Carbonic nanoparticles and C-S-H insertion into cementitious nanocomposite

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Abstract—Use of nanomaterials in cementitious nanocomposites is a possibility to improving mechanical properties as well as increased durability. In this research the insertion of multi-walled carbon nanotubes (MWCNT) and particles of Calcium Silicate Hydrate (C-S-H) with Ca/Si=0.8 and Ca/Si=1.2 ratios were used in microconcrete specimens. The effects on the compressive and tensile strength were tested, besides analysis of the porous structure by mercury intrusion, as well as the microstructure by scanning electron microscopy. Nanocomposites were produced by varying NTCPM insertions at 0.1% and 0.2% and C-S-H inserts at 1% and 2%, all of them based on cement mass. The results showed that the nanocomposites with C-S-H insertion with Ca/Si=0.8 ratio were the least porous and presented the highest tensile and compressive strengths, reaching strength increases in the order of 30% compared to the control material because C-S-H insertion with Ca/Si=0.8 ratio is reactive and causes reduction of the total porosity.
Keywords— nanocomposites, mechanical properties, carbonic nanoparticles, C-S-H, nucleation.

I. INTRODUCTION

The development of nanotechnology has been a great opportunity for the improvement and even the creation of new materials such as the discovery of carbon nanotubes (NTC) [1]. Cementitious materials have high compressive strength, but their low performance in tensile strength limits its use in structural elements subjected to tensile stresses as the case of flexural tensile.

To solve this problem the structural elements, use the steel as reinforcement of Portland cement concrete, in the so-called reinforced concrete. The better understanding of the structure and behavior of concrete at micro/nano-scale could help to improve concrete properties and prevent the illness, such as ASR [2].

The use of nanotechnology should be sought to solve the deficiency problems of conventional materials. A closer look at this assertion reveals that nanotechnology has indeed been sought for material enhancement in specific applications [3].

Applied in a smart way, using advanced mix design tools, nanoparticles can play an important role and can enable a cost effective and more sustainable development of civil and residential concrete structures [4].

The search for materials with homogeneous performance such as compressive strength and equivalent tensile strength has been a goal of many engineering researchers.

In this case the structural elements of constructions would be more durable and would have the calculation and production processes facilitated and safer as with structural elements produced in steel, which is considered for calculation purposes the same strength both to traction and compression.

NTCs are cylindrical shaped particles with a diameter at the nanoscale and composed basically of carbon and hydrogen, which have, among other characteristics, high tensile strength (some researchers report resistances greater than 100 times the tensile strength of steel, high modulus of elasticity and low specific mass). Carbon nanotubes have been used in various fields of applications in recent years due to their high physical, chemical, and mechanical properties [5].

Another alternative for improving cementitious materials is the use of materials that may result in micro-structural modifications based on chemical reactivity with Portland cement components.

The extremely fine size of the particles can alter the specific surface area and hence the properties of concrete. Nano particles added cement composite can increase the workability, strength and durability characteristics [6].

The C-S-H inserts that are of the same chemical composition of the calcium silicate hydrates (present in the Portland cement composition) can be considered.

The C-S-H are particles (monocrystals) whose thickness can be as small as 5 nm [7]. C-S-H represents between 50% and 60% of the volume of solids of the fully hydrated cement paste [8].

[9] investigated laboratory-precipitated C-S-H insertions and concluded that there was an increase in the hydration process of Portland cement pastes measured by thermal analysis.

These researchers recommend the use of inserts that are CSH because they are particles with the same chemical composition of the Portland cement hydrate products and may result in elimination of the induction period (without chemical activity) due to acceleration of hydration in the first hours with higher hydration peaks.

The result of the increased chemical activity produced by the C-S-H inserts can be explained by the crystalline nucleation and growth process that may occur in the porosity regions and does not focus only on Portland cement silicates.

Thus, in addition to maintaining the dense cementitious matrix by reducing the porosity, there is also the formation of nucleation spaces outside the surface of the silicates. in this way the negative effect of the layer formation (barrier) on these silicates is reduced and allows the diffusion decrease and the result is the possibility of increasing hydration of the silicates and formation of heavy crystalline structures such as the C-S-H gel.

