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EROSION RESISTANCE OF PRE-TREATED RICE HUSK ASH CONCRETE UNDER SIMULATED ACID RAIN

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In order to explore the ability of pre-treated rice husk ash concrete to resist acid rain erosion, this study investigates the deterioration law of ordinary concrete and pre-treated rice husk ash concrete under the combined action of acid rain erosion and dry-wet cycles, combining microscopic changes and a series of indicators such as the compressive strength of the concrete, with the dry-wet cycle of clean water as a control to analyse the deterioration law of the concrete. The results show that when the replacement rate of the pre-treated rice husk ash is 10%, the compressive strength of the concrete is the most improved and the splitting tensile strength is negatively correlated with the substitution rate of P-RHA. From the durability of the concrete, with the progress of the dry-wet cycle, the mass, compressive strength, and relative dynamic elasticity modulus show a decreasing trend, and the water absorption shows an upward trend. According to microscopic changes, the two types of concrete are mainly eroded by gypsum. The addition of P-RHA can promote the growth of C-S-H gels, reduce the effective porosity of the concrete, and delay the deterioration time of the concrete. By analysing the depth of the degradation of the concrete's compressive strength, it is concluded that the ordinary concrete is destroyed earlier than the P-RHA concrete.

INTRODUCTION

Modern building products are subject to erosion by a variety of media, which affect the usability and durability of the building. The pH of acid rain is less than or equal to 5.6, which is one of the representative sources of erosion of buildings [1, 2]. Southwest China is located in China's three major acid rain areas, and the composition of acid rain is mainly a composite acid containing sulfuric acid and nitric acid. In addition, it is affected by the subtropical monsoon climate, where there is more rainfall all year round, which causes serious erosion of buildings in southwest China and affects the service life of the buildings [3]. Rice husk is a renewable resource, and rice husk ash (RHA) prepared by specific combustion contains high-purity amorphous SiO_2 and it has high pozzolanic activity, which can be used as an auxiliary material to improve the durability of concrete and improve the ability of concrete to resist acid rain erosion [4].

Many scholars have conducted relevant studies on the application of rice husk ash in concrete materials [5–7]. It was found that when the RHA substitution rate is 5 % ~ 10 %, the mechanical properties of concrete materials are significantly improved. Yao et al. [8] soaked rice husk ash concrete in a sulfate environment for erosion, and found that RHA with 9 % cement mass could greatly improve the mechanical properties of the concrete and improve the resistance of the concrete to sulfate erosion. At the same time, some scholars believe that the substitution rate of RHA exceeding 20 % will enhance the resistance of concrete to Cl^- and acid erosion, improve the compressive strength of concrete specimens, and reduce the splitting tensile strength of the specimens [9, 10]. As an auxiliary material, the calcination temperature, grinding fineness, and different methods of the RHA pre-treatment will affect the concrete performance. Some experts and scholars have found through experiments that rice husk can be calcined at a temperature of 600 °C ~ 800 °C to produce more pure amorphous SiO_2, the rice husk is soaked with acid (pre-treatment), the content of amorphous SiO_2 in the prepared RHA can reach more than 98 %, and the particle size on the ash of the pre-treated rice husk is smaller after calcination [11–15]. Ramezanianpour et al. [16] believe that after the rice husk is calcined at a temperature of 700 °C, the SiO_2 in the ash of the rice husk shows an amorphous state, and when the temperature exceeds 750 °C, the SiO_2 begins to transform into a crystalline state. Park et al. [17] pre-treated rice husk with acid and found that the pre-treatment of rice husk ash could effectively improve the compressive strength of the concrete and improve the frost resistance of the concrete. Ma et al. [18] found that RHA with a small grinding fineness improved the mechanical properties of cement mortar better than RHA with a large fineness.

In summary, the current main research direction is RHA as an admixture to study the erosion resistance of concrete and pre-treated rice husk ash (P-RHA) to improve the mechanical properties of concrete. However, for the pre-treatment of rice husk ash (P-RHA) as an admixture, it is rare to study the erosion resistance of concrete in an acid rain environment. The test imitates the deterioration characteristics of concrete in the acid rain area of southwest China, and the erosion test of ordinary concrete and P-RHA concrete under the action of compound acid solution (H_2SO_4+HNO_3) and a dry-wet cycle (150 days) was carried out. Through the apparent phenomenon of concrete, the changes in the mass, compressive strength, relative dynamic elasticity modulus, and water absorption were analysed, and the microscopic changes of the specimens were analysed by scanning electron microscopy (SEM) and X-ray diffraction (XRD), and the deterioration law of the two types of concrete was explored by combining the macro-micro changes.

EXPERIMENTAL

Test materials

The raw materials tested: Water (tap water in Chongqing), P·O 42.5 ordinary Portland cement (Jidong Cement Chongqing Hechuan Co., Ltd.), river sand (fineness modulus of 2.7), crushed stone (particle size of 5-15mm), water-reducing admixture (Shaanxi Qinfen Building Materials, Q8011HPWR type PCA polycarboxylic acid system), sulfuric acid and nitric acid (Jingqi standard solution, 0.1 mol·L^{-1}), rice husk ash (Chongqing, fineness of less than 50μm). The test samples are shown in Figure 1.

Figure 1. The rice husk ash test samples.

The chemical elements contained in the rice husk ash were determined by EDS, and the oxide content after calcination was determined by semi-quantitative XRD analysis, as shown in Table 1, and the XRD phase analysis of the rice husk ash is shown in Figure 2. It can be seen from the figure that after the pre-treatment with acid, the rice husk ash has a strong diffraction peak in SiO_2, no obvious crystalline phase, and does not change the chemical properties of the rice husk ash, which proves the feasibility of P-RHA as a concrete admixture.

