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Role of Low-cost Nano RHA on Physico-mechanical Properties of Cement Mortar

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THIS WORK compares nano-structured rice husk ash (RHA) before grinding and nano-sized RHA after grinding in terms of the physical properties of cement and mortar performance. Blaine surface area, sieve analysis (45 μm mesh), water of consistency, expansion, initial and final setting time, and compressive strength (at 2, 7, 28, 60 and 90 d of curing) measurements were performed for 0, 2, 4, 6, 8 and 10% RHA replacement of cement by weight. RHA both before and after grinding enhanced the cement physical and mechanical properties, as well as the mortar performance in terms of the long-term aged strength, at a constant water/cement ratio and without the use of any type of super-plasticizer (SP). The enhancement became stable at all long-term ages for 10% replacement in the case of RHA before grinding and 4% replacement in the case of RHA after grinding. More considerable enhancements were observed with a high replacement percentage up to 10% nano-sized RHA due to the small size of its particles, which increased the pozzolanic reactivity and worked as a filler material to produce a denser mortar.

Keywords: Cement mortar, Low-cost, Nano, Rice husk ash.

Introduction

Rice husk ash (RHA) is a type of pozzolan, which is defined as »a siliceous or siliceous and aluminous material, which in itself possesses little or no cementitious value but will, in finely divided form and in the presence of moisture, chemically react with calcium hydroxide at ordinary temperatures to form compounds possessing cementitious properties« according to ASTM C618 [1]. Calcium-silicate-hydrates (C-S-H) will be formed through the chemical pozzolanic reaction between the $Ca(OH)_2$ produced by cement hydration and the amorphous silica of RHA, resulting in a higher matrix density.

The reactivity of the pozzolan depends on various parameters, such as the chemical composition, type of mineralogical phase, proportion of active phases, particle size and specific surface area (SSA), ratio of lime to pozzolan, curing time, water content and temperature [2, 3]. RHA contains silica (80–95%) [4] and has a relatively high SSA (30–80 m^2/g). The residual carbon in and microporous cellular structure of the RHA skeleton, which is essentially composed of silica, also helped the pozzolanic reaction. The cellular material has a high SSA due to its external and internal pores [5]. The pozzolanic reactivity also depends on the RHA burning temperature [6] and retention time [7] used to produce amorphous silica, which is considered the most important property determining the pozzolanic reactivity [3], in addition to the degree of RHA grinding [8]. The dependence on the grinding degree occurs because a decrease in the RHA particle size will increase its pozzolanic reactivity, as indicated by the variation in the strength activity index (SAI) with increasing grinding time, especially if the particle size is on the nano-scale [9]. Because Portland cement (PC) has a particle size range of 0.5–60 μm on average, approximately 100 times that of nano-scale particles, the nano-sized RHA particles will fill the cavities between the

cement and aggregate particles and between the cement particles. This cavity filling results in improvement of the compressive strength and increased durability of concrete due to the increase of the dense packing of aggregate and cement particles, as mentioned for the silica fume performance [10].

According to refs. [11-14], the RHA pozzolanic reactivity can be evaluated with chemical methods, such as measuring changes in the conductivity for a lime/pozzolan solution over time, or mineralogical methods, such as monitoring $Ca(OH)_2$ consumption by X-ray diffraction or by using the SAI. The SAI is measured by moulding two specimens according to a standard specification: one with 100% PC as a reference and the other with replacement of part of the PC by the corresponding amount of the pozzolan to be tested. After curing, both specimens are tested for the SAI to express the effect of the pozzolanic material:

SAI= (compressive strength (pozzolan mix))/ (compressive strength (reference))   Eq. (1)