Seeding with a pure form of laboratory made C-S-H would have a similar effect. Adding this type of C-S-H to C_3S paste increased nucleation sites for hydration to occur [9].

II. RAW MATERIALS AND METHODS

2.1 Production and chemical treatment of NTCPM

The NTCs used were of the multi-wall type (NTCPM) and were produced by the method of chemical vapor deposition (CVD), as shown in figure 1, in the Carbon Nanomaterials Laboratory of the Franciscan University (UFN), where were submitted to treatments and characterization.

This method was adopted because it is relatively simple and reliable, besides providing production in reasonable quantities to meet the expected consumption in the production of the tested nanocomposites.
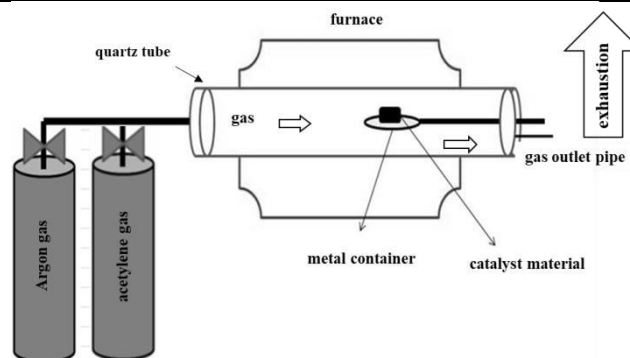

Fig.1: NTCPM production scheme - DVQ method, [10].

The NTCPM were subjected to chemical oxidation with the purpose of adding functional groups such as carboxyl group (-COOH) and hydroxyl radical (-OH), in the existing faults of the tube walls and especially in the extremities. After functionalized the NTCPM were denominated NTCPM-OX differentiating from non-oxidized nanotubes (NTCPM). The functionalization solves the problem of the hydrophobicity of the NTCPM facilitating their dispersion in aqueous solutions that is the case of cementitious materials in the fresh state.

The oxidation process was performed by immersion in an acid solution composed of a 3:1 mixture of H_2SO_4 and HNO_3 submitted sonication (by immersion) for 1 hour, according to a technique proposed by Mokhtar et al. [11], which effectively provides functionalization chemical properties of the material and preserves the structure of the treated material, according to figure 2.
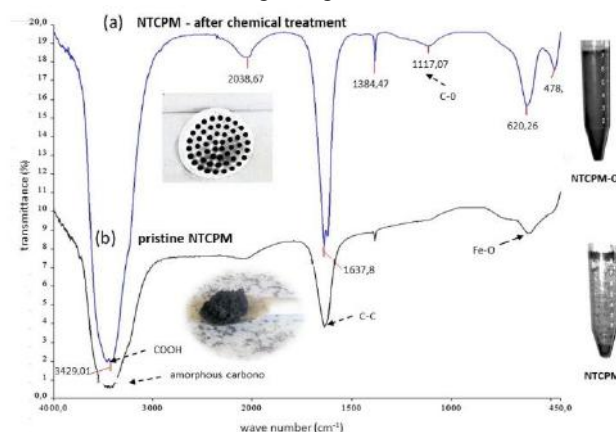

Fig.2: NTCPM Analysis - Fourrier Transform Infrared Spectroscopy (FTIR). Presents NTCPM as produced and after chemical oxidation treatment. The COOH functional groups are well identified in the material after the chemical oxidation process demonstrating effective functionalization and facilitating the dispersion in water.

Dispersion of nanofillers plays a very important role in the use of filler properties in polymeric composites. A technique to achieve good dispersion of nanoparticles is ultra-sonication which can be used also for CNTs [12].

