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CORROSION AND CARBONATION RESISTANCE OF MORTARS INCORPORATING RICE HUSK ASH

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Abstract. The Rice Husk Ash (RHA) was obtained by incinerating Rice Husk with a temperature of 300°C, 500°C, 700°C, and then added into control mortars as replacement of cement to prepare modified mortars. The microstructure of RHA was characterized by FT-IR test, then the corrosion and carbonation resistance of mortars were investigated. Additionally, the microstructure of cement mortars was revealed using the SEM test. Researched results indicated that the cement hydration is improved and the mezzanine structure of RHA at 700°C is compact, while the mezzanine of RHA at 300°C is composed of crisscross plates. Moreover, the incorporation of RHA improves the corrosion and carbonation resistance of mortars.

***Keywords**:* mortar, rice husk ash (RHA), chemical corrosion, mechanical properties, carbonation resistance.

1. INTRODUCTION

Agricultural wastes lead to environmental problems and have increasingly attracted the attention by the government [1–2]. The most widely available agricultural waste throughout the world is rice husk, which is one of the agricultural waste with low nutritional properties for animals, constituting about one fifth of the total rice produced [3]. Rice husk ash (RHA) is a solid residue of rice husk through combustion. It is well known that highly reactive pozzoland RHA can be obtained when the rice husk is combusted under controlled conditions [4]. Therefore, RHA based concrete is recently developed and the application of RHA in cementing materials is of tremendous interest due to the abundance of the rice production [5–7]. However, numerous research publications referring to cementing materials with RHA focused more on the preparation and experimental research on the physical and chemical properties of cementing materials incorporating RHA [8–14].

In this study, rice husk ash (RHA) was produced by combusting rice husk at temperatures of 300 °C, 500°C, and 700 °C. The RHA samples, prepared at these different temperatures, were then added to mortars. The objective of this research is to compare the effects of RHA burnt at different temperatures on the properties of modified mortars, which use RHA as an integrative additive. This will enable the determination of the optimal combustion temperature for producing rice husk ash.

2. EXPERIMENTAL

2.1. Raw materials

Type 42.5R Portland cement, sourced from Huaxin Cement Company in China, was used in this study. The cement is usual hardened(N). Rice husk, obtained from Hubei Province in China, served as an additive. The binder material is the sum of RHA and cement. Medium-coarse sand, with a density of 2.66 g/cm³ and a fineness modulus of 2, was utilized to prepare the cement mortar. The maximum dimension for sand is 0.5 mm. Tap water was used to prepare both the blank and modified cement mortars.

2.2. Preparation of samples and curing conditions

Rice husk was prepared at temperatures of 300 °C, 500 °C and 700 °C and the time duration of 1 hour for all samples. After the combustion, the RHA was pulverized and passed through 100 μm sieve to obtain smaller particles. The chemical and physical properties of Rice Husk Ash is shown in Table 1 and Table 2, respectively. Meanwhile, the RHA have pozzolanic activities. The chemical properties of cement are shown in Table 3. The RHA were used as the integral part in the mortars. Water to cement ratio of 0.4 was used for preparing mixtures incorporating 0%, 5%, 8% and 10% RHA as added replacement by mass of cement. The experiment complies with the proportion requirements as specified in "Test Procedures for Polymer Modified Cement Mortar" (DLT5126-2001). The mass ratio of cement to sand ranges from 1:1.5 to 1:3. Based on previous related studies, this experiment adopts a cement-to-sand mass ratio of 1:2, aiming to maintain the slump of RHA modified cement mortar within the range of 35 m ± 5 mm, with an appropriate water to cement ratio of 0.4. The experiment selects three levels of calcination temperatures for rice husk ash: 300 °C, 500 °C, and 700 °C. Each temperature corresponds to three different levels of incorporation (5%, 8%, and 10%), forming 9 experimental groups. Additionally, there is a blank group of cement mortar for comparison, totaling 10 experimental groups. The mix ratios of cement mortar per cubic meter for the blank group and the 9 RHA modified cement mortar groups are designed as shown in Table 4. The dimension of samples is 70.7 mm × 70.7 mm × 70.7 mm. The samples were cured in a standard curing chamber (20±2°C, 95% RH) until the testing days.

