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Study on Water Absorption and Strength of Cement Base Material under Permeable Crystallization Reaction

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The purpose of this paper was to analyze water absorption and strength of the cement base material under permeable crystallization reaction. The method adopted was selecting common mortar as a main cement base material to study the strength and water absorption of the cement base material after the permeable crystallization reaction. The results indicated that CTAB can effectively reduce the water absorption rate of the mortar, and when the dosage of surfactants was increased gradually, the water absorption rate of the mortar was reduced slowly. Calcium ion additive can play a certain role in porous fractures of the cement base material. In conclusion, active materials and the additives can gradually permeate into the cement base material under the permeable crystallization reaction, so as to inhibite the generation of concrete fractures and pores.

1. Introduction

The cement base material belongs to manmade stone materials and may generate the problem of pore defects or fractures due to long term exposure in the application period of constructional engineering, and safety loopholes are easily caused. Portland cement base material is a common building material, and plays an important role in the aspects of civil buildings, aerospace engineering, etc. The fracture of the cement base material is a common phenomenon, and may be caused by influence factors such as structural external force, materials and construction environment, etc. When fractures appear in the cement base material concrete, a leakage phenomenon easily occurs, thereby generating an influence on material performances.

Figure 1: Porous fracture of cement base material

Figure 1 shows porous fracture of cement base material. A cement base permeable crystallization waterproof material has better waterproof effect and can enhance the permeability of the concrete structure. This paper mainly selects the common mortar to replace the cement base material and explores the water absorption and the strength of the cement base material under the permeable crystallization reaction.

2. Literature review

Since the introduction of cement-based permeable crystalline waterproof material from foreign countries after the reform and opening up in1980s, China has not fully entered the market for various reasons, such as high price, technical secrecy and so on. After many efforts in the middle of 1990s, the Oasis Marine Chemical

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Company of the United States has introduced Saipas to Shanghai subway being constructed for waterproof, and the effect is remarkable. Finally, the relevant technologies are introduced and core master-batch invested and built the plants in Beijing, Shanghai, Urumqi, Kunshan and other places in China, and then promoted and used. But the key technology and core master-batch are still confidential to China. With the emergence of various kinds of cement-based permeable and crystalline waterproof materials in the market, the majority of the scientists and technicians in China conducted alternative research on the active components, and formed their own characteristic technology, which achieved certain use effect and economic benefit. Now, these products are applied in various industrial and civil buildings in China and are well received. Ghashghaei and Hassani, through the research and development of cement-based osmotic crystalline waterproof material, improved the waterproof effect of the continuous investigation of technology and science. More importantly, the foreign technology monopoly is broken and our own products are created (Ghashghaei and Hassani, 2016).

The main active material of the cement-based permeable crystalline waterproof coating developed by Hayakawa and Matsuoka is water-soluble silicate, which is usually alkali metal silicate. The sodium silicate is used to modify cement-based materials (Hayakawa and Matsuoka, 2016). The results show that sodium silicate can improve the impermeability of cement-based materials, and the best quality content is 1.5-2%. The mechanism research shows that sodium silicate promotes the formation of calcium silicate crystals and plugs pores, thus improving the impermeability of cement-based materials. Isikver studied the effect of adding catalyst and auxiliary agent permeable crystalline high effective protectant on the durability of concrete (Isikver, 2017), which is based on alkali metal silicate solution and inert material as base material. The results show that the impermeability of concrete, such as carbonation resistance, chloride penetration resistance and frost resistance, is improved obviously after immersion or brushing.

In addition, anionic, complex agents and other chemicals are used as osmotic crystalline active substances. Jimada et al. studied most anions and complex agents as citric acid, tartaric acid or their soluble sodium salt (Jimada et al., 2017). The reaction of sodium salt will produce NaOH by-products and increase the risk of alkali silica reaction. Stempkowska and so on, through experiments, studied the repair effect of the homemade cement-based osmotic crystalline material made up of active anions to the pores and cracks of concrete (Stempkowska et al., 2017). The results show that after repair, the compressive strength and impermeability are improved, and the self-waterproof effect on concrete members is enhanced. Wang et al. studied the effect of the composite osmotic crystallization on the self-healing properties, strength, setting time and stability of concrete cracks (Wang et al., 2017), which are mainly composed of the complex agent. The results show that the self-healing ability and impermeability of the concrete specimens are obviously improved.