Table 1 - Quantity of material insertion

	Ca/Si	C	S1-0,8	S1-1,2	S2-0,8	S2-1,2	T1	T2	ST1-0,8	ST1-1,2	ST2-0,8	ST2-1,2
C-S-H	0.8	-	1%	-	2%	-	-	-	1%	1%	2%	2%
C-S-H	1.2	-	-	1 %	-	2 %	-	-	-	-	-	-
NTCPM-OX	-	-	-	-	-	-	0.1 %	0.2 %	0.1 %	0.1 %	0.2 %	0.2 %

* Inserton quantity - in relation to cement mass

The result of Fourrier-transform infrared spectroscopy (FTIR) demonstrates the presence of the carboxylic groups after the chemical treatment with acids, indicating that the NTCPM were effectively functionalized. The peak around 3429 cm-1 is a characteristic of the stretching of the hydroxyl group (O=C-OH and C-OH) that can be attributed to the oscillation of carboxylic groups (-COOH) [13].

2.2 C-S-H Production

The production of C-S-H was performed by direct precipitation, according to the method described by Thomas, Jennings and Chen [9]. The chemical reagents used were calcium nitrate tetrahydrate $(Ca(NO_3)_2 \cdot 4H_2O)$ and sodium silicate (Na_2SiO_3). The proportions of the reactants were determined by stoichiometric calculation and then 2 types of C-S-H with different Ca/Si ratios (0.8 and 1.2) were produced. Precipitation occurred after the bath sonication process (immersion for 60 minutes).
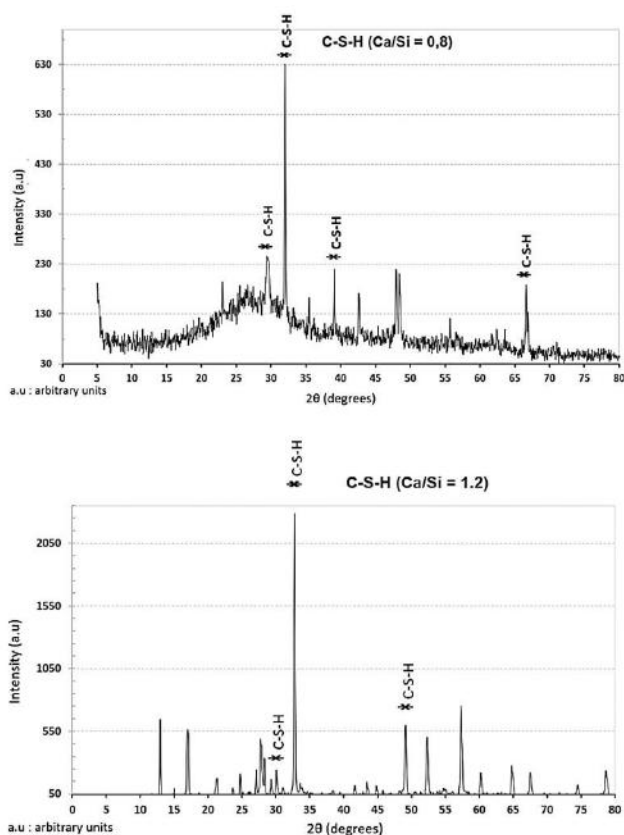

Fig.3: C-S-H. X-ray diffraction analysis (XRD).

Precipitation occurred after the bath sonication process (immersion for 60 minutes). After filtration, the materials were dried in an oven at 100 °C until the material had a constant weight.

Finally, the material was subjected to milling in the ball mill (ceramic beads for 12 hours. X-ray diffraction (XRD) analysis confirms the presence of C-S-H produced, as shown in figure 3.

2.3 Specimens for testing

For the tests of simple axial compressive strength, concrete specimens of dimensions (diameter x height) 32x64 mm were molded in cylindrical molds of wood specially produced for this purpose, and the molding was adapted according to the recommendations of the standard ABNT NBR 5738 [14]. The test was performed according to ABNT NBR 5739 [15].

The fragments of the specimens after the flexural traction test were packed in plastic bags to avoid contamination, to be used in mercury intrusion porosimetry tests in the GREENTEC laboratory in the Chemical Engineering Department of the Federal University of Rio de Janeiro (UFRJ), where the assay was performed on the AutoPore IV 9500 V1.09 equipment of micromeritics and still.

The same procedure was performed for transmission electron microscopy analysis, which was performed at the Analytical Center of the Federal University of Ceará (UFC), in the Quanta FEG 450 equipment, in the secondary electron module (SE).

Fig.4: Fragments packaged for porosimetry and microanalysis assay.