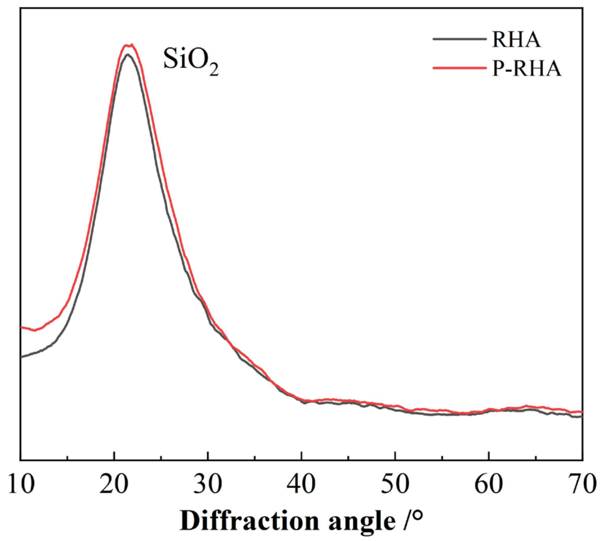


Figure 2. The rice husk ash test samples.

Design of the experiment

In this test, the water-cement ratio is 0.45, the mass ratio of the cement, river sand, and crushed stone is 1:1.93:3, and the proportion of the mixture is

Table 1. Chemical composition of the rice husk ash (%).

	SiO_2	K_2O	Na_2O	Fe_2O_3	MgO	CaO	P_2O_5	Ignition loss
RHA	80.41	4.09	1.52	2.37	1.22	1.20	1.17	8.02
P-RHA	90.77	3.12	0.53	0.83	0.65	0.76	0.21	3.13

shown in Table 2. The substitution rate of P-RHA was 5 %, 10 %, 15 %, and 20 % of the mass of the cement, and H_2SO_4 was selected as the rice husk pre-treatment agent, with a concentration of 0.1 mol·L^{-1}. Imitating the erosion characteristics of acid rain in southwest China [2, 3], a compound acid solution with a concentration of 0.1 mol·L^{-1} composed of H_2SO_4 and HNO_3 is used as the erosion solution. The sulfuric nitric acid volume ratio is 9:1, and, on this basis, to strengthen the erosion intensity to reduce the test cycle, the pH is controlled between 1 and 1.5, and the solution was changed every 15 days in the test..

Test methods

Taking the production of P-RHAC-10 as an example, the rice husk is poured into tap water for cleaning, drained and put into a drying oven to dry (105 °C, 2 h), once dried, it is soaked in H_2SO_4 (2 h), drained, and calcined in a muffle furnace (700 °C, 2.5 h), cooled and ground, replaced with 10 % mass cement after sieving, and mixed for later use. The inside of the mould was brushed with an oil-based release agent before the test block was made. According to the mixing ratio, the aggregate is first mixed for 60 s, then cement is added and mixed for 60 s, and finally, water is added and mixed for 2 min. The mixture is then poured into the mould and vibrated, left for 24 hours, and then de-moulded, and cured for 28 days under standard curing conditions (temperature is 20 °C ± 2 degrees Celsius, relative humidity greater than or equal to 95 %).

The size of the test cube is 100 mm × 100 mm × 100 mm, with three specimens in each group. The deterioration of concrete at 30 d, 60 d, 90 d, 120 d, and 150 d was tested and compared with the concrete under the dry-wet cycles in clean water. The dry-wet cycle system simulates the test methods for resistance to sulfate attack [19]. The specimens were soaked in the compound acid solution for 16 hours, taken out and dried naturally for 1 hour, and then dried at 70 °C with a blast drying box for 6 hours, and placed in a room for cooling for 1 hour, for a total of 24 hours, which was used as a 1d dry-wet cycle test. The test requires a total of 150 d cycles, and the dry-wet cycle system is shown in Table 3. The flow of the test is shown in Figure 3.

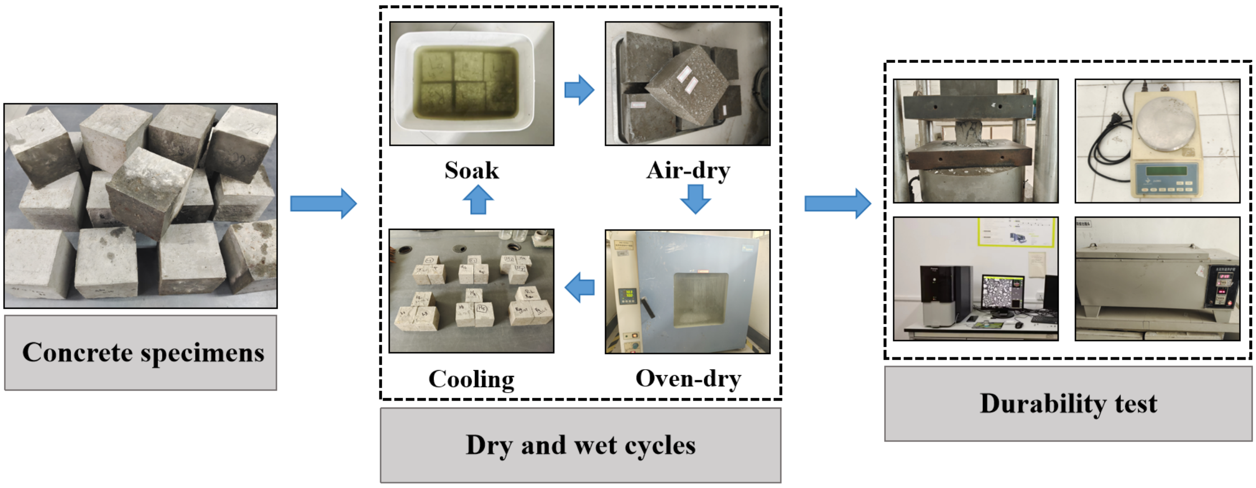


Figure 3. Test flow chart.

