Research Article

Experimental Research on Chloride Erosion Resistance of Rubber Concrete

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Chloride corrosion test was carried out in 4% NaCl solution to study the chloride corrosion resistance of rubber concrete. Rubber concrete was prepared by using 20 mesh, 1–3 mm, and 3–6 mm rubber particles instead of sand by 5%, 10%, 15%, and 20% of the cementitious material mass. The P-wave velocity and compressive strength of rubber concrete were measured. The microstructure of rubber concrete corroded by chloride was analyzed by SEM. The micromorphology was compared with the macrofailure characteristics under uniaxial compression. The results show that the rubber concrete was still in the early stage of erosion. With the increase of immersion time at the age of 110 days, the P-wave velocity and compressive strength of concrete were generally on the rise. Furthermore, during the period of erosion, the mechanical properties of rubber concrete increased with the increase of rubber particle size and decreased with the increase of the content. Therefore, when the rubber particle size was 3–6 mm and the content was 5%, the antierosion performance was the best. This study has a certain guiding significance for the chloride corrosion resistance of rubber concrete.

1. Introduction

In recent years, the demand for automobile and other industries has led to the rapid development of rubber industry, resulting in the increasing number of waste rubber in China year by year [1]. Therefore, the rubber concrete prepared by mixing rubber particles into concrete provides a new way for us to deal with and apply waste rubber. As early as 1993, Professor Eldin of Oregon State University in the United States mixed rubber particles of waste tires into concrete and named it concrete with rubber aggregate [2]. Compared with the ordinary concrete, rubber concrete could effectively improve the micropore structure of concrete, so as to improve the durability and environmental erosion resistance of concrete [3, 4]. Rubber material had the characteristics of superelasticity, lightweight, and incompressibility; compared with sand and stone, it has smaller hardness and lower adhesion with other materials when mixed into concrete, but the impermeability of concrete was improved when mixed with rubber particles [5]. The compressive strength of concrete would be reduced by adding rubber particles into the concrete through experimental research, which has been found by Khatib and Bayomy [6]; Wang et al. [7] found that the compressive strength of concrete at low temperature would be improved by adding rubber particles into the concrete. According to the research of Sang et al. [8], the compressive strength and elastic modulus of concrete would be reduced, but the deformation energy and absorption performance would be improved, and the curvature ductility would be increased by 90%.

At present, concrete is used not only in the above-ground structure but also in the marine environment, so not only should the factors that affect the stability and durability of concrete be the temperature and humidity, but also the impact of chloride corrosion should be taken into account. Penetrating into concrete, some of the chloride ions dissolved in the solution of internal pores, while others reacted with the hydration products of cement in concrete to form chloride binding [9]. The chloride produced would have harmful effects on the mechanical properties and durability of concrete, which had been studied by many scholars at home and abroad. Da et al. [10] found that prolonging the
wet curing age or using magnesium sulfate cement could improve its ability to resist chloride diffusion and extended the service life of the structure. Based on the portable neutron generator, the concentration of chloride ion in various kinds of concrete by single instant gamma ray energy method has been measured by Naqvi et al. [11, 12], and its pollution in concrete has also been analyzed. The micro-morphology and pore structure characteristics of the composite admixture concrete after being eroded by chloride through the comparison of the macroperformance and microcharacteristics test has been analyzed by Li et al. [13]. Zhu et al. [14] found that the type of chloride ion had a great influence on the binding capacity of chloride ion in concrete and the pH value of pore solution. The higher the pH value of the pore solution was, the higher the solubility of the combined chloride released by Friedel's salt was. A number of scholars [15–17] found that chloride ion had a weakening effect on the mechanical and acoustic properties of concrete, and, with the increase of immersion time, the change trend of the two properties was similar, namely, increasing first and then decreasing. Yu et al. [18], combined with field test and artificial model, predicted the life of concrete in chloride environment. Zhou et al. [19] predicted the chloride diffusion coefficient of high-performance concrete in chloride environment. Yang and Jiang [20] studied the influence of random factors on the durability of structural concrete under chloride corrosion and analyzed the reliability of the service life of structural concrete. From the existing data, the research on chloride corrosion test of concrete was mainly in three aspects: first, through field test and micromodel to study the diffusion and transmission law of chloride ion in concrete and to predict and study its diffusion coefficient; second, to analyze the reliability of the service life of concrete in chloride environment; and third, to concrete coagulation under chloride corrosion study on the change of soil mechanical properties and durability. However, there were few studies on the internal damage and bearing capacity degradation of concrete mixed with rubber particles in chloride environment.

