

Study on the compensating calcium ion method for existing concrete based on crystal infiltration waterproof materials

Yang Dishan¹, Yan Tongyu¹, Lin Yubin¹, Li Jiyu¹, Ruan Xiaofei¹, Zhou Hong², Shi Jianguang²

¹National Grid Fujian Electric Power Co., Ltd. Institute of Economics and Technology, Fuzhou 350012, China

²School of Architecture and Civil Engineering, Xiamen University, Fujian 361005, China

Abstract: The quality of the existing concrete surface in its repairing and strengthening is the key factor affecting the together working performance. The effective method to solve this problem is to use permeable crystal waterproof material to strengthen the existing concrete surface. In view of the existing old concrete which lacks free Ca^{2+} in the interior, the method of compensating calcium ion strengthening is proposed based on the action mechanism of permeable crystalline waterproof material. On the basis of DPS, calcium ion compensating agent $\text{Ca}(\text{OH})_2$, Na_2SiO_3 (sodium silicate) and Na_2CO_3 (potassium carbonate) solutes are added to prepare composite reinforcement solution for impregnation strengthening of concrete. Scanning electron microscopy (SEM) was used to observe the microstructure of the concrete before and after strengthening. It showed that after the entry of silicate ions, C-S-H colloid was formed by reaction with $\text{Ca}(\text{OH})_2$, and C-S-H gel blocked some pores, which made the inner microstructure more compact. The results of compressive strength before and after concrete strengthening show that the strengthening effect of calcium ion compensation method for low-strength concrete is better than that of permeable crystallization material strengthening method. The strength of C5 and C15 grade concrete is increased by 36.1% and 6% respectively, and the surface strength of 13.7 MPa concrete is increased by 16.7%.

1 Introduction

Existing concrete is required to have a certain strength in the repair and reinforcement of the existing concrete base. For example, the various reinforcement methods in the GB 50367-2013 <Code for Design of Reinforcement of Concrete Structures> require that the positive tensile bonding strength of the substrate surface of the concrete is not less than 1.5MPa and the strength is above C10 or C20 when the concrete is reinforced. JGJ/T259-2012 <Technical Specification for Durability Repair and Protection of Concrete Structures> divides the repair construction into four processes: base treatment, interface treatment, repair treatment, and surface treatment. Base treatment and interface treatment are important measures to ensure the bonding effect between the base concrete and the repair material. The base treatment is mainly to solve the existing concrete foundation hollowing, cracking, loosening, steel corrosion and other problems that affect the repair treatment and durability in the later use, and create good base conditions for the restoration. Whether it is the repair or reinforcement of the concrete structure, the quality of the existing concrete base and the treatment method of the bonding surface are the key factors that affect the bonding of the existing concrete and the repair or reinforcement materials to form a common force^[1]. In order to ensure the quality of the existing concrete base, surface treatment methods such as flower hammers,

grinders or high-pressure water jets are required to remove loose aggregates, gravel, scum, leaked cracks and dirt or damaged concrete, surface chiseling, surface cleaning, etc^[2]. The surface roughness after base treatment directly affects the bond strength of existing concrete and repair and reinforcement materials^[3]. The more the existing concrete base layer is removed and chipped, the more difficult the construction, the greater the impact on the existing concrete, and the more environmental problems such as dust. Especially for the concrete components with serious carbonization and corrosion of the base layer and the bare leakage of external high-altitude steel bars, the difficulty of the base layer treatment is higher. Taking base reinforcement treatment is an effective technical way to solve these problems. After the surface is cleaned, the existing concrete base can be directly reinforced, so as to improve the quality and strength of the concrete at the base, and create better conditions for subsequent interface treatment, repair or reinforcement. In order to explore the measures of this technical approach, on the basis of summarizing the research results of concrete infiltration crystalline material reinforcement, the method of compensating calcium ion reinforcement was researched and developed.