Table 2. Proportion of the mixture (kg·m^{-3}).

Number	Cement	Sand	Stone	Water-reducing admixture	Water	Rice husk ash
OC	380	732	1140	3.80	171	0
P-RHAC-5	361	732	1140	3.61	171	19
P-RHAC-10	342	732	1140	3.42	171	38
P-RHAC-15	323	732	1140	3.23	171	57
P-RHAC-20	304	732	1140	3.04	171	76

Table 3. Dry-wet cycle system.

Immersion time (h)	Immersion temperature (°C)	Air drying time (h)	Drying time (h)	Drying temperature (°C)	Cooling time (h)	A dry-wet cycle (h)
16	NT	1	6	70	1	24

Evaluation index of the durability

According to the "Standard for Long-term Performance and Durability Performance Test Methods for Ordinary Concrete" GB/T50082-2009, the relative mass loss of the concrete specimen exceeds 5 % as the failure limit of the concrete specimen, and the calculation formula is shown in Equation 1. When the relative compressive strength and relative dynamic elasticity modulus of the concrete specimen drop to 75 % and 60 %, respectively, as the failure limit of the concrete specimen, the calculation formulas are shown in Equations 2 and 3 [19].

$$M = \frac{m_n - m_0}{m_0} \times 100\ \% \tag{1}$$

where m_n represents the mass of the nth cycle of the specimen, g; m_0 represents the mass of the specimen when it is not participating in the cycle, g.

$$F_c = \frac{f_{cn} - f_{c0}}{f_{c0}} \times 100\ \% \tag{2}$$

where f_{cn} represents the compressive strength of the specimen in the nth cycle, MPa; f_{c0} represents the compressive strength of the specimen when it is not participating in the cycle, MPa.

$$E = \left(\frac{v_n}{v_0}\right) \tag{3}$$

Where v_n represents the ultrasonic wave velocity of the nth cycle of the specimen, m·s^{-1}; v_0 represents the ultrasonic wave velocity of the specimen when it is not participating in the cycle, m·s^{-1}.

RESULTS AND DISCUSSION

Substitution rate of the pre-treated rice husk ash

The compressive strength and splitting tensile strength of the concrete under different RHA and P-RHA substitution rates are shown in Figure 4. It can be seen, from the figure, that the increase in the compressive strength is the most significant when the RHA and P-RHA replacement rate is 10 %, and the compressive strength increased by 10.4 % and 15.78 %, respectively, compared with ordinary concrete on the 28th day. When the replacement rate reaches 20 %, the compressive strength is reduced compared to the ordinary concrete. Under the same substitution rate, the splitting tensile strength values of the two types of concrete were similar, and the tensile strength decreased with the increase in the substitution rate.

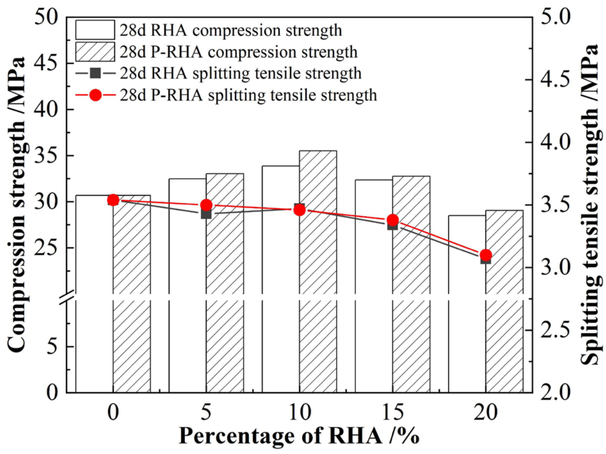


Figure 4. Strength variation of the concrete with the different substitution rates of rice husk ash.

The test found that the effect of the P-RHA on increasing the compressive strength was better than that of the RHA. This is because the rice husk that has been pre-treated with acid and then calcined contains amorphous SiO_2 of higher purity. SiO_2 as an acidic oxide which can be reactive with the cement-hydrate to promote the formation of C-S-H gels (pozzolanic activity), which reduces the effective porosity of the concrete specimen. However, RHA has strong water absorption, excessive incorporation will cause the untimely and insufficient reaction of hydrate and SiO_2, which will increase the porosity and reduce the strength [20]. From the test results, the mechanical properties of the concrete are the best when the P-RHA substitution rate is 10 %, and thus the P-RHAC-10 group was selected for the dry-wet cycle test.

Surface changes in the concrete specimens

The surface changes of the specimen under clean water are shown in Figure 5. From 0 to 150 days, the continuous alternation of the dry and wet cycles promotes the continued hydration of the cement, and as the water continues to penetrate the interior of the specimen to dissolve the residual $Ca(OH)_2$ (CH), the CH precipitates out with the increase in the temperature during the drying process, resulting in the surface colour of the specimen

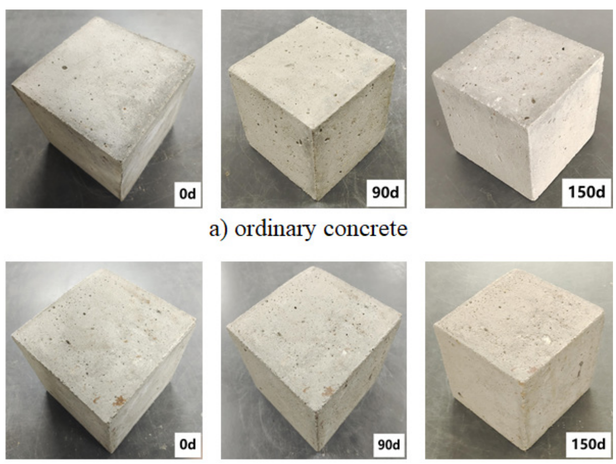


Figure 5. Surface characteristics of the concrete in water: (a) Ordinary concrete; (b) P-RHA concrete.

gradually becoming lighter. From 0 to 150 days, the two specimens maintain their initial integrity throughout the cycle, their edges and corners have not fallen off, their size has not been significantly reduced, and there were no swelling, cracks, etc.