In this paper, ultrasonic testing, static mechanical property test, and microtest were used to study the erosion of rubber concrete in the NaCl solution with a concentration of 4% for a long time. The particle size, mixing amount, and soaking time of rubber particles were used to study the erosion of rubber concrete, and the relationship between the longitudinal wave velocity and compressive strength of rubber concrete test block after erosion was analyzed. This paper provides a useful reference for the application of rubber concrete in chloride environment. It is expected that the research results will contribute to the design of more durable lightweight aggregate concrete structure in chloride environment.

2. Materials and Methods

2.1. Materials and Mix Proportion. The basic material for the preparation of rubber concrete is P·C42.5 composite Portland cement manufactured by Bagongshan cement plant, Huainan City. Its fineness was 342 and standard consistency water was 25.9%. XRD analysis of cement and grade I fly ash is shown in Figures 1(a) and 1(b), respectively; tap water; the particle size of the standard Huaihe River medium sand less than 0.075 mm was not more than 20% and its fineness modulus was 2.8; 5–20 mm continuous graded crushed stone was used; HPWR standard high-performance Water reducing agent produced by Shaxi Qinfen building materials company was adopted, and the main component was polycarboxylic acid, with the proportion of 1.0%, solid content of 15.0%, water reduction rate of 25.0%. Qinshui rate of 42%, and air content of 2.5%. In the test, the rubber was processed from waste rubber tires, and the particle size of rubber was 20 mesh, 1–3 mm, and 3–6 mm, respectively.

The benchmark concrete mix ratio is cement: sand: stone: water: fly ash: water reducing agent = 310: 791: 1115: 150: 50: 3.4, and the specific mix is shown in Table 1. The water cement ratio was 0.41, the concrete density was 2420 kg/m³, and the design strength grade was C40. The rubber particles with the particle size of 20 mesh, 1–3 mm, and 3–6 mm were mixed into the concrete by 5%, 10%, 15%, and 20% of the mass of cementitious materials instead of sand.

2.2. Test Method. Prepare the materials according to the mix proportion of each group and put them into the mixer for mixing, pour out the cube mold of 70.7 mm × 70.7 mm × 70.7 mm, vibrate and compact to form, and remove the mold 24 hours later. Then, the test block was put out into the environment with temperature of (20 ± 2) °C and relative humidity of more than 95% for 28 days, curing in a glass box filled with 4% NaCl solution. 13 groups of concrete test blocks were immersed in NaCl solution for 10 d, 20 d, 30 d, 40 d, 50 d, 60 d, 70 d, 90 d, and 110 d.

NM-4B nonmetallic ultrasonic testing analyzer was used to measure the P-wave velocity of the test block. Before measurement, each test block needed to dry the surface solution. After the concrete was corroded by chloride, the internal structure could be generally divided into three areas: dense matrix area, crack pore area, and liquid filled area [21]. Due to the large difference of P-wave velocity among the three regions, the measured P-wave velocity should be the mean value of P-wave velocity in the three regions:

\[ V_p = \frac{1}{\frac{i_1}{v_1} + \frac{i_2}{v_2} + \frac{i_3}{v_3}}. \]