Using RHA as a supplementary cementitious material has environmental benefits, saves cost, and improves the mechanical properties of mortar and the durability of concrete, especially in aggressive environments. The environmental benefits have been summarized as the trapping of the carbon remaining in the RHA, which is released to the environment over a long storage period, and the reduction of the CO_2 emitted during cement production (900 kg CO_2 emitted/1 ton of cement manufactured); 5–7% of global CO_2 emissions is produced in cement manufacturing [15]. The substitution of cement by a percentage of well-prepared RHA will cause a decrease in cement production and save cost through the enhancement of the mechanical properties and durability of concrete [16]. In the last few decades, several studies have investigated the effects of mineral nano-particles on cement concretes and mortars, but the effect of nano-structured RHA (before grinding) and nano-sized RHA (after grinding) addition to cement mortar is still unexplored, especially the relations of the BET surface area, Blaine SSA and particle size distribution with the cement physical properties and pozzolanic reactivity. In this study, we focused on the effect of nano-structured and nano-sized RHA on the physical and mechanical properties of cement mortar.

Materials and Methods

Raw materials

The raw materials used in the study were sulfate-resisting PC CEM I 42.5 N-SR3 as per ES 4756-1/2013 [17], with the chemical analysis results shown in Table 1, and CEN Standard Sand complying with EN 196-1 [18].

TABLE 1. Chemical analysis of CEM I 42.5N-SR3.

Chemical composition (%)	Specification limit for cement	Cement results
SiO_2	----	21.03
Al_2O_3	----	4.30
Fe_2O_3	----	5.05
CaO	----	62.26
MgO	----	1.19
SO_3	3.5 max.	2.85
Na_2O	----	0.53
K_2O	----	0.37
Cl	0.10 max.	0.02
Insoluble residue	5.0 max.	0.33
Loss on ignition	5.0 max.	1.22
CaO	----	1.12
Equivalent alkalis	----	0.78
C_3A	3.0 max.	2.84

In addition, RHA was prepared using rice husk from Kafr El Sheikh, Delta, Egypt washed with distilled water, dried, combusted at 700 °C for two hours in a muffle furnace (model Eurothengle by VECSTAR) and cooled three times under burning combined with stirring to obtain the highest SiO_2 content with the lowest loss on ignition (LOI), as shown in Table 2. This optimization has done after a lot of trails. It was found that the SiO_2 content in RHA depends on the initial amount of rice husk, the burning and cooling periods. It was observed that when number of cooling periods increased from 1 to 6 times, LOI decreased from 2.28 to 1.3%. This may be attributed to changing of oxidizing conditions during burning. However, the optimum conditions were applied for the production of high yield of SiO_2.

The mineralogy analysis confirmed that the RHA silica is amorphous (Fig. 1) according to XRD (X–ray diffraction, Panalytical Embryean, model no. 202964). TEM micrograph (Fig. 2) showed that the RHA appeared irregular with tendency to be spheres with a particle size around 200 nm using model (JEOL JEM-2100).
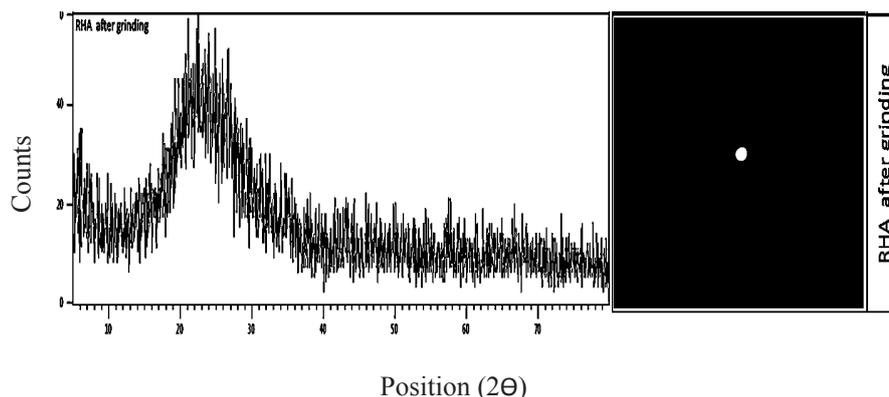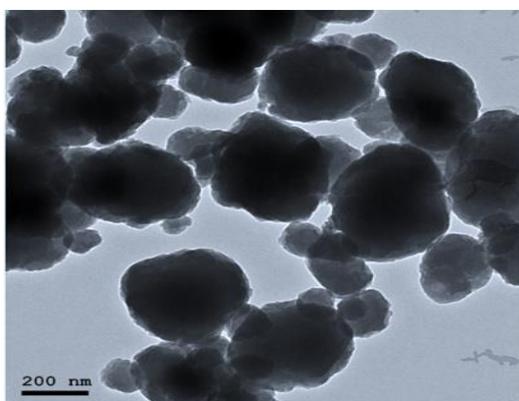
Fig. 1. Mineralogy state of RHA .