The surface changes of the specimen in the compound acid solution are shown in Figure 6. The compound acid solution starts to react with the cement-hydrate in the early stages of the concrete specimen erosion by the compound acid solution, i.e., from 0 to 90 days, as the erosion has just started, the concrete has fewer pores, it is difficult for the erosion solution to penetrate the interior, and the initial reaction is mostly on the surface of the concrete specimen. The reaction between the hydrated cement and an acid solution will lead to dissolution erosion. On the one hand, acid solutions will have a neutralisation reaction with CH, with the consumption of CH in cement hydrate, the colour of the concrete specimen will gradually become darker, on the other hand, H_2SO_4 and HNO_3 will react with cement hydrate to form sulfate and nitrate, which will gradually dissolve with the change of temperature and lead to sanding on the surface of the specimen. At this stage, burrs appear around the specimen, the surface of the specimen is slightly sanded, and the specimen size is relatively complete. In the later stages of erosion, from day 90 to day 150, the dry-wet cycles will accelerate the rate of pore enlargement, and gypsum will appear and begin to accumulate within the concrete, which also accelerates the development of the pores. As shown in Figure 7, the coarse aggregate ($CaCO_3$) is attacked by the acidic solutions in addition to the sulfate and nitrate attack. These acid solutions penetrate through the pores and react with the aggregate to produce insoluble $CaSO_4$ and dissolved nitrate. At this stage, the concrete erosion layer gradually deepens, the cement-hydrate inside the specimen is gradually consumed, the aggregate of the whole specimen is exposed and seriously falls off, and the surrounding area is jagged, and the size of the specimen at this stage is significantly reduced [21–23]. From the surface changes, it was found that the deterioration of the P-RHA concrete was lighter than that of the ordinary concrete from day 0 to day 90, and the deterioration of both types of concrete accelerated after day 90 [24].

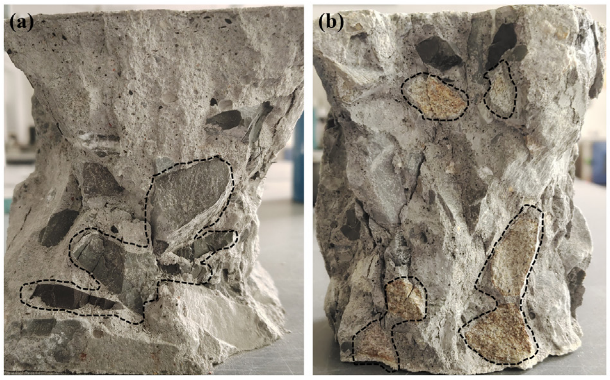
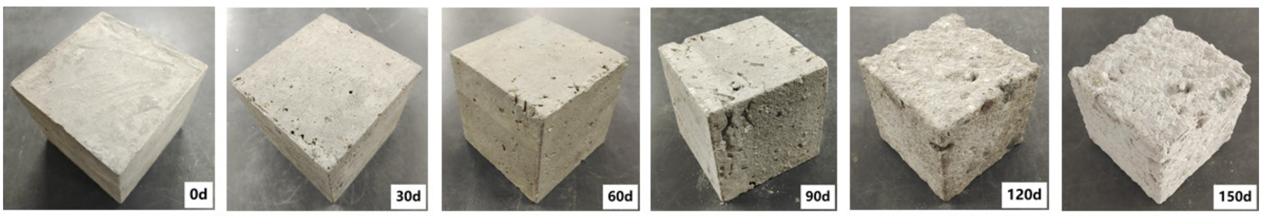


Figure 7. Comparison of aggregates before and after concrete erosion: (a) before erosion; (b) after erosion.

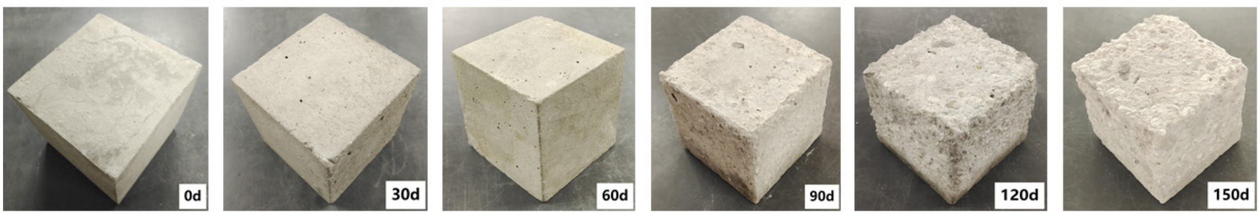
Changes in the physical and mechanical properties of the concrete

Changes in mass

The changes in the mass of the concrete specimen under the action of the dry-wet cycle are shown in Figure 8. As shown in Figure 8a, the mass of the specimens in clean water showed three trends: first an increase, then a decrease and finally stabilisation, and the peak appeared on the 60^{th} and 90^{th} days. Before and after the dry-wet cycle, the mass difference between the two specimens was within 15 g, and there was no obvious change overall.