The fragments were subsequently prepared with a size of about 6 mm in diameter. After being immersed in absolute ethyl alcohol for 24 hours and dried in an oven at 60 ° C for a period of 12 hours.This procedure removes free water and induces the halting of the hydration reactions and serves to avoid changing the microstructure

of the material after the tests have been carried out. They were then packed in a hermetically sealed container and identified, figure 4, until they were properly submitted to microanalysis tests by transmission electron microscopy.

For the flexural tensile strength test, prismatic specimens measuring 4x4x16 cm (height x width x length) were produced. Metallic forms were used, the same ones used for mortar tests and the test was adapted and followed the recommendations of ABNT NBR 13279 [16]. The nanocomposites and the control material were prepared with basic materials (cement, sand, water and chemical additive based on carboxylates) in addition to carbonic material inserts (NTCPM-OX) as well as C-S-H. The terminology for identification of the nanocomposites and the quantities of insertion are shown in table 1.

III. RESULTS AND DISCUSSIONS

3.1 Microstructure analysis

The result of the mercury intrusion porosimetry test revealed the modification of the microstructure of the nanocomposites with inserts when compared to each other and especially as the control material (C).
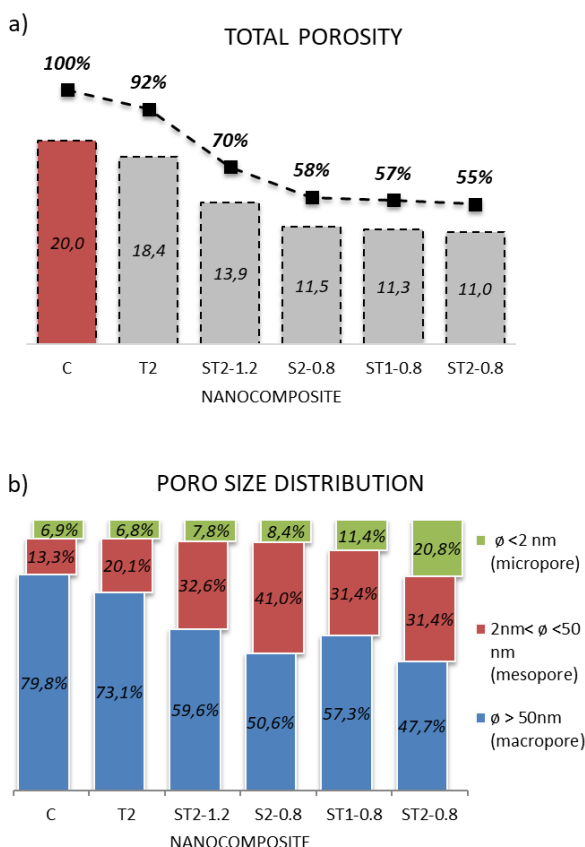

Fig.5: Pore size distribution

The C-S-H insertions with Ca/Si=0.8 ratio resulted in the reduction of the total porosity to values around 55% when compared to the control material (C), as was the case of the nanocomposites ST2-0.8 (mixed insertion 2% of C-S-H ratio Ca/Si=0.8 and 0.2% of NTCPM-OX) and S2-0.8

(insertion 2% CSH Ca/Si ratio = 0.8) and ST1-0.8 (mixed insertion of 1% C-S-H Ca/Si=0.8 ratio and 0.1% NTCPM-OX) according to Figure 5-a.

In addition to the modification of the pore size distribution that resulted in macro and mesoporous reduction and significant increase of micropores, as shown in Figure 5-b.

The nanocomposite ST1-0.8 presented a percentage of macropores of 50.6%, a significant reduction when compared to the control material (C) with a high amount of macropores, 73.1%. If we analyzed the micropores the amount was 8.4% higher than the control material, which presented only 6.8%.

For mesopores, the ST1-0.8 nanocomposite presented the amount of 41% double that of the control material, 20.1%.

It is verified that there was a differentiated porosity distribution for the mixed insertion nanocomposite that resulted in a more compact micro-structure by the substitution of larger pores for smaller pores, which is called refinement.

