Study on the Preparation and Properties of High-Strength Type Internal Curing Agent

Mingbin Shi[1], Kepeng Wang[1], Huawen Li[1], Changjiang Ma[1], Huibo Shen[1], Lihua Wang[2,*] and Zhitao Ma[3]

[1]China Railway No.3 Engineering Group Co., Ltd, Taiyuan, Shanxi, 030000, China
[2]College of Civil Engineering and Architecture, Shandong University of Science and Technology, Qingdao, Shandong, 266590, China
[3]College of Energy and Mining Engineering, Shandong University of Science and Technology, Qingdao, Shandong, 266590, China

*Corresponding author's e-mail: wlh@sdust.edu.cn

Abstract. Internal curing technology is an effective means to improve the crack resistance of concrete. A kind of high strength concrete internal curing agent TD-1 is prepared by monomer polymerization with porous powder quartz as carrier. By comparison with reference concrete samples, adding 0.2 % internal curing agent to ordinary concrete can slow down the evaporation rate of concrete surface, and reduction of heat release rate during hydration of concrete, and the cumulative heat release of concrete decreased by 11.1 %, and Improvement of crack resistance of concrete. Although the porosity increased by 18.8 % and the early strength decreased slightly, the pore size distribution of concrete is more uniform, and 56 d compressive strength of concrete increased by 6.7 %, and the durability of concrete is also improved. The practical application shows that the self-made TD-1 internal curing agent has good ability to restrain concrete cracking. It has a good prospect of popularization and application.

Keywords: internal curing agent; super absorbent polymers; anti-crack concrete; contraction

1 Introduction

For concrete, curing is a very important step. Concrete curing is divided into two forms: external curing and internal curing [1]. External curing is a traditional concrete curing method, which is a method of direct watering on the surface of concrete after demoulding. For concrete with low water cement ratio and dense structure, demand of the whole process of concrete hydration. Scholars and engineers have turned their thinking to internal curing, that is, adding materials that can absorb water in advance into concrete to form a small "reservoir" inside the concrete. With the progress of cement hydration reaction and the decrease of internal humidity of concrete, the mixed absorbent material releases water to maintain a high humidity autogenous shrinkage of concrete [2].

G. Zhao et al. (eds.), *Proceedings of the 2024 7th International Symposium on Traffic Transportation and Civil Architecture (ISTTCA 2024)*, Advances in Engineering Research 241,
https://doi.org/10.2991/978-94-6463-514-0_30

At present, the commonly used concrete internal curing materials mainly include porous lightweight aggregate and super absorbent polymer (SAP). The porous lightweight aggregate internal curing agent uses the free water stored in the aggregate pores to slowly release into the concrete to meet the humidity environment required for the cement hydration reaction. Liu Wei et al. [3] used expanded perlite (EP) as an internal curing agent and incorporated it into concrete to increase the compressive strength of concrete and its growth rate. The main reason is that under the action of EP internal curing, the hydration products produced will fill the microcracks at the interface, and the pores on the surface of EP will provide growth space for the hydration products.

Du Yuhui et al. [4] used pre-water-saturated low-activity slag as an internal curing material and incorporated it into cement mortar. Through experiments, it is concluded that using low-activity slag as an internal curing agent can effectively inhibit the autogenous shrinkage of mortar at all stages, although the strength of mortar is reduced. The internal curing material which is widely used in engineering is still super absorbent resin. Super absorbent resin is a kind of polymer containing a large number of carboxyl, hydroxyl and other hydrophilic groups, can absorb the equivalent of their own quality dozens of times the water. When the relative humidity inside the concrete decreases, the capillary negative pressure appears inside the concrete, and SAP can release the absorbed water one after another, which not only contributes to the further hydration of cement-based cementitious materials, but also significantly alleviates the rapid change of relative humidity inside the concrete, effectively reduces the early autogenous shrinkage of concrete and reduces the risk of concrete cracking.

At present, the super absorbent resins used as concrete internal curing agent mainly include starch and acrylic resin. Wang Xuemin et al. [5] prepared core-shell structure concrete internal curing agent with acrylic acid, styrene monomer and nano-silica as raw materials under the action of composite emulsifier. When the content of internal curing agent is 1.5 %, the water retention rate of concrete at 28 d is more than 90 %, and the compressive strength is significantly improved. Guo Rui [6] synthesized an internal curing agent with acrylamide, acrylic acid and cassava starch as raw materials, which can effectively reduce the hydration heat of concrete, reduce the shrinkage of concrete and improve the durability of concrete.

