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Incorporation of micro and nanoparticles of silica in cementitious composites

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Abstract: In recent years, the incorporation of micro and nanoparticles has been studied as an alternative to improve the characteristics of the cementitious materials. Researches on the reinforcement of cementitious composites per incorporation of micro and nanoparticles of silica have become more frequent and have demonstrated many benefits. However, the scientific literature is still limited, as there are many controversies and gaps on the knowledge about this subject. In this context, this study has compared the mechanical and microstructural behavior of four cementitious composites: a composite used as reference, a composite containing only 8% of silica from rice husk ash (RHA) in substitution for the cement mass and two others containing the same incorporation of 8% of RHA with the addition of 0.2% and 0.4% of nanosilica dispersed in polycarboxylate (NDP) in relation to the mass of cement. The mechanical behavior was assessed by the compressive strength test after both 7 and 28 days curing. It was also performed the test of water absorption after 28 days curing. The results show that the addition of nanosilica was feasible regarding the improvement of mechanical and microstructural properties of the cementitious composites that have been studied. Nevertheless, the composite containing the largest nanosilica content was not the most viable composite, since the results at 28 days were not significant when compared to the composite with the half of this addition. Therefore, the best performance observed was of the composite that had a replacement of its mass of cement by 8% of RHA and had the addition of 0.2% of NDP, which showed a good mechanical behavior, and had also decreased the water absorption of the samples.

Keywords: *Cementitius materials, micro and nano particles, silica from rice husk ash, nanoparticles.*

I. INTRODUCTION

Lately, the incorporation of micro and nanoparticles in cementitious composites has been known as a promising field of research, because it tends to enhance their physical and mechanical properties.Composites are materials of two or more phases that seek to improve certain properties inherent to each product. Researches in the composites area have sought materials that, when combined, improve its properties, especially the mechanical and microstructural [1]. In this context, the incorporation of mineral particles of silica tend to optimize the performance of cementitious materials, as they ensure a better refinement of the microstructure, producing more resistant and durable materials [2-3].At least two forms of performances can be shown with these incorporations: a chemical, acting as high reactivity pozzolanic and a physical, acting as a filler. In the chemical action, the nanosilica rapidly reacts with the calcium hydroxide ($Ca(OH)_2$) released during the hydration of cement, forming resistant hydrated calcium silicate compounds, which tend to fill the capillary voids. In physical acting, the nanoparticles are dispersed in the spaces between the cement grains, resulting in a uniform distribution of the hydration products, filling the interstitial gaps in the skeleton of the microstructure of the cement paste, thus contributing to a denser structure, less porous and consequently, with greater strength. It is also known that the chemical reaction rate is directly proportional to the surface area of the agglomerates; Thus, nanosilica may favor to an increase in the formation of calcium silicate hydrate (CSH) through the pozzolanic reaction with calcium hydroxide [4-6].The silica from rice husk ash (RHA) can be used as a micro particle option to be incorporated in cementitious composites due to the presence of a high amorphous silica content in its chemical composition [7]. In the hardened state the incorporation of low levels of about 3% and 8% of RHA tends to increase the mechanical resistance and reduce porosity, refining the microstructure, while in the fresh state this incorporation tends to decrease segregation and exudation [6].

The combined action of micro and nanoparticles of silica seeks to optimize the particle packing, which is essential to ensure the decrease of the pores and increase the mechanical resistance, improving considerably the quality of the composite [5].Nanoparticles are microscopic particles whose size is measured in nanometers (nm), where at least one of its dimensions is less than 200 nm. Among the nanoparticles commonly used in

cementitious materials is nanosilica [4, 8-11]. The main difference between micro and nanosilica is its particle size since the nanosilica is about 1000 times thinner [12]. Thus, the nanoparticles are more reactive, participating more effectively in chemical reactions [13]. Hence, the present research aims to analyze the influence of the incorporation of micro and nanoparticles of silica in cementitious composites.

II. MATERIALS AND METHODS

2.1 Materials

For the production of the cementitious composites were used the following materials: High-early strength Portland cement (Type III – HES) which do not contain any additions; silica from rice husks (SILCA NOBRE); Nanosilica dispersed in polycarboxylate based superplasticizer (NDP) Type II (SP-II N), according to the classification of the Brazilian standard NBR 11768 [14], and fine quartz aggregate. The specifications of silica fume and nanosilica according to the manufacturer are shown in Tables 1 and 2, respectively.