* Corresponding author: 550818454@qq.com

2 Existing concrete base layer infiltration crystalline material reinforcement method

Permeable crystalline materials are divided into water-based infiltrated crystalline materials and cement-based infiltrated crystalline materials. The water-based osmotic crystallization material is the most famous DPS (Deep Penetrating Sealer) permanent condensate, and it is a kind of chemical permeable waterproof agent. The building materials industry of our country also issued the JCT 1018-2006 <water-based permeable inorganic waterproof agent>. Jiang Qian^[4] applied water-based permeable crystalline material (DPS) on the surface of concrete with different strength grades, the compressive strength and chloride ion penetration resistance of concrete were significantly improved, and the improvement degree decreased with the increase of concrete strength grade. Gong Yunli^[5] used three kinds of water-based osmotic crystallization (seal-100, karst, DPS) materials to do the test of improving the strength of concrete. The three kinds of waterproof agents showed slightly different effect of improving the compressive strength for different water cement ratio. When the water cement ratio was 0.5, the improvement effect was more obvious than that when the water cement ratio was 0.4. Weng^[6] studied the effect of DPS on the surface pore structure, mechanical properties and durability of cement-based composites. Concrete specimens with different water cement ratios ($W/C = 0.35, 0.45, 0.55$) were treated with different amounts of DPS. The results show that DPS improves the compressive strength and chloride ion resistance of concrete, and the penetration depth of DPS is about 2 cm. Zhang Yongchun^[7] sprayed concrete with permeable crystalline material for 72h. The results showed that the maximum penetration depth was 195mm, the maximum penetration depth of side wall was 30mm, and the surface strength and hardness were significantly improved. Zong Shizhen^[8] used the water-based permeable crystalline material in the protection of ancient relics, and found that DPS has strong infiltration ability on the surface of dense (gray pottery) and porous (red pottery). After the treatment test of 10% phosphoric acid and 10% sulphuric acid, the surface has no change, indicating that DPS has strong resistance to chemical corrosion and air invasion.

Cementitious permeable crystalline waterproof material (CCCW) is a new type of waterproof material based on Portland cement, quartz sand and other basic materials mixed with active chemicals. The general use method is to mix the cement-based permeable crystalline material with water and then brush or spray it on the concrete surface. Cement based permeable crystalline materials have developed from VANDEX in Germany to XYPEX in Canada, VANDEX in Switzerland, FORMDEX in Germany and PENETRON in the United States. China has also issued standards for cementitious permeable crystalline materials, such as GB 18445-2001 <cementitious permeable crystalline waterproof materials> .

Chen Guangyao^[9] proposed the crystallization mechanism of cementitious osmotic crystallization

materials: precipitation reaction crystallization mechanism, complex precipitation reaction crystallization mechanism. The active chemical substances in the permeable crystalline materials react with the free alkali ions dissolved in the capillary pore solution to form crystals insoluble in water, which can effectively seal the pores and micro cracks in the concrete, thus playing the role of water resistance and waterproof. The active chemical substances entering into the concrete react with Ca^{2+} to form a water-soluble but unstable calcium complex. The calcium complex dissolved in water and diffused with the water in the coagulation. When the calcium complex met the highly active unhydrated cement gel, the active chemicals were replaced by silicates and aluminates, which had more stable chemical properties. The precipitation reaction took place. $Ca(OH)_2$ was then transformed into a certain strength crystal, filling the micro cracks and capillary pores in the concrete. So as to enhance the concrete strength and waterproof effect.

Xu Minggen^[10] applied cementitious permeable crystalline materials to xiazixi tunnel of Jiaoliu line, SEM combined with energy spectrum analysis shows that the penetration depth increases with the increase of age. The scanning electron microscope shows that the penetration depth of the material in the mortar can reach 29.1 mm after 28 days of curing in the standard state after brushing. Cheng Wei^[11] according to the phenomenon that the concrete surface is uneven and loose, the tunnel wall is wet in a large area, and the local external pressure seepage is serious in the transition section of the downstream impedance surge shaft of No. 3 diversion tunnel of Tianshengqiao II hydropower station, After consolidation grouting, the pores are coated with XYPEX plugging agent. After treatment, the loose pitted surface, pores and local honeycomb are solved. The surface is smooth, the water seepage phenomenon disappears, the surface is gradually dry, the handle is hard, and the strength is improved.

Cement based permeable crystalline materials have their limitations. Now, different scholars do not have the same views on how deep the penetration depth of CCCW can be. Xue Shaozu^[12] observed by scanning electron microscope that the penetration depth of active substances in the base course is about 5cm within 28 days. However, some researchers have shown that the penetration depth of the substance can reach 1.2m, and the active ingredients will continue to penetrate with the passage of time^[13].