Table 1

The chemical properties of RHA

Chemical composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	MnO	Na_2O	K_2O	Cl	Other
Specific gravity(%)	78.29	0.10	0.08	0.78	0.30	0.16	0.04	3.32	0.15	16.78

Table 2

The physical properties of RHA

Physical properties	Density(kg/m^{-3})	Modulus of fineness	Specific area (kg/m^{-3})	Graducation
Index	300	1.5	55	fine

Table 3

The chemical properties of cement

Chemical composition	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3	Na_2O	K_2O	Other
Specific gravity (%)	21.29	5.60	3.00	62.96	2.24	1.47	0.30	0.31	2.83

Table 4

The mix composition of RHA modified cement mortar per cubic meter

Sample	Calcination temperature(℃)	Dosages (%)	Cement (kg)	Water (kg)	Sand (kg)	RHA (kg)
S0	–	–	677	271	1354	–
P1	300	5	643.2	271	1354	33.8
P2	500	5	643.2	271	1354	33.8
P3	700	5	643.2	271	1354	33.8
R1	300	8	622.8	271	1354	54.2
R2	500	8	622.8	271	1354	54.2
R3	700	8	622.8	271	1354	54.2
S1	300	10	609.3	271	1354	67.7
S2	500	10	609.3	271	1354	67.7
S3	700	10	609.3	271	1354	67.7

2.3. The FT-IR of RHA

The FI-IR spectra of RHA was acquired using a model Nexus FT-IR spectrometer from Thermo Nicolet. The scanning area were variable varying from 4 000 cm^{-1} to 400 cm^{-1} with a resolution of 4 cm^{-1}.

2.4. The corrosion resistance test

The experimental method in this paper involves using 40 mm × 40 mm × 160 mm cement mortar specimens. After curing for 1 day in an environment with humidity greater than 90%, the molds are removed. Subsequently, the samples are further cured in a standard curing room for 28 days, after which their masses are measured and compressive strengths are tested. Thereafter, each group of cement mortar samples (3 samples per group) is immersed in a 5% H_2SO_4 solution, ensuring that the liquid level is at least 10 mm above the top surface of the samples during immersion. After another 28 days of immersion, the samples are removed from the solution, thoroughly rinsed with clean water, and samples from each aging period as per experimental design are selected for compressive strength and mass determination, using concrete with the same aging period and ratio in the erosion medium, to calculate mass loss rate and corrosion resistance coefficient. Moreover, the weight loss ratio and corrosion resistance coefficient of mortars without and with RHA were calculated using Eqs. (1) and (2):

– weight loss ratio: $$\Delta W = (M_0 - M_1)/M_0 \times 100 \quad (1)$$

where $\triangle W$ represents the weight loss ratio of mortars after chemical corrosion (in %), M_0 represents the weight of mortars before chemical corrosion and M_1 represents the weight of mortars after chemical corrosion;

– corrosion resistance coefficient: $$K = R_0/R_1 \times 100 \quad (2)$$

where R_1 represents the compressive strength of mortars before corrosion resistance, R_0 the compressive strength of mortars after corrosion resistance and K is the chemical resistance coefficient of mortar (in %).

2.5. The carbonation test

After molding, the samples are placed in a standard curing room for 28 days. Two days before the test, they are taken out of the curing room and placed in a 60 °C oven for 48 hours. The samples are then sealed with paraffin on five surfaces, leaving only one side exposed. They are then placed in a carbonation chamber at a temperature of 20 °C, relative humidity of 70%, and carbon dioxide concentration of 20% for carbonation testing. After 7 days, 14 days, 28 days, and 56 days of carbonation, the samples are taken out, split at the front end, and sprayed with a 1% phenolphthalein ethanol solution on the split surface (the uncarbonated part turns red, while the carbonated part does not change color). The carbonation depth is measured with a millimeter-precision steel ruler. According to the RILEM CPC-18, the carbonation depth of all samples at 7, 14, 28 and 56 days was carried to measure the carbonation depth of non-colored parts.

2.6. The SEM of control and modified mortars

The same Scanning electron microscopy (SEM) was employed to characterize the morphology of modified mortars containing different dosages RHA at a temperature of 300 ℃, 500 ℃ and 700 ℃.

3. RESULTS AND DISCUSSION

3.1. The FT-IR analysis of RHA

The FT-IR spectra of RHA at different temperature were shown in Fig. 1. It is found that, in the infrared absorption band, the asymmetric strength vibration between 1000 cm^{-1} and 1080 cm^{-1} is Si-O-Si. The band about 1700 cm^{-1} may be the bending vibration of O-Si-O. The intensity of bending vibration of O-Si-O of RHA at 500 °C and 700 °C is higher than that of RHA at 300 °C, indicating that the SiO_2 content of RHA at 500 °C and 700 °C is higher, compared with RHA at 300 °C. Therefore, the cement hydration is restrained because of the decrement of SiO_2.

