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Effect of Nano RiceHusk Ash Against Penetration of Chloride Ions in Mortars

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ABSTRACT: These days, in the structural designing, the durability properties of materials should be considered as significant as the other specifications. Deterioration of concretes in corrosive environments leads to considerable costs in order to maintain the reinforced concrete structures. Usage of industrial pozzolans can improve quality and serviceability of concrete structures in such environments. Nowadays, one of the most common pozzolans in structural concretes is the rice husk ash (RHA) which enhances the mechanical and durability properties of concretes. In this paper, effects of nano RHA on chloride permeability, compressive strength, electrical resistivity and capillary absorption of mortars have been investigated. The results showed that the incorporation of RHA nanoparticles gradually increased the compressive strength. It was found that a partial replacement of cement by nano RHA would enhance the durability properties of mortars in the long-term.

Keywords:

Rice Husk Ash
Nano
Durability
Mortar
Mechanical Properties

1- Introduction

Nowadays, production of concrete using Portland cement is popular all over the world. Besides the advantages of this production, it brings lots of disadvantages. Firstly, the production of cement is a major contributor to greenhouse gas emissions that are implicated in global warming and climate change. Secondly, many concrete structures suffer from lack of durability which may leads to several destructive consequences such as reduction of serviceability and strength. Finding a suitable substitute for ordinary Portland cement would be desirable for sustainable development in this area [1].

In the last decades, recycling of waste components contributes to energy savings in cement production, for conservation of natural resources, and in protection of the environment. One of the most suitable sources of pozzolanic material is rice husk, as it is available in large quantities with great pozzolanic reactivity. Rice husks are protective coverings of rice grains and one of the main agriculture industry residues which contains high amount of silica. Rice husk ash (RHA) is a solid residue of rice husk controlled combustion which shows the highest pozzolanic behavior among all plant residues [2]. The usage of rice husk ash as artificial pozzolan not only reduced the fuel demand for cement production and environmental pollution, but also has improved the mechanical properties and durability of concretes especially in aggressive environments [3, 4].

Usage of RHA in cemetitious materials can decrease the total porosity of them, modify the pore structure of the mixture and significantly reduce the permeability against aggressive agents. Improvements in mechanical and durability properties of the concretes containing RHA can be explained by the high pozzolanic reactivity due to the non-crystalline silica and high specific surface area of the RHA particles [4-6]. Pozzolanic reactions between the amorphous silica of RHA and calcium hydroxide (C-H) produced by the cement hydration can form calcium-silicate-hydrates (C-S-H) clusters and result in a higher densification of the matrix [7].

Researchers [8-12] have proven that the utilization of rice husk ash as a pozzolanic material in mortars would enhance the compressive strength. However, researchers have found that this enhancement is limited to optimum replacement of 20% by weight of cement. On the other hand, few other studies have found that the durability properties of the RHA blended mortars could face great enhancement against chloride ions penetration with higher dosages of replacement in comparison with compressive strength [3, 13, 14].

With the advancement of nanotechnology, several studies devoted to investigate the effect of mineral nanoparticles such as nano-SiO_2, Nano-TiO_2 and Nano-Al_2O_3 on cementitious concretes and mortars [15-21]. Nanoparticles can act as centers of crystallization of cement hydrates, therefore accelerating the hydration and pozzolanic reactions. In this

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regard, researchers have found that the binary blended mortars containing RHA and nano-SiO_2 with ultra-fine particles of amorphous silica would lead to prodigious enhancement of the compressive strength [22-26]. Results show that nano-SiO_2 can contribute to the high early age strength and the RHA increases the long-term strength. The nano-alumina blended cement mortars had significantly higher compressive strength compare to that of the mortars without nano-alumina particles even when 30% RHA was replaced [23]. Unfortunately, only limited studies is concerned with durability properties of binary blended mortars containing RHA and nanoparticles such as nano-TiO_2 or nano-SiO_2 [24-26]. Results show that the incorporation of nanoparticles and RHA can contribute to chloride resistivity enhancement in early and long-term ages, respectively. However, the study of using nano-RHA in cementitious materials is still untouched.

Table 1. Chemical and physical characteristics of type

Chemical components	Cement (%)	NRHA (%)
SiO_2	22.28	83.74
AL_2O_3	4.72	0.29
Fe_2O_3	2.75	0.67
CaO	64.12	0.74
MgO	1.23	0.86
SO_3	1.97	0.87
Na_2O	0.28	0.091
K_2O	0.76	2.84
P_2O_5	0.26	0.37
MnO	0.11	0.14
Loss of ignition (LOI)	1.12	8.39
C_3S	50.44	-
C_2S	25.82	-
C_3A	7.86	-
C_4AF	14.36	-
Physical properties	Cement	NRHA
Surface area (cm^2/g)	3035	804410
Specific gravity (g/cm^3)	3.02	2.08

II Portland cement and RHA

In this study, nano rice husk ash (NRHA) was used as a partial replacement of cement in order to investigate its effects on the compressive strength and durability properties of mortars such as electrical resistivity, capillary absorption and resistance to chloride ions penetration.