Although the commonly used internal curing agent has obvious anti-cracking effect on concrete, when the water in the internal curing agent evaporates completely, more pores will be left, and the strength of concrete will generally decrease, which will bring adverse consequences to concrete engineering.

In order to improve the adverse effects of internal curing agent on concrete, an early strength concrete internal curing agent TD-1 was prepared in this paper. Mixing it into concrete raw materials will not reduce the strength of concrete and can effectively reduce the generation of concrete cracks. The water retention performance and its influence on the hydration heat, mechanical properties and crack resistance of concrete were studied to provide theoretical reference for related research and engineering application.

2 Material

The raw materials used in the test are divided into raw materials for synthetic internal curing agent and raw materials for concrete performance test.

2.1 Synthetic Internal Curing Agent Raw Materials

Acrylic acid monomer, acrylamide monomer, allyl polyoxyethylene ether monomer, styrene monomer, ammonium persulfate and sodium hydroxide are all commercially available analytical pure reagents. Water is pure water. Porous powder quartz is a porous powder quartz operated by a company in Shanghai. The particle size is about 5μm, and the shape is approximately spherical.

2.2 Concrete Performance Test Materials

The cement used in the preparation of concrete is P · O 42.5 ordinary Portland cement produced by Shanshui Group. The natural river sand in Weifang area is selected as the fine aggregate, and the fineness modulus is 2.53, which belongs to the medium sand in zone II. The coarse aggregate is limestone gravel with a continuous gradation of 5 ~ 20 mm in particle size, and the grain shape is good.

The polycarboxylate superplasticizer produced by Subote New Materials Co., Ltd. was selected as the water reducing agent, and the water reduction rate was 28 %. The particle size of commercially available SAP is 60 ~ 100 mesh, and the water absorption rate is 850 times. Concrete mixing water is tap water.

3 Preparation of Internal Curing Agent TD-1

Acrylic acid and pure water were mixed evenly. Porous quartz powder was added slowly under stirring condition. After stirring for 20 min, acrylamide monomer, allyl polyoxyethylene ether monomer and styrene monomer were added dropwise. After stirring for 15 min, ammonium persulfate was added dropwise. When the system became thicker, the stirring was stopped and the reaction continued for 2 h. The pH value was adjusted to 7 ~ 8 with sodium hydroxide solution. After spray drying, high strength concrete internal curing agent TD-1 was prepared.

After testing, the water absorption rate of high strength concrete internal curing agent TD-1 is 445 times, the water retention rate is 90.8 %, and the negative pressure water release rate is 82 %. Its water absorption rate is less than that of ordinary SAP, which is due to the fact that the TD-1 internal curing agent contains a certain amount of inorganic porous powder quartz. When calculating the content of TD-1 type internal curing agent, the amount of polymer should be taken as the benchmark.

TD-1 internal curing agent has excellent water retention and water release ability, and it still has certain strength after water release, which will not adversely affect the strength of concrete. This is because the polymer monomer is fully polymerized in the pores of the porous powder quartz to form a stable shell polymer structure, which covers a solid coat for the super absorbent polymer. Adding it to concrete can effectively inhibit the early shrinkage of concrete. In the later stage of concrete hydration, the voids formed by super absorbent polymer after releasing water are occupied by powder quartz, which will not affect the strength of concrete.

4 Concrete Test Mix Ratio

In order to verify the effect of TD-1 internal curing agent, the TD-1 internal curing agent was compared with the commercially available SAP internal curing agent. C45 concrete is configured according to JGJ15-2011 ' Specification for Mix Proportion of Ordinary Concrete ', and the water-binder ratio is 0.33. At the same time, the reference concrete without internal curing agent is made for comparison.

The super absorbent resin has strong water absorption, which makes the super absorbent resin have a certain thickening effect. The dry powder super absorbent resin will absorb part of the water in the concrete, which reduces the fluidity of the concrete to some extent. In order to make the concrete have the same fluidity, a part of external water diversion should be added to the concrete mixed with super absorbent resin. According to Powers ' SAP additional water diversion theory, when the water-cement ratio of the base concrete is not greater than 0.36, the additional water diversion is 0.18 times that of the base water-cement ratio [7].