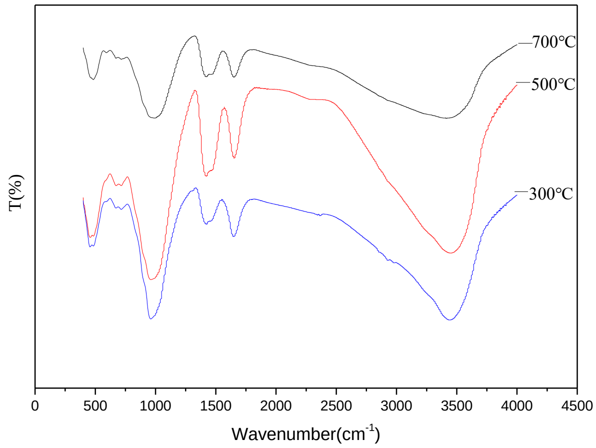

Fig. 1 – The FI-IR analysis of RHA at 300 °C, 500 °C and 700 °C.

3.2. The variation of weight loss ratio in the corrosion resistance test

The variation in weight loss ratios of control and modified mortars containing different dosages of RHA at temperatures of 300 °C, 500 °C, and 700 °C was studied, and the experimental results are presented in Fig. 2. As shown in Fig. 2, it is clear that, compared to the control mortars, the weight loss ratio of the modified mortars decreased, indicating that the incorporation of RHA enhanced the corrosion resistance of the mortars. Additionally, for modified mortars with the same dosage of RHA, increasing the calcination temperature from 300 °C to 700 °C further improved their corrosion resistance. This improvement can be attributed to the more complete calcination of the rice husk and the reduction in the particle size of the RHA at higher temperatures, resulting in a denser internal structure of the modified mortars due to the addition of RHA calcined at higher temperatures.

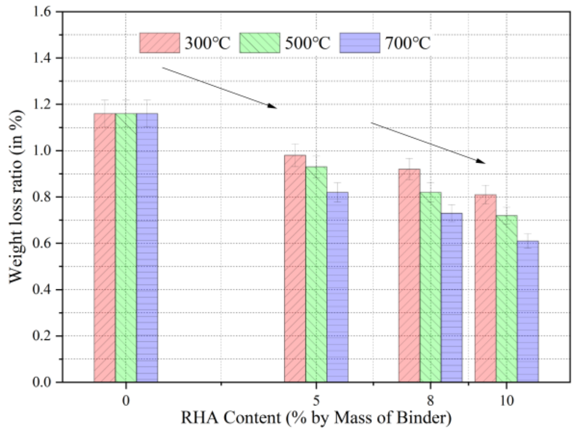

Fig. 2 – The variation of weight loss ratio of control and modified mortars at 300 °C, 500 °C and 700 °C.

3.3. The variation of corrosion resistance coefficient

The variation of corrosion resistance coefficient of control and modified mortars incorporated with different dosages RHA at temperature of 300 °C, 500 °C and 700 °C were studied and the experimental results were shown in Fig. 3 and Table 5. As seen in Fig. 3 and Table 5, the corrosion resistance coefficient of modified mortars was higher than that of control mortars. For example, for modified mortars mixed with RHA with a calcination temperature of 700 °C, the corrosion resistance coefficients of all samples containing 5% RHA were improved by 12.65%, and the corresponding results of these samples mixed 8% and 10% RHA are 17.73% and 22.78%, respectively. The reaction mechanism is as follows: in an acidic environment, the calcium sulphate dihydrate is formed by the reaction combining the sulphuric acid and $Ca(OH)_2$ generated from cement hydration. Then C-S-H and ettringite are formed due to the reaction of oulopholite, cement clinker and ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 18H_2O$), which are line with the result shown in in Fig. 3. The solubility of ettringite is very low, which results in the existence of precipitate. Moreover, crystalline compressive stress caused by the growth of ettringite crystal makes the cement mortar specimen expand and crack. The chemical reaction formula are shown in (3)–(5):

$$Ca(OH)_2+Na_2SO_4+H_2O \rightarrow CaSO_4 \cdot 2H_2O+NaOH \tag{3}$$

$$CaO \cdot A1_2O_3 \cdot CaSO_4 \cdot 18H_2O+CaSO_4+H_2O \rightarrow CaO \cdot A1_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \tag{4}$$

$$CaO \cdot Al_2O_3 \cdot 19H_2O+CaSO_4+H_2O \rightarrow CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O+Ca(OH)_2 \tag{5}$$

The pores and micro-cracks of mortars are filled with RHA, so that it is difficult for sulphuric acid to enter into the interior of mortars. Therefore, the chemical resistance of cement mortars is greatly improved with the addition of RHA.