Fig. 2. TEM micrograph for RHA.

RHA was ground to the nano-scale using an Attritor ball mill (Union Process, model # 1S) with a grinding time of 8.16 min for every 1 g of RHA at a ball weight/RHA powder weight ratio equal to 8/1 and a 1170 rpm mill speed (Fig. 3). Table 2 shows that the chemical and physical properties of RHA before and after grinding comply with ASTM C 618–05 [19].

Experiments and equipment used

The various tests and equipment used to determine the chemical properties, physical properties, and mortar performance of the cement and RHA are shown in Table 3 along with the standard codes for each method.

Mixture proportions

A reference sample (100% PC) without any additive was prepared, and 10 mixtures were prepared with 2, 4, 6, 8 and 10% RHA replacement of cement by weight using RHA before and after grinding to evaluate changes in the Blaine surface area, sieve analysis result (45 µm mesh), water of consistency, expansion, initial and final setting times, and compressive strength (at 2, 7, 28, 60 and 90 d of curing).
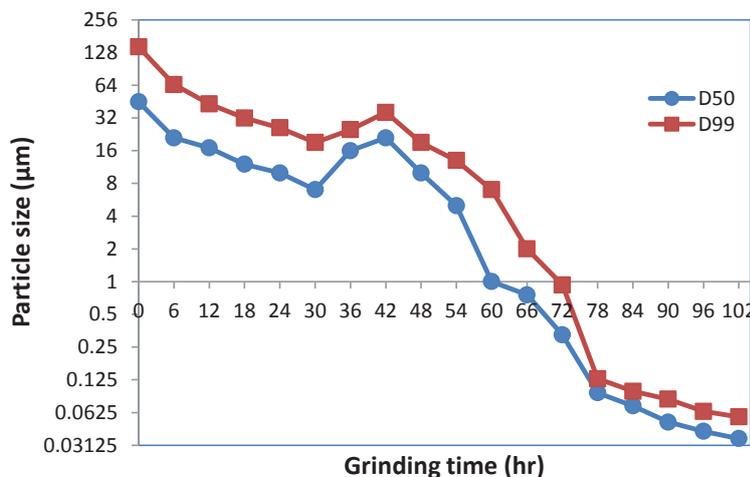

Fig. 3. Effect of grinding time on particle size distribution of RHA.

TABLE 2. Chemical analysis and physical properties of RHA.

Chemical analysis			
Chemical composition (%)	Specification limit	RHA before grinding	RHA after grinding
SiO_2		90.78	81.21
Al_2O_3	Summation= 70 min.	0.93	4.94
Fe_2O_3		0.42	0.65
CaO	----	4.34	4.61
MgO	----	0.58	0.47
SO_3	4 max.	0.13	0.10
Na_2O	----	0.00	0.00
K_2O	----	0.74	0.87
LOI	10 max.	1.73	6.73
Free CaO	----	0.34	0.34
Moisture	3 max.	0.70	0.90
Physical properties			
Retained sieve analysis result [45 μm mesh]	34 max.	33.2	0
Particle size distribution D_{50} [μm]	----	45.00	0.036
Particle size distribution D_{99} [μm]	----	144.00	0.057
Blaine surface area [m²/g]	----	0.2997	2.0849
Laser diffraction surface area [m²/g]	----	0.0864	29.4811
BET surface area [m²/g]	----	87.517	29.794
Mineralogy	----	amorphous	amorphous
Bulk density [g/cm3]	----	0.70	1.00
Shape texture	----	irregular	regular

TABLE 3. Experiments and equipment used.