With regard to the study of the mechanism of osmotic crystallization, Wright used scanning electron microscopy (SEM) and X-ray diffractometer (XRD) to study the chemical effects of active substances on concrete, the formation of crystallization products and the penetration depth of active ions (Wright, 2017). The results show that the active substances can infiltrate into the concrete micro cracks well, and the penetration depth deepens with the increase of age. The positions of the main diffraction peaks in cement paste mixed with permeable crystalline materials did not change, but the relative intensity of the peaks was changed. The effect of permeable crystalline material on the permeability coefficient of plastic concrete was studied by Zander and so on. The results show that the interfacial transition zone of plastic concrete with permeable crystalline material is dense, the proportion of small damage holes increases, and the proportion of multiple damage holes decreases (Zander et al., 2016). Infiltrating crystalline materials can help reducing the permeability coefficient and improving the impermeability of concrete.

To sum up, the above research work mainly studies the combination of soluble silicate, carbonate, calcium chloride and sodium fluoride, tartaric acid, citric acid and other complexagents of osmotic crystalline active substances. These active substances react with $Ca(OH)_2$ in concrete to generate C-S-H gels to block pores and cracks, while producing the by-product NaOH or other soluble salts, which increases the risk of alkali silica reaction. Therefore, based on the above research status, the water absorption and strength of cement-based materials by osmotic crystallization is systematically studied. In the face of the complex cement hydration system, the thermodynamic and kinetic mechanism of the osmotic crystallization reaction is not thorough enough. It is basically in the experiential qualitative analysis, and there is no systematic and in-depth theory research, thus hindering its scientific development and application.

3. Methods

3.1 Experimental Materials

In the experiment, common cement mortar was used as the cement base material to study various performances of the mortar after processing of the permeable crystallization waterproof material. In the experiment, when there was no particular note, the specification of the mortar was that a cement-sand ratio was 1:3, and a water-cement ratio was 0.55, and the mortar was molded into prismatic test blocks of 4×4×16 cm by adopting a tri-mould, and the preparing method thereof was: weighting quantitative water and cement and stirring them at a slow speed in a cement mortar stirrer for 30s, quantitative sand was added, stirring was continuously performed at a slow speed for 30s, a fast stirring manner was adopted to continuously stir for 150s, and after being loaded into a standard mould, the mortar was cured for 24h after jolt ramming and demoulded under the conditions of 20±3 oC，RH=95%. Table 1 raw materials and reagents. Table 2 shows concrete proportions.

Table 1: Raw materials and reagents

Name	Specification	Manufacturer
Cement	Common Portland Cement 42.5 MPA	Tianye cement plant, Shihezi City
Water	Tap water	Ownership
Sand	Common River sand, particle size < 2.36 mm	Outsourcing
Ban-80	Analysis Pure	Tianjin Sheng O Chemical Reagent Co. Ltd.
Calcium formate 96 %	Analysis Pure	Aladdin Reagent Company
Sodium silicate, ammonium carbonate, AMMONIUM PHOSPHATE	Analysis Pure	Institute of Light Complex Fine Chemical Industry, Tianjin
Op-10 emulsifier	Analysis Pure	Institute of Light Complex Fine Chemical Industry, Tianjin

Table 2: Concrete proportions

Materials	Sand（kg/m3）	Cement（kg/m^3）	Water（kg/m^3）	Pebbles（kg/m^3）	Water Gel Ratio	Sand Rate (%)
Cement concrete	6.55	3.50	1.75	12.70	0.5	52

3.2 Painting Processing Method for Mortar

The dosage of each mortar TEOS was 10ml, according to the exploration under different conditions in the experiment, the surfactants and the calcium ion additive were added into a solution, the surfactants were dissolved in absolute ethyl alcohol (50% of the dosage of TEOS) under a magnetic stirring condition, and then the TEOS was added, and the solution was continuously stirred to be uniform and was painted on the mortar surface at two steps. The calcium ion additive was dissolved with water (50% of the dosage of TEOS) and then painted, and the TEOS was painted after the surface was dried. In the exploration experiment with other influencing factors, according to a specific experimental design, if there is no particular note, twice paintings were performed. After the active substances were screened, the TEOS was mainly selected as the main component of the cement base permeable crystallization waterproof material. The mortar of every 10mL was painted on the surface at two steps, and influence on freezing and melting resistance and immersion resistance of the mortar was inspected, and meanwhile, the mortar performances in different ages after the painting were also studied.