Table 5

The physical characteristic of control and modified cement mortar

Sample	Mass (g)		Compressive strength (MPa)		Apparent density (g/cm^3)
	M_1	M_0	R_0	R_1	
S0	846	730	38	48	2.07
P1	730	745	49	61	2.11
P2	666	716	47	55	2.03
P3	608	742	57	64	2.11
R1	651	708	47	56	2.01
R2	592	722	46	52	2.04
R3	545	746	61	66	2.11
S1	565	698	41	48	1.98
S2	516	716	46	51	2.03
S3	432	708	51	53	2.01

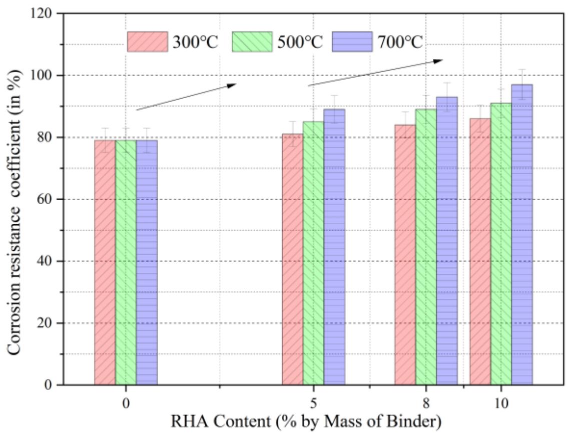

Fig. 3. – The variation of corrosion resistance coefficient of control and modified cement mortars at 300 °C, 500 °C and 700 °C.

3.4. The variation of carbonation depth

The variation in carbonation depth of modified mortars containing 10% RHA at 7, 14, 28, and 56 days is shown in Fig. 4. As illustrated in Fig. 4, the carbonation depth of control mortars is greater than that of the modified mortars with RHA at various curing ages. This indicates that the incorporation of RHA positively affects the hydration process, resulting in a denser internal structure. Furthermore, as the curing age progresses, the carbonation depth of the mortars tends to decrease, suggesting an improvement in hydration over time. This observation is consistent with the results shown in Fig. 2 and Fig. 3 and is further supported by Fig. 5.

Another significant finding from Fig. 4 is that with the improvement of calcination temperature for RHA, the carbonation depth is decreased, demonstrating that the calcination products become fuller and the internal structure of modified mortars become denser, which can be testified by means of the shown in Fig. 1.

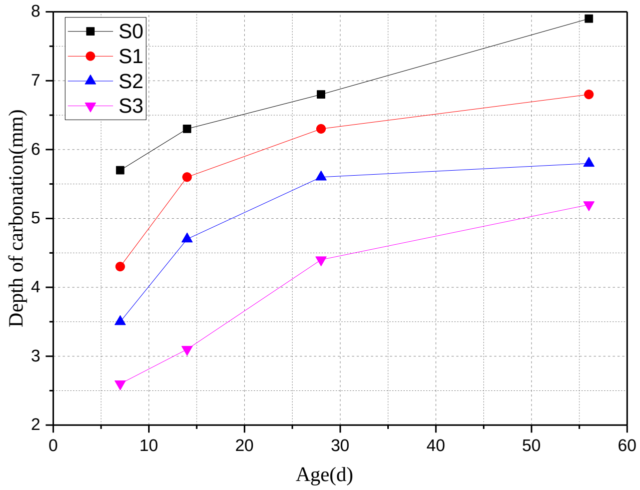

Fig. 4 – The variation of depth of carbonation of control and modified mortars at 7 days, 14 days, 28 days and 56 days.

3.5. The microscopy examination of control and modified mortars

The SEM images were adopted to evaluate the microstructure of mortars without and with RHA at different temperatures. As shown in Fig. 5a–c, "needles" regarded as ettringite appear in modified mortars when RHA are added into control mortars, resulting in that the inner interleaving capacity of mortars is enhanced and microstructure become denser. Hence, integrity and stability of mortars matrix are improved, and sulphate can't be easily immersed into it, which testifies experimental result shown in Fig. 3 and Fig. 4. At the time, increasing calcination temperature of RHA improves the quantity of "needles" in mortars matrix.