Experiment name	Equipment used	The method conformed to
Chemical analysis	X-ray fluorescence apparatus (model ARL 9900 by Thermo Scientific)	EN 196 – 2.2:2005 [20] & ASTM C114 [21]
LOI	Muffle furnace (model Eurothengle by VECSTAR)	EN 196/2 [22]
Free CaO	Titrimetric method	ES 474 – 1994 [23]
SSA	Blaine method, ToniPERM apparatus (model 3301/204/06 Zwick/Roell by Toni Technik)	EN196-6 [24] and ASTM C204 [25]
	BET method (model TriStar II by Micromeritics)	ISO 9277 [26]
Particle size distribution	Laser diffraction apparatus combined with laser diffraction SSA and laser particle size analyser (model BT-9300S by Bettersize)	ISO 13320 [27]
Initial and final setting times & water of consistency	Vicat's apparatus	ES 2421-3 [28] & (UNIEN 196-3) [29]
Soundness of cement	Le Chatelier Moulds Code 62-L0025	ES 2421-3 [28]& (UNIEN 196-3) [29]
Compressive strength	Compression and bending test apparatus (model Toni/Technik)	UNIEN 196-1 [30]

According to previous studies [31-34], 10% was chosen as the maximum level of replacement because this ratio is the optimum replacement to achieve the best strength. In all cases, we preferred to avoid using a SP to avoid the increase of the SAI up to 34% that occurs for various SPs (modified polycarboxylate, sulfonated melamine, modified lignosulfonate or polycarboxylate derivatives). This variation was studied for a mixture of cement and submicron 995 (nano-silica) [35], measured according to the European (EN) standard, as shown in Fig. 4. Therefore, the variation in the SAI in the present study will only be produced by the RHA effect.

Results and Discussion

Effect of RHA on the cement Blaine surface area

The effect of the RHA particle size distributions D_{50} and D_{99} before and after grinding on the cement Blaine surface area is shown in Fig. 5. D_{50} and D_{99} before grinding were 45 and 144 µm, respectively, with irregular shapes observed, and after grinding, these values were 36 and 57 nm, respectively, with regular shapes observed. The results confirmed that the cement Blaine surface area increased with increasing percentage of RHA replacement, and the nano-sized RHA had a stronger effect than the nano-structured RHA on the cement Blaine surface area at all replacement percentages. For example, the Blaine surface area increased from 3259 cm^2/g to 4543 cm^2/g when using 10% RHA before grinding, achieving a 39.4% increase in the Blaine surface area due to the irregular shapes, and few of the RHA particles were smaller than the cement particles. In contrast, the Blaine surface area increased from 3259 cm^2/g to 6009 cm^2/g when using the same ratio after grinding, achieving an 84.4% Blaine surface area enhancement. Because the regularly shaped RHA particles are smaller than the cement particles, the cement hydration reaction will accelerate. However, replacement percentages >10% were not studied to avoid the influence of the higher cement volume produced from the higher Blaine surface area and the problems in cement packing caused by the bulk densities of RHA before and after grinding (0.7 and 1.0 g/cm^3, respectively) being lower than the sulfate-resisting PC 42.5 N bulk density (1.83 g/cm^3).

