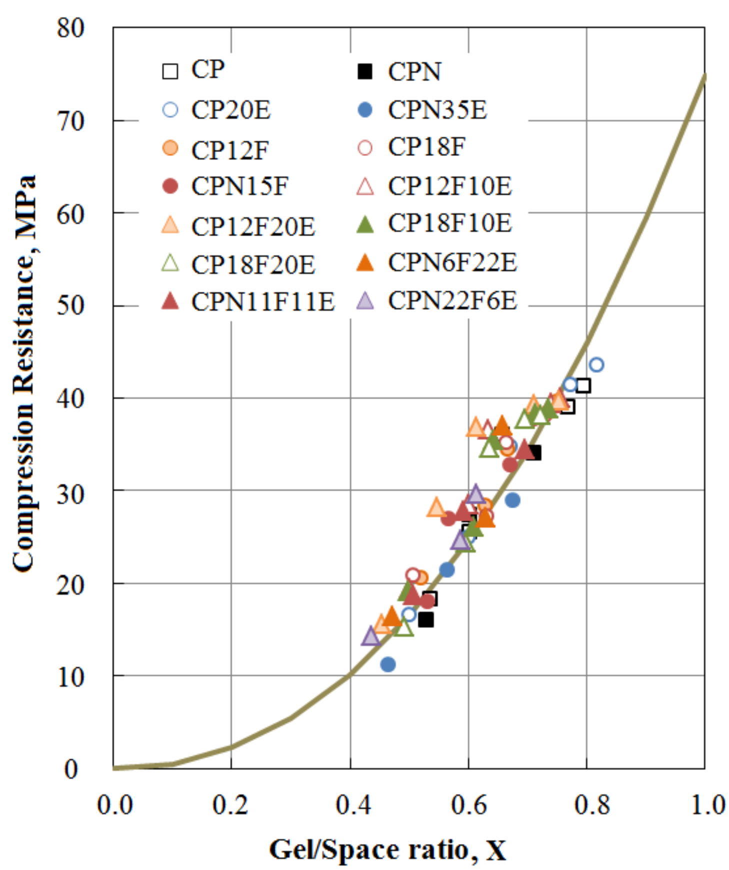

Figure 2: Compression resistance vs. gel/space ratio for all the concretes studied.

Table 2: Coefficients of the equation that relates *f'c* and the gel/space ratio.

Concretes included in the correlation	f_0	*n*	R^2
Portland Cement (CP, CPN)	74.1	2.2	0.84
Binary cements with calcareous filler (CP12F, CP18F, CP15F)	76.7	2.1	0.95
Binary cements with slag (CP20E, CPN35 E)	75.8	2.3	0.96
Ternary cements	76.3	2.0	0.92
All cements	74.9	2.06	0.90

To ensure the durable performance of the concrete before the deterioration processes, the first measure that must be taken is the reduction of the transport processes of water and aggressive substances in its mass. For concretes of Portland cement, it has been assumed that a decrease in the a/c ratio below 0.53 produces a drastic reduction on the permeability when the same has been properly cured and is related to the capillary porosity (Soroka, 1979).
The capillary porosity (ϕ) according to the Powers model for Portland cement depends on the a/c ratio and the degree of hydration (α) of the same (3).

$$\phi\ (\%) = (a/c - 0.37\ \alpha) * 100 \tag{3}$$

In terms of pore connectivity, the reduction of permeability occurs when the volume of capillary pores in the mixture is below 18% (Winslow et al., 1994). In the case of Portland cement with an a/mc ratio of 0.50, a hydration degree of 0.70 is required to archive a capillary porosity of 18% and thus segment the pores impeding the transportation of water. In concretes of binary or ternary cement, the calculation of capillary porosity also emerges from the analysis of the content of the hydrated cement material in function of the space available to be filled. For this reason, the capillary porosity increases with the increment of the effective a/c and decreases when the degree of hydration of the cement material increases. In function of this model, it is possible to estimate the volumes of the various stages that are found in the cement paste at any of its hydration stages.
Figure 3 shows that for concretes CP and CP20E, when the 18.5% capillary porosity is achieved, segmentation of the pores occurs and the capillary absorption rate changes very little after the first 28 days once the degree of hydration that produces segmentation of the pores is reached. Between 90 and 360 days, the capillary absorption rate does not significantly change. For all the binary and ternary cements that contain 12 and 18% of calcareous filler, even though the degree of hydration is greater, the absorption rate presents a higher value up to the first 28 days due to the increase of the effective a/c ratio. However, the capillary porosity threshold that does not make significant changes in the capillary absorption rate is greater (22 to 24%). This situation is attributable to the fact that the models utilized do not take into account the blockage effect of the pores, which can produce the incorporated calcareous filler particles.
In this manner, it can be concluded that in order to obtain an impermeable concrete with a low water transportation rate per capillarity, it can only be achieved when the segmentation of the pores of the cement matrix is produced; whether through a reduction of the a/mc ratio or an increase in the degree of hydration of the cement material.

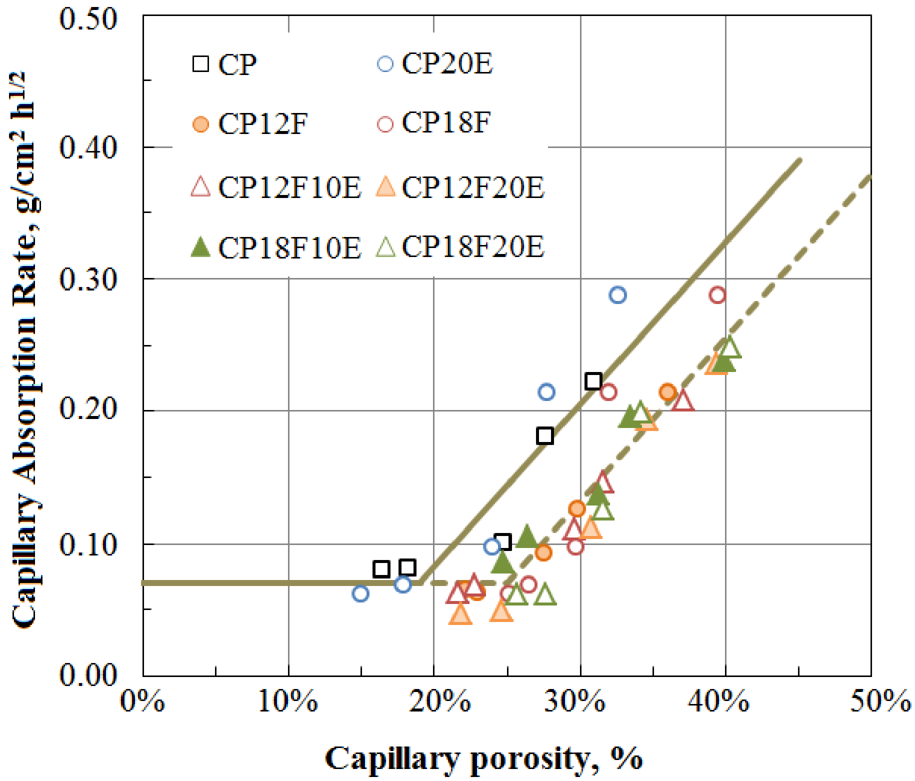

Figure 3. Relation between the capillary absorption rate and the capillary porosity of the matrix.

4. CONCLUSIONS

According to the experimental results and the suppositions made to implement the existent hydration models, the following conclusions can be expressed:

- The evolution of the hydration of the cement matrix of the concrete determines the development of the porous structure and with it, the compression strength and the capillary absorption rate independent of the formulation of the cement mixture utilized.
- For binary compound cements, the evolution of the hydration of the cement can be controlled and modified with the calcareous filler or in the case of cement, with slag through a change in the finesse and the ratios in the mixture. In general, it can be observed that the properly ground calcareous filler contributes to the early hydration and slag contributes to the late hydration. This supplementation allows the development of ternary cements.
- The Powers model and the considerations of Chen & Brouwers for the hydration of slag allow the modeling of the gel/space ration and the capillary porosity of the matrix in the ternary cements. The relation between the results of the models and the experimentally determined properties of the concrete reasonably correspond.

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Carbon Nanotubes in Portland cement concrete: Influence of dispersion on mechanical properties and water absorption

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ABSTRACT
Carbon nanotubes (CNTs) are carbon structures which take the shape of cylinders in nanometric scale. This work presents an evaluation in regard to the addition of CNTs in concrete made with Portland cement, focused on the importance of performing the CNTs dispersion in water ultrasound before its incorporation to the concrete mass. Therefore, three concrete mixtures were performed, one without CNT (reference series) and two with CNTs (one mixture with previous dispersion in water and additive using ultrasound and the other without dispersion). Then properties of fluidity, compressive and tensile strength and water absorption were analyzed. The amount of CNT added was 0.30% with respect to cement mass. In all cases, the previous dispersion of CNTs using ultrasound increased the effect of CNTs addition, evidencing the importance of the efficiency of such material when added to cement.
Keywords: carbon nanotubes; concrete; strength; water absorption.

RESUMO
Os nanotubos de carbono (NTCs) são estruturas de carbono que obtêm forma de cilindros em escala nanométrica. Este trabalho apresenta uma avaliação da adição dos NTCs em concreto de cimento Portland, com foco na importância da realização de dispersão dos NTCs à água com uso do ultrassom antes de sua incorporação a massa de concreto. Para isto, três traços de concreto foram preparados sendo um sem NTC (série de referência) e dois com os NTCs (uma série com dispersão prévia em água e aditivo com o uso de ultrassom e outra sem dispersão). Analisou-se então as propriedades de fluidez, resistência à compressão, tração e absorção de água. O teor de NTC adicionado foi de 0,30% em relação à massa de cimento. Em todos os casos a dispersão prévia dos NTCs usando o ultrassom potencializou o efeito da adição de NTCs, mostrando-se importante para a eficiência deste material, quando adicionado ao cimento.
Palavras-chave: nanotubo de carbono; concreto; resistência; absorção de água.

RESUMEN
Los nanotubos de carbono (NTC) son estructuras de carbono que se obtienen en forma cilindrica de escala nanométrica. Este artículo presenta una evaluación de la adición de NTC en hormigón de cemento Portland, centrándose en la importancia de llevar a cabo la dispersión de los NTC en el agua con el uso del ultrasonido antes de su incorporación en la masa de hormigón. Para ello, tres mezclas de hormigón se prepararon con un NTC libre (referencia) y dos NTC (con una serie previa de dispersión en agua y el aditivo con el uso de ondas ultrasónicas y otras sin dispersión). A continuación, se analizó las propiedades de fluidez, resistencia a la compresión, tracción y la absorción del agua. El NTC añadió contenido de 0,30% a respecto de la masa de cemento. En todos los casos, la dispersión previa de NTC usando ultrasonido potenció el efecto de la adición de nanotubos de carbono, siendo importante para la eficiencia de este material cuando se añade al cemento
Palabras clave: nanotubo de carbono; concreto; resistencia; absorción del agua.

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1. INTRODUCTION

Research performed in the fields of cement and nanotechnology have appointed that some nano composite cement additions allow major changes in its microstructure, which provides a more resistant production of concrete, less porous and more durable (Marcondes, 2012). Among the row of possible nanomaterials exists the carbon nanotubes (NTC), to be the focus of this work.

Carbon nanotubes (CNTs) are carbon structures which after synthesized, tend to form cylinders at the nanometer scale and measure approximately 3 nm in diameter and 1000 nm long (Couto, 2006).

From a structural point of view, there are two types of carbon nanotubes: the single wall, consisting of a single graphene sheet rolled on itself to form a cylindrical tube, and multi-walled, comprising an assembly of carbon coaxial nanotubes with several graphene sheets rolled into tube form wise (Zarbin, 2007). Single-walled carbon nanotubes (NTCPS) are difficult to be synthesized, which increases their cost and virtually precludes its application on a large scale (Herbst et al., 2004).

This test used the CNTs of multiple walls, due to its lower cost and availability in relation to single wall. They were purchased from a company in Belgium and added to the concrete, in order to review the effect of CNTs in water absorption, the fluidity of fresh concrete and mechanical properties of compressive and tensile strength via diametrical compression.

2. NTC IN PORTLAND CEMENT COMPOSITES

The addition of NTCs cement compounds is a topic which has been studied in several national and international universities, as showed in Table 1.

Table 1. Some of the leading universities players towards nano materials research applied to cement compounds

Institution	Department	Researchers
BRAZIL		
Federal University of Minas Gerais – MG	Physics Deptartment / Structural Engineering Department	M. Pimenta; Luis Orlando Ladeira; André F. Ferlauto e José M. Fonseca Calixto
Federal University of Paraná - PR	Civil Construction Department	Carlos G. Nastari Marcondes e Marcelo H. F. de Medeiros
Federal Universtity of Santa Catarina – SC	Civil Engineering Department	Philippe J. P. Gleize e Wellington L. Repette
INTERNATIONAL		
University of Minnesota Duluth, USA	Department of Mechanical and Industrial Engineering / Department of Civil Engineering	Xun Yu; Eil Kwon
Chiang Mai University, Tailândia	Department of Physics and Materials Science	Arnon Chaipanich
The State University of New Jersey, USA	Department of Civil and Environmental Engineering	P.N. Balaguru

Berkeley University, USA	Department of Civil Engineering, Structural Engineering and Structural Mechanics (SESM)	Paulo Monteiro
University Shanto, China	Department of Civil Engineering, Shantou	Geng Ying Li; Pei Ming Wang; Xiaohua Zhao
Politecnico di Torino, Itália	Physics Department / Structural Engineering Department	Simone Musso; Giuseppe Ferro
Northwestern University, USA	Center for Advanced-based Materials	Surendra P. Shah
Democritus University, Grécia	Department of Civil Engineering	Maria S. Konsta-Gdoutos

The reason for several researches held in this area is that in some studies [such as those by: Marcondes (2012), Batiston et al. (2010), Makar et al. (2005), Chaipanich et al. (2010), Melo et al. (2011) and Li et al. (2004)] attest the performance of nanoparticles when added to paste and Portland type cement mortars. Due to its minuscule proportions, these particles contribute to the void fill and, consequently, for the improvement of various properties of these materials. In this case, there are still some barriers to overcome. According to Batiston et al. (2010), the two major challenges to the introduction of carbon nanotubes into cementations matrices are: homogeneous distribution of the carbon nanotubes in the cement composite and to study the interaction between CNTs with compounds due to the cement hydration. This previous aspect can be interpreted as the necessity to understand the changes caused by the addition of CNTs in Portland cement composites, such as changes in microstructure, in kinetic hydration reactions, the paste/aggregate adhesion, among others.

In regard to distribution of CNTs to a cementations matrix, several methods have been used, especially the sonification and functionalization of CNTs using mixture of nitric and sulfuric acid (Li et al., 2004; Konsta-Gdoutos et al, 2010).

From the scope of researchers Koshio et al. (2001), ultrasound can be considered an effective technique in dispersing carbon nanotubes in water, oil or polymers. For these researchers, the sieving forces triggered by ultrasound had overcome the bonding forces between the nanotubes, turning out to split them. This was attested by researchers Konsta et al. (2010) who achieved an efficient dispersion by application of ultrasonic energy and the use of a surfactant. The results appointed an adequate dispersion with the application of ultrasonic energy and the multi-walled carbon nanotubes to enhance the cement matrix, to increase the amount of CSH and reduce the porosity.

Chaipanich et al. (2010) analyzed the addition of carbon nanotubes in Portland cement mortars (0.5 and 1% by mass relative to the cement). The CNTs were initially dispersed in water using ultrasound for a 10 min of timeframe. In that case, the authors rendered with fly ash cement and the compressive strength of the composites (paste and mortar) also investigated. Research has appointed the use of carbon nanotubes increased strength of composite Portland cement with 20% of fly ash. The highest strength was obtained with the addition of 1% NTC where the compressive one at 28 days indicated 51.8 MPa representing a 10% of increase in compressive strength when compared to the reference mixture without nanotube carbon, which evidenced strength of 47.2 MPa. Furthermore, according to Chaipanich et al. (2010), the analysis towards scanning electron microscopy also evidenced a good interaction between carbon nanotubes and cement with fly ash in comparison to mixture without CNTs.

3. EXPERIMENTAL PROCEDURE

The works published until now focused on the influence of CNTs into pastes and Portland cement mortars and this experimental was conducted fin this study focused in the effect of adding CNTs in Portland cement concrete. The key feature was to explore the feasibility of using conventional NTC dosing in concrete with compressive strength between 25 and 40 MPa, and measuring some effects on the mechanical strength and water transport through the concrete pore network with and without the addition of NTC.

3.1 Materials.

3.1.1 Cement.

The cement used was Portland cement type CPV-ARI. The cement was selected because it has no pozzolanic ash and contain higher amount of clinker in its composition. It eliminates another variable in the study, since pozzolanic materials may interact with CNTs and interfere in results (Chaipanich et al., 2010).

The physical and chemical composition of the cement are evidenced in Table 2. The specific cement average weight is 3.12 g/cm³ in accordance with the NM NBR 23/2001 (NBR NM 23, 2001).

Table 2. Physical properties and chemical composition of cement CP V – ARI

Chemicals composition										
	Al_2O_3	SiO_2	Fe_2O_3	CaO	MgO	SO_3	Loss of ignition	CaO Free	Resid. Insol.	Total alkalies as Na_2Oe*
	%	%	%	%	%	%	%	%	%	%
CP V - ARI	4.12	18.34	2.52	59.72	5.35	3.05	3.2	1.49	0.63	0.62

Physical properties											
	Expansion	Initial set	Final set	Normal Cons.	Blaine	# 200	# 325	1 day	3 days	7 days	28 days
	mm	h:min	h:min	%	cm²/g	%	%	MPa	MPa	MPa	MPa
CP V - ARI	0.5	02:15	03:00	27.6	4370	0.10	2.80	23.40	37.60	42.70	51.10

* $Na_2Oe = Na_2O + 0.658\ K_2O$

3.1.2 Aggregates.

The fine aggregate was a natural sand compound from Balsa Nova city – Paraná. The properties of fine aggregate are appointed in Table 3.

Table 3. Fine aggregate properties

Properties	Result	Standard method
Maximum dimension (mm)	4.8	NM 248/2001
Fineness Modules	2.92	NM 248/2001
Powdery Materials (%)	2.00	NM 46/2003
Specific gravity (g/cm³)	2.61	NM 52/2009
Bulk Density (g/cm³)	1.487	NM 45/2006
Absorption (%)	0.37	NBR 9777/1987
Organic Content (ppm)	< 300	NM 49/2001
Clay Content (1%)	0.1	NBR 7218/1987

The coarse aggregate was employed for the production of concrete derived from one granite gravel crushing. The coarse aggregate is in accordance to ABNT NBR 7211 (2005).
The coarse aggregate was initially washed to remove impurities and powdery materials and, after that, was dried in an oven until mass constancy. Its characterization was conducted in accordance with national standards and is represented in Table 4.

Table 4. Coarse aggregate properties

Properties	Result	Standard method
Specific gravity (g/cm³)	2.62	NM 52
Bulk Density (g/cm³)	1.348	NM 45

3.1.3 Carbon nanotubes and Admixture.

The CNTs used in this study were produced from Nanocyl SA Company, located in Belgium. The CNTs cost 120 euros per kilo. These are multi-walled CNTs synthesized by the chemical vapor deposition method or also called CVD - chemical vapor deposition. Commercially the product is specified by the name of NC 7000. Figure 1 shows an image of this material with the use of scanning electron microscopy (SEM).

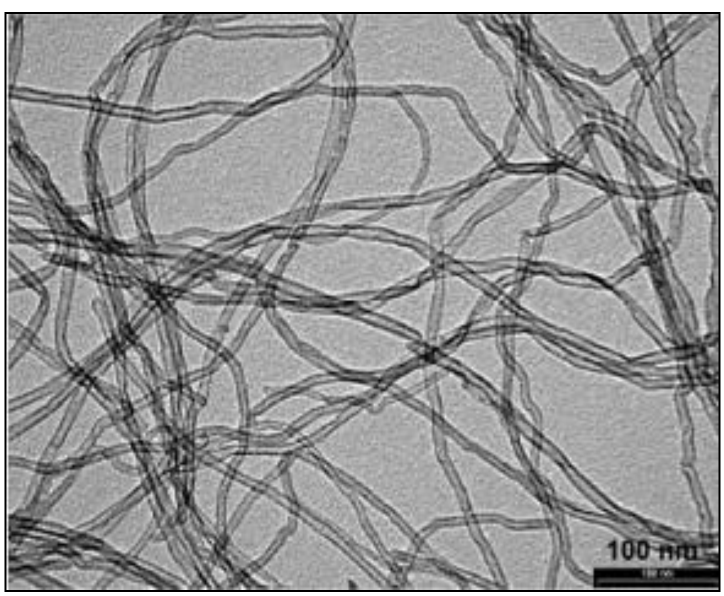

Figure 1. SEM Image of carbon nanotubes multi-walled produced by Nanocyl SA.