This refinement has several advantages for cementitious materials such as increased mechanical strength, reduced permeability and consequently increased durability of these materials against aggressive agents.

The transformation of the microstructure of the nanocomposites with insertions can be explained by the nucleation and growth of crystalline structures, stimulated by C-S-H insertions with Ca/Si=0.8 ratio, which were chemically active and compatible with the hydrated products (Portland cement silicates) which made the matrix (micro structure) of these materials denser since crystal growth also occurred in the weakened pores or sites, as shown in Figure 6.

The growth in the porous region has positive characteristics of reducing the total porosity, refining the porous micro structure and also reinforces the matrix resulting in increased mechanical strength.
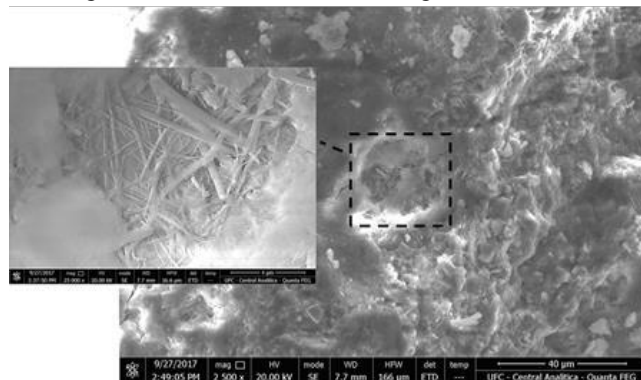

Fig.6: SEM-FEV nanocomposite ST2-0.8 - It shows the formation of interlaced crystalline structures occupying a region with filling failure.

3.2 Compressive strength

The use of C-S-H inserts with Ca/Si = 0.8 ratio resulted in the increase in the compressive strength of the nanocomposites when compared to the control material. The most resistant were the nanocomposite ST2-0.8 (mixed insertion of 2% CSH Ca/Si ratio = 0.8 and 0.2% NTCPM-OX) and S2-0.8 (insertion 2% of CSH ratio Ca/Si = 0.8) that showed resistance 30% and 26% higher than the control material (C), according to figure 7.

On the other hand, isolated inserts of NTCPM-OX did not present significant results considering error (5%) as was the case of T1 nanocomposites (insertion of 0.1% of NTCPM-OX) and T2 (insertion of 0.2% of NTCPM -OX). The nanocomposites with C-S-H insertion with Ca/Si=1.2 ratio had considerable performance only for mixed insertion such as the case of the nanocomposite ST2-1.2 (insertion 2% of C-S-H Ca/Si=1.2) that presented strength 17% higher when compared to the control material.

This result shows that the C-S-H with ratio Ca/Si =1.2 has a lower chemical reactivity than the C-S-H Ca/Si=0.8 ratio resulting in lower nucleation and growth of hydrated products, such as secondary C-S-H, as happened with the isolated inserts of NTCPM-OX.

The increase of the compressive strength can be explained by the transformation of the microstructure and consequent reduction of the total porosity and reinforcement of the cementitious matrix of the nanocomposites with insertions of C-S-H with Ca/Si=0.8 ratio that proved to be more active and stimulated the growth of resistant hydrated products such as secondary C-S-H.

Compression tests are performed on cylinders of seeded cement pastes with the understanding that a dense microstructure should cause high compressive strength [17].
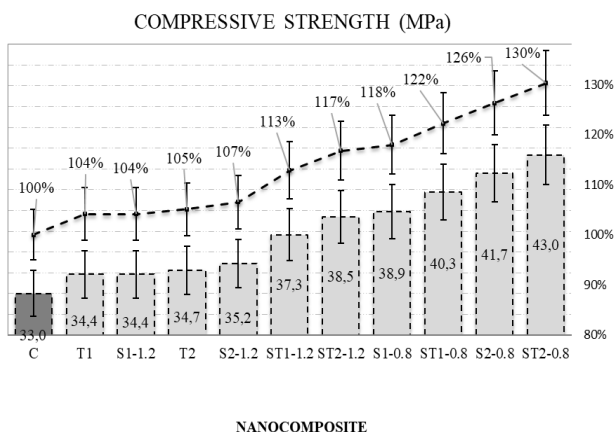

Fig.7: Compressive strength

An increase in compressive strength accompanies the development of a denser, less porous, microstructure for cement materials because C-S-H gel acts as a seed for nucleation sites for further C-S-H growth, an increase in

compressive strength would reinforce this observation [18].