2- Materials

The following materials were used in the preparation of the mortar specimens. River sand was graded according to ASTM C778 with specific gravity of 2350 kg/m^3, water absorption of 1.00% and fineness modulus of 3.49; a polycarboxylate based superplactiizer called ZP with pH of 7±1 and specific gravity of 1.1±0.02; Tehran potable water, Type II Portland cement according to Iranian national standards 389 and rice husk ash incinerated at a controlled temperature of 650 °C and time duration of 60 minutes and pulverized to nanoparticles with mean size of 35.86 nm for 13 hours using planetary ball mill. This mean size of particles is about 170 times smaller than usual average size of RHA in other studies which is around 6 μm. The results of zetasizer analysis for NRHA is shown in Figure 1. Table 1 present the chemical composition and physical properties of type II Portland cement and NRHA.

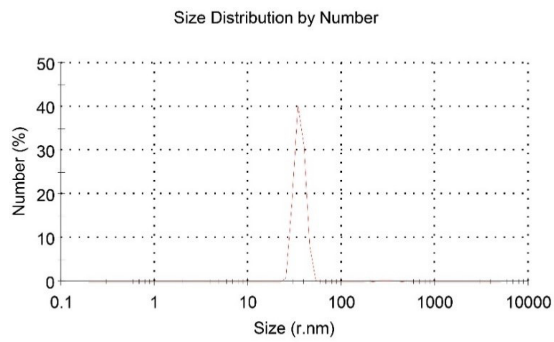


Figure 1. Zetasizer analysis of NRHA

3- Testing Methods

A total of four concrete mixtures were designed; one corresponding to ordinary Portland cement mortar (OPC) and three others with 2.5%, 5% and 7.5% NRHA replaced with cement by weight. The proportion of mixtures are presented in the Table 2.

The preparation procedure involved: (a) materials weighing, (b) initial mixture of RHA powders with 30% of the mixture water to produce additive gel, (c) adjusting pH value of the gel up to 9 by adding NaOH to the gel in order to control surface charges of the RHA microspheres and better dispersion of the small particles (Figure 2), (d) mixing of gel, cement and remained water, (e) addition of sand, (g) performing workability test using flow table according to ASTM C230, (h) addition of super-plasticizer and mixing, (i) casting the specimens in two layers and vibrating each layer for entrapped air removal using vibration table.

Three cubes of 50 mm were cast for every mixture and used for compressive strength test at ages of 3, 7, 28 and 90 days according to ASTM C109. For each mixture, three 50 mm cubic specimens were used for capillary absorption test at ages of 7 and 28 days in accordance with BS EN 480-5:2005 standard. Using non-destructive Wenner four electrode method, the surface resistivity of a 100×200 mm cylindrical specimen of every mixture was measured at ages of 7, 28 and 90 days.

According to NT Build492, for every mixture, a cylindrical specimen of 100×200 mm were cast for rapid chloride migration test (RCMT) at ages of 28 and 90 days. Specimens were prepared by cutting and discarding 25 mm slices from the top and bottom of them, and the remaining section cut into three 50 mm thick slices.

Table 2. Mortar mixture proportions

Mix	Water/binder (%)	Cement (Kg/m^3)	Water (Kg/m^3)	Sand (Kg/m^3)	NRHA (Kg/m^3)	Superplasticizer (%)
OPC	0.46	582	268	1269	0	0.22
2.5% NRHA	0.46	567.4	268	1269	14.55	0.46
5% NRHA	0.46	552.9	268	1269	29.1	0.57
7.5% NRHA	0.46	535.35	268	1269	43.65	0.68

Figure 2. Adjusting pH value of the mixture gel up to 9 for better dispersion of the nanoparticles

After casting, the specimens were covered by wet towel for 24 hour; and then demolded and cured in water (saturated with calcium-hydroxide) at 23±2 °C until the test day.