3.3 Test Method of Mortar Water Absorption

The mortar water absorption is the most intuitive representation for experimentally inspecting the waterproof effect of the cement base permeable crystallization waterproof material through experiment, and is also the performance that gains the most attention in actual waterproof engineering application. This experiment screened the permeable crystallization active substances with a change of the water absorption rate, and the smaller the water absorption rate was, the smaller the water content permeated into the mortar relative to the blank, and the better the waterproof effect was.
The specific test method for the water absorption rate was as follows:
(1) the curing of the painted mortar that was cured to the specified age was terminated, the mortar was placed in an oven of 55℃ for drying for 5h, and then cooled to the room temperature and weighing.
(2) the mortar was transversely placed in a plastic box, water was added till one third of the mortar was immersed in water, and scribing was performed to mark the height of the water surface, the water absorption of the test block after 0.25, 0.5, 1, 2, 4, 8, 12, 24 and 48 hours was tested respectively, the water on the surface was wiped out before weighing, placing back into the water tank after weighing, and well covering the

lid. The water was supplemented in the tank anytime in the test process to ensure that the water level was at the marked scale.
(3) The water absorption rate was the percentage of the water absorptions at different moments to the total water absorption amount of the blank test block of 48h.

3.4 Test Method for Mortar Strength

The mortar strength was used to represent the change of the mortar strength after the cement base material was painted, and indirectly indicated that the surface layer mortar was more compact and waterproof after printing, and was also improved in strength. The strength test referred to BS EN 196-1: 2005, firstly, the mortar test pieces of 4×4×16 cm were subjected to fracture resistance strength test, each test piece was fractured into two parts, one was subjected to the pressure resistance test, every three test pieces were taken as a group for determination, and the average value of the values of the three test pieces were taken as the strength of the test piece. When a difference value between one of the maximum or minimum of the three test values and a median exceeded 15% of the median, it was abandoned, and the average value of the remaining two values was taken as the strength value. If the difference value between the two test values and the median exceeded 15% of the median, then the experimental result of the test piece was ineffective.

4. Results and analysis

4.1 Influence of Surface Active Material on the Mortar Strength and Water Absorption

The surface tension of the permeable crystallization active substance solution was reduced, and the active substance was enabled to faster and more thoroughly permeate into the pores and fractures of the cement base material, so that the material's waterproof effect was improved and the waterproof material was enabled to be absorbed much faster to reduce loss, and to be more effectively used. Surfactants were divided into a nonionic type, a cationic type and an anionic type. The property of the ampholytic surfactants was similar to that of the anionic surfactants under the alkali condition and was thus not adopted. In addition, TEA was also compared in the experiment as a common early strength agent for the concrete. The OP-10 emulsifier and span-80 were selected as the nonionic surfactant, CTAB was selected as the cationic surfactant and SDS was selected as the anionic surfactant.
The mortar strength was not obviously changed after surfactants were added, and was basically close to the reference, indicating that the addition of the surfactants had no influence on the cement hydration reaction in the mortar. In addition, the permeable crystallization waterproof material only changed the compactness of the mortar surface layer, while the strength was closely related to the mortar integral porosity, therefore the mortar integral strength was not changed obviously. The addition of TEA improved the mortar fracture resistance by 10%, and the reason should be that the TEA was permeated into the pores and the fractures to facilitate the continuous hydration of the unhydrated cement in aggregate's interface, the binding strength between the aggregate and a matrix was enhanced, and the mortar fracture resistance was improved. Figure 2 shows Influence of surfactants on the strength of mortar.

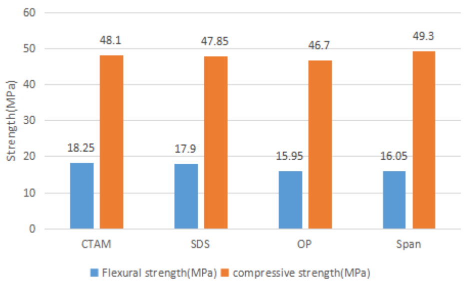

Figure 2: Influence of surfactants on the strength of mortar

After the surfactants were added, the mortar water absorption rate was reduced to different extents, wherein the reduction of the cationic surfactant was the most obvious, the water absorption rate was merely 13.5% and was reduced for 50% relative to the reference, the improvement effects of the nonionic surfactants, expect for tween-20, on the water absorption rate were close, and the effect of the anionic surfactants with the SDS as the representative was very close to that of the nonionic surfactants. It was indicated that the addition of the surfactants improved the repair effect of TEOS for the pores and fractures of the cement base material, such that the mortar surface layer was more compact and waterproof which was mainly resulted from reduction of a surface tension of the paint after the surfactants were doped, and the surfactants can faster and more deeply permeate into the mortar surface layer to react with calcium ions or calcium hydroxide in the pores to generate sediment crystallized substances to block pore passages.