Among them, \( V_p \) was the measured longitudinal wave velocity; \( i_1, i_2, \) and \( i_3 \) represented the volume fraction of the dense matrix area, the crack pore area, and the liquid filled area, respectively; and \( v_1, v_2, \) and \( v_3 \) were the propagation velocity of ultrasound in the dense matrix area, the crack pore area, and the liquid filled area, respectively. The strength of rubber concrete test block was measured according to the standard for mechanical properties test of ordinary concrete (GBT 50081–2002). The loading method of constant speed displacement control was adopted, the displacement speed was 0.3 mm/min, monotonic loading until the compression failure of the test piece. The strength value measured by the nonstandard test piece could be multiplied by the size conversion coefficient of 0.9. The
The equipment used was CSS-YAW3000 electrohydraulic servo pressure tester. To further study the internal mechanism of rubber concrete corroded by chloride, the micromorphology of concrete was observed by scanning electron microscope (SEM), and the relationship between macrocharacteristics and microstructure was analyzed. The small pieces crushed by uniaxial compression test were used as the observation samples of SEM test. The interface between rubber concrete cement mortar and rubber particles was selected from the test samples. The size side length was less than or equal to 10 mm without water and pollutants. Before the test, the samples were dried at 60°C for 2 days, sprayed with a small amount of conductive colloid, and sprayed with gold.

3. Result and Discussion

3.1. Change in P-Wave. Under normal curing conditions and NaCl solution immersion, the P-wave velocity and moisture content of rubber concrete at the age of 110 d are shown in Table 2.

It can be seen from Table 2 that the P-wave velocity and moisture content of rubber concrete after standard curing for 110 d are greater than those after soaking in NaCl solution for 110 d; the maximum difference of wave velocity and moisture content of rubber concrete under standard curing and chloride corrosion is 0.893 km/s and 1.41%, respectively. With the increase of the content of rubber particles, the P-wave velocity and moisture content of rubber concrete decreased.
concrete decrease, and, with the increase of particle size, the P-wave velocity and moisture content decrease.

Under the immersion of NaCl solution, chloride ion intrudes into the inner part of rubber concrete test block and reacts with the product of cement hydration, resulting in concrete damage, internal microcrack expansion, water content increase, and P-wave velocity decrease. This phenomenon is called salt solution erosion damage, which belongs to elastic loss [22]. When rubber particles with the same particle size are added, the P-wave velocity decreases and the moisture content increases with the increase of rubber content, which indicates that the more rubber particles are added, the more concrete internal pores are, and the more concrete internal defects are. The reason is that the rubber particles are nonpolar and hydrophobic, which makes the surface of rubber particles easier to absorb air, so the adhesion between rubber particles and cement-based is low, and cracks are more likely to occur around rubber particles.

From Figure 2, it can be seen that, just in chloride environment, the wave velocity of various rubber concrete is a little different, and the wave velocity of ordinary concrete is larger, which shows that the internal defects of ordinary concrete are less and denser. When the content of rubber concrete is 5% and 10%, the wave velocity of rubber concrete with particle size of 3~6 mm is relatively large, so its interior is relatively dense.

From Figure 2, it can be seen that the wave velocity change trend of rubber concrete with different content is basically the same. As shown in Figure 2(c), taking the rubber concrete with particle size of 3~6 mm as an example, it is analyzed that the wave velocity of rubber concrete increases by 7.74%, 1.37%, 8.29%, and 8.31%, respectively, when it is immersed in NaCl solution for 20 days and when the content is 5%, 10%, 15%, and 20%; when it is immersed in concrete for 30 days, the wave velocity decreases and a “inflection point” appears. From the inflection point to the end of the test, the wave velocity of rubber concrete with the content of 5%, 10%, 15%, and 20% increases, the rising rate is 16.01%, 12.10%, 12.18%, and 11.29% respectively, and the overall rising rate is relatively slow. The reason is that the immersion time of the rubber concrete test block in NaCl solution is short, and the chloride ion has not yet reacted with the concrete interior. Moreover, the cement hydration reaction is greater than the chemical reaction corroded by chloride. The chemical equation of cement hydration in concrete is as follows:

\[
2(3\text{CaO} \cdot \text{SiO}_2) + 6\text{H}_2\text{O} = 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 3\text{H}_2\text{O} + 3\text{Ca(OH)}_2
\]

(2)

\[
2(3\text{CaO} \cdot \text{SiO}_2) + 4\text{H}_2\text{O} = 3\text{CaO} \cdot 2\text{SiO}_2 \cdot 2\text{H}_2\text{O} + \text{Ca(OH)}_2
\]

(3)

\[
3\text{CaO} \cdot \text{Al}_2\text{O}_3 + 6\text{H}_2\text{O} = 3\text{CaO} \cdot \text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}
\]

(4)