Its properties and composition are showed in Tables 5 and 6.
From the scope of the experiment, it was used a polycarboxylate as superplasticizer, used to set the desired consistency.
The admixture used in the experiment is a carboxylic ether polymer modified, with concentration average of 49%. It is in accordance to ASTM C 494 (2011) (Type A and F), ASTM 1017 (1998) and NBR 11768 (2011).
Polycarboxylate macromolecules are used as dispersants in cementitious compositions as high efficiency by reducing the viscosity and minimizing the amount of water used for processing (Mehta; Miller, 2008).
Some properties of admixture is showed in Table 7.

Table 5. Physical properties of NTCs

Property	Unit.	Value
Average diameter	Nanometer	9.5
Average Length	Mícron	1.5
Surface Area	m^2/g	250-300
Average Density	g/l	60

Table 6. NTCs composition

Components	% (weight)
Synthesized graphite (NTC)	90%
Cobalt Oxide	< 1%
Metal Oxide	10%

Table 7. Superplasticizer informations

Suggested dosage (by cement mass)	pH (ABNT 10908)	Specific gravity (ABNT 10908)
0.3% to 2%	5.5 + 1.0	1.10 + 0.02 g/cm^3

3.2 Specimens.
The concrete without CNTs was called REF (without adding CNTs) and was used to compare with the concrete with the addition of CNTs. Thus, it was adopted a simply conventional concrete mix as a reference and then reproduced series adding the CNTs. The mix proportions established are appointed in Table 8. It should be noted that the CNT content relative to the cement mass was maintained at 0.3% for all composites. This settlement was made based on the studies of Melo et al. (2011) that indicated 0.30 % (in cement mass) as the optimum content.
The nomenclature used in Table 8 refers to the REF as the mark without the carbon nanotubes; the CD, such as the insertion mark with the additive and carbon nanotubes (with dispersion in water and additive ultrasound); and SD, the mark containing only the NTC added powder (without the dispersion in the additive and without application of ultrasonic energy - mixed into the cement powder using only with mixer attached to a drill).
The water/cement ratio used in this study was set at 0.55. During this work, it was noted that the addition of CNTs to the concrete caused reduction of fluidity to the SD serie, which damaged its feasibility and prevented the use of smaller ratio values water/cement ratio. On the other hand, it is

considered the limit value as specified by the NBR 6118 (2007) for the purpose of application of concrete in marine environments.

Table 8. Concrete mix proportions

Mix Proportions	Cement	CNT*	Fine aggregate	Coarse aggregate	α	C (cement content)	a/c	Admixture*
	(kg)	(g)	(kg)	(kg)	%	(kg/m^3)		(g)
	1.00	**0.30%**	**2.25**	**2.75**			**0.55**	**1%**
REF	10.9	0	24.4	29.8	58	352	0.55	108.5
CD	10.9	32.55	24.4	29.8	58	352	0.55	108.5
SD	10.9	32.55	24.4	29.8	58	352	0.55	108.5

*in reference to cement mass.

Cement content is 352 kg/m^3 and is in accordance to the suggested consumption established by NBR 12655 (2006), which in the case of concrete placed in class III environment indicate the lower limit of 320 kg of cement per cubic meter of concrete.

From the scope of tests, they were made in the mixer 3 mixtures, one for each mix proportion, and to prepare the solution to be used for CD feature of preparation, there was the addition of CNTs water with superplasticizer and was followed with sonification. The wave application time was 1 hour. This time was predetermined based on work done by Marcondes (2012) due to a visual analysis indicated that after 60 minutes the samples did not appoint any changes to the tonality and turbidity.

Furthermore, as of 40 minutes sonication the samples are not presented (visually) CNTs decantation elapsed time of 24 hours in the solution rest, as can be seen in Figure 2.

The ultrasonic equipment rendered low frequency, model 0-14 C / I manufacturer Thornton INPEC Electronics SA with a nominal frequency of 40 kHz and 100W of power. The dispersed solution was used within 30 minutes after sonication.

Figure 2. Visual analysis of samples with 40 minutes of sonification elapsed in 24h rest (MARCONDES, 2012).

3.3 Tests procedures.

3.3.1 Compressive strength.

The compressive strength is the key to evaluate mechanical properties of concrete Portland cement. The molding test specimens was performed in accordance to the NBR 5738 (2003) using cylindrical molds Ø 10 x 20 cm. Six specimens were prepared for each mix proportion, on the total of 18 specimens.

3.3.2 Tensile strength by diametrical compression.

The tensile strength by diametrical compression test was carried out according to the NBR 7222 (2011). This test is focused on evaluating the tensile strength in the analyzed concrete by applying a diametrical compression load to the specimen. Similarly to the previous test, it was prepared six cylindrical specimens Ø 10 x 20 cm for each mix proportion.
The Equation 1 was used to calculate the tensile strength by diametrical compression.

$$f_{t,D} = \frac{2.P}{\pi.d.L} \qquad (1)$$

Where: P = maximum applied load, kN; d = specimen diameter, mm; L = specimen height, mm.

3.3.3 Immersion water absorption.

The immersion absorption test was performed based on NBR 9778 (2005) and was performed according to the following steps:
1 - Drying of specimens until they reach constant mass (the dry out temperature was 60 °C to avoid very high temperatures, which may cause microcracks in the specimen and influence the results);
2 – After the dry out in an oven, it was rendered the immersion of the sample in water at 23 ± 2 °C for a total of 72 h. The samples were kept immersed up to 1/3 of its volume during the first 4 h, 2/3 in the subsequent 4 h, remaining completely immersed in 64 h;
3 - It was determined the mass of the test specimens at 24 h, 48 h and 72 h of immersion. The determinations were made after dry up the sample surface with a cloth.
The water absorption by immersion was defined by Equation 2.

$$\frac{M_{sat} - M_s}{M_s} \times 100 \qquad (2)$$

Where: M_{sat} = saturated mass of specimen; M_s = mass of oven dried specimen

3.3.4 Water absorption by pipette method.

This test also renowned as pipette test or RILEM pipette test (Test Method II.4: Water absorption test tube, 2006). It was proposed by German researcher Karsten and approved by RILEM (*Reunion Internationale des Laboratoires d'essais et de Recherches sur les Materiaux et les Constructions*) (RILEM, 2006) for the control of water infiltration in walls.
Each specimen was cut into 5 cm thick slices. These slices were placed in an oven at a temperature of 60 °C during four days. Then, the pipettes were fixed on the circumference of the specimens with silicone as shown in Figure 3. We used four slices of each series formulated for the measurements.

With fixed pipette, they were filled with water until the zero degree (highest) and the water inlet on the substrates was monitored by the decrease in the water level on the graduated scale (Figure 3). The readings were taken at 15 minute intervals to complete 2.5 hours of testing and, after that, we proceeded with readings 24h, 48h and 72h.
In order to consider the loss of water by evaporation, a pipette was fixed on a glass plate and it was used considering the variation of water level, in this case, as the water evaporated. These were subsequently evaporating discounted values of all the tested series concrete.

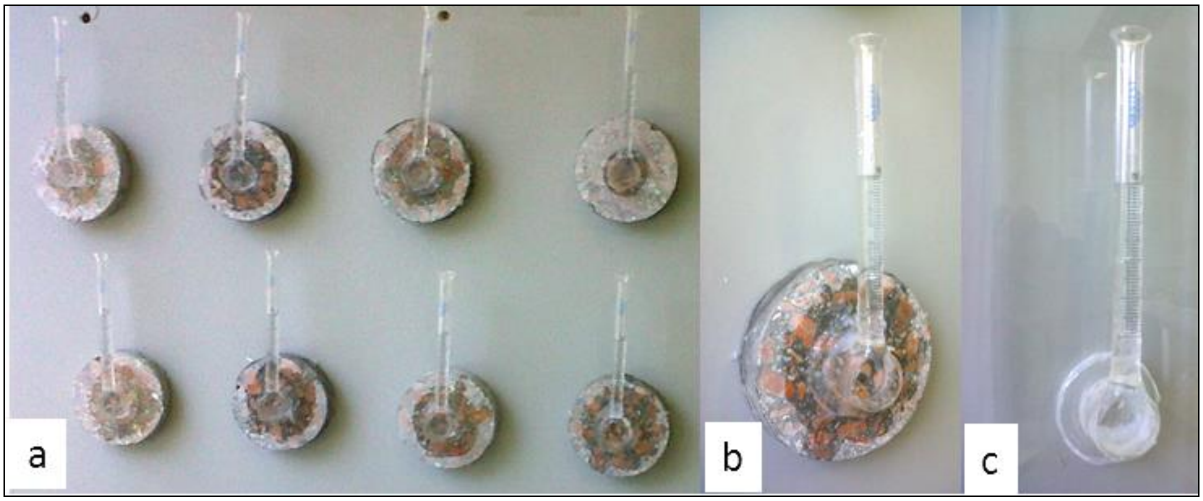

Figure 3. a) Pippete Positions; b) Pipette details; c) Pipette *in vitro*.

4. RESULTS AND DISCUSSION

To obtain more reliability it was carried out statistical processing of results of compressive strength and tensile strength by applying analysis of variance (ANOVA) aiming 95% of reliability.

4.1 Influence on consistency.

The consistency results of fresh concrete mixtures obtained by the slump test upon the determined mix proportions for this experiment are showed in Figure 4.

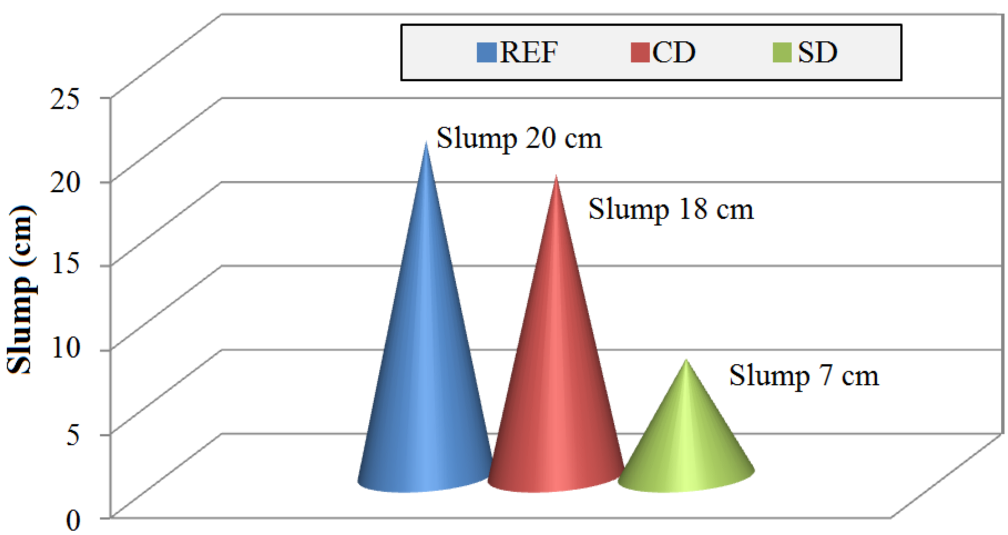

Figure 4. Slump test results (cm).

The test results evidenced that the form of dispersion and the presence of CNTs in the concrete have a strong influence on consistency. As it can be seen in Figure 4, the presence of CNTs Without dispersion increased the consistency of the concrete (reduced its slump), while the series with the presence of CNTs in ultrasound dispersed form presented similar results compared to the reference series. In comparison to the reference series, the powder mixture without dispersion caused the reduction of slump results from 20 cm to 7 cm.
These results highlights the difficulty in performing feasible concrete with CNTs, therefore indicating to be possible only with the use of chemical admixtures to increase the plasticity of the concrete, due to the high amount of water required for the concrete with CNTs. On the other hand, it was appointed that the prior dispersion by sonification had considerably reduced the locking effect of the fluid mass submitted by the addition of powdered CNTs.
Experience shows that the slump results reduction on the addition of powdered CNTs to be due to the large specific surface of the material (250-300 m_2/g) about 650 times higher than CP-V ARI as used in this study. The high slope consumption surface evidenced a splitting towards the entire area of the particles as per CNTs addition. The improvement in the slump results with the ultrasound usage for scattering technique (CD series) led to the better distribution of the CNTs in an aqueous medium and admixture incorporation as presented on the surface of CNTs. This means, the dispersion of ultrasound as evidenced to ensure a preview area and efficient water splitting to the carbon nanotubes particles.

4.2 Compressive strength.
The results of the compressive strength test at 28 days of cure may be observed in Figure 5.

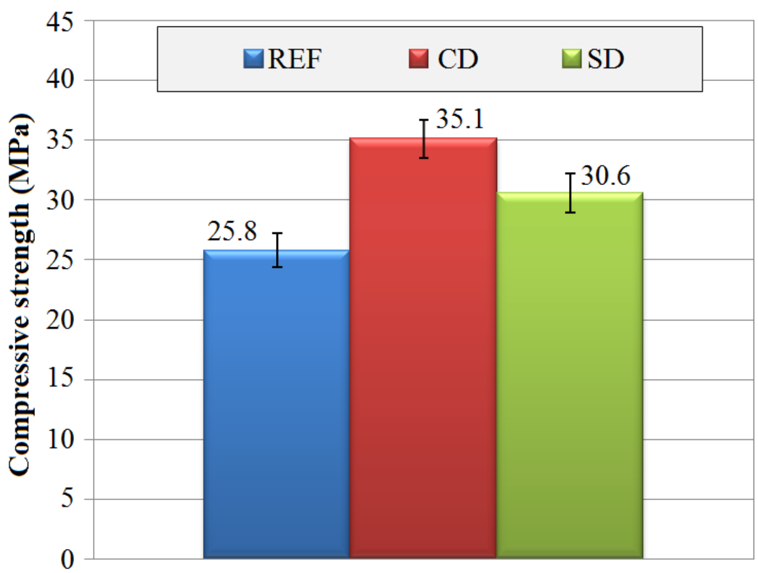

Figure 5. Compressive strength (MPa) for reference series and the two forms of NTCs addition.

The data had evidenced in both cases when CNTs were added, to estate significant improvements in compressive strength effects. To acknowledge these results it was applied the analysis of variance (ANOVA) and it appeared the averages to be significantly different, 95% of certainty. The ANOVA data can be seen in Table 9 and the difference between the averages is confirmed by the fact of F to be higher than $F_{critical}$.

Table 9. Analysis of variance (ANOVA) between compressive strength values

Anova: single factor

SUMMARY				
Group	*Count*	*Sum*	*Average*	*Variables*
Column 1	6	154.6	25.8	2.0
Column 2	6	210.5	35.1	2.6
Column 3	6	183.3	30.5	2.7

ANOVA						
Source Variable	*SQ*	*gl*	*MQ*	*F*	*value-P*	*F critical*
Between groups	260.5	2	130.2	54.0	1.4E-07	3.7
Inside groups	36.2	15	2.4			
Total	296.6	17				

The mix proportion with higher elevation of the compressive strength was the CD series, where there was 37% of increase in compressive strength compared to the reference series. The series without dispersion (SD series) showed 19% of compressive strength increase compared to the reference series.

The results show that the dispersion with ultrasound is extremely important to maximize the benefits brought about by the addition of CNTs in Portland cement concrete.

4.3 Tensile strength by diametrical compression.

Figure 6 shows the results of tensile strength by diametrical compression from the concrete series screened in this study.

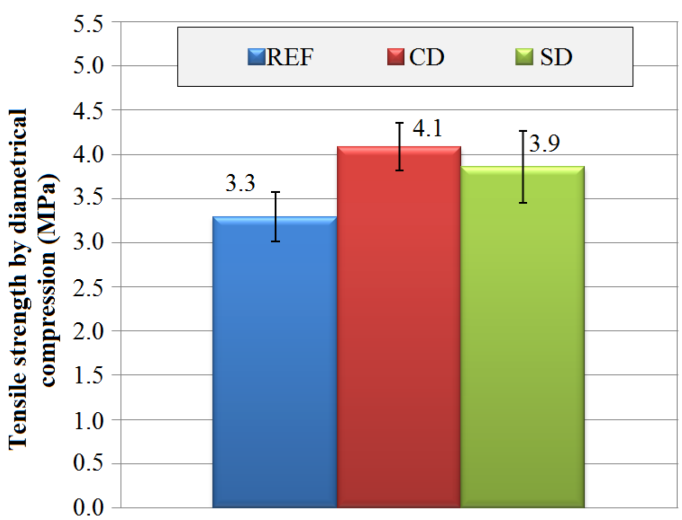

Figure 6. Tensile strength by diametrical compression for reference series and the two forms of NTCs addition.

These results indicate increase in tensile strength between 18 % and 24% with the NTCs addition to the concrete, as compared to the reference series. Although the SD series had resulted in a similar increase of tensile strength compared to the series with dispersion, the SD series presented the largest standard deviation among samples. This is an indication of which the addition of NTCs powder in the mixer resulted in less uniformity of distribution of NTCs in the concrete mass creating considerable variability in tensile concrete strength tests.
To obtain greater reliability in the comparison between the series of concrete studied, the ANOVA tool was used, of which indicated 95% reliability appointing significant differences between the results. This can be better detailed in Table 10, with F higher than $F_{critical}$.

Table 10: Analysis of variance (ANOVA) between the results of tensile strength by diametrical compression for 95% significance

ANOVA: Single Factor

SUMMARY						
Group	*Count*	*Sum*	*Average*	*Variables*		
Column 1	6	19.75127	3.291879	0.079457		
Column 2	6	23.49777	3.916295	0.068453		
Column 3	6	23.14968	3.85828	0.163137		
ANOVA						
Variable source	*SQ*	*gl*	*MQ*	*F*	*value-P*	*F critical*
Between groups	1.428143	2	0.714072	6.887118	0.007554	3.68232
Inside groups	1.555233	15	0.103682			
Total	2.983377	17				

4.4 Immersion water absorption.

Figure 7 evidences that samples with the NTCs there have been improvements in the immersion absorption propertie. This may be related to a better distribution of the pores, resulting in reduced macro porosity. On the other hand, to prove this it is necessary other tests, as the mercury porosimetry test to be able to better quantify the pore size.
It is easy to see the trend of reduced absorption caused by addition of NTCs in concrete as reviewed in this research. However, the reduction level not to be as high as expected, presenting a decrease of 4.4% for the SD series and 3.9% for CD series.

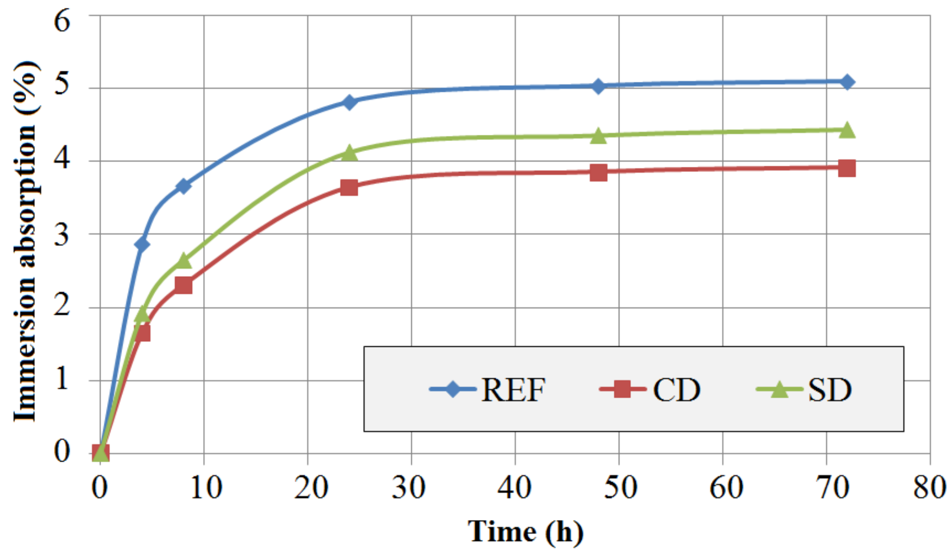

Figure 7. Immersion absorption (%) X time (h) for reference series and the two forms of NTCs addition.