3.2 Tensile strength by flexural stress

In this parameter it is verified that the insertion of NTCPM-OX was relevant in the results, especially in the mixed inserts as

the case of the nanocomposites ST2-0.8 (mixed insertion of 2% C-S-H Ca/Si=0.8 ratio and 0.2% NTCPM-OX), ST1-0.8 (mixed insertion of 1% C-S-H Ca/Si=0.8 ratio and 0.1% NTCPM-OX) and ST2-1.2 (mixed insertion of 2% of C-S-H Ca/Si=1.2 ratio and 0.2% of NTCPM-OX), resulting in a tensile strength increase of up to 33% higher than the control material, according to figure 8.
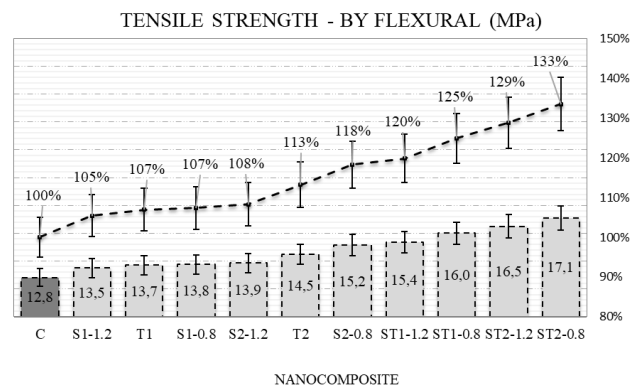

Fig.8: Tensile strength by flexural stress

Furthermore, the isolated insertion of NTCP-OX as the nanocomposite T2 (insertion of 0.2% of NTCPM-OX) presented tensile strength 13% higher than the control material, which can be explained by the fact that materials such as NTC exhibit high tensile strength and when well distributed in the matrix results in a nanoscale reinforcement [19,20], according to figure 9, preventing the appearance of the first cracks, which results in the increase of tensile strength.
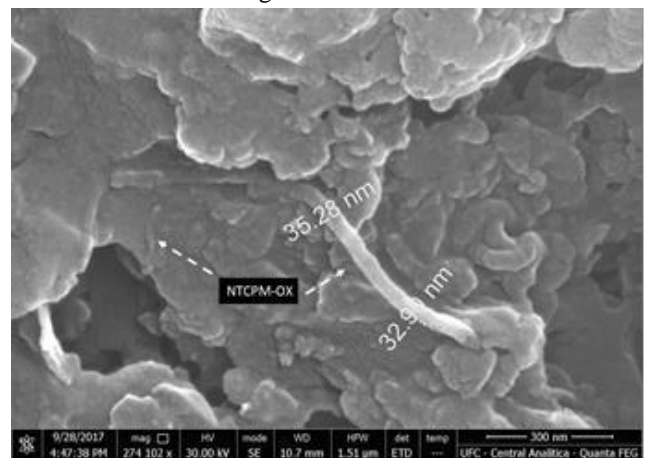

Fig.9: SEM / FEG nanocomposite image ST2-0,8.
Presence of nanotubes adhered and reinforcing to the cementitious matrix.

IV. CONCLUSIONS

Analyzing the numerical results and also the microscopy images, it was possible to verify that the insertions of C-S-H ratio Ca/Si = 0.8, result in the modification of the microstructure of the cementitious nanocomposites because they cause the nucleation and growth of resistant materials, especially in the region porous, in this way the matrix becomes more compact and resistant to both compression and traction.

The addition of functionalized carbon nanotubes caused relevant results because the nanoparticles were well distributed in the matrix and acted as reinforcement in this way the result in the flexural tensile strength was demonstrated for the nanocomposites with this type of insertion, especially those with mixed insertion.

REFERENCES

[1] S. Iijima, Helical Microtubules of graphitic carbon. Nature, v. 354, p. 56-58, 1991.