These studies and engineering practices have proved that both water-based permeable crystalline materials and cement-based permeable crystalline materials can improve the compressive strength and durability of concrete on the basis of increasing the waterproof capacity of concrete base. In order to improve the reinforcing effect of water-based permeable crystalline material DPS, the method of compensating calcium ion was formed by adding calcium ion compensating agent.

3 Research on strengthening technology of existing concrete base with permeable crystalline material

3.1 selection of reinforcement materials and preparation of reinforcement solution

The reinforcement material of permeable crystalline material is made of Keluo permanent condensate DPS produced by Keluo waterproof technology (Shenzhen) Co., Ltd. the basic properties of the product are shown in table 2-1.

Table 2.1 basic properties and applicability of DPS

Basic attribute name	Attribute characteristics
Environmental protection	Pure environmental protection materials
Acid and alkali resistance, gasoline and freeze thaw resistance	have
Improvement of water absorption of concrete	83% reduction, with secondary impermeability
Strengthening effect on concrete	Surface strength increased by 20% - 25%
Anti cracking (automatic crack sealing)	seal 0.3mm crack automatically
Requirements for drying degree of base course	Dry and wet base surface can be constructed normally
Requirements for flatness and regularity of base surface	No
Construction environment requirements	All weather

DPS liquid is colorless and transparent. In order to determine which anions are contained in DPS, CaCl₂ solution is added to it and a large number of white flocculent substances are found. Therefore, it can be concluded that there may be SiO₃²⁻, CO₃²⁻ and OH⁻ in DPS, as shown in Figure 2.1. The pH test showed that the test paper was blue purple and the liquid was alkaline. When sodium silicate solution was added, a very small amount of precipitation was formed, as shown in Figure 2.2. There was a small amount of Ca(OH)₂ in DPS. It can be judged that the internal "active substances" are silicate, carbonate and a small amount of Ca²⁺.



Figure2.1 DPS permanent condensate and massive precipitation

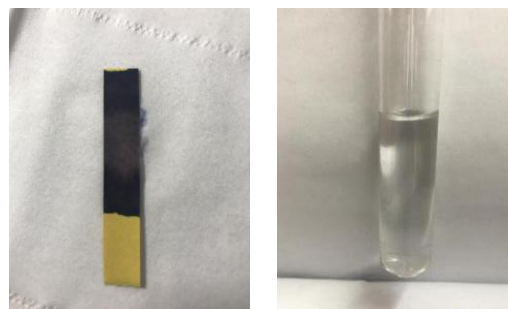


Figure2.2 Alkaline pH test paper and white precipitation

Because the content of Ca²⁺ in DPS is very limited, in order to obtain better reinforcement effect, more Ca²⁺ must be added as compensation. Due to the age of the old concrete is too long, the free Ca²⁺ in the concrete has been basically consumed by the influence of carbonation and other conditions. At this time, it is more necessary to compensate more Ca²⁺ in the concrete, so that the reinforcement liquid can react with Ca²⁺ after penetration to play a reinforcing role. For the choice of Ca²⁺ compensation agent, the solubility and acidity and basicity are mainly considered. Because Ca²⁺ needs to penetrate into the interior of the concrete substrate in order to have a better reinforcement effect, the calcium ion compensation agent needs to dissolve into the water and immerse into the concrete substrate with the water, which requires the calcium ion compensation agent to have good solubility. The solubility of common compounds containing Ca²⁺ is shown in table 2.2.

Table 2.2 solubility of Ca²⁺ compounds (unit: g)

Ca ²⁺ containing compounds	Solubility of 100g water at 20°C
Ca(OH) ₂	0.17
CaCl ₂	74.5
Ca(NO ₃) ₂	129
CaSO ₄	0.25

It can be seen from the table that the solubility of Ca(NO₃)₂ and CaCl₂ is very high, while the solubility of Ca(OH)₂ and CaSO₄ is small. In theory, the effect of using Ca(NO₃)₂ and CaCl₂ as calcium ion compensators is very good, but considering that the reinforcement inside the concrete can not be eroded, the acidity and alkalinity of calcium ion compensators should also be considered. Because the acid solution will not only react with the hydration products of cement and the stones in concrete, but also destroy the alkaline environment in concrete, which has a very negative impact on the internal reinforcement, the calcium ion compensation agent must be alkaline solution. It is reasonable to choose Ca(OH)₂ as calcium ion compensation agent, the solubility of Ca(OH)₂ can meet the requirements, and the pH value of saturated Ca(OH)₂ solution is 12 ~ 13, which has a positive effect on the protection of internal reinforcement of concrete.