Combined with the fluidity test of cement paste, for C45 concrete, in the case of dry mixing of internal curing agent 0.2 %, the additional water-cement ratio of concrete mixed with commercially available SAP needs to be increased to 0.059, and the additional water-cement ratio of concrete mixed with self-made TD-1 internal curing agent needs to be increased to 0.051. The specific test mix ratio is shown in Table 1.

Table 1. Test mix proportion of concrete (unit: kg / m^3)

No.	Cement	Sand	Stone	Water	Water reducer	Internal curing agent
C0	430	750	980	142	7.6	0
C1	430	750	980	166.8	7.6	0.88(SAP)
C2	430	750	980	163.2	7.6	1.25(TD-1)

5 Test Method

The cement hydration heat test, concrete water evaporation test, concrete strength test, slab crack resistance test and pore structure analysis of concrete were carried out in the laboratory.

5.1 Hydration Heat Analysis

According to GB / T12959-2008 “Test Methods for Heat of Hydration of Cement ”, the hydration heat of cementitious materials in different concretes was measured by 8-channel isothermal calorimeter, and the ambient temperature was 20 °C.

5.2 Water Evaporation Test

According to JG / T477-2015 “Evaporation Retardants for Concrete During Plastic Stage”, concrete specimens with dimensions of 300 mm × 150 mm × 30 mm were made. After forming, they were put into the environmental test chamber within 5 minutes and weighed. The mass of the specimens was weighed every 15 minutes to calculate the mass loss of concrete.

5.3 Internal Relative Humidity

The internal relative humidity of concrete is 150mm × 150mm × 150mm cube specimen, and a test hole with a diameter of 30mm and a height of 75mm is reserved at the bottom of the specimen. After 24 hours of molding, the specimen was demoulded, and the humidity sensor was placed in the test hole. The specimen was wrapped with tin paper and placed in a thermostat with a temperature of (20 ± 2) °C and a relative humidity of (50 ± 4) %.

5.4 Compressive Strength

According to the “Standard for Test Methods of Concrete Physical and Mechanical Properties” (GB / T50081-2019), 150mm × 150mm × 150mm standard cube test blocks were prepared, demoulded after 1d of molding, and placed in a standard curing box. Curing to 3d, 7d, 28d and 56d, the compressive strength of concrete at different ages was tested.

5.5 Crack Resistance

According to the early crack resistance test method specified in GB / T50082-2009 “Standard for test methods of long-term performance and durability of ordinary concrete”, a plane thin plate specimen with a size of 800mm × 600mm × 100mm was made. From the beginning of concrete mixing and adding water, the crack width and crack length of concrete were observed by HC-CK101 crack width observation instrument after 24 hours, and the crack area was calculated.

5.6 Pore Structure Evolution

Auto Pore IV 9500 automatic mercury porosimeter produced by Micromeritics company was used to detect the pore structure of 56 d concrete samples.

6 Experiment Results and Analysis

6.1 Hydration Heat Analysis

Reducing the adiabatic temperature rise of concrete is one of the effective measures to control concrete cracks [8]. The temperature change of concrete is caused by the hydration reaction of cementitious materials. Remove the coarse and fine aggregates in the concrete, refer to the mix ratio of the cementitious material in Table 1, and test the thermal power of the corresponding cementitious material paste. The corresponding cementitious materials are numbered C0 *, C1 * and C2 *. Fig.1 and Fig.2 are the heat release rate and cumulative heat release curves of cementitious materials in concrete during hydration heat release process.

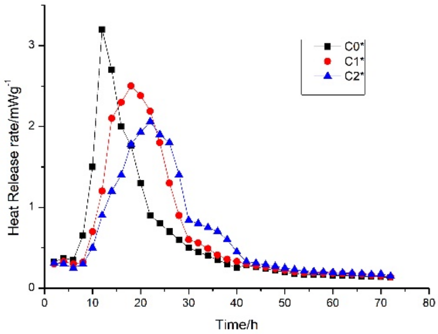

Fig. 1. Heat release rate of cementitious

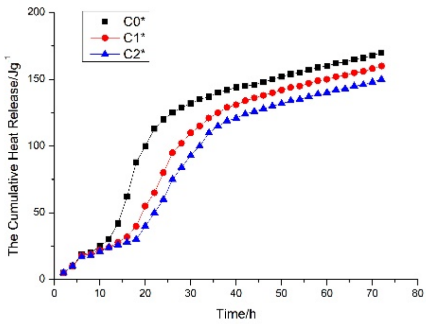

Fig. 2. The cumulative heat release of materials in concrete. cementitious materials in concrete.