During hydration of cement, C₃S and C₃A also react with other components in cement to form hydrated reaction of ettringite (Ca₆Al₂(SO₄)₃(OH)₁₄⋅26H₂O), namely, three sulfur hydrated aluminum sulfate type AFt, single sulfur hydrated aluminum sulfate calcium AFm, calcium hydroxide CH, and calcium silicate C-S-H gel, and the microstructure
is shown in Figure 3(a). With the increase of time, the hydration reaction of cement is gradually sufficient, and the increase of aft content makes the internal cracks of rubber concrete decrease, and the wave velocity increases. With the increase of immersion time, the chloride ion erosion is greater than the cement hydration reaction, the inner part of rubber concrete is eroded, the cracks increase, and the wave velocity shows a temporary decline phenomenon. When the chloride ion gradually invades the inner part of the test block along the pores in the concrete and reacts with the hydration product of cement, calcium chloride hydrate $(\text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O})$, namely, Friedel’s salt, and Ca(OH)$_2$, to form soluble CaCl$_2$ and C$_3$A, and CaCl$_2$ reacts with C$_3$A to produce calcium chloroaluminate hydrate [23–26]. The micromorphology is shown in Figure 3(b), and the chemical equation is

$$\text{NaCl} + \text{Ca(OH)}_2 = \text{CaCl}_2 + 2\text{NaOH}$$  \hspace{0.5cm} (5)

$$2\text{NaCl} + \text{C}_3\text{A} + 15\text{H}_2\text{O} \rightarrow \text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$$  \hspace{0.5cm} (6)

$$\text{Ca}_2\text{S} \cdot 4\text{H}_2\text{O} + 2\text{NaOH}$$

$$\text{C}_3\text{A} + \text{CaCl}_2 + 10\text{H}_2\text{O} \rightarrow \text{C}_3\text{A} \cdot \text{CaCl}_2 \cdot 10\text{H}_2\text{O}$$  \hspace{0.5cm} (7)

Calcium chloride aluminate hydrate has a certain volume expansibility. This kind of chemical reaction hinders the expansion of microcracks caused by expansion stress in the...
concrete, thus reducing the internal defects of the concrete and increasing the wave velocity. With the increase of time, the content of chloride ion increases, the content of calcium chloride aluminate hydrate increases gradually, the internal microcracks of concrete continue to narrow, and the wave velocity slowly increases.

3.2. Compressive Strength. See Table 3 for the compressive strength of rubber concrete in different conditions and times.

It can be seen from Table 3 that the compressive strength of rubber concrete increases after immersion in NaCl solution for 60 d while the compressive strength of rubber concrete after normal curing for 60 d is less than that after immersion in NaCl solution. The compressive strength of rubber concrete is still increasing after soaking in NaCl solution for 110 d, but its compressive strength is smaller than that of rubber concrete under normal curing conditions. When corroded by chloride for 110 d, the compressive strength of rubber concrete with particle size of 3–6 mm and 5% content is greater than that of ordinary concrete, and the increase of rubber concrete strength is greater than that of ordinary concrete, which shows that the rubber concrete with 3–6 mm and 5% content can improve the resistance to chloride penetration. With the increase of time, the compressive strength of rubber concrete increases both in NaCl solution and under normal curing conditions. Under normal curing conditions, the growth rate of compressive strength is relatively large from 60 d to 110 d. For example, the growth rate of compressive strength of rubber concrete with particle size of 20 mesh fluctuates greatly. When the content is 5%, 10%, 15%, and 20%, the growth rates are 17.05%, 30.65%, 32.53%, and 22.59%, respectively. It can be seen that the growth rate of compressive strength of rubber concrete with particle size of 20 mesh and 10% ~ 15% is relatively large. However, the compressive strength of rubber concrete mostly soaked in NaCl solution increased greatly from 0 d to 60 d and decreased after 60 days. For example, the growth rate of rubber concrete with particle size of 1–3 mm is 1.45%, 0.27%, 5.47%, and 2.80%, respectively, when the content of rubber concrete is 5%, 10%, 15%, and 20%.