Table 1 – Specifications of RHA, Silca Nobre SCI (Source: The manufacturer).

Properties	Data
Humidity (%)	< 3,0
Amorphous silica content (%)	> 95
Bulk density (kg/m³)	550 - 600
Specific gravity (g/cm³)	2,16
Average Diameter	< 8,0 μm
Specific area (m²/kg)	20000
pH	≤ 10,0
Amorphous Silica (SiO2) (%)	≥ 90,0
Crystalline Silica (SiO2) (%)	≤ 2,0

Table 2 – Specifications of NDP, Silicon ns high 200 (Source: The manufacturer).

Property	Values
Color	Honey
Relative density	1.09
Conventional solids content	48.5
pH	2.99
Chloride content	< 0.1%
Alkali content	-

2.2 Methods

In order to achieve the aims of this study, it was made a comparison of four types of cementitious composites: a reference composite and other three modified with the incorporations, with the silica from rice husk ash (RHA) being incorporated in substitution to the cement mass and the nanosilica dispersed in polycarboxylate (NDP) being utilized as an addition, also in relation n to the cement mass. In Table 3 are shown the composites in study, their constituent materials and their respective nomenclatures.

Table 3 – Component materials and nomenclatures of the cementitious composites

Composite	Constituent materials	Nomenclature
Reference	Cement + sand + water	CC I (0:0)
With RHA	Cement + sand + water + 8% de RHA [1]	CC II (8:0)
With RHA e NDP	Cement + sand + water + 8% [1] de RHA + 0,2% de NDP [2]	CC III (8:0.2)
With RHA e NDP	Cement + sand + water + 8% [1] de RHA + 0,4% de NDP [2]	CC IV (8:0.4)

(1) Substitution in relation to the cement mass;
(2) Addition in relation to the cement mass.

In order to optimize the particle size distribution of the fine aggregate it was studied the particle size composition of two sands, a medium and a fine grained. For this purpose, it was carried out assays of compressed unitary mass for different compositions of these sands, from 100% of medium grained to 100% fine grained sand, in order to select the composition with the lowest empty index and greater compacted unitary mass.The tests that were carried out to verify the characteristics of the aggregates compositions are described in Table 4, and were realized in accordance to Brazilian standards.

Table 4 – Tests carried out for characterization of fine aggregate and their respectives standards.

Test	Brazilian standards
Unitary mass	NBR NM 45/2006 [15]
Granulometric composition	NBR NM 248/2003 [16]
Specific Gravity	NBR NM 52/2009 [17]
Water absorption	NBR NM 30/2001 [18]

Besides the characterization of the fine aggregate, the nanosilica dispersed in polycarboxylate (NDP) was lyophilized and characterized from X-ray fluorescence assay, through the equipment of energy dispersive spectrometry (ED-XRF). This test is a qualitative and quantitative method based on the measurement of the intensities of the characteristic X-rays emitted by the chemical elements in the sample [19].

In order to analyze the properties of the cementitious composites, tests in fresh and hardened state were carried out. The assays carried out in the fresh state and their respective Brazilian standards are shown in Table 5 and the experimental planning of the tests realized in the hardened state and their respective Brazilian standards are shown in Table 6.

Table 5 – Tests carried out in fresh state and their respective Brazilian standards.

Test	Brazilian standards
Consistency index	NBR 13276/2005 [20]
Specific Gravity	NBR 13278/2005 [21]

Table 6 – Planning of tests carried out in hardened state and their respective Brazilian standards.

Test	Specimen size (mm)	Specimen by age		Total of samples	Brazilian standards
		7 days	28 days		
Compressive strength	50 x 100	4	4	8	NBR 7215/1997 [22]
Water absorption	50 x 100	-	3	3	NBR 9778/2009 [23]

2.3 Mix Ratio Definition

The mix ratio adopted for the preparation of composites was 1: 1. For the production of the composites was determined the consistency of 260 mm ± 10 mm in the consistency table, then varying the water/cement ratio (w/c) in the composite, as water was being added until obtaining the desired consistency. Table 7 shows the consumption of materials in each composite.