4.5 Water absorption by pipette method.

The absorption by the pipette method was performed to add more knowledge of water absorption of concrete produced with the addition of NTCs. Their results are shown in Figure 8. Note that the reference series and the SD series showed the worst results demonstrating once again the importance of employment dispersion with ultrasound, the CNTs in the additive and water before mix the concrete.

The test was conducted on the cut face and it is important to emphasize the fact that the presence of coarse aggregate in the concrete may affect the water absorption results in this method. However, the trial also showed the importance of the dispersion in the variation of water penetration results and showed reduction trend in series with CNTs pre-dispersed with ultrasound technique.

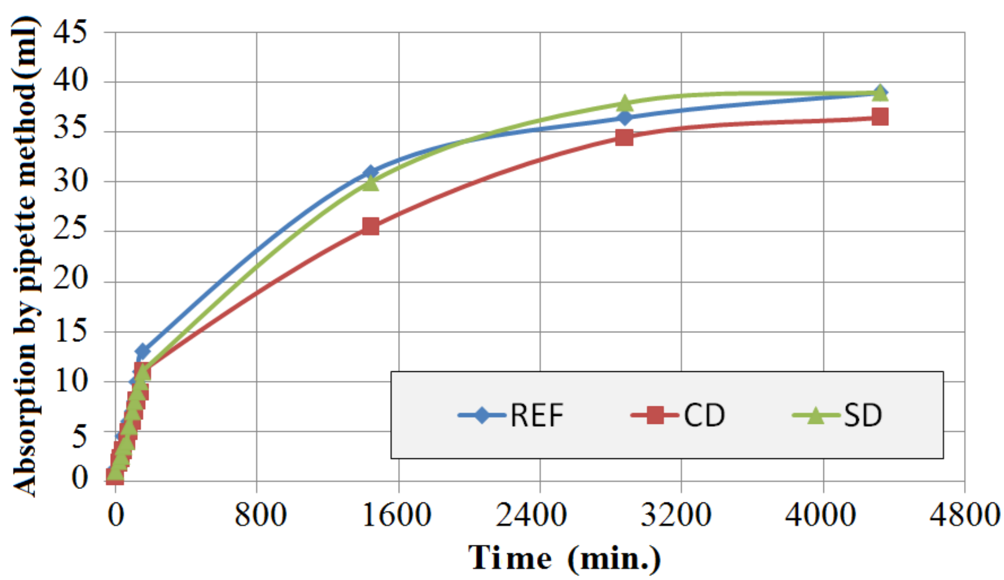

Figure 8. Absorption by pipette method.

4.6 Discussion.

Chaipanich et al. (2010) showed that the addition of carbon nanotubes increased strength of cement with fly ash. In such research, the levels of 0.5% and 1% NTCs relative to the cement mass was analyzed, and the second with 20% fly ash showed a 10% increase in compressive strength. Comparing study data hereby presented with data Chaipanich et al. (2010), it appears that the first case was obtained higher level of compressive strength (increase of 19 % to 37%) and this is probably due to the use of higher levels of CNT in the work of Chaipanich et al. (2010). Due to its high specific surface, the CNT tends to make the cementitious composite less fluid and this may have been a causative point of difference between the results of two research work. However, it is not possible to compare the effect of CNTs on the fluidity in both works because the study of Chaipanich et al. (2010) was carried out on cement paste and consistency was not measured.

Melo (2009) showed an increased compressive strength and tensile strength in Portland cement products with the addition of CNTs. Melo (2009) and Nochaiya; Chaipanich (2011) in their respective studies proved a reduction of the average size of the pores caused by the incorporation of NTC in Portland cement pastes, which can increase the durability of concrete structures, since smaller diameters tend to hinder the movement of aggressive agents within the concrete. According Melo (2009), the content of 0.3% nanotubes showed the highest strength lifting capacity. According to Makar et al. (2005), an increase in the durability of concretes and mortars with addition of CNTs should the adhesion bridges that form in the mass microstructure (Figure 9). They control cracks generated in the cementitious matrix and hence promote greater strength and decrease in porosity. Li et al. (2004) also report a connecting bridge between the hydrated cement and nanomaterials on one of the reasons of increased strength mortars had the incorporation of carbon nanotubes. Other explanations cited in the work of Li et al. (2004) and Nochaiya; Chaipanich (2011) imply the fact that the nanoparticles fill the voids of the cement paste and increases the mechanical strength of the cementitious composite.

Despite being used in various fields, carbon nanotubes also have a high cost, which can be an obstacle to the use of this material in cement composites. Experience shows that with the increasing demand and the ability to synthesize CNTs in the manufacture of clinker, which is being studied at UFMG as reported by Ludving et al. (2011) and Melo et al. (2011), the material will become more accessible. Thus, although the cost of the material is a negative aspect at present, the tendency is that this drawback be overcome over time.

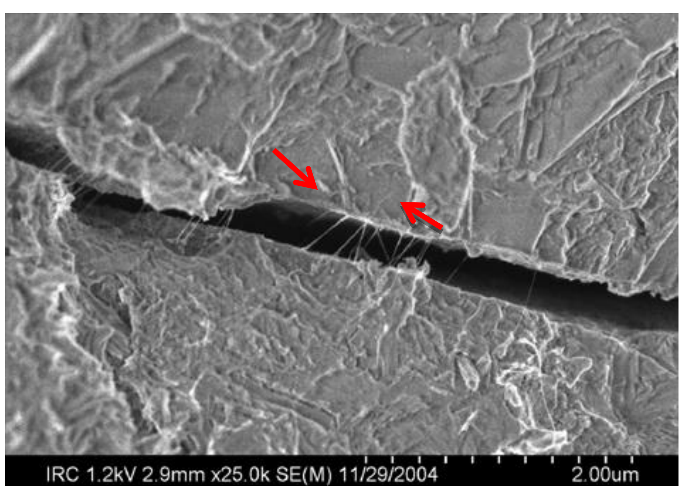

Figure 9. Micro fissure in the cement paste with addition of CNTs acting as adhesion bridges (Makar et al., 2005).

4. CONCLUSIONS

This study focused on the contribution to the effect of addition of carbon nanotubes in Portland cement concrete. Once upon a field of study underway of development and to be prominent and with a few initial results available in the literature. These data is applied to studies of pastes and Portland cement mortars and this test give evidence of different application of CNTs in Portland cement concrete.
The work is based on Marcondes master's dissertation (2012), developed in Federal University of Paraná and in attention to the importance of conducting dispersion of CNTs in water and additive to ultrasound prior to its use in concrete mass. The main findings in this work can be seen as below:

- With 95% of significance, it had acknowledged the mechanical effects of compressive strength and tensile strength by diametrical compression, to be affected by the efficiency of the dispersion of carbon nanotubes in Portland cement concrete.
- The increase of compressive and tensile strength by diametrical compression from CNTs had been found. In this research such increase in compressive strength is represented by 19 % for the SD series and 37 % for CD series, and 17 % for SD series and 19 % for CD series of increase in tensile strength by diametrical compression;
- Addition of CNTs reduced to concrete fluidity of this material. In the case of adding the CNTs prior to ultrasonic dispersion, this reduction was very small, triggering the concrete frame into the same consistency range of the reference concrete, which achieved a reduction of 20 ± 3 cm. Since the addition of powdered CNTs directly into the mixer and without dispersion, caused a sharp drop in the feasibility of the concrete, decreasing its reduction to 7 cm, of which affects material applicability. In such case, this addition of water or more admixtures to adjust the consistency would be required;
- Addition of CNTs reduced absorption of water by immersion in pipette test. In such case it was also found that the series of ultrasound dispersion escalated the advantages arising from the incorporation of CNTs to it.

5. ACKNOWLEDGEMENTS

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The potential of a method for the synthesis of ceramic-cementitious materials processed by an alternative route

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ABSTRACT
Formulations of thermochemically bonded ceramics based of silicoaluminate raw materials were characterized. The mixtures were prepared using low water:solid and these were pressed under up to 30MPa. The specimens were cured for 2 hours at 200°C and were further characterized. The flexural strength registered 6.9-15.7 MPa, which was higher than common cements conventionally processed. The microstructures were dense, suggesting a favorable response of the mixtures to the activation process. The flexural strength varied with the type and amount of mixed raw materials. X-ray diffraction indicated that the crystalline phases from the raw materials did not react; the formation of zeolites was not observed. The proposed processing is promising in order to obtain high strength in short curing times.
Keywords: geopolymers; ceramics chemically bound; activated clays; precast products.

RESUMEN
Se estudiaron formulaciones de materiales cerámicos ligados termoquímicamente empleando materias primas silicoaluminosas. Se prepararon mezclas con baja relación agua:sólidos y se procesaron mediante prensado hasta de 30 MPa. Las probetas se curaron a temperaturas de 200°C por 2 horas. Se evaluó la resistencia a la flexión después del tratamiento térmico; los valores registrados alcanzaron entre 6.9 y 15.7MPa, lo cual es superior a los cementos procesados por rutas convencionales. Las microestructuras obtenidas indicaron la formación de matrices densas, sugiriendo una respuesta favorable de las materias primas al proceso de activación. Las propiedades mecánicas variaron con la cantidad y tipo de materiales mezclados. La difracción de rayos X indicó que no hubo formación de fases zeolíticas y las fases cristalinas no reaccionaron durante el proceso de curado. El procesamiento propuesto es prometedor para obtener altas propiedades mecánicas en tiempos de curado cortos.
Palabras clave: geopolímeros; cerámicos químicamente ligados; arcillas activadas; prefabricados.

RESUMO
Estudaram-se o comportamento mecânico de cerâmicos-cimetício silicoaluminosos, ligados termo quimicamente. Empregou-se traços com baixa relação água/sólidos que foram prensados com até 30MPa, para obtenção dos corpos de prova. As amostras foram curadas a temperaturas de 200°C por 2h. Avaliou-se a resistência a flexão depois do tratamento térmico; os valores registrados alcançaram entre 6,8MPa e 15,7MPa, o qual é superior ao normalmente obtido com esses cimentos à temperatura ambiente. As microestruturas observadas indicaram a formação de matrizes densas, sugerindo uma resposta favorável das matérias primas ao processo de ativação. As propriedades mecânicas variaram com a quantidade e tipo de materiais utilizados. A difração de raios X indicou que não houve formação de fases zéoliticas e as fases cristalinas não reagiram durante o processo de cura. O processamento proposto é promissor para obter altas propriedades mecânicas em curtos períodos de cura.
Palavras-chave: geopolímeros; cerâmicos termoquimicamente ligados; arcillas activadas; produtos prensados.

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1. INTRODUCTION

The tile production industry is an important consumer of water and energy due to the various stages of the processing and production, such as wet grinding, drying and firing. During the latter, the temperatures may reach above 1000°C by means of the use of fossil fuels. The mentioned operations contribute to the total cost of production, so savings in the number of operations is of importance. Moreover, in order to promote the sustainability of the production, the industry is interested in strategies leading to reductions in the consumption of fuels, which would in turn reduce CO_2 emissions. This can be achieved by designing alternative routes of production, while preserving as much as possible the properties and quality demanded for the products, i.e. mechanical strength, wear resistance, etc.

A family of cementitious materials are those known as Chemically Bonded Ceramics (CMC), also known as geopolymers, which have been promoted by Davidovits since the decade of the 80, who registered several patents (Davidovits, 1982, Davidovits, 1991). The CMC are inorganic polymers, and some authors consider that the name of alkali activated cements is more adequate. In this paper the materials investigated will be referred as CMC.

The CMC can be of silicoaluminate nature, the structure of which is based on three dimensional arrangements of SiO_4 and AlO_4 tetrahedra bound by sharing oxygen atoms. These materials can be processed as cements and display properties of ceramic-like materials; the consolidation takes place via the dissolution of the raw materials under high pH conditions, and the co-polymerization of the referred species; the reaction temperatures commonly range from ambient to around 100°C.

1.1 Raw materials for the synthesis of CMC.

The raw materials useful to prepare silicoaluminate CMC must comply with some specific requirements: (1) Chemical composition rich in SiO_2 and Al_2O_3; (2) An abundant fraction of glassy phase, fundamental for the susceptibility to the alkaline attack; (3) Sufficiently small particle size in order to promote its reactivity.

Clays are silicoaluminate raw materials, and are among the most abundant minerals in the earth crust. Calcined clays have been used as raw materials in the production of CMC (Barbosa et al, 2000); most of the reports have been based on the use of metakaolin ($Al_2Si_2O_7$) (Davidovits, 1982), which is obtained after firing kaolinite ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$). The latter is a clay of SiO_2:Al_2O_3 configuration of the type 1:1 (Rowles y O´connor, 2003), constituted by one layer of Silicon atoms in tetrahedral coordination with Oxygen atoms and one layer of aluminum atoms in octahedral coordination with oxygen and OH^- ions (also known as gibbsite layer). The chemical composition of kaolinite is (wt %) *46.54%*SiO_2*; 39.50%*Al_2O_3 *39.50%;* H_2O *13.96%;* it shows little reactivity towards alkali under normal conditions. However, after firing at 650-900ºC, the kaolinite losses the OH^- groups and the aluminum layer collapses (Shvarzman et al, 2003) and the aluminum coordination changes to tetrahedral, while the layer of Silicon remains (Kakali et al, 2001). The resulting product is metakaolin, which is amorphous to X-ray diffraction. This conversion increases the reactivity towards alkaline environments even at room temperature, which is the key for the CMC materials. The kaolinitic minerals may contain impurities such as quartz and other clays, as well as the substitution of iron and/or titanium for aluminum. Regarding the purity, previous work in Cinvestav Saltillo (Arellano-Aguilar et al., 2014, Burciaga-Diaz et al., 2012, Burciaga, 2014) has shown that even low purity metakaolinitic minerals are useful to produce CMC.

1.2 Processing of CMC materials.

Compared to the processing of conventional Portland cements, the CMC have lower environmental emissions and better technological properties; moreover, these can be prepared using widely available raw materials, processing fluid and moldable pastes. The CMC harden by virtue of chemical reactions that advance gradually with time, reaching properties of interest for a wide range of applications. The preparation of CMC depends on various factors, for which their effect has not been completely understood according to the literature, some of these are:

(a) Type and amount of chemical activator
(b) Thermal treatment
(c) Chemical composition of the mineral
(d) Glassy fraction of the mineral
(e) Particle size
(f) Amount of water

The chemical composition of the overall formulation plays a major role that defines the mechanical strength (Burciaga-Diaz et al, 2012); it is defined on the basis of molar ratios such as: SiO_2/Al_2O_3, M_2O/Al_2O_3 y M_2O/H_2O (Burciaga-Diaz and Escalante-García, 2004). The literature indicates variable compositional ranges for several raw materials; the ratios reported by the patents of Davidovits, do not always result in the best properties for any raw material. The chemical composition of the CMC can also be reported including the concentration of mineral raw materials and alkaline activators. The most common among the latter are the alkaline silicates of the type $M_2O{:}xSiO_2$, which promote high pH values (Palomo et al, 1999; Davidovits, 1984), where M can be Na or K.

The chemical reactions during the synthesis of CMC have been proposed to take place in three stages: **(1)** Destruction of the atomic structure of the mineral. The alkaline media offers chemical stimuli such as the variation of the ionic strength caused by the presence of alkaline metals that perform as electron-donors; this causes the breaking of the bonds Me-O, Si-O-Si, Al-O-Al y Al-O-Si, caused by the alteration of the electronic density around the Si and Al atoms. Some of the species formed include silicic acid ($Si(OH)_4$), and anions such as $Si\text{-}O^-$, $Al(OH)_4^-$, $Al(OH)_5^{2-}$ y $Al(OH)_6^{3-}$. **(2)** The mentioned species saturate the solution and a policondensation takes place, forming new chemical products, leading to the setting, and a reduction of the pH takes place due to the interaction of the hidrosilicates and hydroaluminates with the alkalis. **(3)** Precipitation of products as a result of the particles formed in the previous stage, which results in an enhancement of the mechanical strength; the reduction of pH leads also to de condensation of silica gel from the alkaline activator, which favors the strength.

The conventional synthesis of CMC involves mixing the mineral raw materials with the alkaline solutions of activators, as well as the molding and curing to attain solidification. The curing commonly takes place at temperatures from ambient to 120°C (Barbosa y McKenzie, 2003; de Vargas et al, 2011; Burciaga-Diaz et al, 2012). Curing at high temperature allows gains of high early strength, some authors have pointed that higher strengths are reached with higher temperatures, e.g. 60MPa after curing 24 h at 85°C (Palomo et al, 1999, Rowles y O´connor, 2003); however, it has also been reported that after curing at high temperature the strength gains are negligible (Arellano-Aguilar et al, 2014). Information about the use of curing temperatures above 100°C is scarce in the literature.

1.3 This investigation.

There exist in the literature a considerable number of reports related to the synthesis of geopolymeric materials based on high purity clay minerals and industrial by products such as metallurgical slags, fly ash, muds, etc. Nonetheless, there exists a limited number on reports based on kaolinitic minerals of low grade (Burciaga-Diaz et al., 2012; Arellano-Aguilar et al., 2014). The latter are an abundant resource worldwide, so their potential is considerable and the opportunities must be explored (Davidovits, 2002), such is the case of this investigation. On the other hand, there are only a few papers on the synthesis of CMC materials that combine the CMC processing under the conditions proposed in this research (Asbridge et al., 2002, Zivica et al., 2011), i.e.: very low water/solid ratios and uniaxial compression.

This paper presents the results of an investigation to develop a strategy to synthesize CMC materials in the shape of small tiles, using those raw materials commonly consumed by the traditional ceramic industry of tile production, which are in turn of lower purity than those used in CMC synthesized as cementitious binders. In contrast to the traditional ceramic industry, this paper proposes a simpler route, with less processing steps, using less water, less energy and generating less CO_2 emissions, but with the potential of preparing ceramic-like materials of properties similar to those currently produced by conventional routes but in a more sustainable way.

2. EXPERIMENTAL PROCEDURE

2.1 Materias Primas.

Some experimental details are omitted to protect authorship rights and industrial secrets. Three silicoaluminate minerals were employed, labelled as MA, MB y MC; the MA was fired at 700°C and was labelled as MAc. Table 1 shows the chemical composition obtained by X-ray fluorescence spectroscopy (FRX), from which the differences in chemical composition among the silicoaluminate minerals were evident; MA shows high content of iron. The mineralogy of the raw materials was characterized by X-ray diffraction, the results are shown with the results in Figure 4 for reasons of space and for a better comparison and understanding of the results. The difference among MA and MAc was the disappearance of the reflections of kaolinite, although the other crystalline phases persisted after the firing at 700°C; on the other hand, MB and MC showed an amorphous hump in the 2theta position typical for silicoaluminates.

Table 1. Chemical composition of the raw materials, obtained by X-ray fluorescence.

Mineral	**Weight % of oxides**						
	SiO_2	**Al_2O_3**	**Fe_2O_3**	**K_2O**	**TiO_2**	**CaO**	**Na_2O**
MA	54.5	20.6	10.1	5.7	1.65	0.219	0.15
MB	72.1	14.8	0.916	5.13	-	3.39	3.21
MC	68.66	12.82	0.94	4.76	0.04	4.15	-

2.2 Processing of materials.

After a series of preliminary tests carried out to determine a set of experimental parameters, 4 mixtures were prepared using the raw materials from Table 1; here the mixtures are made of MAc and any of the other 3 raw minerals. Table 2 lists the formulations prepared. The alkaline activators were chemical compounds of $Na_2O{\cdot}SiO_2{\cdot}H_2O$ with weight ratios SiO_2/Na_2O lower than 2. The amounts of Na_2O used were similar to those commonly reported for CMC from the literature using calcined clays. The amount of water used was the minimum necessary to provide the mixtures a consistency useful for the conformation of green bodies ready for the subsequent processing stage.

Table 2. Systems investigated.

Mixture	Component 1	Component 2	Ratio Component/Component2
M1	MAc	MB	High 2/1
M2	MAc	MB	Low 3/1
M3	MAc	MA	Low 3/1
M4	MAc	MC	Low 3/1

The powdered minerals and activator solutions were mixed using a high speed mixer. The semi-dry mixtures were placed in the cavities of molds of dimensions of 4x16cm, the thickness of the resulting specimens was of 0.8-1.0cm. The mixtures were subjected to uniaxial compression using pressures up to 30.4 MPa. The tile specimens were demolded and thermally treated at 200° for 120 minutes and then left to cool to room temperature before characterization.