[2] Ge, Z. e Gao, Z. Applications of nanotechnology and nanomaterials in construction. First International Conference on Construction In Developing Countries (ICCIDC-I), Karachi, Pakistan, 2008.

[3] M. C. Roco, R. S. Williams, P. Alivisatos, Nanotechnology Research Directions: IWGN Research Report. Committee on Technology, Interagency Working Group on Nanoscience, Engineering and Technology (IWGN), National Science and Technology Council.1999.

[4] Brouwers,H.J.H. Proceedings of ACI Session on "Nanotechnology of Concrete: Recent Developments and Future Perspectives" Nov. 7, Denver, USA. 2006.

[5] Baughman, RH, Zakhidov, AA, de Heer, WA: Carbon nanotubes—the route toward applications. Science 297, 787–792 (2002).

[6] Jemimah, C. M. and Prince, A.G. IRACST – Engineering Science and Technology: An International Journal (ESTIJ), ISSN: 2250-3498, Vol.2, No.1, 2012.

[7] A. Nonat, The structure and stoichiometry of C-S-H. Cement and Concrete Research 34. p 1521–1528. Elsevier, 2004.

[8] P.K. Mehta and P. J. M. Monteiro. Concreto: Estrutura, Propriedades e Materiais. São Paulo, Ed. Pini, p.573, 1994.

[9] J. J. Thomas, H. M. Jennings and J. J. Chen, Influence of Nucleation Seeding on the Hydration Mechanisms of Tricalcium Silicate and Cement. The Journal of Physical Chemistry. 2009.

[10] M. A. Duart, Efeitos da adição de nanotubos de carbono e C-S-H precipitado nas propriedades de nanocompósitos cimentícios. 2017. Tese (doutorado em nanociências) – Universidade Franciscana, Santa Maria, 2017.

[11] A. Mokhtar et al. Functionalization and characterization of carbon nanotubes / polypropylene nanocomposite. World Academy of Science, Engineering and Technology. v. 58, p. 421-425, 2011.

[12] M. M. Shokrieh, A. S. and M. C Mechanical properties of multi-walled carbon nanotube/polyester nanocomposites. Journal Of Nanostructure in Chemistry 2013, 3:20 http://www.jnanochem.com/content/3/1/20.

[13] M. A. Atieh et al, Effect of Carboxylic Group Functionalized on Carbon Nanotubes Surface on the Removal of Lead from Water. Bioinorganic chemistry and applications, 2010. DOI- 2010. 603978. 10.1155/2010/603978.

[14] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. NBR 5738: Concreto - Procedimento para moldagem e cura de corpos de prova. Rio de Janeiro, 2015.

[15] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. NBR 5739: Concreto - Ensaios de compressão de corpos-de-prova cilíndricos – Método de ensaio. Rio de Janeiro 2007.

[16] ASSOCIAÇÃO BRASILEIRA DE NORMAS TÉCNICAS. NBR 13279: Argamassa para assentamento e revestimento de paredes e tetos - Determinação da resistência à tração na flexão e à compressão. Rio de Janeiro 2005.

[17] T.C. Powers and T.L. Brownyard, Studies of the physical properties of hardened Portland cement paste, Bull. 22, Res. Lab. of Portland Cement Association, Skokie, IL, U.S. (1948), reprinted from J. Am. Concrete Inst. (Proc.) 43 (1947) 101-132, 249-336, 469- 505, 549-602, 669-712, 845-880, 933-992.

[18] Hubler, M. H.; Thomas, J. J. and Jennings, H. M. Influence of nucleation seeding on the hydration kinetics and compressive strength of alkali activated slag paste. Cement and Concrete Research, v. 41, p. 842-846, 2011.

[19] Kawashima, S. et al. Modification of cement-based materials with nanoparticles. Cement & Concrete Composites, n. 36, p. 8-15, 2012.

[20] Z. S. Metaxa, M. S. Konsta-Gdoutos and S. P. Shah. Carbon nanofiber cementitious composites: Effect of debulking procedure on. Cement & Concrete Composites, n. 36, p. 25-30, 2013.