Table 7 – Consumption of materials in each composite.

Composites	Quantitative of components			
	Cement (g)	Sand (g)	RHA [1] (g)	NDP (ml)[2]
CC I (0:0)	3300	3300	0	-
CC II (8:0)	3036	3300	264	-
CC III (8:0.2)	3036	3300	264	5.57
CC IV(8:0.4)	3036	3300	264	11.14

(1) Substitution in relation to the cement mass;
(2) Addition in relation to the cement mass.
(3)

III. RESULTS AND ANALYSES

3.1 Characterization of fine grained aggregate

It were carried out many tests of compressed unitary mass, mixing fine grained sand with medium grained one, in order to choose the best composition, with the lowest void index, in order to optimize the particle size distribution. The results obtained are shown in Table 8.

Table 1 – Compressed unitary mass of the mixture.

Medium sand amount (%)	Fine sand amount (%)	Compressed unitary mass (Kg/dm³)	Void index (%)
100	0	1.748	33.0
90	10	1.758	32.6
80	20	1.765	32.4
70	30	1.760	32.6
60	40	1.744	33.2

50	50	1.742	33.3
40	60	1.726	33.9
30	70	1.711	34.4
20	80	1.690	35.3
10	90	1.676	35.8
0	100	1.645	37.0

The chosen composition chosen was composed by 80% of medium grained sand and 20% of fine grained one, as the mixture showed the higher compressed unitary mass, and consequently the lowest void index.After choosing the composition, tests were carried out in order to determine the characteristics of the composed aggregate. The particle composition and its grading curve are shown in Table 9 and Figure 1, respectively.

Table 2 – Particle composition

Strainer (mm)	**Retained mass (g)**	**Retained percentage (%)**	**Percentage retained accumulated (%)**
4.8	2.40	0.24	0
2.4	21.20	2.12	2
1.2	82.30	8.23	11
0.6	279.60	27.96	39
0.3	421.00	42.10	81
0.15	165.80	16.58	97
Fundo	27.70	2.77	100

From the results obtained and shown in Table 9, it can be verified that the fineness modulus of the composition of the composed aggregate is 2.29, which is characterized as a medium sand. The density that was found is 2.61 g/cm³, the water absorption is 0.57% and the compacted bulk density is 1.765 kg/dm³. Figure 1 presents the grading curve of the chosen particle size distribution that was used.

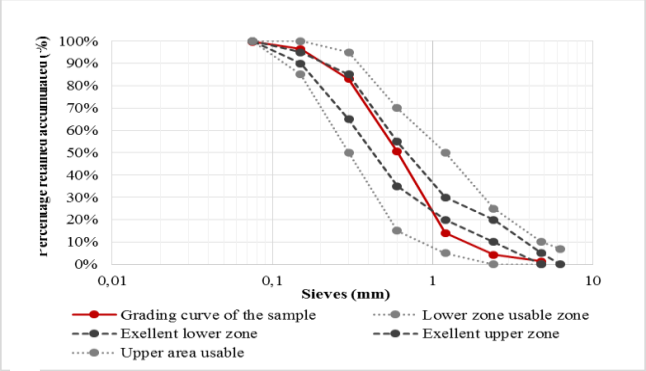

Figure 1 – Grading curve.

It can be noticed t the grading curve of the chosen composition is within the working limits, having a continuous particle size d ibution.

3.2 Characterization of nanosílica dispersed in polucarboxylate

The results obtained by the X-ray fluorescence assay realized through the equipment of energy dispersive spectrometry (ED-XRF) are shown in Table 10. The image from the spectrometry that was originated by the equipment is shown in Figure 2.

Table 10 – Chemical elements detected in the NDP sample (Silicon ns High 200) from the ED-XRF assay.