2.3 Characterization of materials.

The specimens were tested by flexural strength using an hydraulic machine following the ISO 10545-4; due to difficulties associated to the processing of the specimens, only the flexural strength was measured, which is more important than the compressive strength for tile samples. The density was measured by the Archimedes method using liquid mercury. After the mechanical testing, the sample relics were used for further characterization. A fraction of the samples was ground in a planetary mill with agate media in order to pass the 105μm mesh, before characterization by DRX (Phillips PW3040) under the following operating conditions: CuKα radiation (1.542 Å), range 10-70° 2θ, step of 0,03° 2θ and incidence time of 3s per step. Solid fragments of specimens were mounted in resin for characterization by scanning electron microscopy (MEB Philips XL30ESEM coupled with energy dispersive spectroscopy, EDS) at an acceleration voltage of 20 ekV. The specimens were polished and coated with carbon. EDS spot analysis were performed to determine semi-quantitatively the chemical composition of specific areas in the samples, the measuring time was of 30 seconds for each analysis.

3. RESULTS AND DISCUSSION

Table 3 presents the results of compressive strength and density of the formulations investigated, which showed notable variations in flexural strength. The highest strength was for the mixture M1 (MAc-MB with low content of MB), this was close to the requirements for conventional ceramic tiles and 35% higher than the strength of the mixture M4 (MAc-MC with high content of MC). Higher contents of MB among mixtures M1 and M2 resulted in a reduction of 43% of the strength. The density values did not correlate to those of strength, i.e. M3 was denser and also weaker than mixtures M1 y M4; this could be due to differences in the intrinsic mechanical properties of the reaction products formed during the thermochemical activation.

It is noteworthy that the flexural strength values registered were superior to those reported for CMC processed in a conventional way, which are commonly much lower than 10 MPa after 28 days; this indicates that the proposed processing method is quite efficient to attain high strength in considerably short curing times. Considering that for concretes, the flexural strength is approximately 10% of the compressive strength of the specimen, the mixtures investigated would be expected to potentially show compressive strengths of 69 to 157 MPa after only 2 h of preparation. The obtained flexural strength results could be considered similar to those reported previously using uniaxial compression and low water/solid ratios (Zivica et al., 2011); they reported compressive strengths of up to 146 MPa, which would correspond to an estimate of approximately 15 MPa of flexural strength. Nonetheless, the minerals used in this investigation are of far lower grade that those of the referred report, which makes our route more economical.

Table 3. Mechanical properties and density of the mixtures investigated.

Mixture	Flexural Strength (MPa)	Density (g/cm^3)
M1	15.7	2.01
M2	8.9	1.76
M3	6.9	2.21
M4	11.6	1.88

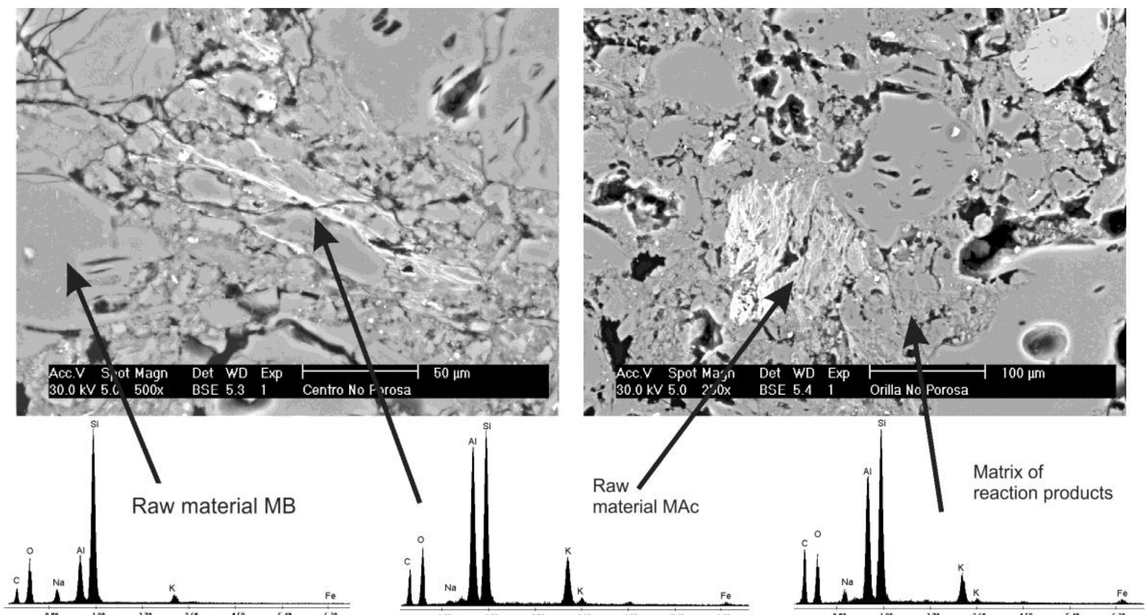

Figure 1. Microstructure obtained by scanning electron microscopy and backscattered electrons of mixture M1.

Figure 1 presents the microstructure of the mixture M1, obtained by backscattered electron imaging. The matrix of reaction products was dense, in agreement with the good flexural strength. Some particles of MB showed internal porosity. Some particles of MAc showed bright zones, which occasionally showed an elongated morphology; the brightness of such zones is attributed to a higher emission of backscattered electrons due to the presence of compounds of higher average atomic number, such zones could be unreacted particles that have not incorporated water, as happens in the reaction products that appear of a darker gray tone.

Figure 2 shows the microstructure of mixture M3 (the lowest flexural strength). The densification of the matrix of reaction products was similar to that of mixture M1, so the reduced strength is attributed to the formation of reaction products of lower intrinsic strength. The microstructure shows some bright zones, which were rich in Fe y Ti, in agreement with the chemical composition of the MAc.

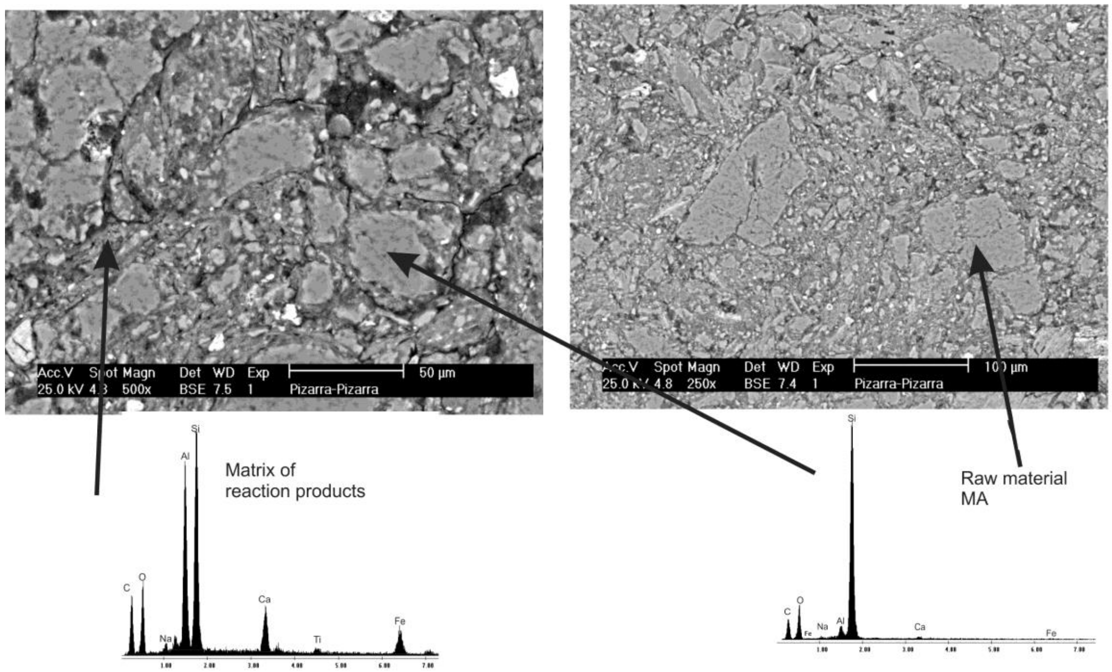

Figure 2. Microstructure obtained by scanning electron microscopy and backscattered electrons of mixture M3.

Figure 3 shows the micrographs from the microstructure of mixture M4, which displayed a similar densification as mixtures M1 and M3. The bright zones showed high contents of Fe and Ti (high atomic number) in the matrix corresponding to MA, while the matrix of MC showed a chemical composition consistent with a silicoaluminate in most of the particles (similar to MB).

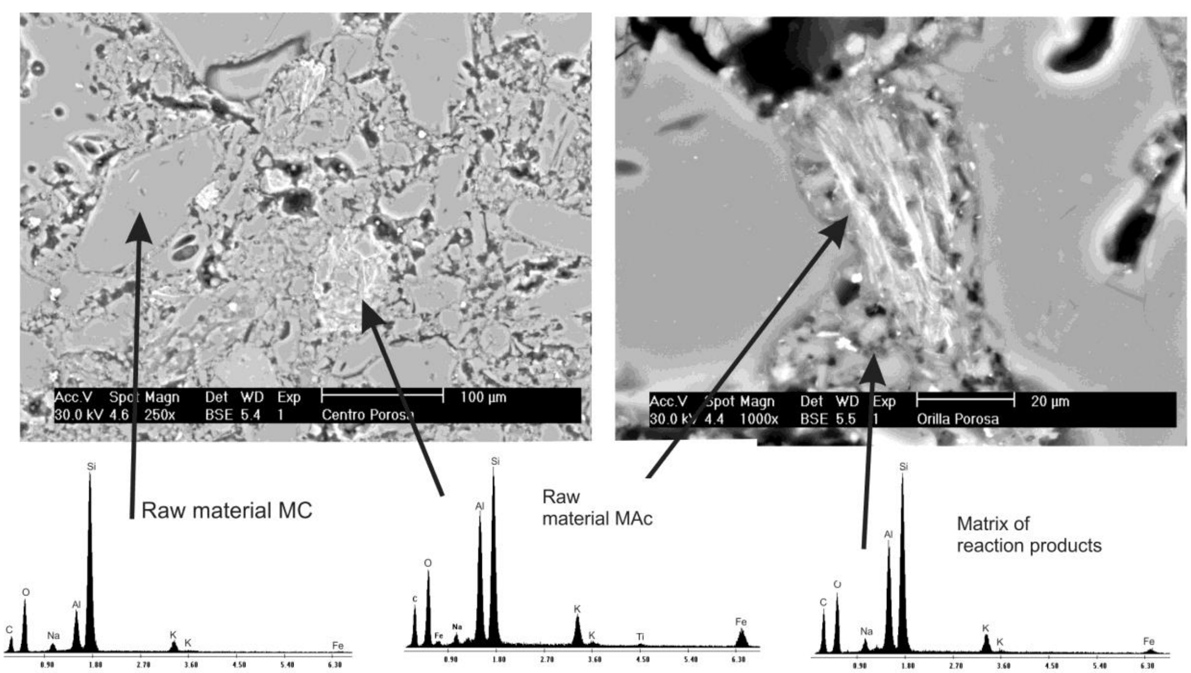

Figure 3. Microstructure obtained by scanning electron microscopy and backscattered electrons of mixture M4.

The results show that the type and amount of Component 2 (see Table 2) influences directly on the resulting properties. The differentiation among reaction products and unreacted raw materials is complicated in the micrographs, as both are silicoaluminates, so the differentiation by means of the gray tone is not as easy as in the case of hydrated conventional Portland cement. However, due to the high flexural strength obtained, it can be inferred that the reaction cementitious products are intimately intermixed with the unreacted raw materials.
Figure 4 presents the XRD patterns of the investigated mixtures, the patterns of the unreacted raw materials are included for reference purposes. In general terms, it was noted that the crystalline fractions remained unreacted after the solidification, indicating that these are inert during the curing process at 200°C for 2h. The formation of zeolites was not observed as reported for some CMC materials. On the other hand, the reaction products of cementitious CMC are characterized by an amorphous nature. For the mixtures M1, M2 y M4 the amorphous hump persisted, although it was noted that such humps were widened and shifted slightly to the left, indicating the formation of new reaction products of amorphous nature but different to those of the starting raw materials. In contrast, for the mixture M3 the amorphous hump was not clear, although the consolidation and mechanical strength indicated the formation of reaction products, so it is possible that the high crystallinity of the specimens overlaps and overshadows the presence of amorphous products.

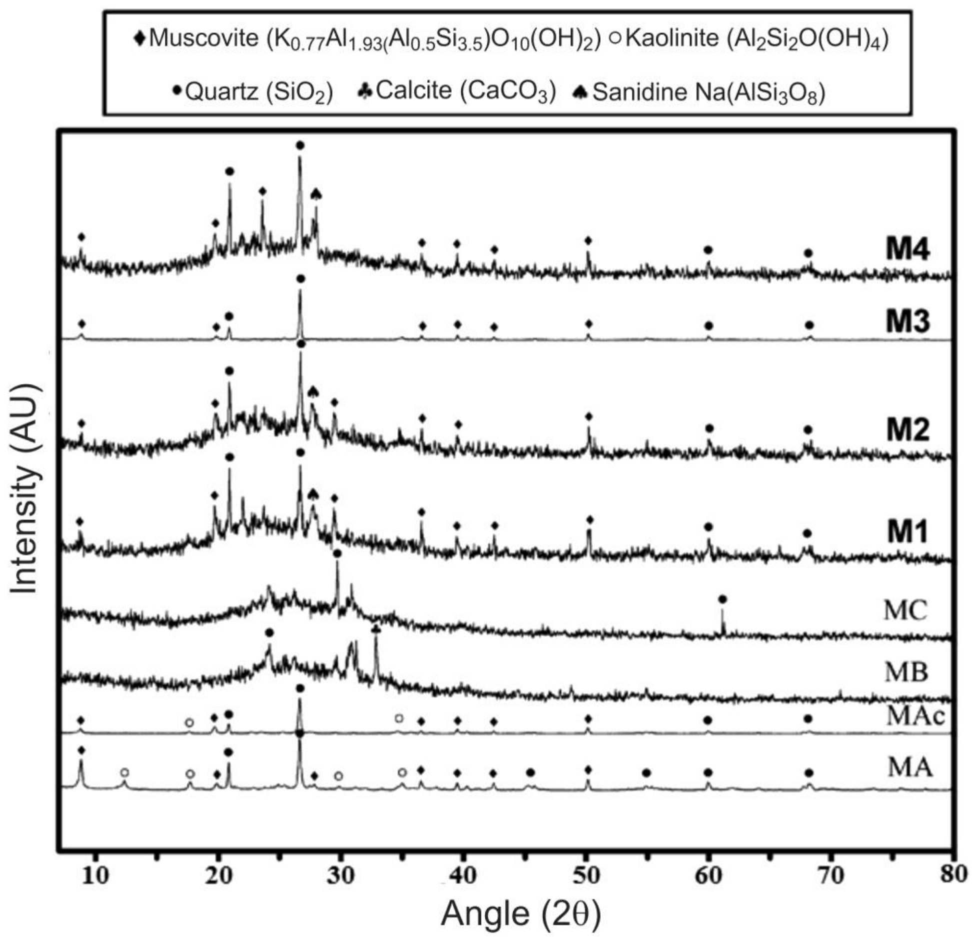

Figure 4. X-ray diffraction patterns of the mixtures and raw materials investigated.

4. CONCLUSIONS

- The uniaxial pressing favors the densification of the matrices of the chemically bonded binders, which resulted in high flexural strengths of 6.9-15.7 MPa
- The thermal processing accelerates the reaction processes, promoting the formation of the reaction products of cementitious nature, which are intimately intermixed with the unreacted raw materials in dense microstructures.
- The chemical activation process was reinforced by the uniaxial pressing and thermal activation, using Na2O concentrations similar to those reported for common chemically activated binders
- The combination of chemical activation and thermal treatment, could be called thermochemical activation and has the potential to produce ceramic-like materials of similar properties as those processed at more than 1000°C, but with savings in the energy and water demands.
- More research is required to optimize the processing and for a better understanding and characterization of the structure of the mixtures, in order to understand the mechanisms of reaction.

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Structural strengthening of a historical building in Rio Branco city – Acre

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ABSTRACT

This work presents the use of the technique of structural reinforcement for jacketing applied in the reform of the historical building called "Casarão", due to the architectural need to remain as faithful to the original design,justifying the need for increased resilience without substantial increase in the cross section of the pillars. The results obtained by analyzing the reinforcement relative to rectangular columns subjected to bending, shearing and torsional, in accordance with the NBR 6118 (ABNT, 2014), indicated that the studied technique was efficient because all reinforced parts had a greater bearing capacity and met the current requirements without compromising the structural safety of the building's characteristic architectural.
Keywords: historical building; structural strengthening; jacketing.

RESUMO

Este trabalho apresenta o emprego da técnica de reforço estrutural por encamisamento aplicada na reforma da edificação histórica denominada “Casarão”, devido à necessidade arquitetônica de permanecer o mais fiel ao projeto original, justificando-se pela necessidade do aumento de capacidade de resistência sem que haja aumento substancial na seção transversal dos pilares. Os resultados obtidos através da análise do reforço em relação aos pilares retangulares submetidos à flexão composta, esforços cortantes e torsores, em concordância com a NBR 6118 (ABNT, 2014), indicaram que a técnica estudada foi eficiente, pois todas as peças reforçadas tiveram uma capacidade portante maior e atenderam aos requisitos atuais de segurança estrutural sem comprometer as caracteristicas arquitetônicas da edificação.
Palavras-chave: edificação histórica; reforço estrutural; encamisamento.

RESUMEN

Este artículo presenta el empleo del método de refuerzo estructural por revestimiento aplicada en la reforma del edificio histórico llamado "Casarão" en portugués, debido a la necesidad arquitectónica de permanecer tan fiel al diseño original, justificado por él interés de aumento de resistencia sin aumento sustancial de la sección transversal de los columnas. Los resultados obtenidos mediante el análisis del refuerzo con relación a las columnas rectangulares sometidos a flexión compuesta, esfuerzos de cizallamiento y de torsión, de acuerdo con la NBR 6118 (ABNT, 2014), indican que la método estudiada fue eficiente, porque todas las partes reforzadas tuvieron una mayor capacidad portante y cumplieron con los requisitos actuales de seguridad estructural, sin comprometer las características arquitectónicas del edificio.
Palabras clave: edificio histórico; refuerzo estructural; revestimiento.

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1. INTRODUCTION

The "Casarão" (Figure 01), public building built in the 1930s, has mixed structure of reinforced concrete and wood in good condition in its central part, maintaining eclectic Syrian and Lebanese architectural features with European influence, representing a regional style of great cultural importance of the city of Rio Branco, in Acre state. Its revitalization meets a society demand for the state government, which received a petition with hundreds of signatures to this choice. The historic building was listed by the State Board of Historical and Cultural Heritage on August 13, 2009, at the initiative of civil society, and approved on April 30, 2010, by the decree number 5,235, under the protection and supervision of the state government, through the Department of History and Cultural Heritage Foundation of Culture and Communication Elias Mansour.

Figure 1. The Casarão.

In this case study, the building’s columns were analytically and computationally evaluated to check their resistance, to meet the existing requirements of structural safety. As well as several old buildings in the city of Rio Branco, the concrete of these columns was dosed with brick shards as coarse aggregate to replace commonly used ones, such as pebble and gravel. There is no technical evidence of the strengthening of this material to meet the NBR 6118 (ABNT, 2014), testimonies extraction procedures were performed and the results showed compression strength of concrete below the specified on the structural revitalization project of the building, carried out with the help the computer program. The verification of the results of this enhancement becomes important because jacketing technique with reinforced concrete is the most common and also presents implementation difficulties in historical buildings works due to architectural necessity, considered culturally indispensable to the architectural heritage of the city and should remain as true to its original form, without any substantial increase in the cross section of the columns, the jacketing of reinforced concrete is feasible due to economic advantages, speed of execution and consistency with the architectural design.

2. METHODOLOGY

2.1 Characteristics of the historical building.

The building to be revitalized is called Casarão and is located at Brazil avenue number 310 in the city of Rio Branco, Acre state. Featuring 405.1 m² of built area, the Casarão is composed of basement, ground floor and upper floor, with a parking with 705.0 m² and a free area of 154.7 m² in front of the building. All stages of the building revitalization process were the Acre State Government responsibility and followed an executive chronogram previously established and detailed. The municipal director plan, by law 1611 of 27 October 2006, classified Casarão as a building located in ZPHC (Cultural Historic Preservation Zone), with occupancy rate of 70% (810.0 m^2), coefficient of utilization 6 (7800.0 m^2) and 10% of permeability rate (130.0 m^2). During the process of revitalization it was found the need for structural strengthening only for the underground stretch of the columns P21, P30 and P41 for new loadings, which did not occur with the other columns. Figure 2 (top floor wood molds) shows the original situation of the columns and the strengthening proposal.