4- Results and Discussion

4- 1- Compressive strength

The average compressive strength results of the mortars, which were determined from three cubic specimens are shown in Figure 3. The results indicate that, at ages of 7, 28 and 90 days, the compressive strength of mixes containing NRHA has gradually improved in comparison with that of control mix due to the high surface area and reactivity of nanoparticles leading to acceleration of C-S-H gel production process. Among the mixes containing NRHA, 7.5% NRHA mix shows the best performance by increasing the compressive strength of about 31.85% and 26.16% at ages of 28 and 90 days, respectively. However, at the early age of 3 days, the addition of NRHA mostly has led into the decreasing trend of compressive strength, except for 2.5% NRHA mix. This slight reduction can be explained by the partially replacement of the Portland cement with NRHA particles having slower reactivity, resulting in lower amount of $Ca(OH)_2$ and gel formation through the hydration of cement at early ages. It should be noted that the standard deviation of the results was between 1 to 2 MPa.

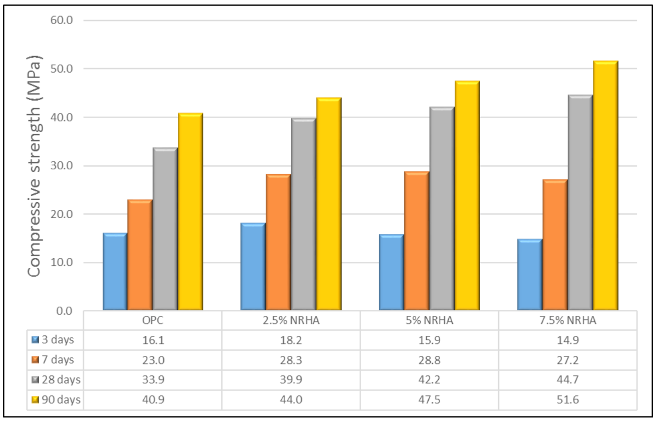


Figure 3. Average compressive strength results of mortar mixes

4- 2- Electrical resistivity

The electrical resistivity results at ages of 7, 28 and 90 days are presented in Figure 4. The results show that products of pozzolanic reactions due to the addition of NRHA, reduce the volume of capillary pores, consequently increase the electrical resistivity of mortars.

It can be observed from the results that 7.5% NRHA mix has the highest electrical resistivity at all ages than other mixtures. As a matter of fact, due to high surface area and filler effect of nanoparticles, incorporation of NRHA leads to gradual development of electrical resistance in mortars.

For instance, the electrical resistivity at 90 days is improved by 49.19% for 7.5% NRHA compared to the control mortar. According to the fact that slow reactivity is an inherent characteristic of pozzolanic materials, the electrical resistivity is not expected to be increased at early ages. In contrary with former studies conducted on incorporation of RHA with the same size as cement particles [25], in this study, the addition of NRHA has enhanced the electrical resistivity at age of 7 days compared to the control mixture because of its higher surface area, therefore higher densification of the matrix.

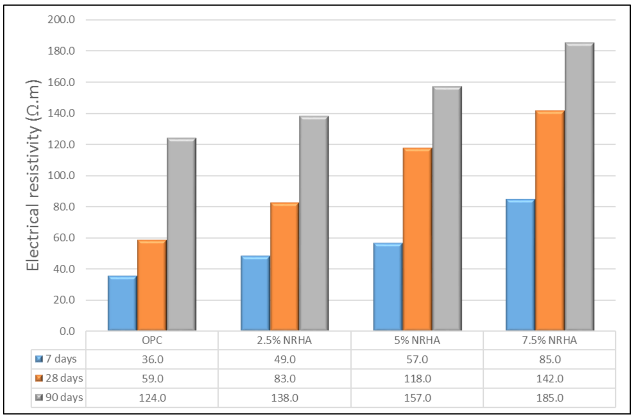


Figure 4. Electrical resistance of mortar mixes

4- 3- RCMT

Figure 5 shows the rapid chloride migration test results after 28 and 90 days of curing. According to the results, the ability of NRHA to reduce chloride intrusion into mortar is clearly evident. Hence, the increase in replacements level of cement with NRHA, has led to higher chloride resistivity. As a matter of fact, NRHA particles possess high pozzolanic activity and as a result, the hydration of cement is accelerated and larger volumes of reaction products are formed.

It is found, in general, that the rate of compressive strength development is slower at early ages, whereas the rate of increase in chloride penetration resistance is significant between 28 and 90 days. For instance, 7.5% NRHA mix shows the best performance by increasing the chloride penetration resistivity by 124.48% and 148.48% at ages of 28 and 90 days, respectively.