Because the strength of concrete mainly comes from the high stability hydrated calcium silicate compound (C-S-H) generated by cement clinker such as tricalcium

silicate and dicalcium silicate under the action of water, and the internal concrete is still carrying out C-S-H hydration reaction slowly after its initial setting, in addition, the CaCO_3 in concrete also contributes to the strength. Therefore, three principles should be followed in the preparation of reinforcement solution: it is easy to dissolve in water and can penetrate into concrete with water; It can react with Ca^{2+} to form insoluble silicate or carbonate which contribute to the strength; It does not react with other substances in the concrete. Na_2SiO_3 (sodium silicate) and Na_2CO_3 (potassium carbonate) are selected to form a composite reinforcement solution. CaSiO_3 and CaCO_3 are insoluble, which can effectively seal the internal pores of concrete and enhance the strength of concrete.

The calcium hydroxide used is produced by Tianjin Damao chemical reagent factory, the molecular formula is $\text{Ca}(\text{OH})_2$, the purity is 95%, the sodium silicate is produced by Wuxi Yatai United Chemical Co., Ltd., the molecular formula is $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$, the molecular weight is 284, the potassium carbonate is produced by Tianjin Damao chemical reagent factory, the molecular formula is K_2CO_3 , the molecular weight is 138.21. The purity is 99%.

Through the preparation of composite reinforcement solution, the calcium ion compensation reinforcement method based on the osmotic crystallization material reinforcement method is formed.

3.2 preparation of concrete test block and impregnation of reinforcement solution

The main materials of concrete test block are Portland cement, water, coarse aggregate and fine aggregate. The cement is P·O 32.5 ordinary portland cement, which conforms to the national standard GB 175-1999 <Portland cement, ordinary portland cement>. Its 3-day and 28 day flexural strength is 4.0Mpa and 7.6Mpa respectively, and its 3 day and 28 day compressive strength is 18.8Mpa and 37.4Mpa respectively. The fine aggregate used is machine-made sand from Quanzhou, Fujian, with an apparent density of 2680kg/m^3 . According to GB/T 14684-2011 <the requirements of sand for building>, the percentage of sieve residue meets the requirements. The coarse aggregate is crushed stone from Xiamen, Fujian Province, with a continuous grading of 5-25mm. According to GB/T 14685-2011 <the requirements of pebbles and crushed stones for construction>, the cumulative sieve residue percentage of crushed stone aggregate meets <the requirements of the specification>. The water is tap water.

In order to explore the reinforcement effect of low-strength concrete, concrete test blocks with C5, C10 and C15 different mix proportions are designed. According to the selection table of concrete sand ratio in JGJ55-2011 <code for design of common concrete mix proportion>, the sand ratio is determined to be 45%, and then the amount of coarse and fine aggregate is determined by absolute volume method. The mix proportion of three kinds of concrete is shown in table 2.3.

Table 2.3 mix proportion of three concrete test blocks

Concrete grade	Material consumption (kg/m ³)			
	Cement	Water	Sand	Gravel
C5	156	195	915	1118
C10	207	195	894	1092
C15	256	195	875	1069

In order to make the reinforcement liquid penetrate deeply in the concrete, the concrete test block is infiltrated by immersion method. Three concrete test blocks of different strength are put into impermeable PE plastic bags, and then the reinforcement liquid is added. The closed opening ensures that the reinforcing liquid is not evaporated, and it is soaked in the ambient temperature of 20 °C and the relative humidity of 70% for 7 days.