Mechanism analysis: the change of macromechanical properties of concrete corroded by chloride ion can be divided into two stages [22]: the first stage is chemical erosion. When the concrete is in water, it mainly absorbs water by capillary tension. In chloride environment, except for capillary tension, there is a solution concentration difference between the inside and outside of the test block, resulting in osmotic pressure. Chloride ion diffuses from the concrete surface to the capillary. In addition, it reacts with the hydration products of cement in the pores to form soluble CaCl₂ crystal and hydrated calcium chloroaluminate, which is several times the original volume. The expansion materials gradually accumulate to fill the internal voids of concrete so that the compressive strength of rubber concrete is improved. In the second stage, the concrete corrosion cracking, chloride ions, and concrete continue to react when the expansion materials continue to form until reaching a threshold value, and the cracks in the concrete will further expand, and there will be new cracks due to extrusion; the bearing capacity of the concrete will decline in this process.

The results show that (1) with the increase of immersion time in NaCl solution, the negative damage (strength increase) occurs first and then the damage (strength decrease) occurs. In the test, the compressive strength of rubber concrete is still increasing after soaking in NaCl solution for 110 d, which indicates that rubber concrete is still in the stage of negative damage. Due to the filling effect of reaction products in rubber concrete, the pores are reduced; when the concrete is compressed, the compressive strength is increased due to the inner compactness of the concrete, resulting in stronger constraints. (2) P·C42.5 composite Portland cement is used in the test carrying the characteristics of high early and later strength, good water retention, and low hydration heat, and the concrete is not easy to crack. Therefore, the strength of rubber concrete increases more in 110 d of normal curing. (3) The compressive strength of rubber concrete increases first and then decreases due to chloride corrosion. The strength of rubber concrete under normal curing is less than that under chloride corrosion when it is soaked for 60 d, and the strength of rubber concrete under normal curing is greater than that under chloride corrosion when it is soaked for 110 d, which shows
that the hydrated calcium aluminate expansion material has filled the inner pores of rubber concrete and is expanding continuously, and the inner part of concrete is squeezed due to the expansion of hydrated calcium aluminate. As a result, the strength of rubber concrete tends to decrease.

According to the test results of ultrasonic testing and static mechanical properties, it can be found that the results of tests are similar. The wave velocity increased first, then decreased, and finally increased. The compressive strength increased after being immersed in chloride for 110 d. The reason is that the cement hydration reaction only occurs in the rubber concrete under normal curing conditions while, in the chloride environment, the rubber concrete not only has the cement hydration reaction, but also is corroded by chloride ion. When the rubber concrete is soaked in NaCl solution, only cement hydration occurs in the initial stage of the rubber concrete, and the chloride ion has not penetrated into the concrete, so the wave velocity of the rubber concrete rises. With the increase of immersion time, chloride ions intrude into the inner part of rubber concrete, which leads to the loss of concrete. Subsequently, the chemical reaction with the hydration product of cement causes the cracks in rubber concrete to be filled by the hydrated calcium chloroaluminate produced by the reaction, which leads to the negative loss state; that is, the wave velocity increases, and the compressive strength increases. It can be predicted that with the increase of immersion time, the performance of rubber concrete will weaken.

### 3.3. Microstructure Test Results

As shown in Figure 4, there are the SEM images of various rubber concrete under natural curing conditions and soaking in NaCl solution for 110 d. It can be seen from Figures 4(a) and 4(b) that a large number of fibrous crystals appear in the process of ordinary concrete eroded by chloride ions, which are distributed in the concrete and filled in the cracks of concrete. However, it is found in (a) and (b) that the cracks of the corroded rubber concrete are wider than those of the standard curing rubber concrete, indicating that the volume expansion of Friedel’s salt fills the internal cracks of the concrete and reduces the defects, but, with the increase of time, the volume of Friedel’s salt increases gradually, which makes the cracks larger and larger but destroys the internal tightness of concrete and reduces the bearing capacity of concrete.