a) ordinary concrete

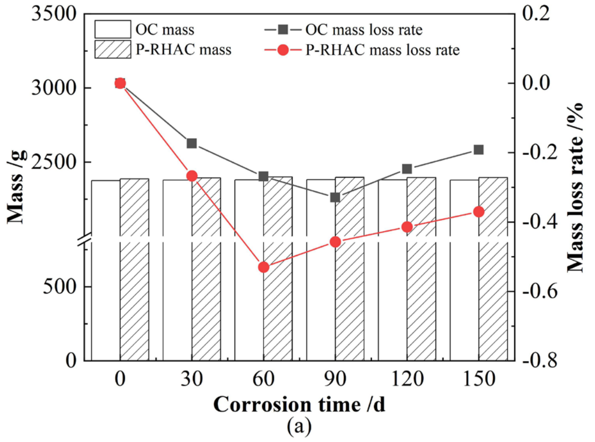


b) P-RHA concrete

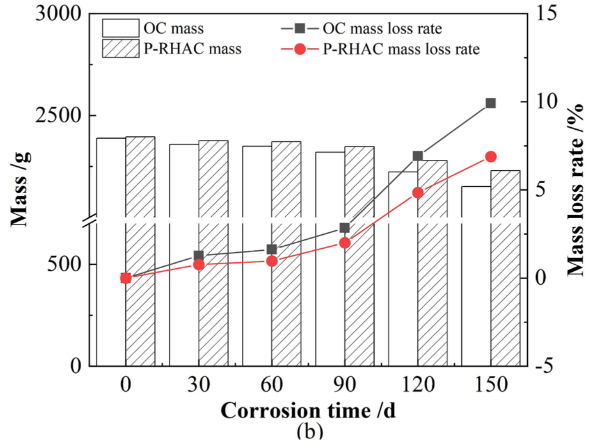
Figure 6. Surface characteristics of the concrete in the compound acid solution.

The overall mass of the concrete has a decreasing trend under the action of the erosion of the compound acid solution. As shown in Figure 8b, the loss of concrete mass is slower before 90 days and begins to accelerate after 90 days. When the cycle reaches 120 days, the mass loss of ordinary concrete and P-RHA concrete is 6.91 % and 4.85 %, respectively, at this time, the ordinary concrete specimen fails, and when the cycle reaches 150 days, the relative mass loss of P-RHA concrete is 6.89 %, and the concrete specimen is damaged.

It can be seen from Figure 9b that the compressive strength of the two types of concrete in the compound acid solution shows a slow downward trend from 0 to 90 days, and an accelerating downward trend from 90 to 150 days. When eroded for 150 days, the compressive strength loss rates of the ordinary concrete and P-RHA concrete were 28.74 % and 18.47 %, respectively, at which time the compressive strength of the ordinary concrete reached the failure limit, and the P-RHA concrete was not damaged.



a) water



b) compound acid solution

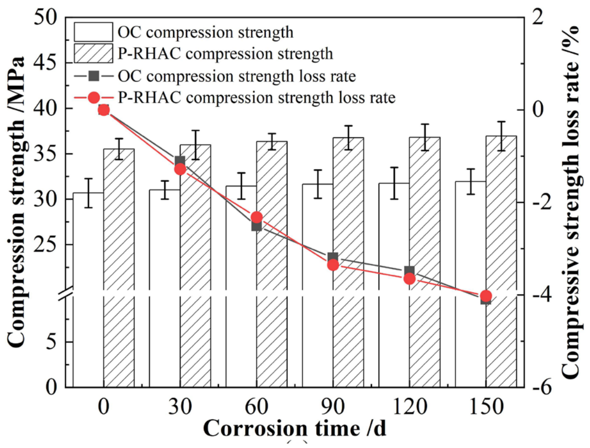
Figure 8. Changes in the mass of concrete.

Changes in the compressive strength

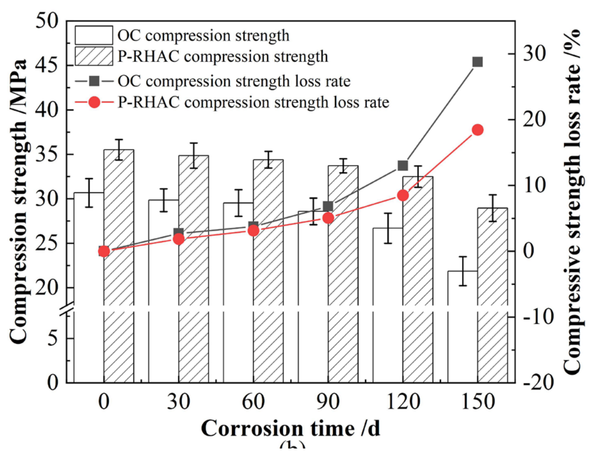
The changes in the compressive strength of the concrete under the action of the dry-wet cycle are shown in Figure 9. It can be seen from Figure 9a that from 0 to 150 days, the compressive strength of the two types of concrete in the clean water shows a slow growth trend, and the growth rate of the two is close, and there is no obvious downward trend after 150 days of cycling.

Changes in the water absorption

The water absorption of the concrete specimens is affected by the combined influence of the environment and temperature during erosion. The magnitude of the water absorption performance reflects the erosion resistance of the concrete in this environment, and can also characterise the effective porosity of the concrete, and the water absorption rate of the specimen is calculated in Equation 4 [25].



a) water



b) compound acid solution

Figure 9. Changes in the compression strength of the concrete.

$$W = \frac{m_w - m_d}{m_d} \times 100\,\% \quad (4)$$

where m_w represents the saturated mass of the test piece in the n^{th} cycle, g; m_d represents the drying mass of the test piece in the n^{th} cycle, g.

The changes in the water absorption of the concrete under the action of the dry-wet cycles are shown in Figure 10. In clean water, the water absorption rate of the two types of concrete from 0 to 150 days is between 2 % ~ 3 %, and there is no obvious fluctuation. In the compound acid solution, the change in the water absorption is inversely proportional to the compressive strength and mass loss rate, with the prolongation of the erosion time, the water absorption of two kinds of specimens continued to rise, from 0 to 90 days the specimen's water absorption grows slowly, and from 90 to 150 days the water absorption begins to accelerate the growth, at 150 days of erosion, the water absorption of the ordinary concrete and RHA concrete is 4.92 % and 4.65 %, which is 2.41 % and 2.51 % higher than before erosion, respectively. The greater the water absorption of the specimen, the worse the compactness and the lower the compressive strength, the test shows that the change in the water absorption is consistent with the change in the compressive strength and mass.