3.3 influence of penetration reinforcement materials on concrete strength

According to GB 50081-2002 <standard for test methods of mechanical properties of ordinary concrete>, the compressive strength of concrete reinforced by permeable crystalline material and compensated calcium ion is shown in table 2.4, and the comparison of compressive strength of reinforced concrete is shown in Figure 2.3. It can be seen that the permeable crystalline material DPS has a reinforcing effect on low strength concrete. The lower the strength of concrete is, the better the reinforcing effect is. The strength of C5 concrete is increased by 33.4%, and that of C15 concrete is only increased by 6%. Low strength concrete has larger water cement ratio, more internal pores and poor anti permeability, which makes it easier for DPS to penetrate. The deeper the penetration depth is, the better the reinforcement effect is.

Table 2.4 comparison of compressive strength improvement of concrete reinforced by permeable crystalline material and compensated calcium ion

Group	Concrete grade	Compressive strength (MPa)			Average (MPa)
		1	2	3	
Control group	C5	4.8	4.8	4.6	4.7
	C10	8.6	8.1	8.6	8.4
	C15	14.7	13.8	14.0	14.2
Strengthening method of osmotic crystalline materials	C5	6.3	6.2	6.4	6.3
	C10	9.8	9.5	10.0	9.8
	C15	15.9	14.2	15.2	15.1
Compensation calcium ion Reinforcement method	C5	6.3	6.4	6.5	6.4
	C10	10.0	10.3	9.8	10.0
	C15	15.9	14.3	15.2	15.1

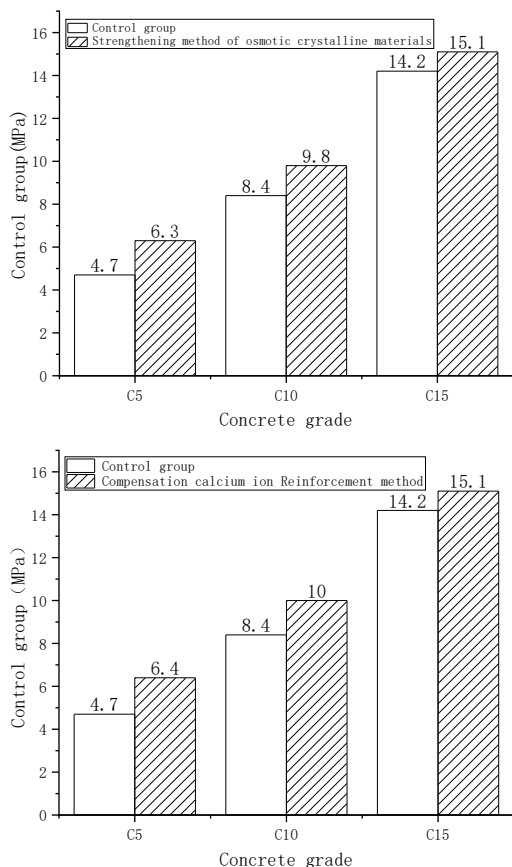


Fig. 2.3 comparison of compressive strength of concrete reinforced by permeable crystalline material and compensated calcium ion

The results show that the reinforcing effect of calcium ion compensation method for low strength concrete is similar to that of osmotic crystallization material. The strength of C5 concrete is increased by 36.1%, and that of C15 concrete is only increased by 6%.

3.4 influence of penetration reinforcement materials on concrete surface strength

According to JGJT23-2011 <the technical specification for testing concrete compressive strength by rebound method>, the surface rebound strength of concrete before and after reinforcement is tested. After the surface rebound strength and carbonation depth are obtained, the compressive strength of concrete can be obtained (see table 2-5 and table 2-6). It can be seen that the surface strength of concrete with 14MPa strength is increased by 2.5MPa, i.e. 17.8%, and the surface strength of concrete with 13.7mpa strength is increased by 2.3mpa, i.e. 16.7%, after using the calcium ion compensation reinforcement method.