Sieve analysis (45µm mesh)

When using RHA before grinding, the sieve analysis result (Fig. 6) increased with increasing RHA replacement % due to the RHA particle size distribution D_{99} being higher than the normal PC particle size, ranging from 0.5 to 60 µm on average. When using RHA after grinding, the sieve analysis result decreased at all RHA replacement percentages due to both the RHA D_{99} and D_{50} particle size distributions being lower than the PC particle size.
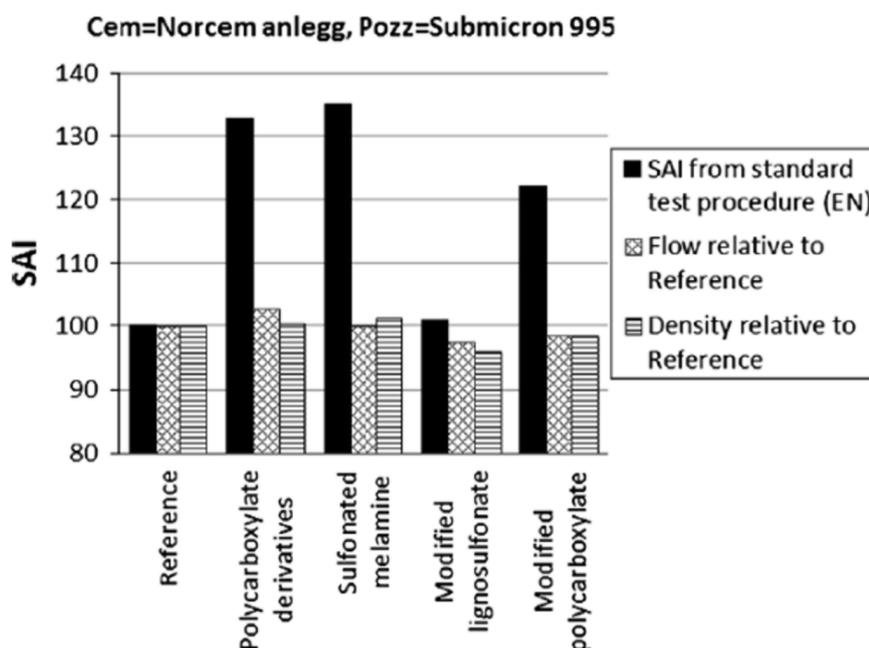

Fig. 4. Typical effect of varying the type of SP on the SAI, flow and density for one mixture of cement and pozzolan (according to the EN standard) [35].
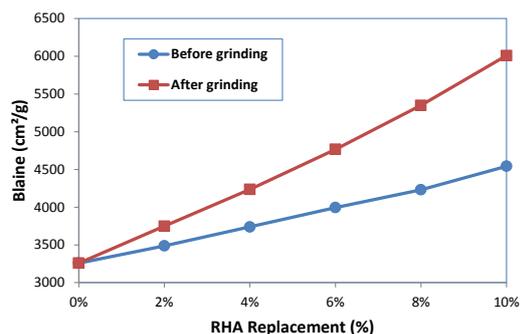
Fig. 5. Effect of RHA replacement % on the cement Blaine surface area.
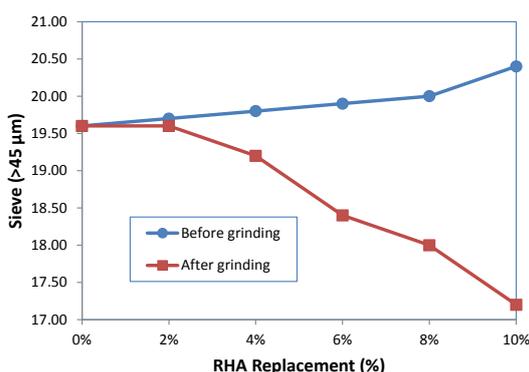

Fig. 6. Effect of RHA replacement % on the results of sieve analysis (45 µm mesh).