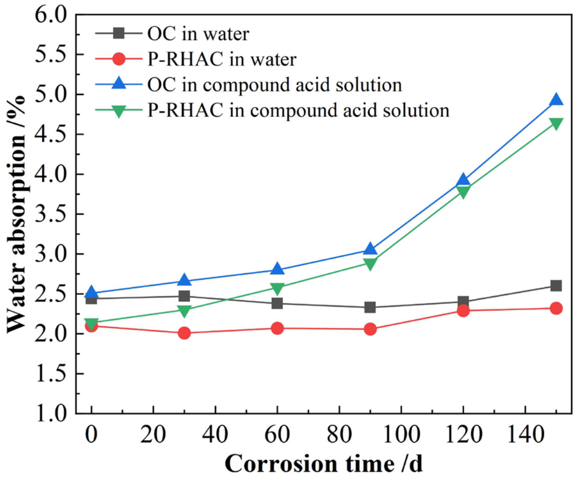


Figure 10. The water absorption rate of the concrete.

Changes in the relative dynamic elasticity modulus

The relative dynamic elasticity modulus of the specimen is calculated by measuring the propagation velocity of the ultrasonic waves in the concrete, and the size of the relative dynamic elasticity modulus reflects the compactness of the concrete. The changes in the relative dynamic elasticity modulus of the concrete are shown in Figure 11. In clean water, the relative dynamic elasticity modulus of two types of concrete shows an increasing trend, of which the growth rate is faster from 0 to 60 days and slows down after 60 days. In the compound acid solution, the relative dynamic elasticity modulus of both specimens continued to decrease with the extension of the erosion time, indicating that the compactness of the specimens was gradually decreasing under the long-term erosion in the compound acid environment, and the relative dynamic elasticity modulus loss rate of ordinary concrete was 41.6 %, which reached the damage limit, and the relative dynamic elasticity modulus loss rate of the RHA concrete was 38.1 %, which was close to the damage when the erosion reached 150 days.

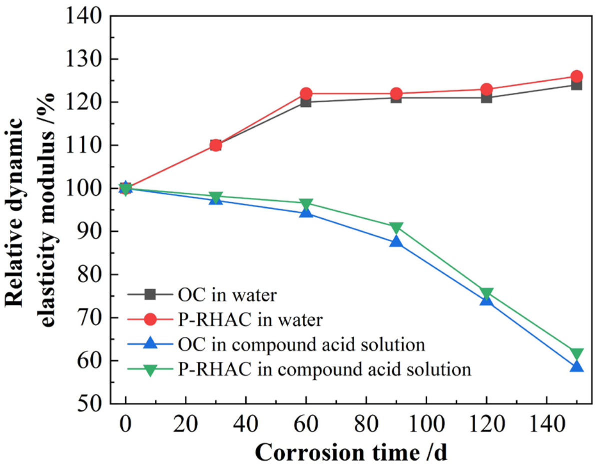


Figure 11. The relative dynamic elasticity modulus of the concrete.

The test shows that the physical properties of the ordinary concrete and the P-RHA concrete under the action of the dry-wet cycle in clean water are similar, the overall change trend is the same, and the addition of P-RHA can effectively maintain the performance of the original concrete without changing the basic characteristics of the concrete. Under the action of the dry-wet cycle of the compound acid solution, the mass of the two concrete specimens reached the failure limit earlier than the compressive strength reached the failure limit, and the addition of P-RHA delayed the loss of the relative dynamic elasticity modulus and compressive strength of the concrete specimens [26]. The test also found that the water absorption rate of the ordinary concrete is always greater than that of the P-RHA concrete, indicating that the addition of P-RHA optimises the particle gradation and can reduce the effective porosity of the concrete specimen.

The addition of P-RHA promotes the production of C-S-H gel, consumes CH, improves the compactness of the concrete, hinders the penetration of the erosion solutions, and retards the loss of compressive strength in the early stages. However, at the late stage of erosion, the loss of compressive strength of the P-RHA concrete is less than that of ordinary concrete, but gradually accelerates, and the relative dynamic elasticity modulus and water absorption of the two types of concrete gradually approach. It indicates that P-RHA acts more as an inhibitor of concrete degradation in the early stage, as AFt and C-S-H are decomposed in an acidic environment, the porosity of P-RHA concrete increases, and its degradation rate gradually accelerates.

Microscopic analysis under the erosion of the compound acid solution

The concrete specimens in clean water have no obvious changes in the surface, mass, and strength after 150 days of circulation, so no microscopic analysis is undertaken here, and the following analysis is conducted for the microscopic morphology of the concrete in the compound acid solution.

The microscopic morphology of the normal concrete at day 0, day 90, and day 150 is shown in Figure 12. From Figure 12a, it can be seen that on day 0, AFt in the form of rods is present and relatively dispersed within the ordinary concrete. From Figure 12b, on the 90th day, under the continuous erosion of the compound acid solution, the AFt disappeared, and there were obvious gaps inside the specimen under the action of the erosion solution and the swelling substance. From Figure 12c, at day 150, the main erosion product found within the specimen was dense gypsum crystals. From Figure 12d, at day 150, the SEM at ×500 magnification revealed that microcracks within the specimen had expanded rapidly.