Table 2.5 surface strength of concrete before and after reinforcement with permeable crystalline materials

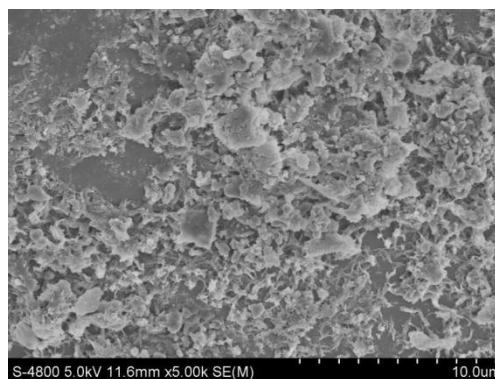
Group	Rebound value Rm				Average	Strength conversion (MPa)
Before reinforcement of infiltration crystalline material	22	22	28	21	23.3	14.0
	23	24	28	24		
	26	28	32	22		
	28	28	26	25		
After the reinforcement of infiltration crystalline material	21	25	24	25	25.2	16.5
	25	25	25	26		
	24	31	35	21		
	25	32	25	27		

Table 2.6 concrete surface strength before and after calcium ion reinforcement

Group	Rebound value Rm				Average	Strength conversion (MPa)
Before compensating calcium ion reinforcement	23	26	30	24	23.0	13.7
	28	26	23	22		
	20	22	21	22		
	22	23	22	20		
	25	28	28	26		
After calcium ion compensation	28	28	25	24	24.8	16.0
	22	24	23	24		
	24	25	22	22		

3.5 microstructure of concrete after penetration reinforcement

After being permeated with crystalline material, the concrete inside is covered by wormlike C-S-H gel. According to the mechanism of precipitation reaction and crystallization, after infiltration of crystalline material into concrete, its active substances react with a large number of alkaline substances such as $\text{Ca}(\text{OH})_2$ and free Ca^{2+} in concrete, forming insoluble calcium silicate gel (Fig. 2.4).



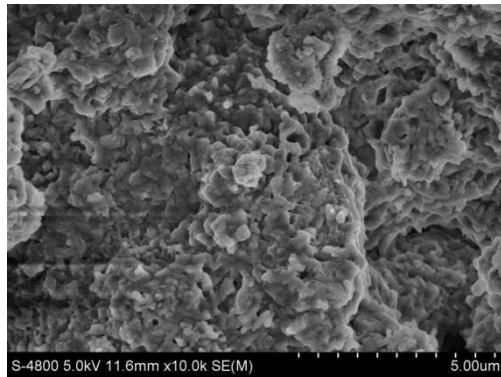


Figure. 2.4 The internal microstructure of concrete after reinforcement by infiltrating crystalline material (5000 times, 10000 times)

The microstructure of the concrete after calcium compensation is similar to that of the concrete after strengthening by infiltration and crystallization. (Fig. 2.5), there are hardly any six corner lamellar $\text{Ca}(\text{OH})_2$ on the surface. All of them are wrapped by C-S-H. After considering the entry of silicate ions, C-S-H colloids react with $\text{Ca}(\text{OH})_2$, and C-S-H gel blocks some pores. So that the internal microstructure is more compact.

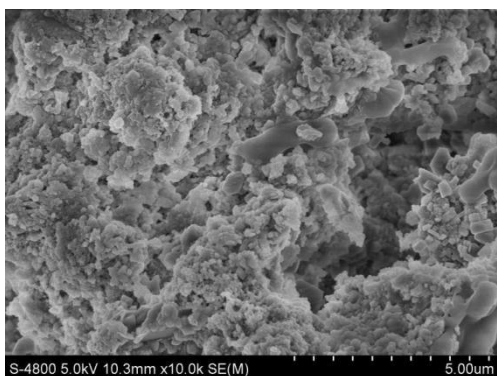
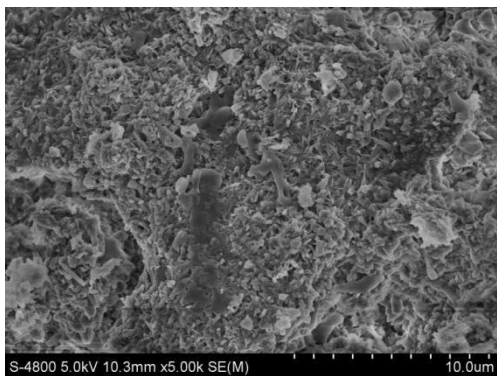


Figure. 2.5. The internal microstructure of concrete after calcium ion compensation (5000 times, 10000 times)