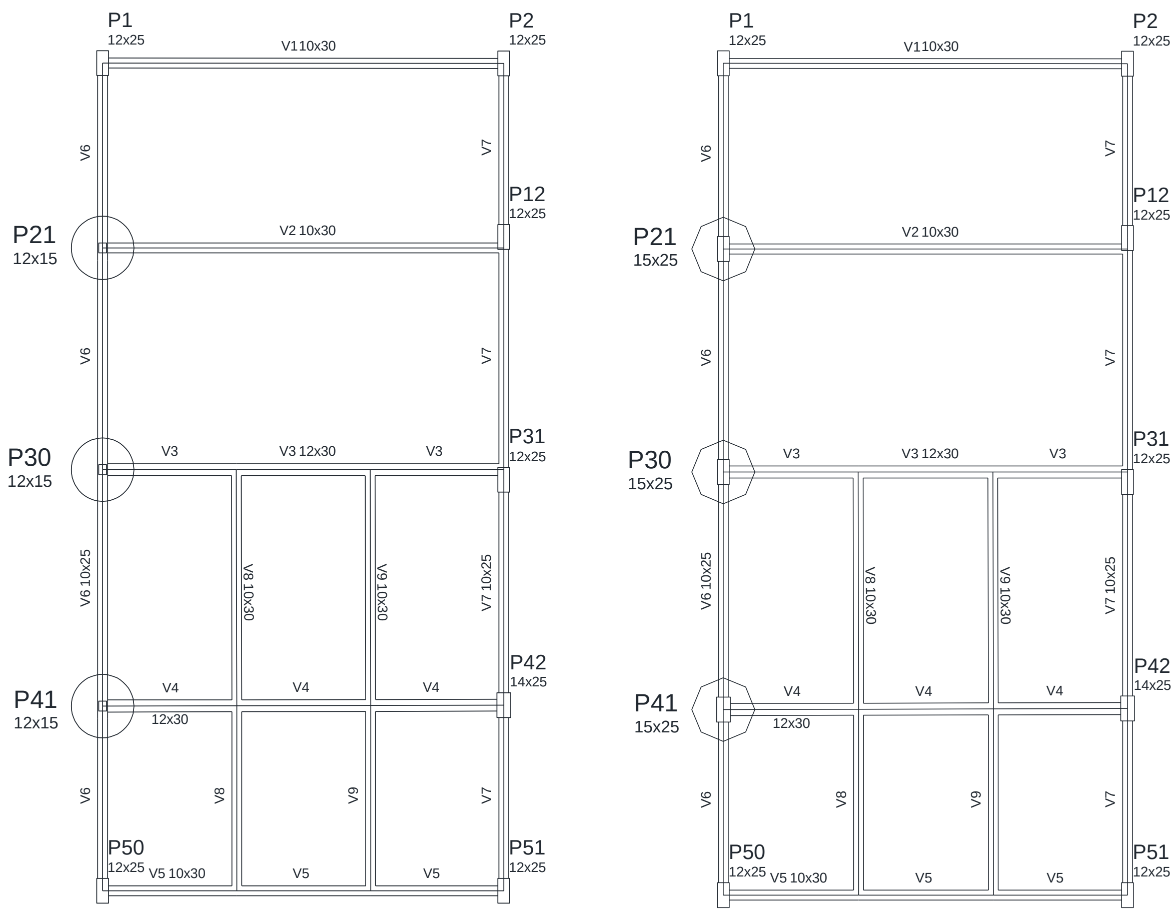

Figure 2. Location and dimensions of columns P21, P30 and P41 before and after structural strengthening (right).

In the reform of the building, period features have been retained and built-up areas that were not in the original architectural design have been removed. The services performed were the revitalization of the original wood walls, structural strengthening of the columns, replacement of the roof structure, the roof, the floorboards of the ground and upper floors, replacement of electric installations, logic, water and sewer pipes, fire-fighting system, creating a seating area with benches and bins, maintenance of three rooms upstairs and manufacture of masonry in the three floors. Figure 3 shows the appearance of the side and front facades of the revitalization project.

Figure 3. Final aspect designed for Casarão.

2.2 The finding of the problem.

To check the existing structural safety, inspection visits and monitoring of the construction site during the execution of the revitalization work were carried out, where the procedures, techniques and equipment used in operations were identified and the photographic record being held at all stages of the executive process in 2009 and 2010. Before performing any procedure on the structure, the technical team highlighted the importance of axial compression tests on concrete testimonies to enable identification of any eventual problems related to concrete strength, since the old concrete was originally made with ceramic pieces of bricks and roof tiles. The test results indicated that, in general, the structural concrete has low compressive strength and contained coarse aggregate larger than 50 mm, which contributed to the formation of voids inside of some columns. It notes that the use of coarse aggregates derived from reducing of ceramic elements such as bricks and tiles is still a common practice in the city of Rio Branco, where there is shortage of gravel and rolled pebble. Figure 4 shows the location of extraction of the concrete testimonies in a column and Table 1 shows the results for concrete compressive strength of concrete testimonies from columns P21, P30 and P41, which further analysis indicated the need for structural strengthening in the basement level columns.

Besides the low compressive strength, it was also found that the reinforcements of some columns had advanced corrosion and severe weight loss, compromising bearing capacity to service loadings and even to permanent ones, once some bars were completely sectioned by corrosion. Figure 5 shows the appearance of the corroded reinforcement bars of the columns. It was concluded that the damage was characteristic of deterioration processes with systemic nature, i.e. related to the quality of the concrete used in the manufacturing of the structural system and especially the thickness of reinforcements coatings that showed values between 10 mm and 15 mm, considered inadequate to provide the required service life of a structure made of concrete containing such porous aggregates.

Figure 4. Testimonies' extraction hole in a column.

Table 1. Concrete's compressive strength.

Pilar	Testemunhos (MPa)	Projeto de reforço (MPa)
P21	13.7	25.0
P30	20.1	
P41	14.7	
Average	16.2	

Figure 5. Columns' longitudinal reinforcement eroded (corrosion).

2.3 Structural strengthening.

The applied methodology for defining the structural strengthening technique considered the set of information on the conservation status of the entire structure in order to drive the strengthening designer engineer to draw up a more accurate diagnosis of the causes and consequences of the pathologies found, because, according to Julio *et al.* (2003), the success of rehabilitation activities or intervention in the structure depends on a clear and precise definition about the problems encountered, including a diagnosis and prognostic evaluation of the acting causes. This preliminary study was instrumental in determining the level of intervention to be performed in the structure, which can range from simple repairs located to the need for demolition and reconstruction. For structural reinforcement was chosen the reinforced concrete jacketing technique, as the concrete can be cast into molds or projected, making it the most versatile material for the enhancement or restoration of reinforced concrete structures, and used in all kinds of structural elements and in different situations and conditions (Mehta & Monteiro, 2014). The structural reinforcement was then indicated to the columns P21, P30, P41, in the basement floor lengths, with the main steps consist of superficial concrete scarification, positioning of additional reinforcement, installation of wooden molds and placing of concrete with compressive strength (f_{ck}) of 25 MPa.

2.3.1 Concrete. The concrete used for structural strengthening was monitored and supervised following the recommendations of the Brazilian standard for concrete structures design, NBR 6118 (ABNT, 2014), and the design of the concrete mix to reach the compressive strength of concrete (f_{ck}) 25 MPa provided the volume ratio of 1: 2: 3 with water/cement factor of 0.5 using coarse aggregate maximum diameter of 9.5 mm. Verification of the compressive strength of concrete was performed by specialized laboratory that conducted the casting "in loco" of cylindrical proofs with 100 mm diameter and 200 mm height. Three proofs were molded from each concreted held by employees of the executive company of the structural strengthening, who received training and quality control so that the concrete mix reached the compressive strength specified by the designer of the structural strengthening.

2.3.2 Reinforcements. The longitudinal and transverse reinforcement (stirrups) before and after the structural strengthening of the columns were composed of steel bars with diameters, numbers and spacing presented in Table 2. The concrete cover for the columns was 25 mm and 15 mm at the short and long sides' dimensions, respectively. Figure 6 shows details of the cross sections of the columns before and after the structural strengthening with reinforced concrete jacketing, and Figure 7 shows details of the transverse and longitudinal bars. The columns P21, P30 and P41 were only strengthened in the basement floor length because these columns presented safety factors below the recommended by the Brazilian standard for reinforced concrete structures design for the future loadings. Figure 8 shows the placement of the reinforcements, where it is possible to see that, despite efforts to preserve as much original architecture, the smaller final dimensions of the columns, plus the 20 mm thick coating mortar layer, would be greater than the wall thickness.

Table 2. Columns' cross section dimensions and reinforcements.

<table>
<tr><th rowspan="3">Column</th><th colspan="2">Columns dimensions</th><th colspan="3">Steel</th></tr>
<tr><th colspan="2">Cross section (mm)</th><th colspan="2">Reinforcement (mm)</th><th rowspan="2">Design yield stress (MPa)</th></tr>
<tr><th>Original</th><th>Strengthening</th><th>Original: Longitudinal / Stirrups</th><th>Strengthening: Longitudinal / Stirrups</th></tr>
<tr><td>P21</td><td rowspan="3">120 x 150</td><td rowspan="3">150 x 250</td><td rowspan="3">4Ø10.0 / Ø5.0e150</td><td rowspan="3">4Ø12.5 / Ø5.0e150</td><td rowspan="3">435</td></tr>
<tr><td>P30</td></tr>
<tr><td>P41</td></tr>
</table>

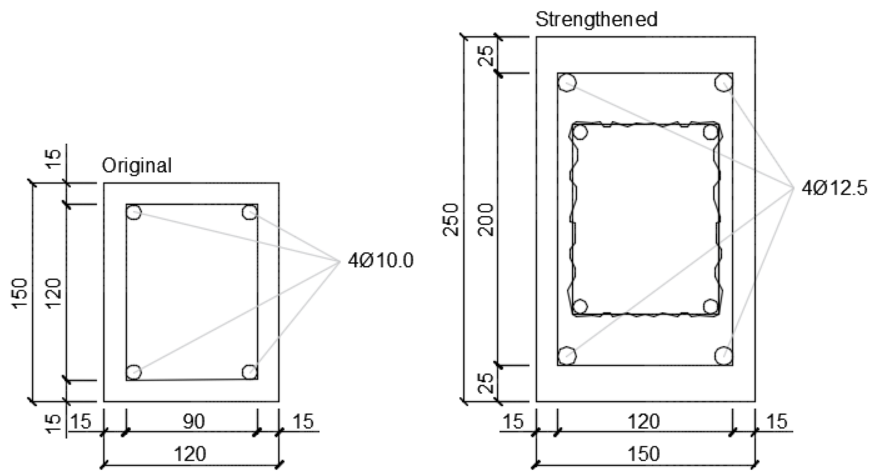

Figure 6. Columns’ cross section before and after the structural strengthening.

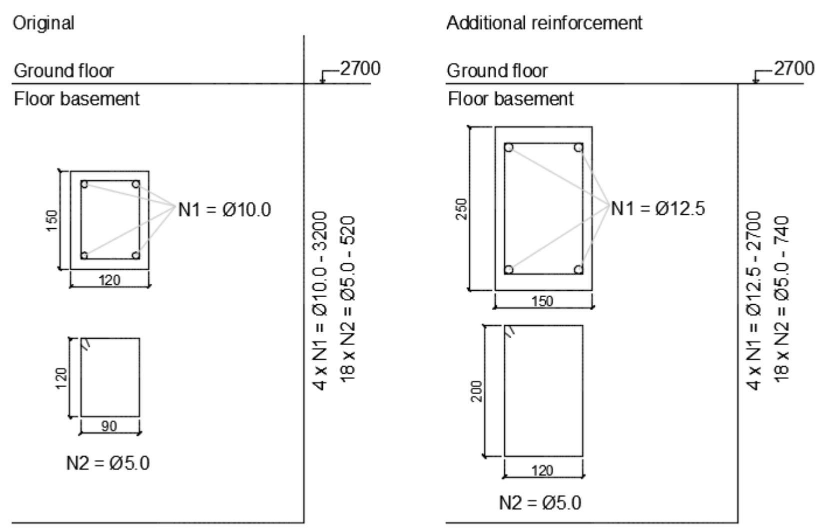

Figure 7. Original and additional reinforcement.

Figure 8. Longitudinal reinforcement and stirrups of the structural strengthening.

2.3.3 Concrete casting. So that there was greater adherence between the old and new concrete its surfaces of the columns were wet before the concrete casting. The concrete was carefully released (Figure 9) and the density was achieved with immersion vibrator with a head diameter of 20 mm, first in 50% of the volume of concrete cast in each column and then the remaining volume. After removal of the wooden mold the columns received a mortar coating layer to allow the finishing, or painting. Figure 10 shows the final appearance of the columns with smaller dimensions exceeding in 35 mm the wall thickness.

Figure 9. Concrete casting of the structural strengthening.

Figure 10. Final aspect of the strengthened columns.

3. RESULTS AND DISCUSSION

3.1 Current columns' safety evaluation.

The calculation methodology to check the columns' safety with and without structural strengthening followed the prescriptions of NBR 6118 (ABNT, 2014). A simplified analysis which were determined and compared only the normal loading and resistant capacity for P21, P30 and P41 columns before the strengthening with its normal loading force multiplied by γ_u (Equation 1) and an additional increase coefficient (Equation 2). Since design normal resistant force was determined by Equation 3, Equation 4 was used to determine the concrete's design compressive strength (f_{cd}) and Equation 5 enables the determination of the safety factor for each column.

a) Cross section's parameters. The cross section of solid columns and wall-columns, whatever its form, should not present dimension smaller than 190 mm. As the smallest dimension of the column is less than 190 mm, the acting loads must be multiplied by an additional factor γ_n indicated in Table 3, where *b* is the smaller dimension of the cross section of the column. For the columns analyzed, γ_n = 1.35 (b = 120 mm).

Table 3. Additional coefficient γ_n of NBR 6118 (ABNT, 2014)

***b* (mm)**	**≥ 190**	**180**	**170**	**160**	**150**	**140**	**130**	**120**
γ_n	1,00	1,05	1,10	1,15	1,20	1,25	1,30	1,35

b) Applied normal force

$$N_{Sd,Eq} = \gamma_u \, . \, \gamma_n \, . \, N_{Sk} \quad (1)$$

$$\gamma_u = 1+(6/b) \quad (2)$$

c) Cross section's resistant normal force

$$N_{Rd} = 0{,}75 \cdot f_{cd} \, A_c + f_{yd} \cdot A_s \quad (3)$$

$$f_{cd} = \frac{f_{ck}}{1{,}4} \quad (4)$$

d) Safety evaluation

$$\gamma_f = \frac{N_{Rd}}{N_{sd}} \quad (5)$$

Normal acting force (N_{Sk}) was obtained from Altoqi Eberick 2002 software and the results found with the preliminary analysis for the safety factors of the columns P21, P30 and P41 before strengthening not meet the normative safety requirements, as shown in Table 4. Figure 11 shows the interaction envelopes of resistant forces of these columns, i.e. the consideration of acting and resistant characteristic bending moments without any coefficient of increase or decrease in these actions. In this case, it is observed that the bending moments are more important and destabilize the columns (Marí & Hellesland, 2005), which did not occur because the current actions were lower than those considered in the structural design up to now. It is also possible to conclude with more refined analysis that the progress of corrosion on the flexural reinforcement could significantly reduce the resistant capacity of the columns to flexure and even if the maximum designed loads did not occur, small additions could cause the loss of stability of these columns (Tang & Yang 2011), evidencing the need to strength these structural elements.

Table 4. Columns' safety coefficient before and after the structural strengthening

Column	f_{ck} (MPa)	f_{cd} (MPa)	f_{yd} (MPa)	A_c (mm^2)	A_s (mm^2)	γ_u	γ_n	N_{Sk} (kN)	$N_{Sd,Eq}$ (kN)	N_{Rd} (kN)	γ_f
P21	13.7	9.9						119	240	155	0.65
P30	20.1	14.4	435	18000	482	1.5	1.35	198	400	215	0.54
P41	14.7	10.5						176	356	164	0,46

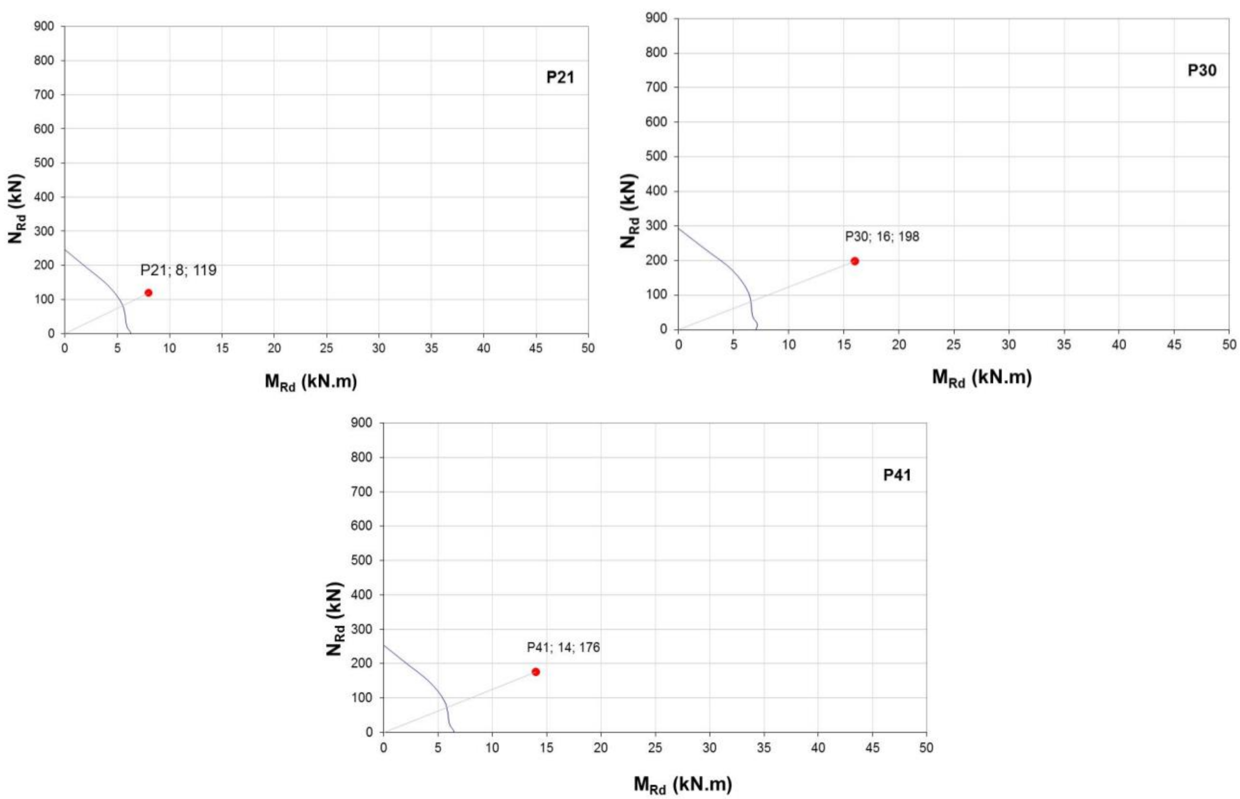

Figure 11. Envelopes for columns P21, P30 e P41 before the structural strengthening.

3.2 Strengthened columns' safety evaluation.

Columns' design safety factors for P21, P30 and P41 strengthened columns was based on the prescriptions of NBR 6118 (ABNT, 2014) following the same criteria used for the original columns without strengthening. The results are presented through the interaction envelopes of Figure 12. The safety factors of each column were determined by the ratio between the length of the straight line from the origin to the outer envelope, passing through the acting loads point, and the distance from this point to the origin, and results are presented in Table 5.