From Figures 4(c), 4(e), and 4(g), it can be seen that most of the corrosion products appear in the cement state around the cement base, and as the diameter of the rubber increases, the packages are gradually tight, and the corrosion products and cement base are bonded together, which makes the internal cracks in the rubber concrete filled. Needle-like, rod-shaped, and flocculent Friedel’s salt crystals and fibrous crystals are randomly distributed in the cement-based materials and are alternately bonded together. NaCl crystals are not found in the microscopic images of various rubber concrete, which indicates that during the process of chloride ion invading the rubber concrete for 110 d, the cement hydration products inside the test block will solidify chloride ion, one part of which will be absorbed on the surface of cement base in the way of physical solidification, the other part of which will generate Friedel’s salt in the form of chemical solidification, filling the internal pores of rubber concrete, making the concrete coagulate. The internal defects of the soil are reduced, which is in accordance with the above results.

According to Figures 4(d), 4(f), and 4(h), columnar crystals are randomly arranged in the cracks between the rubber and the cement-based on the fracture surface of the concrete mixed with 20 mesh rubber. The cement-based is thick and flaky, and the hydration products are distributed on the surface of the cement-based to wrap it. There are columnar crystals in the cracks between the rubber and the cement-based on the fracture surface of the concrete mixed with 1–3 mm rubber, but the number is obviously reduced, the thick sheet cement-based disappears and separates into thin sheets, the hydration products tightly wrap them, and the two are bonded together. Columnar crystal was not found in the crack between the rubber and the cement-based on the fracture surface of the concrete mixed with 3–6 mm rubber. The cement-based showed lamellar tearing. The
hydration product is fibrous crystal interlaced in the middle of the lamellar, which makes the inner bond. It can be seen that, with the increase of rubber particle size, the coarser the surface of rubber particle is, the closer the bond with cement base is and the smaller the crack is, so the larger the rubber particle size is, the better the bearing capacity of rubber concrete is.

Figures 4(a) and 4(b) show the microimages of ordinary concrete corroded by chloride and cured by standard, respectively; Figures 4(c) and 4(d) show the microimages of 20...
mesh rubber concrete corroded by chloride and cured by standard, respectively; Figures 4(e) and 4(f), respectively, show the microimages of 1–3 mm rubber concrete corroded by chloride and cured by standard; and Figures 4(g) and 4(h) show the microimages of 3–6 mm rubber concrete corroded by chloride and cured by standard curing microimage, respectively.

**4. Conclusions**

The macromechanical properties of rubber concrete corroded by chloride are studied, and the microtest results are analyzed; the following conclusions can be made:

1. The wave velocity (moisture content) of rubber concrete under normal curing was higher than that under chloride environment, the maximum difference of wave velocity was 0.893 km/s, and the maximum difference of water content was 1.41%. It was observed that the wave velocity of rubber concrete soaked in NaCl solution for different times was basically the same. When the content of rubber particles was fixed, the larger the rubber particle size was, the larger the wave velocity was; and when the particle size was fixed, the smaller the rubber content was, the larger the wave velocity was. Therefore, the rubber concrete with the particle size of 3-6 mm and the content of 5% had the highest wave velocity, so the inner part was more dense. Compared with ordinary concrete, the wave velocity of rubber concrete with 5% content was higher than that of ordinary concrete, which indicated that rubber concrete with small content improved the resistance to chloride ion erosion.

2. When the rubber concrete was corroded by chloride ion for 110 d, the compressive strength increased, and the larger the particle size of the rubber concrete was, the larger the compressive strength was, that is, the maximum the compressive strength of rubber concrete with particle size of 3–6 mm and content of 5%. The compressive strength of rubber concrete soaked in NaCl solution for 110 d was less than that of normal curing for 110 d, which indicated that the internal part of the rubber concrete has reached the damage stage.

3. By analyzing the cracks between the rubber and cement-based on the fracture surface of rubber concrete, it can be seen that, with the increase of the particle size of rubber, the coarser the particle surface was, and the salt corrosion products in the pores wrapped the internal hydration products to be closer, and there were less internal defects in rubber concrete, leading to the better mechanical properties of rubber concrete as well as the higher wave speed and compressive strength in terms of macroscopic performance, which is more consistent with the actual macroscopic test results.

**Data Availability**

The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

**Conflicts of Interest**

The authors declare no conflicts of interest.

**Authors’ Contributions**

Tingya Wang and Xin Huang performed the experiments; Ruonan Zhu analyzed the test data and wrote the manuscript; and Jianyong Pang conceived the experiment and provided the guidance and suggestion.

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