4 Summary

There are two kinds of strengthening materials for existing concrete base: water-based permeable crystalline materials and cement-based permeable crystalline materials. Different strengthening materials provide different technical measures for various engineering needs. In order to improve the reinforcing effect of compressive

strength, the composite reinforcing solution was prepared by adding calcium ion compensating agent $\text{Ca}(\text{OH})_2$, Na_2SiO_3 (sodium silicate) and Na_2CO_3 (potassium carbonate) on the basis of permeating crystallization reinforcing material DPS. Through the comparison of concrete immersion tests, it is found that:

(1) The permeable crystalline material DPS can reinforce the low strength concrete. The lower the strength of concrete, the better the reinforcement effect. The strength of C5 concrete is increased by 33.4%, and that of C15 concrete is only increased by 6%.

(2) The results show that the compensation calcium ion reinforcement method is better for low strength concrete, the strength of C5 concrete is increased by 36.1%, and the strength of C15 concrete is increased by 6%. It can be determined that calcium ion and silicate ion play a major role in the reinforcement of permeable crystalline materials

(3) The results show that the surface strength of 14MPa concrete is increased by 17.8%. The surface strength of the concrete with 13.7mpa strength increased by 16.7% after being strengthened by the calcium ion compensation method.

(4) The internal microstructure of concrete reinforced by calcium ion compensation and the microstructure of concrete reinforced by osmotic crystallization method show that, after the entry of silicates, C-S-H colloid was formed by reaction with $\text{Ca}(\text{OH})_2$, and C-S-H gel blocked some pores, which made the inner microstructure more compact.

The results show that the method of compensating calcium ion is proposed based on the mechanism of osmotic crystallization waterproof material, which can improve the old concrete which lacks free Ca^{2+} in the interior.

Reference:

1. Tian Wenling, Zhao Zhifang, Zhao Guofan, et al. Review on bond mechanism and test methods of new and old concrete[J]. *Journal of Hebei institute of technology*, **1**(1998):84-94.
2. GB 50550-2010, building structure reinforcement engineering construction quality acceptance specification. [3] Ao Jintao, Chen Zhaoyuan. Main factors affecting the bond strength of new and old concrete[J]. *Engineering mechanics*, A02(1997):328-333
3. Jiang Qian, Mu Song, Liu Jianzhong, Shi Liang. Research and Mechanism Analysis on performance improvement of concrete with water-based permeable crystalline materials[J]. *New building materials*, **43**, 03(2016):49-52, 89.
4. Gong Yunli. Study on the influence of water-borne permeable inorganic waterproof agent on the performance of waterproof concrete[D]. Central South University, (2012).
5. Tasi-Lung Weng. Effect of Surface Penetrating Sealer on the Microstructure Properties of Cement-based Composites[A]. Information Engineering Research

- Institute, USA.Proceedings of 2012 International Conference on Engineering Materials (ICEM 2012 V651)[C].Information Engineering Research Institute, USA:Institute of intelligent information technology applications,2012:6.
6. Zhang Yongchun.Application of permeable crystalline waterproof material in construction[J]. *Scientific management of Railway Materials*, **04**(2003):25-26.
 7. Zong Shizhen.Application of DPS permanent coagulant in the protection of ceramic cultural relics[J].*Restoration and research of cultural relics*, 2003(00):176-179.
 8. Chen Guangyao,Wu Xiaomei, Fan Yueming. Mechanism analysis of cementitious permeable crystalline waterproof material[J].*New building materials*,**36**, 08(2009):68-71.
 9. Xu Minggen, SEM and EDS analysis of penetration depth of cementitious permeable crystalline waterproofing materials[J].*Journal of Railway Science and Engineering*,03(2005):67-70.
 10. [11] Cheng Wei, Action mechanism of XYPEX material and its application in Tianshengqiao secondary structure. *Construction organization design*, **2**(2001):21-24
 11. Development status and market of cementitious permeable crystalline waterproofing materials, Waterproofing engineering and materials "conference news" No.6 (total 101) compilation of special materials of waterproofing technology committee of construction and building materials branch of Chinese Architectural Society
 12. Shang Xiaohua,Jing Denghu.Experimental study on CCCW improving performance of low strength concrete[J]. *Journal of water conservancy and Construction Engineering*, **78**,02(2018),:42-47.