The microscopic morphology of the P-RHA concrete at day 0, day 90, and day 150 of erosion is shown in Figure 13. From Figure 13a, it can be found that on day 0 of erosion, AFt in the shape of rods existed within P-RHA concrete, and the AFt was concentrated within the pores, which were more robust compared to the AFt in ordinary concrete, and it can also be found that a reticular gel was generated within the P-RHA concrete, as shown in Figure 13b. The presence of gel and AFt can reduce the effective porosity of the specimen, slow down the penetration rate of the erosion solution and reduce the loss of concrete specimens [27]. On the 90th day of the cyclic erosion, the gel and AFt were decomposed under the action of the erosion solution, the pores of the specimen began to increase, and cracks were created inside the specimen under the action of the erosion solution and swelling material, as shown in Figure 13c; The same slight cracks were observed in P-RHA concrete when the specimens were eroded for 150 days and the electron microscope was magnified by the same magnification. As the addition of P-RHA improved its resistance to erosion in the early stage, at the later stage, the width of the cracks becoming larger in the P-RHA concrete was smaller than that of the normal concrete, as shown in Figure 13d [27].

From the tests and micromorphology, it was found that the action of the hydration products before erosion (day 0) and the effect of erosion products on the concrete cracks after 90 days of erosion caused differences in the erosion resistance of the P-RHA concrete. The following two types of concrete minerals were analysed by XRD diffraction for the non-eroded and eroded concrete on day 90. As shown in Figure 14, the initial main minerals of the two types of concrete were gypsum, quartz (SiO_2), ettringite (AFt), CH, $CaSO_4$, feldspar, incompletely hydrated dicalcium silicate (C_2S), and tricalcium silicate (C_3S). Comparing the diffraction peaks of the two concretes, it was found that the diffraction peaks of the new minerals did not appear after the addition of P-RHA, but the diffraction peaks of CH were weakened and the diffraction peaks of AFt were enhanced compared with the ordinary concrete. The reason is that the addition of P-RHA stimulates the reaction of SiO_2 with cement hydride (CH), which consumes CH, promotes the generation of C-S-H, and improves the compactness of the specimen, which is consistent with the results of

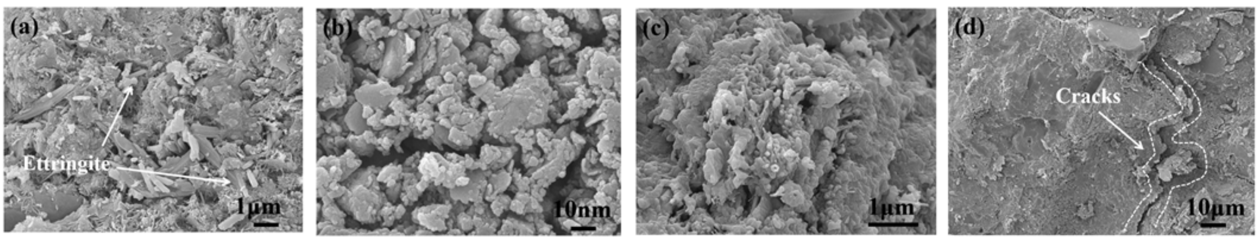


Figure 12. . SEM of the ordinary concrete: (a) 0 d; (b) 90 d; (c) 150 d; (d) 150 d.

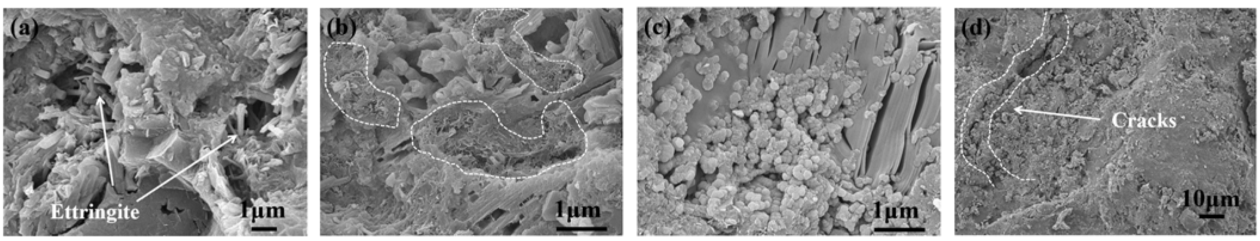


Figure 13. . SEM of the P-RHA concrete: (a) 0 d; (b) 0 d; (c) 90 d; (d) 150 d.

the preliminary mechanical property tests and electron microscopy observations [27]. At day 90 of erosion, the main minerals in both types of concrete are gypsum, quartz, $CaSO_4$, and feldspar. The diffraction peaks of CH and AFt disappeared in the previous period, which is consistent with the morphological analysis of electron-microscopic images. Under the acidic environment, AFt decomposes into gypsum and aluminium sulfate, making the value of the diffraction peak of gypsum increase to the detriment of AFt, while CH is neutralised by the acid solution, releases Ca^{+}, and makes the diffraction peak of CH disappear. As can be seen in Figure 14, at day 90 of erosion, the diffraction peaks of the major minerals in both concretes are the same and the peak intensities are close. The main erosion products in both concretes are gypsum crystals at this time, indicating that the improvement in the concrete properties by P-RHA has been greatly diminished by the long-term erosion in the acidic environment [28-29].

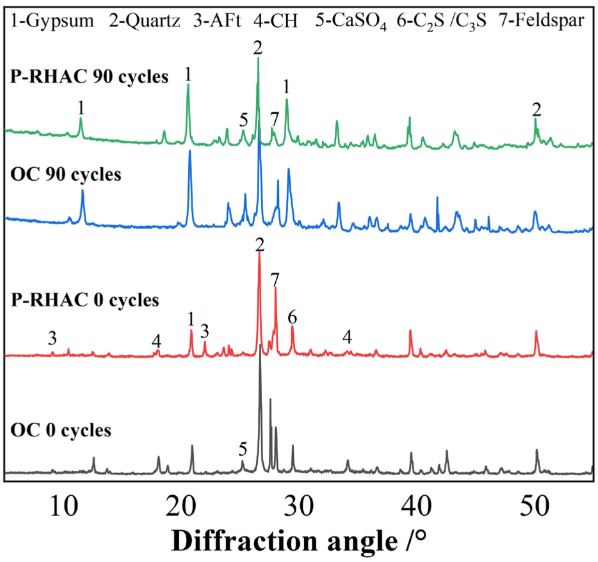


Figure 14. XRD of concrete erosion by the compound acid solution.