Water of consistency

According to the RHA skeleton cellular and porous structure, the RHA before grinding has a higher BET SSA (87.517 m²/g) than the RHA after grinding (29.794 m²/g). This result may be attributed to the fact that grinding destroys the cellular structure, and the fine particles fill the pores, resulting in decreases in the internal and external porosity and thus reducing the internal surface area. Therefore, grinding caused a higher water demand with increasing RHA replacement % in the case of RHA before grinding compared to RHA after grinding, and both RHA materials required more water to achieve the standard consistency than the control sample, as shown in Fig. 7.
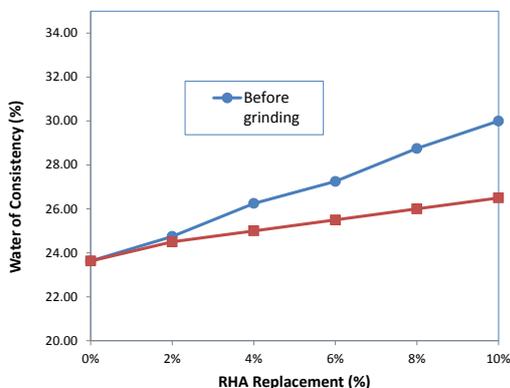

Fig. 7. Effect of RHA replacement % on the water of consistency.

Setting time

According to Fig. 8, both the initial and final setting times of cement increased with increasing RHA % compared with the reference sample because both types of RHA sample consumed more water to achieve the standard consistency than the reference sample. This result was due to the low rate of hydration in the paste containing RHA, which replaced an amount of PC with a higher rate of hydration. This increase was especially pronounced in the short term because of the amounts of tricalcium aluminate (C3A) and tricalcium silicate (C3S) phases, which affect the early-age rate of hydration and the total heat of hydration [36]. At all percentages, the rate of increase for RHA before grinding was higher than that for RHA after grinding because grinding causes RHA particles to fill the spaces between larger cement particles, thus decreasing the frictional forces of the RHA-PC matrix and improving the packing ability, resulting in a denser paste.
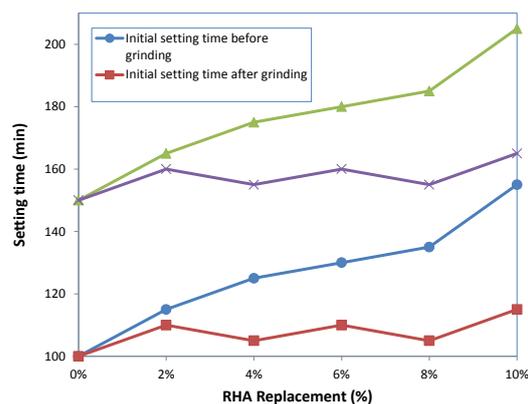

Fig. 8. Effect of RHA replacement % on the setting time.

Expansion

Table 4 shows that no considerable expansion occurred with increasing RHA replacement %, except in the case of RHA before grinding. This result may be due to the RHA cellular structure. However, if the reason of the expansion is CaO or MgO, this will be appeared in both cases of RHA "before and after grinding". But the expansion occurred only before grinding and the only factor changed after grinding is RHA cellular structure. This also confirmed by the large drop in surface area from 87.52 to 29.8 m²/g for RHA before and after grinding, respectively. This may be attributed to the particles agglomeration and cellular structure deformation which happened during grinding process. That retained an amount of water but without a continuous increase. Thus

helping in complying with the ES 2421-3 [28] and (UNIEN 196-3) [29] Le Chatelier expansion specification requirements (10 mm maximum).

TABLE 4. Effect of RHA replacement % on expansion.

RHA replacement (%)	Le Chatelier expansion (mm)
Before grinding	
0%	0
2%	1
4%	1
6%	1
8%	1
10%	1
After grinding	
0%	0
2%	0
4%	0
6%	0
8%	0
10%	0

Compressive strength and RHA pozzolanic reactivity according to the SAI

A constant water-cement ratio was applied without using any type of SP to avoid the occurrence of extra strength when using various SPs, as previously discussed. Table 5 shows the compressive strength results. Figures 9 and 10 present the effect of the RHA (before and after grinding, respectively) replacement % on the SAI.