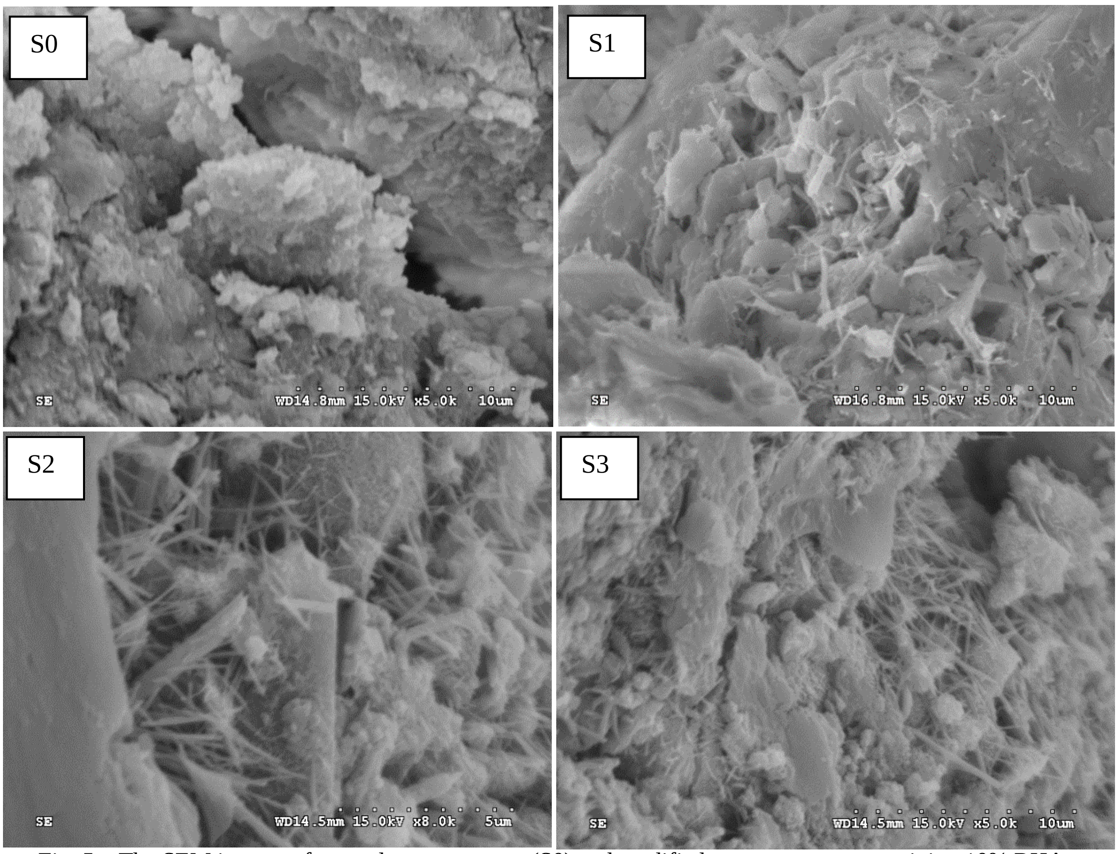

Fig. 5 – The SEM images of control cement mortar(S0) and modified cement mortar containing 10% RHA at a temperature of 300 °C (S1), 500 °C (S2) and 700 °C (S3).

4. CONCLUSION

The article mainly aims to research the characterization of RHA, and the influence of RHA at 300 °C, 500 °C, 700 °C on modified cement mortars. Additionally, a possible mechanism for the behavior of the modified cement mortars was revealed using SEM. The specific conclusion was as follows:

1. The mezzanine structure of RHA at 700 °C is compact, while the mezzanine of RHA at 300 °C is composed of crisscross plates which are loose honeycomb and contain a large number of holes.
2. The intensity of bending vibration of O-Si-O of RHA at 500 °C and 700 °C is higher than that of RHA at 300 °C.
3. The corrosion resistance of modified mortars were improved greatly due to the incorporation of RHA.
4. The incorporation of RHA increase the corrosion resistance and the carbonation resistance of cement mortars.
5. Compared with control mortars, the inner structure of modified cement mortars became more denser.
6. The ettringite of modified mortars incorporated with RHA were more than that of control mortars.

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