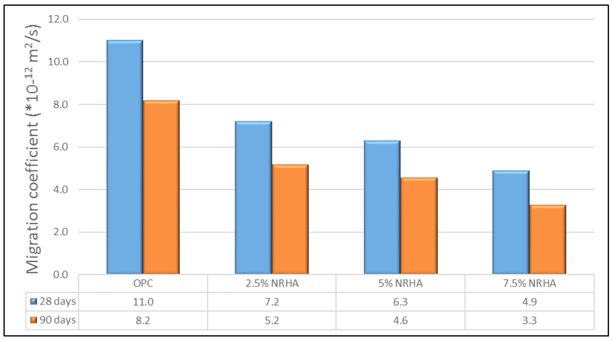
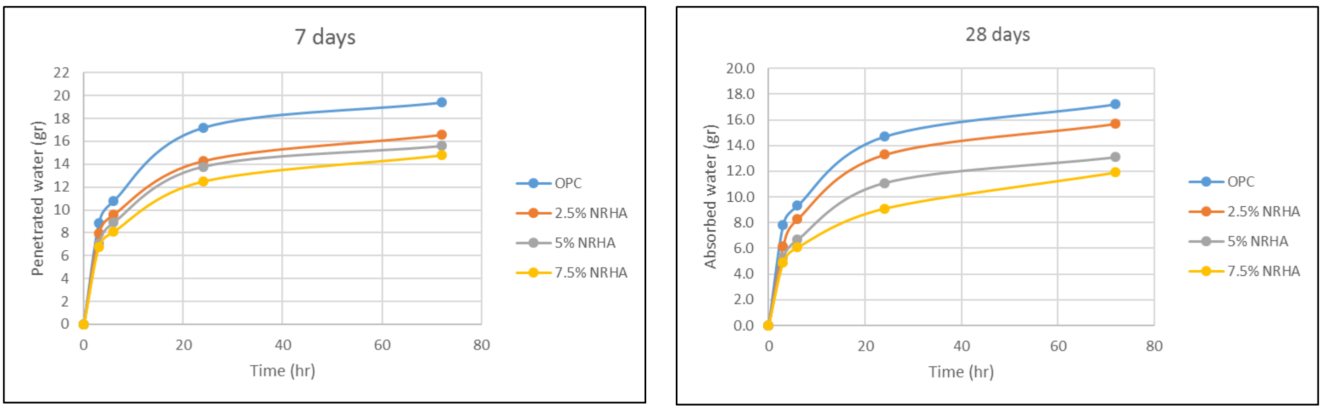


Figure 5. Migration coefficient value of mortar mixes

4- 4- Capillary absorption

The results of capillary absorption at 7 days and 28 days for different time intervals are shown in Table 3. To provide a better comparison, the results are also presented in Figure 6. As seen from the results, the incorporation of NRHA has slightly decreased water absorption into specimens and the increase in replacement levels has further improved capillary absorption. This reduction is the consequence of high reactivity of nanoparticles due to their high surface area. It is important to note that the particles of NRHA which are non-reactive with $Ca(OH)_2$ can act as filler and make the microstructure and interfacial transition zone (ITZ) denser, and consequently reduce the rate of water absorption. According to the table, mortar that contains 7.5% NRHA has the best performance in reduction of water absorption. After 72 hours, it has reduced water absorption by 23.7% and 30.8% in comparison with control mixture at 7 and 28 days, respectively.



(a) (b)

Figure 6. Capillary absorption values of mortar mixes: (a) 7 days, (b) 28 days

Table 3. Capillary absorption values of mortar mixes

Mix	Water absorption (g)							
	7 days				28 days			
	3h	6h	24h	72h	3h	6h	24h	72h
OPC	8.9	10.8	17.2	19.4	7.8	9.4	14.7	17.2
2.5% NRHA	7.9	9.6	14.3	16.6	6.2	8.3	13.3	15.7
5% NRHA	7.1	8.9	13.8	15.6	5.3	6.7	11.1	13.1
7.5% NRHA	6.8	8.1	12.5	14.8	4.9	6.1	9.1	11.9

5- Conclusion

In this study, the effects of nano rice husk ash on development of compressive strength, electrical resistivity, capillary absorption and chloride resistance of mortars was investigated. It was observed that the addition of NRHA enhanced the electrical resistivity and mortars' resistance to water and chloride ions penetration which are in many cases the most significant properties concerning with durability and corrosion prevention. Active nanoparticles provided considerable surface area, which accelerated the pozzolanic reactions, especially at higher percentages of replacement. Moreover, non-reactive nanoparticles acted as fillers and resulted in higher densification of the matrix. However, incorporation of NRHA reduced the compressive strength at the age of 3 days due to slow reactivity of pozzolanic particles. On the other hand, in the long-term ages, addition of NRHA contributed to significant enhancement of the compressive strength, especially at the age of 90 days.

Finally, the effectiveness of using NRHA in mortars has proven.

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