Chemical element	**Amount (%)**
Carbon	60.19
Oxygen	39.04
Sodium	0.38
Silicon	0.16

Sulfur	0.24
Aluminum	-
Total	100

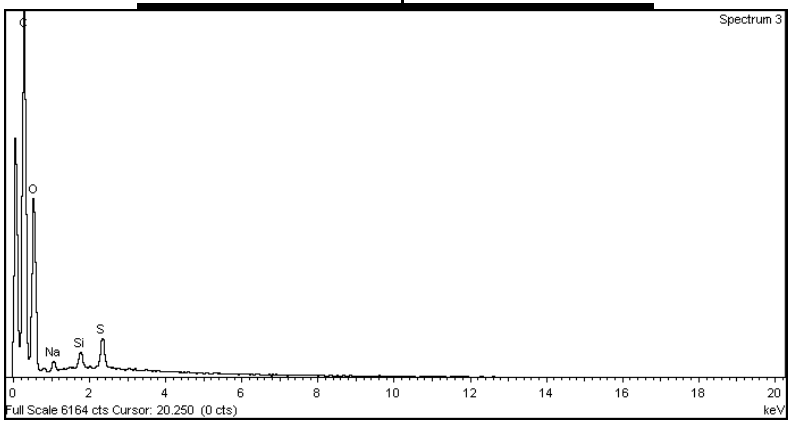

Figure 2 – Spectrum of the NDP sample (Silicon ns High 200).

In the ED-XRF assay it was detected the presence of silicon in the sample which can be correlated to the presence of nanosilica since silica is a compound of silicon dioxide (SiO_2).

3.3 Properties in fresh state

The amount of water that was added in each composite in order to obtain the consistency of 260 mm ± 10 mm, the values of consistency index, the ratio water/cement (w/c), water/dry materials (w/dm) and the density of mass of the composites are shown in Table 11.

Table 11 – Water amount added, ratios, consistency index and density of mass of the composites.

Samples	**Amount of water added (ml)**	**w/c ratio**	**w/dm ratio**	**Consistency index (mm)**	**Specific Gravity (g/cm^3)**
CC I (0:0)	1254	0.38	0.19	266	2.20
CC II (8:0)	1070	0.35	0.16	262	2.20
CC III (8:0.2)	1010	0.33	0.15	263	2.23
CC IV (8:0.4)	911	0.30	0.14	264	2.25

From the data of Table 11, it was observed that the consistency index has respected the consideration limits of 260 mm ± 10 mm. Also, it is possible to see that the addition of NDP increased the mass density in the two studied levels, probably caused by the action of nanosilica, as the replacement with, only, RHA didn't showed any increase in the density of mass.

3.4 Properties in the hardened state

3.4.1 Compressive strength

The results from the compressive strength assay in the ages of 7 and 28 days were obtained through the average of 6 specimens and are shown in Table 12.

Table 3 – Results from compressive strength assay in ages of 7 and 28 days.

Cement Composites	**Age (days)**	**Compressive strength (MPa)**	**Standard deviation (MPa)**	**Coefficient of variation (%)**
CC I (0:0)	7	60.0	0.9	1.4
CC II (8:0)		58.6	1.3	2.2
CC III (8:0.2)		80.2	4.8	6.0

CC IV (8:0.4)		87.2	7.1	8.1
CC I (0:0)	28	63.7	7.9	12.3
CC II (8:0)		95.5	1.1	1.1
CC III (8:0.2)		96.1	0.9	0.9
CC IV (8:0.4)		92.2	5.7	6.2

The values shown in Table 12 were drawn in a graphic and are illustrated in Figure 3.

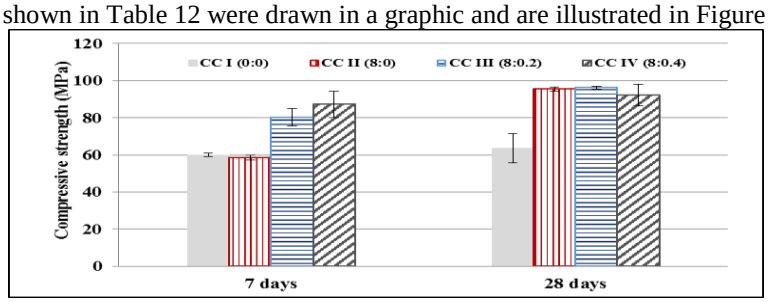

Figure 2 – Compressive strength of the composites.