The compressive strength at early curing ages (2 and 7 d) decreased at all percentages of RHA before and after grinding due to the low rate of hydration in the mortar containing RHA compared with the reference sample containing C3A and C3S, as previously discussed. Starting from the curing age of 28 d, the pozzolanic reactivity began to produce more C-S-H, resulting in higher strength for the longer curing ages (28, 60 and 90 d). The enhancement was stable at higher than 100% SAI for the longer curing ages (60 and 90 d) with 10% RHA before grinding and 4% RHA after grinding. More considerable enhancements occurred under replacement by up to 10% nano-sized RHA due to the small size of the particles, which worked as fillers of the spaces within the cement mortar matrix and increased the pozzolanic reactivity.

Effect of particle size and SSA on the pozzolanic reactivity

According to the concept that the reactivity increases with increasing SSA, the compressive strength for 10% RHA replacement at longer curing ages (60 and 90 d) was compared with the SSA measured by different methods for RHA before and after grinding, as presented in Table 6. A good relation exists between the external SSA (measured by using the Blaine method and laser diffraction, which is associated with the RHA particle size distribution) and the pozzolanic reactivity of the RHA. In contrast, no relation was found between the pozzolanic reactivity and the internal plus external SSA (measured by using the BET method), which clarifies the cellular nature of the internal structure of the RHA.
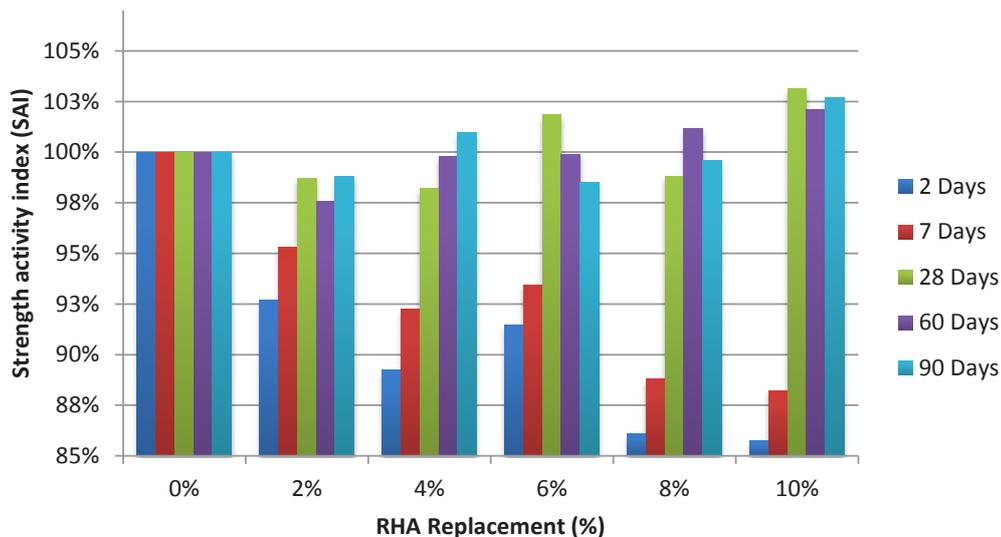
TABLE 5. Effect of RHA replacement % on compressive strength.

RHA Replacement (%)	Compressive Strength N/mm²				
Before grinding	**2 d**	**7 d**	**28 d**	**60 d**	**90 d**
0%	20.04	29.59	43.73	47.70	49.64
2%	18.58	28.20	43.17	46.55	49.05
4%	17.88	27.30	42.95	47.60	50.13
6%	18.33	27.65	44.53	47.65	48.90
8%	17.25	26.27	43.20	48.25	49.43
10%	17.18	26.10	45.10	48.70	50.98
After grinding	**2 d**	**7 d**	**28 d**	**60 d**	**90 d**
0%	20.04	29.59	43.73	47.70	49.64
2%	18.77	28.32	42.13	47.65	48.63
4%	17.25	26.62	42.05	48.85	50.38
6%	16.67	25.83	42.58	49.80	50.08
8%	16.30	25.98	46.13	50.35	51.78
10%	15.25	24.28	44.73	50.35	52.30