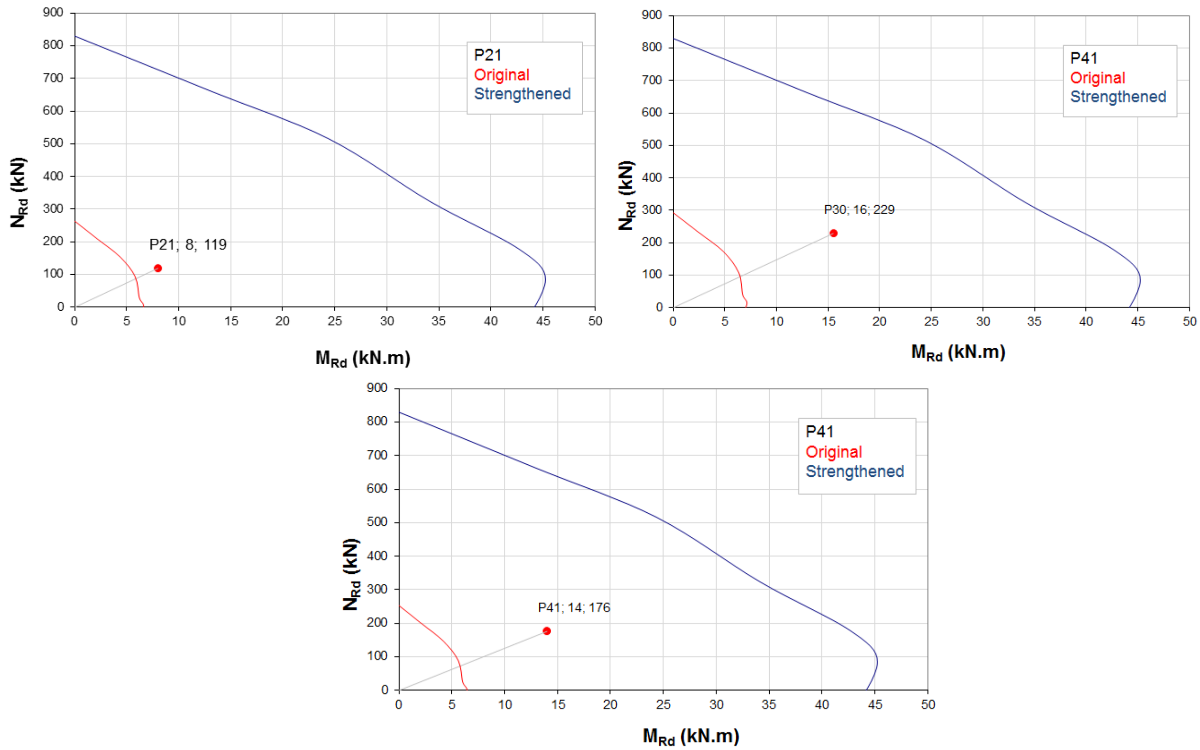

Figure 12. Envelopes' for strengthened columns P21, P30 and P41.

Table 5. Final safety factors

Column	Safety factor
P21	3.5
P30	1.8
P42	2.1

4. CONCLUSIONS

Structural problems which led to the need to strength the columns P21, P30 and P41 of the historic building Casarão were presented, because these columns not meet the recommendations of the Brazilian NBR 6118 (ABNT, 2014). It is considered that the structural strengthening technique proposed for these columns through the reinforced concrete jacketing was feasible because of economic advantages, speed of execution and consistency with the architectural design. Its approval was proven in the verification of normative design parameters, pointing out that the intervention performed on structural elements, however simple it may be, was preceded by structural analysis with current computer programs and increased the columns' saffety of the historic building to satisfactory levels.

5. ACKNOWLEDGEMENTS

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Integrated technical management systems: inspection and repair of non-structural elements

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ABSTRACT

The international scientific community has devoted a great deal of attention to the vast area of knowledge of inspection, diagnosis, maintenance and renovation of buildings, which may be used in the development of integrated building management systems. In this article, we provide a framework for the evaluation methods of the pathology of non-structural elements of buildings, based on current methods, presenting some of the challenges in this area. We present a model to be enforced in the integrated management systems of a building, along with some of the challenges of this area. We also introduce a model to be enforced in the integrated management systems of a building, forming a conductor line and a consistent foundation for a system to be put in place.
Keywords: construction pathology; expert system based on performance; evaluation method; building management.

RESUMO

A comunidade científica internacional tem dedicado a maior atenção ao vasto campo do conhecimento da inspecção, diagnóstico, manutenção e reabilitação das construções, o qual pode ser utilizado no desenvolvimento de sistemas de gestão integrada de edifícios. Neste artigo, é feito um enquadramento aos métodos de avaliação da patologia em elementos não-estruturais de edifícios, com base nos actualmente existentes, apresentando-se alguns dos desafios neste domínio. É também apresentado um modelo a implementar em sistemas de gestão integrada de um edifício, constituindo uma linha condutora e uma base de trabalho consistente para que um sistema deste tipo seja posto em prática.
Palavras-chave: patologia da construção; sistema pericial baseado no desempenho; método de avaliação; gestão de edifícios.

RESUMEN

La comunidad científica internacional ha dedicado mucha atención a la vasta área de conocimiento de la inspección, diagnóstico, mantenimiento y rehabilitación de edificios, que se puede utilizar en el desarrollo de sistemas de gestión de edificios integrados. En este artículo, se realiza un encuadramiento de los métodos de evaluación de patología en elementos no estructurales de los edificios, basado en los actuales, presentando algunos de los desafíos en esta área. También se presenta un modelo a implementar en sistemas integrados de gestión de un edificio, formando una línea conductora y una base consistente para un sistema que se ponga en su lugar.
Palabras clave: patología de la construcción; sistema experto basado en el desempeño; método de evaluación; gestión de edificios.

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1. PRELIMINARY CONSIDERATIONS

The period of use of buildings is the most important in their useful life from an economic and environmental perspective. The useful life of a building corresponds to the period of time after the construction during which a building or its elements exceed the minimum functional requirements for which it was built (Haapio and Viitaniemi, 2008). Therefore, the consensus today is that the extension of the useful life of buildings, as a consequence of their deterioration, is the most viable option (de Brito, 2009).

At a national level, the absence of policies that encourage restoration and maintenance activities, along with an economic scenario that promoted new construction, favored the suburban growth for decades. In this context, Portugal presents a change of paradigm in the construction sector, which includes a change in focus from new construction to the renovation of existing buildings. In fact, when buildings are subjected to maintenance and rehabilitation, the duration of the construction elements is augmented, increasing the expected useful life of the building (Amaral and Henriques, 2013).

Taking into consideration the uniqueness of each building and the different types of defects, it is possible to identify patterns when analyzing a selection of building samples. The databases that offer information on maintenance and repair, through the systematical analysis of the data collected from inspections, were initiated in this manner. Maintenance and renovation activities are fundamental for the durability of the buildings; it is therefore essential to have an accurate interpretation of their defects, based on objective inspections and diagnoses. However, the inspection and diagnosis procedures of the buildings are very complex, a factor which influences the precision of the underlying intervention measures (Aguiar et al., 2006).

The national and international scientific communities have devoted a great deal of attention to the vast area of knowledge of inspection, diagnosis, maintenance and renovation of buildings, including their use in the development of integrated building management systems. A great deal of effort has been put into the incorporation of computer models in order to help engineers in the decision-making processes (Farinha et al., 2005). Even when the building management systems are tritely used in companies, the main focus of such systems is usually the management of the heritage value and the planned maintenance (Chang and Tsai, 2013). However, the defects in buildings may compromise their performance on a structural and/or non-structural level, occasionally making it necessary to intervene several times at great costs in order to return the building to its original state. Therefore, not using management systems that incorporate the inspection and assessment of buildings could compromise performance in the long term (Amaral and Henriques, 2013).

The construction pathology studies have received much attention presently. In this article, we review the area of evaluation methods of building pathology, presenting some of the challenges in this regard when it comes to the implementation of an integrated building management system that is reliable and applicable.

2. BUILDING PATHOLOGY EVALUATION METHODS

Developments regarding the subject of information technologies have favored the automatization of decision-making processes in engineering. At the end of the 1980s, intense activity in the engineering areas led to the implementation of several management systems in regards to the different areas of engineering (Farinha et al. 2005). With respect to the construction pathology, the most important building pathology evaluation methods are chronologically presented, focusing on the non-structural elements.

2.1 DEFECT ACTION SHEETS (1982)

The British BRE (*Building Research Establishment*) organization, specialized in buildings, published a series of building defect action sheets comprising a significant database (Trotman, 2006). In short, 144 defect action sheets were published between 1982 and 1990. The aim of these action sheets is to provide the necessary information to the professionals of the construction sector, in aspects of prevention and correction of defects in buildings. Each action sheet is comprised by two A4 sheets structured in the following manner: i) Description of the defect; ii) Description of the causes; iii) Prevention measures; and iv) References and complementary information. Subsequently, these sheets were grouped and re-published (BRE, 2001; CIB - W086 Building Pathology, 2013).

2.2 DEFECT REPAIR SHEETS (1985)

In the proceedings of the 1st Meeting on Conservation and Rehabilitation of Residential Buildings, carried out in Lisbon in June 1985, a methodology for the evaluation of building pathology was presented, which would be adopted in the elaboration of the defect repair sheets published by the National Civil Engineering Laboratory (LNEC, 1985). The set of these sheets is segmented in the following manner: i) Structural anomalies; ii) Non-structural anomalies; and iii) Facilities and equipment. A group of defect repair sheets corresponds to each one of the segments. Each sheet was structured in the following manner: i) Symptoms; ii) Examination; iii) Diagnosis of the causes; and iv) Repair.

2.3 FAILURE CASES, INFORMATION SHEET (1993)

The International Council for the research and Innovation in Buildings and Construction - CIB (*Conseil International du Bâtiment*) has a work group focused on the research of construction pathology, named *W086 Building Pathology*. In June 1993, this work group published a model of pathology sheets entitled *Cases of failure information sheet*, completely devoted to the pathology records, noting the need for the systematization of knowledge in the field (CIB - W086 Building Pathology, 1993). A structure was suggested for the preparation of pathology sheets: i) Constructive element; ii) Description of the problem; iii) Description of evident defects; iv) Description of the defects that can be monitored; v) Graphical representation (photo, picture); vi) Description of the defect; vii) Identification of the agents that cause the defect; viii) Mistakes; and ix) Diagnosis report

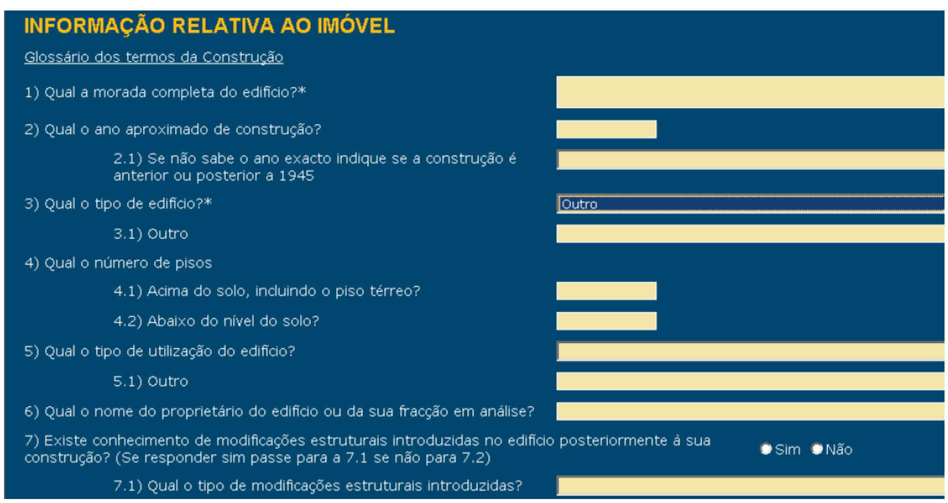
2.4 FICHES PATHOLOGIE DU BÂTIMENT (1995)

In 1995, the French agency AQC (*Agence Qualité Construction*), in partnership with the SMA foundation, developed a set of pathology sheets, entitled *Fiches pathologie du bâtiment* (AQC, 2014). These sheets were elaborated in order to evidence the main anomalies in French buildings, based on the analyses of incidents reported to the insurance companies. The 61 sheets were created in 1995 and have been available online since 2003 (see figure 1). These were grouped and sectioned according to the parts of the affected building. In a similar fashion to the aforementioned cases, these sheets are structured in the following manner: i) Description of the defect; ii) Diagnosis; iii) Sensitive points; iv) Prevention councils; and v) Additional information.

2.5 CONSTRUDOCTOR (2003)

The Portuguese company OZ - Diagnóstico, Investigación y Control de Calidad de Estructuras y Fundaciones, Lda. developed a service of pre-diagnosis of defects in buildings, called Construdoctor (Ribeiro and Cóias, 2003). The service arises as a system that provides an *on-line* diagnosis, the main objective of which is to help correct defects in buildings, providing basic explanations of the probable causes, forming a preliminary diagnosis and defining corrective measures. The service offers a pre-diagnosis based on an *on-line* form (see figure 2). After the submission of the form, the responses of the interviewee are evaluated by specialists in construction pathology and rehabilitation, who fill out an *on-line* report identifying the defect and specifying the possible causes and corrective actions.

Figure 1. *Fiches pathologie du bâtiment* (AQC, 2014)



INFORMAÇÃO RELATIVA AO IMÓVEL

Glossário dos termos da Construção

1) Qual a morada completa do edifício?*

2) Qual o ano aproximado de construção?

2.1) Se não sabe o ano exacto indique se a construção é anterior ou posterior a 1945

3) Qual o tipo de edifício?* Outro

3.1) Outro

4) Qual o número de pisos

4.1) Acima do solo, incluindo o piso térreo?

4.2) Abaixo do nível do solo?

5) Qual o tipo de utilização do edifício?

5.1) Outro

6) Qual o nome do proprietário do edifício ou da sua fracção em análise?

7) Existe conhecimento de modificações estruturais introduzidas no edifício posteriormente à sua construção? (Se responder sim passe para a 7.1 se não para 7.2) Sim Não

7.1) Qual o tipo de modificações estruturais introduzidas?

Figure 2. *On-line* form *(*Construdoctor) (Ribeiro and Cóias, 2003)

2.6 "LEARNING FROM MISTAKES" (2004)

The Italian pathology catalogue “Learning from mistakes” (BEGroup, 2004) was developed by the BEGroup of the Department of Science and Technology of the Constructed Patrimony (BEST) in the Polytechnic University of Milan. The aforementioned catalogue can be accessed *on-line* in Italian (see figure 3) where the pathology files can be found. Similar to the cases previously mentioned, these sheets are structured in the following manner: i) Material records; ii) Mechanisms of deterioration; iii) Pathology records; iv) Records of case studies; and v) Records of defects.

2.7 PATORREB (2004)

The Group of Studies of Construction Pathology created a website dedicated to the circulation of a catalogue of pathology sheets (Freitas et al., 2007). Since 2004, registered users have access to the area of Pathology, where the layout of a building presents the pathology sheets according to the constructive element (see figure 4). When selecting the corresponding element, the list of associated pathology sheets is presented. Similar to the other cases, these sheets are structured in the following manner: i) Identification of the pathology; ii) Description of the pathology; iii) Surveys and measurements; iv) Causes of the pathology; and v) Possible repair solutions.

Figure 3. "Learning from mistakes" (BEGroup, 2004)

Figure 4. Layout of a building (Patorreb) (Freitas et al., 2007)

2.8 WEB-BASED PROTOTYPE SYSTEM (2009)

In 2009, Fong and Wong created the prototype of an integrated building management system (see figure 5), having several objectives in mind: i) provide a friendly approach to the user; ii) provide a simple approach in the process of information presentation; and iii) allow for the communication between the different users of the system, improving the exchange of knowledge and experience in the scope of construction pathology (Fong and Wong, 2009). With this purpose, a questionnaire was used in order to investigate the opinions of construction professionals as well as the capture and re-use of their knowledge and experience. After the preliminary upload, interviews will be done to interested professionals, and the accumulated knowledge and experience will be recorded in forms free of any structure, which will be subsequently introduced to the prototype of the integrated management system.

2.9 MAINTENANCE OF THE WEBSITE (2010)

In 2004 at the National University of Singapore (NUS), a two-year project was developed; it was conceived in order to study the problems that affected different types of buildings in tropical weather. In 2005, the *Maintainability website* was created (see figure 6), which was updated until 2010. The website seeks to create awareness among the construction professionals in regards to the obstacles for the good maintenance of a building (Chew, 2010). This website was developed in English and is divided into the following modules: i) Library of defects/anomalies, with information on the types of defects and their causes, maintenance and diagnosis method; ii) Manual of materials, with information about the development and durability of the materials; and iii) Evaluation system of the maintenance, developed in order to facilitate the selection of sustainable alternatives. The module i) Library of defects, is directly related to the scope of this article, based on the information of defects and is grouped in the following manner: i) Defects on facades, ii) Defects in humid areas, iii) Defects on warehouses; and iv) Defects on roofs. In regards to the records of defects, these are organized in the following manner: in the first two sections, the type of defect is illustrated and the possible causes are explained; the good constructive practices are compiled in the third section in order to avoid systematic mistakes; in the fourth section the techniques of diagnosis and maintenance are illustrated; the possible corrective techniques are illustrated in the fifth section.

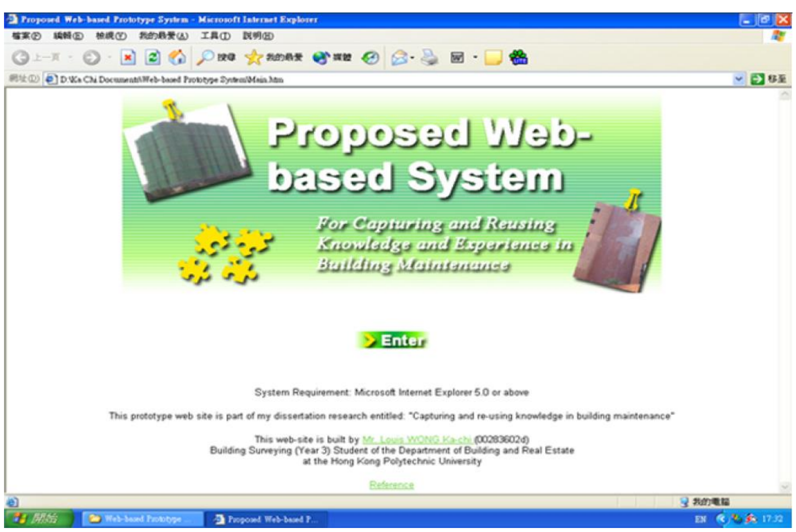


Figure 5. *Web-based prototype system* (Fong and Wong, 2009)

Figure 6. Maintenance of the Website (Chew, 2010)

2.10 BUILDING A MEDICAL RECORD (2013)

In 2013, Chang and Tsai proposed the concept of "building medical records", similar to human medical records (Chang and Tsai, 2013), presenting a diagnosis system. In the application of this system, an expert on the research of pathological situations with a database can be assisted for the diagnosis of defects in buildings. The user receives the notification through an Internet connection on the site of the construction. This system is comprised of four main modules: i) Processing of documents; ii) Extraction of the key solution; iii) Calculation of the simulation; and iv) Classification of the importance. According to the authors, construction companies may offer specialized services in response to the maintenance and management problems using this system. The efficient accumulation and reuse of repair records may also be done during the project phase of a building.

3. CRITICAL AND COMPARATIVE ANALYSIS

Even though in building rehabilitation each case is unique, the majority of defect occurrences in non-structural elements can be resolved in a systemic manner. Using data from inspections or from the crossing of information and an integrated building management system, an inspector may diagnose the defect and define the best repair technique. In this context, the acquisition of data on the development of defects in construction is of vital importance for the planning of maintenance and repair actions. The reliability of this information is fundamental in making rational decisions.
From the analysis of the evaluation methods of building pathology, we can easily conclude that they all have a similar structure when it comes to the description of defects: i) description / identification of the defect; ii) probable causes; and iii) Diagnosis and repair technique. Undoubtedly, it seems that all pathology evaluation methods for the buildings found in literature have a similar organization, but none of them is completely dedicated to intervention, which enforces the importance of research in regards to this topic.
In relation to the evaluation methods based on defect sheets, *Defect action sheets* (1982), Repair defect sheets (1985) and *Cases of failure information sheet* (1993), these represent the starting point for the systemic analysis of building pathology. Through the systematic analysis of the collected data in research studies, it was possible to establish reliable databases, which provide some orientation in the prevention and repair of defects of non-structural elements of buildings; it is an important contribution in the development of integrated management. In this sense, the content of

the information could be in disagreement with the common constructive practices, due to the continuous advancements in the construction and repair techniques.