Analyzing the Figure 3 it is possible to notice that the replacement of RHA by cement (CC II) showed a greater influence after 28 days curing because the increase of the resistance at this age was of 49.9% in relation to the reference, confirming with the study made by Gomes and Marton [6]. In 7 days, the resistance has remained basically in the same value. This behavior may have occurred due to the presence of RHA as pozzolan, increasing the compressive strength over time.It is observed that the composites containing the two incorporations showed higher mechanical performance at early ages, when compared to the composite with only the incorporation of RHA, probably by the high reactivity of the NDP, confirming with the studies submitted [5;24], who analyzed the incorporation of silica alone and also of this combined with nanosilica. At 7 days CC II and CC IV showed an increase in compressive strength of 36.8% and 48.7%, respectively, when compared with CC II.After 28 days curing, the composite CC III showed an increase of 0.6% in its resistance when compared to the composite with activated silica (CC II), then verifying that this addition of 0.2% of NDP did not act in as significantly as at 7 days curing. While the composite CC IV had its compressive strength 3.4% lower than the composite CCII. It is possible to note that the addition of 0.4% NDP in conjunction with the RHA showed no significant results at this analyzed age. This may be due to some error that occurred while molding the specimens, since the water/cement ratio of CC IV, with 0.4% of NDP, was lower than the CC III.When evaluating the variation of nanosilica content from 0.2% to 0.4%, there is an increase in resistance of 8.7% at 7 days, which is not very significant, since the addition was the double. While, at 28 days this behavior did not occur because the increase in NDP content reduced the compressive strength in 3.4%.

3.4.2 Water Absorption

3.4.3

The Figure 4 shows the results from water absorption assay after 28 days of saturation.

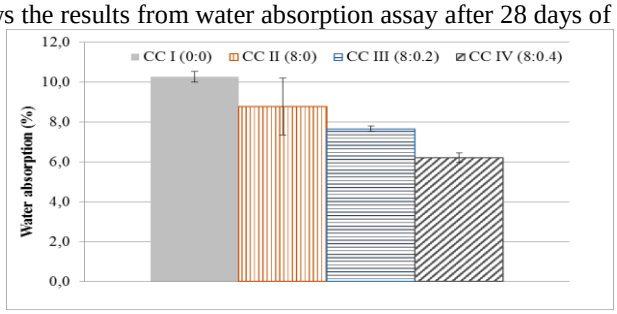

Figure 3 – Water absorption of the composites after 28 days curing.

Analyzing the results, it is possible to observe that the replacement of RHA promoted a decrease of 14.5% in water absorption after saturation.Furthermore, it was found that the joint action of RHA and NDP significantly decreased the water absorption, since the composite CC II showed a decrease of 25.4% and the composite IV, of 39.6%, both compared to the reference.Analyzing the action of the addition of NDP in 0.2% and in 0.4%, it is possible to note that the lower level decreased the absorption in 12.8% and the higher, in 29.3%, when compared to CC II.

When the variation of the level of nanosilica is assessed, from 0.2% to 0.4%, it is also noted a decrease in water absorption of 19.0%. It should be noted that the composite IV, which had the lowest absorption, also had the lowest ratio w/c and the highest mass density. It is believed that this fact happened due to the refinement of the microstructure and to the performance of the NDP.

IV. CONCLUSION

Analyzing the results, it is possible to verify that the incorporation of micro and nanosilica in cementitious composites ensures the increase in density and the improvement of its mechanical characteristics.

In a comprehensive analysis from the collected data it is possible to be concluded that all the composites with incorporations of micro and/or nanoparticles showed improvements in results of all assays, when compared to the reference composite.The composite with the higher level of nanosilica (0.4%) was not the one which presented the best mechanical performance, as its results after 7 days curing were not significant when compared to the composite with the half of the addition (0.2%) and also at 28 days its mechanical resistance was lower. It is believed that this may have occurred due to some error while molding the specimens.

Therefore, the composite that demonstrated a more feasible result in all assays was CC III, with replacement of 8% of the cement mass by RHA and addition of 0.2% of NDP, as it showed the best mechanical performance and had a decrease in its water absorption in the two analyzed conditions.

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