4.2 Influence of calcium ion additive on the water absorption rate and strength of cement base material

The calcium ion additive was one of factors explored specific to the properties of the mortar and a mechanism of the permeable crystallization reaction. The main gel substance cement of the cement base cement also generated calcium hydroxide of about 20% during the hydration reaction, in the experiment, the insufficient soluble calcium content of the surface layer was considered, meanwhile, the reaction efficiency was also improved, a water solution of the calcium ion additive was painted on the mortar surface layer before painting of the TEOS, then the TEOS solution was painted after the surface was dried, for each mortar block, the TEOS dosage was 10mL, the water dosage was 5mL, and water instead of the calcium ion additive was added into the reference group.
In order to improve the reaction efficiency of the TEOS and the APTES, EDTA calcium disodium and calcium formate were selected in the experiment as the calcium ion additive since it had good water solubility and friendliness to the cement base material. Meanwhile, the calcium formate was often used as an early strength agent to improve the easy strength of the concrete material. In the experiment, it not only facilitates the hydration process of tricalcium silicate, but also provides sufficient calcium source for ethyl silicate to repair the material pores.
After TEOS and APTES were painted, the mortar water absorption rate was reduced by about 60% relative to the blank, which indicated that the pores and the fractures of the mortar were blocked to some extent, this was because calcium silicate hydrogel generated by the reaction between the silica sol obtained by hydrolysis of the TEOS in the pores and calcium hydroxide was deposited in the fractures to make the mortar more compact. After the APTES was painted, active silanol groups would be generated on the surface and the inner surface layer of the mortar by hydrolysis, wherein one part of the silanol groups was coupled to hydroxide radicals on the surface of the cement mortar, and meanwhile coupling polymerization per se also occurred to form a net structure. Due to the hydrophobic performance of such layer of net structure, a certain waterproof effect was also achieved, and meanwhile, part of the ports would be filled to compact the mortar. From the drawing, it can be seen that after the APTES was painted, the water absorption rate was lower than that after the TEOS was painted, and this was because the hydrophobic film on the mortar surface layer had good waterproof effect, while the TEOS only formed some calcium silicate hydrogel on the surface layer. In addition, the water absorption rate of the mortar if the calcium ion additive was painted at first was reduced by about 80% relative to the blank, which possibly because that the calcium ion content on the surface layer of the mortar was increased to make its reaction with the TEOS hydrolysate more sufficient, and more calcium silicate hydrogel was generated. Figure 3 shows Effect of calcium ion additive on water absorption of Mortar.

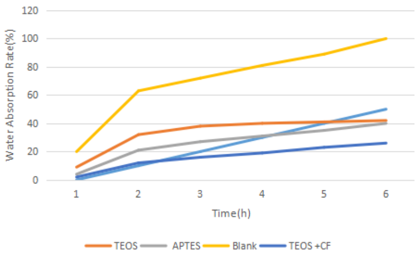

Figure 3: Effect of calcium ion additive on water absorption of Mortar

After the mortar was painted with the TEOS and the APTES, the fracture resistance and pressure resistance were both improved to some extent because the calcium silicate hydrogel and the net structure formed by coupling of massive silanol groups were generated on the mortar surface layer to fill the pores and fractures of the surface layer. The reason why the strength after the calcium ions were added was not obvious was mainly that only the mortar surface layer became compact while the internal structure was not obviously changed. In addition, the TEOS only blocked the pore passages of the mortar, and has no obvious blockage effect on large pores closely related to the strengths, which can be verified by aperture distribution in mercury intrusion analysis. Figure 4 shows Effect of calcium ion additive on mortar strength.

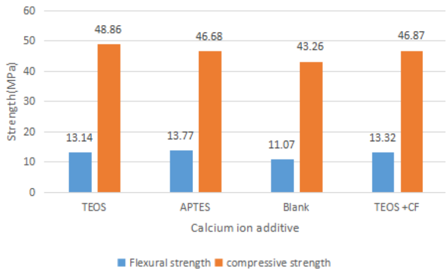

Figure 4: Effect of calcium ion additive on mortar strength

5. Conclusion

The active substances reacted with the cement hydration product calcium hydroxide to generate indissolvable sediment to block the fractures and pores, by taking the TEOS as an example, the TEOS was permeated into the cement base material and was hydrolyzed to form the active silica sol which then reacted with the cement hydration product Ca(OH)2 or nomadic Ca2+ ions to generate the calcium silicate hydrogel to block the pores and the fractures, such that the material achieved the compact and waterproof effects. The TEOS as the optimal active substance of this experiment can reduce the water absorption of the mortar for about 70%, and also can improve the mortar's strength to some extent. For the active substances adopted in this experiment, painting was the best introduction manner. In the exploration for the single condition of the TEOS waterproof effect, the waterproof effect was the best when the optimal conditions were that the concentration was 50%, the dosage was 400mL/m2, and the dosage of the surfactant CTAB was 1% of the mass of the TEOS. The calcium ion additive calcium formate can improve the calcium ion content on the surface layer of the mortar to promote the crystallization reaction and reduce the mortar water absorption rate.

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