In regards to those evaluation methods that make use of the most recent information technologies, it is possible to identify three similar methods in their creation: *Fiches pathologie du bâtiment* (1995), "Learning from mistakes" (2004) and Patorreb (2004). In these cases, several defect sheets are accessible through a website from which they can be downloaded and printed. Through these methods, the divulgation of the pathology records became a reality. However, no measures were taken in order to filter the content of the pathology sheets in order to offer the users an expedited repair solution.

The Construdoctor (2003) and *Building medical record* (2013) evaluation methods emerged as systems that offered an *on-line* diagnosis. After completing the form, the user's responses are evaluated by construction pathology specialists who create an on-line report. It can also be observed that the information offered in the report is just a pre-diagnosis offered by technicians, without previously having had a view of the building. For this reason, the report cannot be as accurate as desired.

In regards to the *Web-based prototype system* (2009) method, it is important to note that the system was not conceived to offer any systematized rule. According to the authors, the investigations concluded that the knowledge in regards to construction pathology is obtained from a specific context and cannot be generalized. Instead, the system allows the users to share and recover the experience of other professionals in order to facilitate their own decision-making process.

Finally, it is important to give greater attention to the *Maintainability website* (2010) method. This method can provide an objective diagnosis through the development of a library of defects, including a manual of materials and a classification system for the maintenance techniques. In regards to the library, the defects and their corresponding causes are explained and illustrated through photographs. The diagnosis and repair techniques are also included. In this manner, the users of this evaluation method are encouraged to find a diagnosis based on images. However, statistical information was not found, specifically when it comes to correlations between defects, diagnoses and repair techniques. As a result, the diagnosis may not be as accurate as expected, as it is clearly dependent on the experience of the user / inspector. Due to this, the method presents some challenges regarding intervention.

Among other identified challenges on the evaluation methods of building pathology found in literature, the objectivity of the information given is a pre-requisite for the making of rational decisions. In order to overcome some of the challenges found, researchers from the Instituto Superior Técnico of the Universidad de Lisboa developed inspection and diagnosis systems, applied to several non-structural constructive elements. These systems are characterized by the definition and classification of the four most important variables in the pathology: defects, causes, diagnosis techniques and repair techniques, as they also established quantitative correlations (de Brito, 2009). Following a systemic approach, studies were published about the following non-structural elements in buildings:

i) Waterproofing of roofs (Walter et al., 2005);

ii) Ceramic coverings for floors and walls (Silvestre and de Brito, 2009; Silvestre and de Brito, 2010; Silvestre and de Brito, 2011);

iii) Epoxy coatings for industrial floors (Garcia and de Brito, 2008);

iv) Slab walls (Gonçalves et al., 2013, 2014);

v) Coatings for wood floors (Delgado et al., 2013);

vi) Natural stone claddings for floors and walls (Neto and de Brito, 2011; Neto and de Brito, 2012)

vii) Divisions made of laminated plaster (Gaião et al., 2011; Gaião et al., 2012);

viii) Common friezes on internal facades (Palha et al., 2012; Pereira et al., 2011);
ix) Coatings on inclined roofs (Garcez et al., 2012; Garcez et al., 2015a; Garcez et al., 2015b);
x) Plaster on walls (Sá et al., 2015a; Sá et al., 2015b);
xi) Frieze paint (Pires et al., 2015a; Pires et al., 2015b);
xii) ETICS (Amaro et al., 2013; Amaro et al., 2014);
xiii) M (Santos, 2012; Vicente, 2012).

Through an intense literature research based on scientific international publications, current available information on the pathology of non-structural elements was collected. This information was complemented with the execution of field work with extensive representative samples, allowing for the creation of a better understanding in relation to the origin of the defects, offering a systemic method for the diagnosis and facilitating the election of intervention methods for repair. These systems have the following tools:

i) List of classifications of defects: identification and classification of the more common defects in each element;
ii) Clarifying list of causes: identification and classification of the most probable causes of different identified defects;
iii) Classification list of diagnosis techniques: classification of the type of test that allows for the characterization of the identified defects, as well as helping in the determination of the possible cause;
iv) Classification list of repair techniques: classification of the type of intervention technique that is more adequate for each one of the defects identified;
v) Correlation matrix of defects-causes: attribution of null relation, indirect or direct between each defect and each cause listed;
vi) Correlation matrix of inter-defects: probability of the development of a defect, in the presence of another;
vii) Correlation matrix of defects-diagnosis techniques: attribution of a null, average or high relation to a diagnosis technique necessary for the characterization of a defect, or the understanding of their conditions in order to obtain some knowledge of the origin;
viii) Correlation matrix of defect-repair techniques: attribution of a null, average or high relation to a relative repair technique to its adequacy in the resolution of defects.

In the meantime, none of the systems created are dully computerized, making them still vulnerable to inaccurate interpretations and for errors in their use.

4. FUTURE PERSPECTIVES

In the area of building rehabilitation, it is established that the rehabilitation procedure shall start with an inspection, ensuring the correct characterization of the existing defects, which will finish with the presentation of a diagnosis and the corresponding repair technique. Having verified the importance of establishing evaluation methods for the building pathology, it is important to create a trustworthy integrated building management system, which will facilitate access to the wide field of construction pathology.

Starting with the analysis of the evaluation methods of building pathology found in literature, it has been concluded that all have a similar organization but that none of them is entirely dedicated to intervention. In order to create a trustworthy integrated management system, the partial systems developed in the Instituto Superior Técnico of the Universidad de Lisboa are featured as reliable sources, once they operate by the same systematical approach, anchored in the knowledge of the areas of inspection, diagnosis and rehabilitation of non-structural elements in buildings. Through

this systemic approach, the most important parameters of the pathology of several elements of construction were defined and classified, as well as the quantitative correlations between them. In this context, the creation of a global integrated management system, including all developed partial systems up to date, arises as a future and credible perspective.
The implementation of an integrated building management system supported by the partial systems developed in the Instituto Superior Técnico will put in to practice all the tools mentioned in section 3 of this article. However, there is a long road ahead in order to implement this system. The creation of a global system based on normalized lists of defects, causes, inspection methods and repair techniques represent a great challenge due to the large amount of information. The analysis and normalization of the partial systems include the joint appreciation of defects, causes, diagnosis techniques and repair methods of each constructive element.
In order to implement an integrated building management system, the different stages through which a building goes shall be considered, including the general and specific periodic inspections for the elements that comprise the building, be it the subsequent maintenance interventions, repairs and/or substitutions. In order for a system of this kind to be implemented, it is necessary to build a computerized tool that is based on the building and its elements. This system shall include a database that allows for the storage of relevant information about the building; a module that allows for the normalization of the inspection activities and the resulting reports; it is a decision module about the action to be taken after the inspection and the diagnosis of eventually existing defects, dedicated to the maintenance operations of the building. Using the aforementioned attributes, a decrease in subjectivity of building elements inspections is expected, as well as the elimination of the dependence on the inspector's experience, that represent some of the challenges associated to the evaluation methods for the pathology of existing buildings.
Finally, it has been expected that the proposed computerized inspection system has the following practical application: i) use in inspections; ii) use in the area of proactive maintenance plans for buildings; iii) support in the decision of rehabilitation projects; iv) preparation of reports on the dilapidation of buildings; v) use for official acknowledgement; vi) preparation of the final report on the diagnosis with a normalized structure; vii) use as a pre-normative base of normalized methodology for inspections to buildings that must be officially acknowledged; and viii) evaluation and management of property assets.

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AgNO3 spray method for measurement of chloride penetration: the state of art

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ABSTRACT
The durability of the buildings has been evaluated through visual inspections associated with field and laboratory tests. Nowadays, for analysis of the carbonation colorimetric method by spraying phenolphthalein is widely used, due to the ease and high reliability. However, when there is the presence of chlorides, the tests are long and expensive. As an alternative, there is a colorimetric method (AgNO3). The method is easy to use, low cost and allows for on-site reviews. But when there is presence of carbonation, the analysis becomes more complex, since reducing the pH and leads to discoloration of the concrete. This paper presents studies on the use of the colorimetric method for evaluation of the depth of chloride penetration in concrete. There is no consensus in academic circles as to eliminate this influence and to determine the turning point, however there is research demonstrating the influence of cement type on the colorimetric method.
Keywords: concrete; corrosion; chloride penetration; silver nitrate; colorimetric method.

RESUMO
A durabilidade das construções tem sido avaliada através de inspeções visuais associadas a ensaios de campo e laboratório. Hoje, para análise da carbonatação o método colorimétrico por aspersão de fenolftaleína é amplamente utilizado, devido à facilidade e alta confiabilidade. Porém, na presença de cloretos, os ensaios não são expeditos e possuem alto custo. Como alternativa, há a aspersão de nitrato de prata (AgNO3). O método é de fácil aplicação, baixo custo e permite avaliações in loco. Mas quando há presença de carbonatação, a análise torna-se mais complexa, devido a redução do pH e alteração da coloração do concreto. Esta pesquisa apresenta estudos sobre o uso do método colorimétrico para avaliação da profundidade de penetração de cloretos no concreto. Ainda não há consenso de como eliminar essa influência ou determinar o ponto de viragem, entretanto há pesquisas que demonstram a influência do tipo de cimento no método colorimétrico.
Palavras-chave: concreto; corrosão; penetração de cloretos; nitrato de prata; método colorimétrico.

RESUMEN
La durabilidad de las construcciones se ha evaluado mediante inspecciones visuales asociados a los ensayos de campo y de laboratorio. Hoy, para el análisis de carbonatación método colorimétrico por pulverización fenolftaleína se utiliza ampliamente debido a la facilidad y alta fiabilidad. Sin embargo, en la presencia de cloruros, los ensayos no son expeditos y tienen un alto costo. En su lugar, se utiliza la pulverización de nitrato de plata (AgNO3). El uso del método es simple, de bajo costo y permite evaluaciones in situ. Pero cuando, hay presencia de carbonatación, el análisis se hace más compleja debido a que la reducción del pH y los cambios en la coloración de hormigón. Esta investigación presenta estudios sobre el uso del método colorimétrico para evaluar la profundidad de penetración de cloruro en el hormigón. No hay todavía uno consenso sobre la forma de eliminar esa influencia o determinar el momento decisivo, sin embargo, hay investigaciones que muestran la influencia del tipo de cemento en el método colorimétrico
Palabras clave: Hormigón; corrosión; penetración por cloruros; nitrato de plata; método colorimétrico.

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1. INTRODUCTION

It is well known that highly alkaline environment provided by the cement matrix maintains this steel in reinforced concrete liability to corrosion. However, the corrosion occurs when chloride ions reach the armature.

The phenomenon of depassivation occurs mainly by two main reasons: First, due to the reduction of the concrete alkalinity caused by carbonation. Second, due the presence of chlorides, even if the concrete has a high pH, the reinforcement depassivation occurs, causing pitting corrosion which reduces the cross section of the bar and reduces its bearing capacity (FRANCE, 2011).

The chloride ions can be found in cementitious matrix in two forms: free (dissolved in pore water) or combined with the hydrated C_3A and C_4AF (from the cement hydration reaction) forming cloroalumintos (Friedel's salt). The chlorides that are really harmful to the steel in concrete are the free. The combined chlorides can become free due the carbonation of concrete or due to the rise of the concrete temperature (HELENE, 1993; PEREIRA & CINCOTTO, 2001; CAVALCANTI & CAVALCANTI, 2010).

In the context of corrosion induced by chlorides, as well as by carbonation, it is reasonable to consider the lifetime of the concrete structures in two stages: the first is when the critical chloride content reaches the surface of the steel inside the concrete (being this the useful lifetime of the structures) and the second is the subsequent spread of corrosion, in which the structure is damaged by steel corrosion (HE *et al*., 2011).

The durability results from the interaction of concrete structures, the environment, conditions of use, operation and even maintenance. Thus, to assess the performance of the buildings, it is often used visual inspections combined with field and laboratory tests, making it possible to identify the causes of pathological manifestations and choose the most appropriate recovery techniques and protection and the most cost-effective to maintain building (MOTA, 2011).

In order to assess the condition of concrete structures, the useful life of the construction can be estimated from the diffusion coefficient chlorides in concrete. The most representative current method to determine current status is based on the second Fick's Law. But this is a time consuming procedure and to improve this situation, accelerated methods, as proposed by ASTM C 1202/05, have being used in association with the identification of chloride penetration depth (KIM *et al*., 2013).

There are several methods to identify and quantify free and total chlorides along the depth of the concrete (chlorides profile), such as gravity (PEREIRA & CINCOTTO, 2001; SILVA, 2006). For the sake of determination of the chloride profile - which requires cutting or drilling, milling and chemical analysis of specific samples - once held towards various equipment and analysis timetable (He et al, 2011). In contrast, the colorimetric method based on $AgNO_3$ for measuring penetration depth of chlorides in the cement matrix is practical and fast (JUCÁ, 2002; MECK & SIRIVIVATNANON, 2003; YUAN *et al*, 2008; FRANCE, 2011; HE *et al*. 2011; MOTA, 2011; KIM *et al*, 2013). Yet, its efficiency and application conditions must be well driven and self-understood to perform the method and to provide the possible application of advantages of such technique.

Silver nitrate spray has been used in association with accelerated test chlorides migration prescribed by ASTM C 1202/05. It consists on sprinkling aqueous solutions of $AgNO_3$ 0.1 M on the slices of fractured concrete after the migration assay. This procedure leads to the formation of two well-defined regions (Figure 1): a whitish, with AgCl precipitation, indicating the presence of chlorides and the other is brown, corresponding to region free of chlorides (MEDEIROS, 2008; TRINITY, 2011; MARRIAGA & CLAISSE, 2011; MARCONDES, 2012).

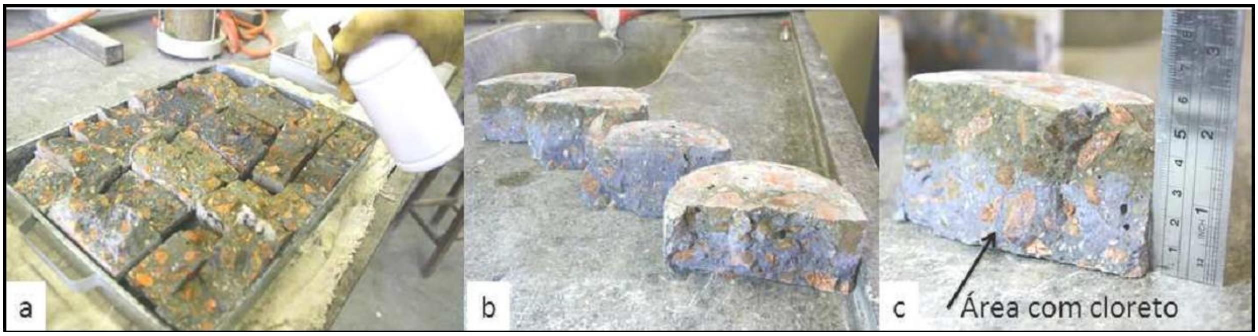

Figure 1. a) Spray silver nitrate solution; b) Comparison of the specimens; c) Measurement of the chloride penetration depth (MARCONDES, 2012)

In 2010, Cavalcanti & Cavalcanti applied the colorimetric method upon a pier located on the beach of Tambaú in João Pessoa/PB/BR. The authors were able to prove the depassivation and reinforcement corrosion occurred because the chloride ions exceeded the thickness of the cover.
Regardless of, despite the simplicity of the method, the chemical reaction that triggers the color to change is affected by the concentration of silver nitrate solution, the pH of the concrete, the presence of carbonates and the chloride content of concrete. Consequently, the method is affected by the presence of carbonation (which leads to reduction of the pH) and the level of contamination at which the material is subjected to (OTSUKI *et al*., 1993; ANDRADE *et al*., 1999; MECK & SIRIVIVATNANON, 2003; JUCA, 2002; BOUNY *et al*, 2007;. HE *et al*, 2012;. FRANCE, 2011; KIM *et al*, 2013). In this context, the purpose of this article is to evaluate the applicability of the colorimetric method towards silver nitrate spraying once analyzing and comparing researches conducted and published.

2. COLORIMETRIC METHOD

The development of the colorimetric method for silver nitrate spraying began in Italy in 1970 by Collepardi. It is a qualitative method for identifying the presence of free chlorides in cementitious materials (FRANCE, 2011; MOTA, 2011). The method became standard in this country, however, according to Colombo (2001) *apud* Juca (2002), it did not present reliable results. So the standard "UNI 7928" was removed from service with no foreseeable replacement.
The main application of colorimetric method is to measure the depth of chloride penetration. When the silver nitrate solution is applied on the concrete surface, a photochemical reaction occurs (Figure 2). The reaction with free chlorides forms a white precipitate silver chloride. In the region of combined chlorides, it is formed a brown precipitate of silver oxide (MECK & SIRIVIVATNANON, 2003; FRANÇA, 2011; MOTA, 2011).

Figure 1. Potential precipitation of free chlorides (white) and combined chlorides (brown) (Medeiros et al, 2009).

As the chloride penetration is not uniform, NT Build 492 (2000) recommends performing seven measurements in every 10 mm. The result is the average of all of them (Figure 3). If some reading failure due the presence of aggregates, it should be changed to the next point or this measurement should be ignored if five other are valid.

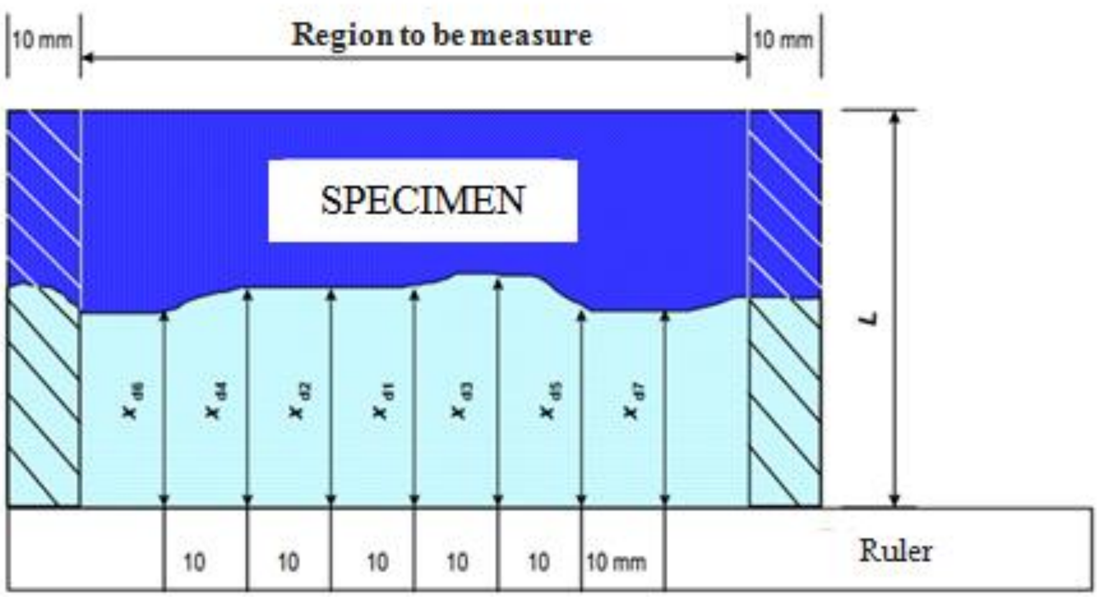

Figure 3. Measurements of chloride penetration depth (NT BUILD 492, 2000).

The chemical reaction occurs with the free chloride ions (1). Although, in the presence of carbonates, the reaction also leads to the formation of a white precipitate, as indicated by the reaction (2). Therefore, Jucá (2002) recommends the use of realkalisation technique, once a carbonated concrete without contamination of chlorides may result in false positive.

$$AgNO_3 + Cl^- \rightarrow AgCl \downarrow + NO_3 \Rightarrow white \tag{1}$$

$$2Ag^+ + CO_3^{2-} \rightarrow Ag_2CO_3 \downarrow \Rightarrow white \tag{2}$$

3. INFLUENCE OF CEMENT TYPE

The colorimetric method only indicates the presence of free chlorides, therefore, the result could also be influenced by the ability of the cement to react with the chlorides (JUCÁ, 2002). As described above, the chlorides combine to C_3A and C_4AF, products of hydration of the Portland Cement. The lower the aluminate content, the less is the ability to immobilize chloride ions.
Althoug, Pereira & Cincotto (2001) evaluated the ability of combination of chlorides in concrete with different types of Portland cement (Brazilians types of Portland Cement: CP I S, CP II F, CP III, CP IV e CP V ARI) and no significant differences in the content of chlorides combined where found.
In contrast, Jucá (2002) tested concretes with the same five types of cement (CP I S, CP II F, CP III, CP IV e CP V ARI), incorporating 1% and 2% of chloride on the cement mass into the specimens. After spraying the silver nitrate solution on the samples, the results indicated that there is a period of chlorides combination and that the aluminate content of the cement is an important factor on chemical combination process.
France (2011) evaluated the combination of chlorides using the colorimetric method with 0.4 and 2% of chloride on the cement mass for the types CP II F, CP IV e CP V – ARI, and so as to Jucá (2002), the results evidenced there was influence of cement type into the amount of free chlorides.
The results of Mota (2011) also indicated the fixing of chlorides throughout the time. For a mortar produced with 2% of chloride on the mass of cement, the white region of the samples (which indicates the free chlorides) has changed. Although there was not a front of chloride penetration, since contamination in this study had internal chlorides, it can be seen in Figure 4 that the area of chloride contamination, as indicated by the whitish discoloration when spraying for silver nitrate, decreased over time. This probably means the chlorides combined with C_3A. It is remarkable that the clear edge in Figure 4 are related to the effect of carbonation.