Degree of damage

The effect of the acid solution on the depth of degradation of the compressive strength of the concrete specimen can characterise the degree of the damage to the concrete. It is assumed that the erosion around the specimen is vertical and uniform, i.e., the thickness of the erosion layer on each surface of the specimen is the same, and the erosion layer no longer has a bearing capacity [29]. The depth of degradation of the compressive strength of the concrete is calculated according to Equation 5.

$$\frac{F_0}{a^2} = \frac{F_{cn}}{(a-2d_f)^2} \tag{5}$$

where F_0 represents the initial compressive strength of the specimen, MPa; F_{cn} represents the compressive strength of the specimen after n times of erosion, MPa; a represents the side length of the specimen, mm; d_f represents the depth of degradation of the surface layer of the specimen, mm.

The side length of the concrete test specimen, i.e., a = 100 mm, is brought into Equation 5 to obtain Equation 6.

$$d_f = 50 \times \left(1 - \sqrt{\frac{f_{cn}}{f_0}}\right) \tag{6}$$

The depth of degradation of compressive strength of concrete specimens can be obtained from Equation 6, and its variation with dry-wet cycles is fitted, and its fitted regression curve is shown in Figure 15. It can be seen from the graph that the depth of degradation of the compressive strength for both types of concrete varies non-linearly. The Equation 7 is as follows:

$$d_f = \mathrm{A}t^2 + \mathrm{B}t \tag{7}$$

where t represents the time of erosion, d; A and B represent the fitting parameters.

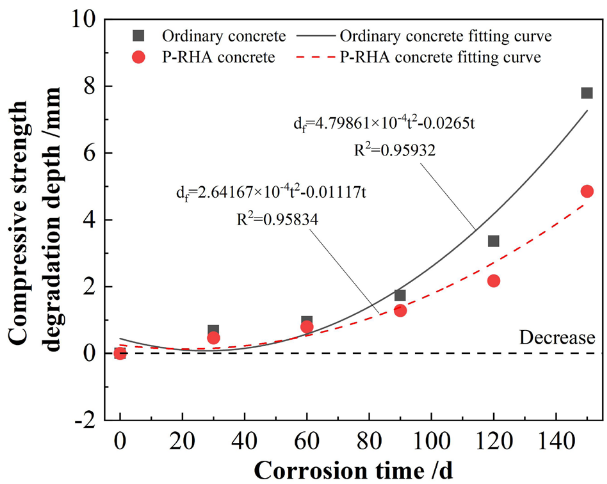


Figure 15. Compression strength degradation depth fitting curve.

As the wet-dry cycle proceeds, the greater the value of A and B, the greater the depth of degradation, and the fitted regression equation is shown in Equation 8. According to Equation 6 and GB/T50082-2009, the depth of degradation of compressive strength of concrete with a volume of 100 mm × 100 mm × 100 mm reaches the damage of 6.699 mm, and it can be found that under this erosion environment, the ordinary concrete is damaged on day 148.9 and the P-RHA concrete is damaged on day 181.8.

$$d_f = \begin{cases} 4.79861 \times 10^{-4} \times t^2 - 0.0265t,\ R^2 = 0.95932, & \text{Ordinary concrete} \\ 2.64167 \times 10^{-4} \times t^2 - 0.01117t,\ R^2 = 0.95834, & \text{P-RHA concrete} \end{cases} \tag{8}$$

CONCLUSIONS

The main conclusions of the experimental studies on the erosion resistance of ordinary concrete and P-The RHA concrete under the action of dry-wet cycles of compound acid solutions are as follows:

(1) When the substitution rate of P-RHA is 10 %, the compressive strength of the concrete is the most significantly improved, which is 15.78 % more than that of the ordinary concrete. The splitting tensile strength decreases with the increasing substitution rate of P-RHA. The changes in the physical properties of the two types of concrete under the action of the dry-wet cycle of clean water are small and the trends are similar, indicating that the addition of P-RHA does not change the basic properties of the concrete.

(2) Under the action of the dry-wet cycle of the compound acid solution, the mass, compressive strength, and relative dynamic elasticity modulus of the two types of concrete showed a decreasing trend and the water absorption rate showed an increasing trend. The water absorption of the specimens was inversely proportional to the compressive strength, and the concrete mass reached the limit of damage earlier than the strength reached the limit of damage. The combination of water absorption and relative dynamic elasticity modulus found that the P-RHA can effectively reduce the porosity of concrete specimens, and each index of durability evaluation of the P-RHA concrete reaches the limit of damage later than that of the ordinary concrete.

(3) Combined with the microscopic analysis, it is found that the addition of P-RHA to the cement results in a pozzolanic reaction that consumed the cement hydrate (CH) while promoting the production of C-S-H gel enhancing the performance of the specimen, which reduces the loss of concrete in the pre-erosion period and, thus, prolongs the time for concrete to reach damage limit.

(4) The analysis of the depth of the degradation of the compressive strength revealed that the P-RHA concrete was destroyed later than ordinary concrete, with a difference of 33 days between the two being destroyed. According to the changes in the specimen's surface, physical properties, and microscopic analysis, it is found that the P-RHA can effectively improve the resistance of the concrete to acid rain erosion.

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