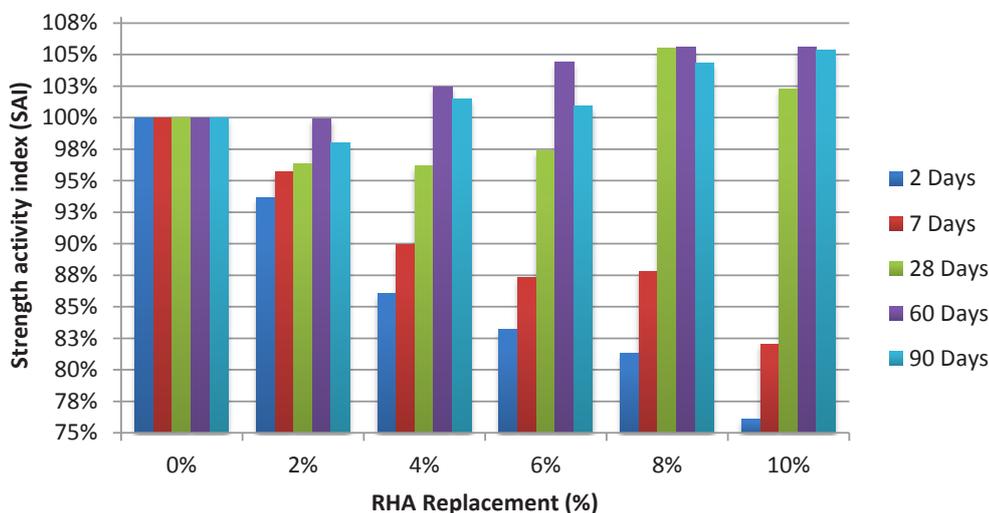**Fig. 9. Effect of replacement % of RHA before grinding on the SAI.**

Fig. 10. Effect of replacement % of RHA after grinding on the SAI.

TABLE 6. The relation between the SSA, particle size distribution and compressive strength of cement after adding RHA before grinding and after grinding.

	RHA before grinding	RHA after grinding	The relation
Blaine surface area [m²/g]	0.2997	2.0849	Increasing 7 times
Laser diffraction surface area [m²/g]	0.0864	29.4811	Large increasing
BET surface area [m²/g]	87.517	29.794	Decreasing 3 times
Particle size distribution D_{50} [μm]	45.00	0.036	Large decreasing
Particle size distribution D_{99} [μm]	144.00	0.057	Large decreasing
Compressive strength [N/mm²] at 60 d	48.7	50.35	Increase by 3.4 %
Compressive strength [N/mm²] at 90 d	50.98	52.3	Increase by 2.8 %

ROLE OF LOW-COST NANO RHA ON PHYSICO-MECHANICAL PROPERTIES ...

1053

Conclusion

1- When using 10 wt. % RHA to replace cement, the enhancement of the cement Blaine surface area reaches 39.4% for RHA before grinding and 84.4% for RHA after grinding.

2- The SSA_{BET} of RHA has a much greater effect on increasing the mortar water demand to achieve the standard consistency than the SSAs obtained by other methods.

3- Increases in the initial and final setting times occur at a higher rate when using RHA before grinding compared to RHA after grinding.4- By using a constant water/cement ratio and without using any type of SP, the SAI stabilizes at higher than 100% for the longer curing ages (60 and 90 d) with 10% RHA before grinding and 4% RHA after grinding, and the enhancements increase under replacement by up to 10% nano-sized RHA after grinding.

5- The pozzolanic reactivity is more highly correlated with the external SSA measured using the Blaine method and laser diffraction than with the internal and external SSA measured by using the BET method.

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