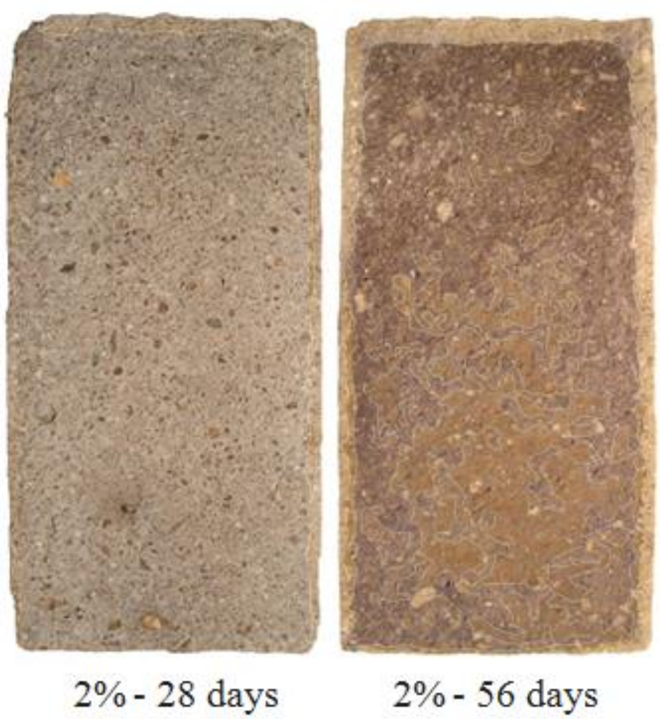

Figure 2. Evolution in chloride combination (Mota, 2011).

4. TURNING POINT AND pH INFLUENCE

When applying the colorimetric method, there is a turning point staining appearance. That means that a certain concentration of chloride and silver nitrate solution cause a color change (the boundary formation; border-color change), in order to determine the depth of penetration in opposition of free chlorides. According to Otsuki *et al*. (1993), the concentration of $AgNO_3$ solution suitable for colorimetric method is equal to 0.1N. This value has been a general consensus among the various authors of the area (ANDRADE *et al*., 1999; MECK & SIRIVIVATNANON, 2003; JUCÁ, 2004; FRANCE, 2011; MOTA, 2011).
Additionally, in accordance to Otsuki *et al*. (1993), for concentration of 0.1N AgNO3 equal to the minimum content of free chlorides it may change the color is equal to 0.15% relative to the cement mass. On the other hand, Collepardi (1997) argues that this minimum level is equal to 0.01% (JUCA, 2004; FRANCE, 2011; MOTA, 2011). Andrade *et al*. (1999) found, with 95% reliability, the turning point is 1.14%±1,4 on the mass of cement. This value is in compliance with the argument leverage by Meck & Sirivivatnanon (2003), which is equal to 0.9% chloride on the mass of cement. In 2011, He *et al*. found the critical chloride content between 0.011 and 2.27% on the cement weight. It should be noted that there is no consensus on the free chloride content which causes a color change in $AgNO_3$ 0.1N solution, since available data in the studies cited are so disparate.
Recently, Kim et al. (2013) reassessed the variables that can influence the technique. The study intended to identify if the is a change in color by altering the pH of the environment, the concentration of $AgNO_3$ and the chloride content. Additionally, if the rated water/cement ratio influence towards the concentration of chlorides in the color-changing border (border-color change), and if the colorimetric method could be applied on site to real structures. The evaluated items and their details are shown in Table 1.

Table 1. Essay Variables (Adapted from Kim *et al*., 2013).

Item	What was assessed?	Details
Colorimetric method clockwork	pH	10; 11; 12 e 13
	Concentration of NaCl (kg/m³)	0,1-1,0
a/c influence towards chloride concentration and color change	Water / cement ratio	0,4; 0,5 e 0,6
Optimal $AgNO_3$ concentration to perform the essay	Concentration of $AgNO_3$	0,03N; 0,04N; 0,05N e 0,1N
Concrete application	Lab.	Cl concentration in the colored area
	In situ	Carbon influence

Initially the tests were made at pH = 12 and change in chloride concentrations and silver nitrate solutions were made, as shown in Figure 5. According to Kim *et al.* (2013), the color change was more clearly observed for concentrations of $AgNO_3$ over 0,03N. As the silver nitrate concentration increases, color change was observed change. In low concentrations, this change was not clearly displayed and can generate errors (especially in concentrations of 0.03 and 0,04N). Therefore, to measure the depth of penetration of chloride ions, the authors recommend using silver nitrate concentration to 0.05N.

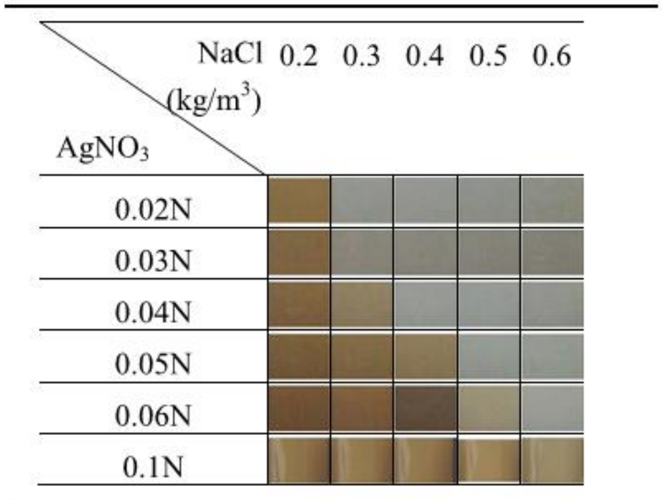

Figura 3. Determination of optimal concentration of the silver nitrate and the minimum chloride content (KIM *et al.*, 2013).

Following the study by Kim *et al.* (2013), four test specimen were submerged in seawater for 3 months, were subjected to spray test of silver nitrate to different concentrations of $AgNO_3$, as shown in Figure 6.

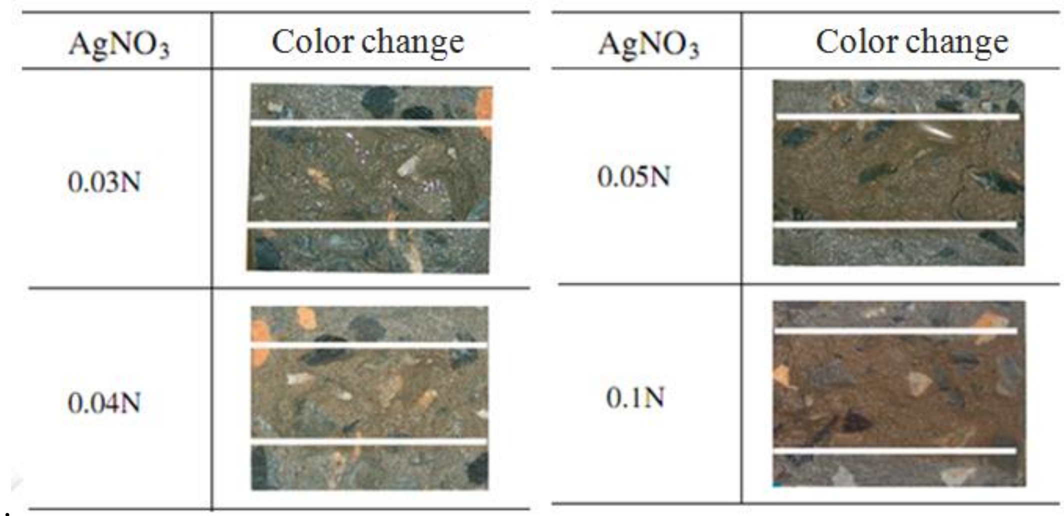

Figure 4. Change of color as per $AgNO_3$ concentration (Adapted to KIM *et al*., 2013).

By analyzing the values held by different authors, it can be said that the concentration of $AgNO_3$ solution most suitable for the colorimetric method is 0.1N. However, there is still no consensus on the chloride content which leads to color change. Even the most current research (HE *et al*., 2011 and KIM *et al*., 2013) have not yet reached values close to each other, as shown in Table 2

Table 2. Concentration summary of $AgNO_3$ and % chloride threshold to turning point.

Author	**Concentration of $AgNO_3$**	**% chloride per cement (weight)**
Otsuki *et al.* (1993)	0,1N	0,15%
Collepardi (1997)	0,1N	0,01%
Andrade *et al.* (1999)	0,1N	1,14% ±1,4%
Meck & Sirivivatnanon (2003)	0,1N	0,90%
He *et al.* (2011)	0,1N	0,011% a 2,27%
Kim *et al.* (2013)	Above 0,05N	0,05%

To evaluate the influence of pH on the coloration, Kim *et al.* (2013) tested, as Figure 7 shows, several silver nitrate and chloride concentrations at different pH values.

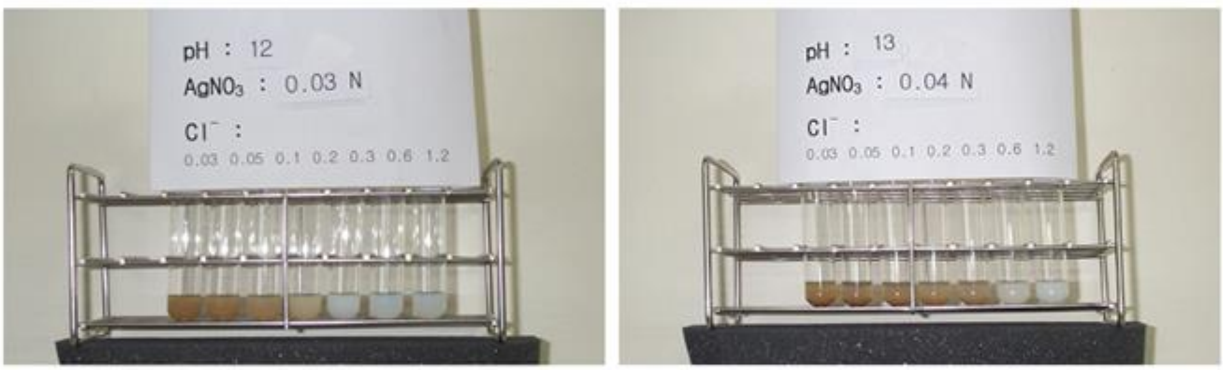

Figure 7. Analysis of the influence of pH on the color change (KIM *et al*., 2013).

The results evidenced when the pH is below 10, the extent of penetration of chlorides turns to become impractical (Figure 8). Therefore, when the structure is exposed to the attack by chlorides and CO_2, the depth of carbonation should be measured before the depth of chlorides. When the carbonation depth exceeds the penetration of chlorides, it is impossible, according to Kim *et al.* (2013) determining a second variable (penetration free chlorides) by spraying silver nitrate.

The ratio water/cement did not influence the concentration of chlorides in the color-change boundary (Kim *et al*., 2013), ie, it does not affect the turning point to the colorimetric method.

The colorimetric method using silver nitrate spray can be used at least as a first step to quantify the penetration into the concrete of chlorides (Bouny et al., 2007). In the case of structures exposed to marine environments and CO_2, the use of silver nitrate spray method becomes complicated, it is necessary to associate the method with other tests (JUCÁ, 2004; FRANCE, 2011; MOTA 2011). Kim *et al*. (2013) applied the colorimetric method to reinforced concrete structures exposed to chlorides and highways exposed to deicing salts to confirm the applicability of the test. As carbonation was deeper than the penetration of chlorides, it was impossible to apply the colorimetric method, since the spray is silver nitrate, the color change region would indicate the presence of carbonation and not just contamination chlorides.

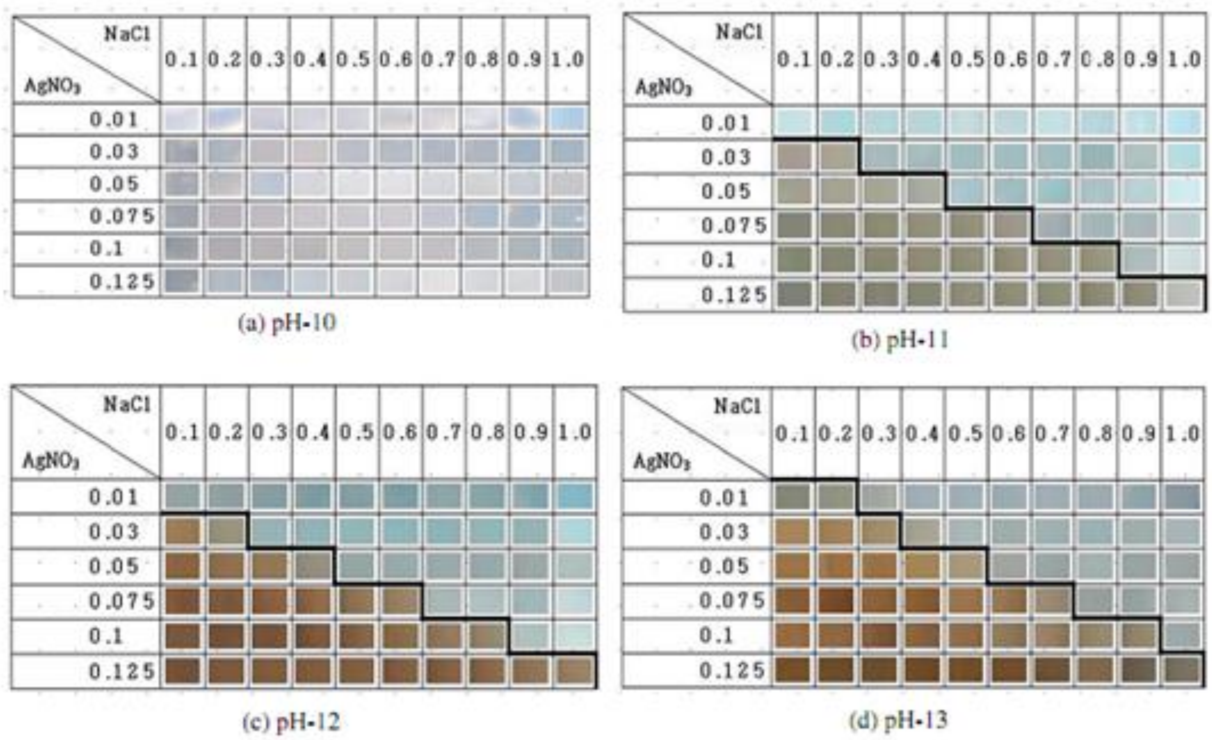

Figure 8. a) Staining to pH = 10 b) Staining to pH = 11 C) Staining to pH = 12 d) staining to pH = 13 (KIM et al., 2013)

5. OTHER METHODS RENDERING COLORIMETRIC SILVER NITRATE

Since 1970, three colorimetric methods based on $AgNO_3$ ($AgNO_3$ + fluorescein, $AgNO_3$ + $AgNO_3$ and K_2CrO_4) have been proposed to measure the depth of penetration of chloride ions in the concrete field and in the laboratory. Both methods are as follows (He *et al*, 2011.):

$AgNO_3$ + fluorescein: in the 70s, Collepardi *et al.* (1970; 1972) developed a colorimetric method to determine the free chloride contained in concrete, in which, firstly, a fluorescein solution (1g / L in a solution of 70% ethyl alcohol in water) was sprayed on a concrete section with chloride penetration. Then it was applied to 0.1 mol / L silver nitrate solution. Immediately after spraying silver nitrate, there was the formation of Ag_2O and AgCl. Fluorescein a weak organic acid, which dissociates in solution in a yellowish green ion. This method was defined as the Italian Standard 79-25 (1978).

$AgNO_3$ + K_2CrO_4: In this method, first, a solution of 0.1 mol / L $AgNO_3$ pH = 3-5 is sprayed onto a concrete section. After one hour of natural drying, applies the K_2CrO_4 solution (5 wt%). Since potassium chromate solution is sprayed, the zone contaminated by chlorides turns yellow due to the formation of AgCl blank, and then applying the K_2CrO_4 solution yellowish leaves.

Comparison of three methods: Colorimetric method which uses only silver nitrate is the simplest of them all; using potassium chromate and fluorescein requires higher reaction time to achieve better coloring effect. The use of $AgNO_3$ results in a clear change in most cases is therefore the most rendered method. In Figure 9 it can be seen that the color change limit between the zone containing chloride and the zone free of chlorides is visible in the three cases. Among the three, the use of fluorescein and $AgNO_3$ + $AgNO_3$ method are very similar. However, the method fluorescein + $AgNO_3$ does not evidence a very clear boundary.

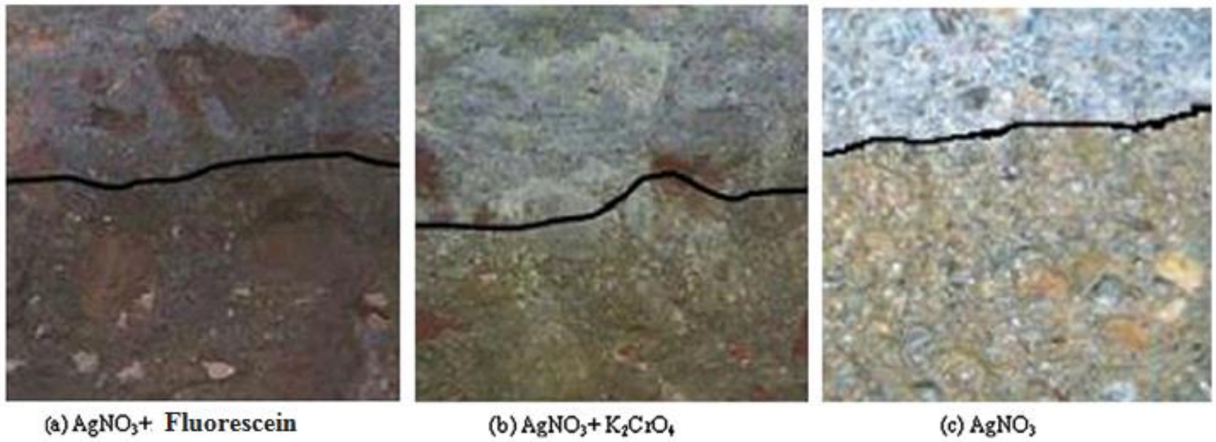

Figure 5. a) $AgNO_3$ + fluorescein b) $AgNO_3$ + K_2CrO_4 c) $AgNO_3$ (Adapted from HE *et al*., 2011).

4. CONCLUSIONS

The purpose of this article was to produce an overview of the state of the art on the use of the colorimetric method by spraying silver nitrate. In this context we attempted to assess the applicability of the method and following are some observations made with the study:

- The type of cement influences the results of the colorimetric method by combining chlorides. As the concrete passes from 28 to 56 days, for example, it combines more chlorides, reducing the free chlorides, which are responsible for the color change;
- It is recommended that the concentration of 0.1N $AgNO_3$, as this allows a clear color change, but studies with 0.1N above concentrations were found and could be developed to verify if there was improvement in contrast;
- There is still no consensus on the chloride content which leads to discoloration, because the studies found out the subject to be very contradictory with very disparate findings together;
- When the pH of the concrete is less than 10, or the carbonation is deeper than the chloride penetration, the colorimetric method cannot be used all alone. One should employ a realkalisation technique, but this kind of practice to enable the use of the method is not merely an idea as an effective procedure which is not quite defined into the technical environment.
- In cases where the attack is exclusively chlorides, the colorimetric method is a qualitative technique efficient, practical and low cost.

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