It can be seen from Fig.1 that in the absence of aggregate, the shape of the exothermic curves of the three cementitious materials is similar. The induction period of ordinary concrete is the shortest, only about 10h. The induction period of concrete mixed with commercially available SAP and self-made TD-1 internal curing agent is extended, which is about 14h and 16h respectively. Ordinary concrete ushered in the main peak of hydration heat at 20h, which was about 3.2 mW/g, while the time of the main peak of hydration heat of concrete mixed with commercially available SAP was extended to 24h, and the peak value was also reduced to 2.8 mWg^{-1}. Concrete mixed with self-made TD-1, the exothermic peak appeared the latest, about 28h, and the peak value was the smallest, only 2.1 mW/g.

From the cumulative heat release curve of concrete in Figure 2, it can be seen that after adding SAP and TD-1 internal curing agent to concrete, the cumulative heat release of concrete in 72 h is reduced from 171J /g to 163J /g and 152J /g, respectively. The cumulative heat of hydration of concrete is significantly reduced, and the process of hydration heat release is delayed, so that the temperature difference cracks of concrete can be effectively avoided.

6.2 Water Evaporation Test

The water evaporation per unit area of concrete is shown in figure 3.

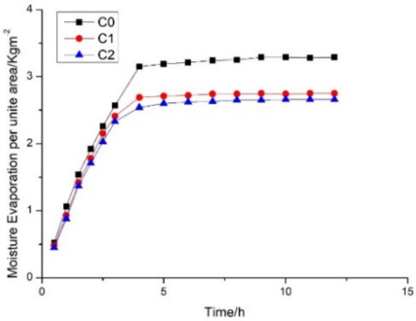

Fig. 3. Moisture evaporation per unit area

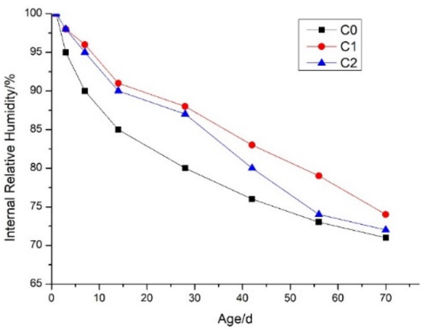

Fig. 4. Internal relative humidity values of concrete.of concrete at different ages.

It can be seen from Fig.3 that in the first 3 hours, the water evaporation of concrete with SAP and TD-1 internal curing agent is not much different from that of ordinary concrete. After 3 hours, the surface evaporation of concrete with two internal curing agents gradually decreases. This is because, in the early stage, due to the high water content of the internal curing agent, the amount of water released is large, the surface free water is almost the same as that of ordinary concrete, and the amount of water evaporation is almost the same. With the evaporation and hydration reaction of the water on the surface of the concrete, the water release rate of the internal curing agent slows down, and the unsaturated internal curing agent increases the water binding force inside the concrete. At the same time, the pores formed after the release of water hinder the diffusion of water inside the concrete, resulting in a decrease in the evaporation of water on the surface of the concrete, which plays a role in retaining water and retaining water. It can also be seen from Fig.3 that the ability of commercially available SAP and self-made TD-1 internal curing agent to inhibit water evaporation on the surface of concrete is not much different.

6.3 Concrete Internal Relative Humidity

The internal relative humidity test results of concrete at different ages are shown in figure 4. It can be seen from Fig.4 that after the incorporation of SAP and TD-1 into the concrete, the relative humidity inside the concrete is higher than that of the ordinary concrete specimen, especially in the first 14 days of cement hydration. After the incorporation of SAP and TD-1 internal curing agent, the relative humidity inside the concrete specimen is always maintained at more than 90 %, which creates a good hydration environment for the cement and makes the cement hydration more sufficient. At the same time, such a high relative humidity can reduce the negative pressure caused by the loss of water in the capillary pores of the concrete, thereby improving the autogenous shrinkage performance of the concrete. The internal humidity of concrete mixed with TD-1 is slightly lower than that of concrete mixed with SAP, which is due to the reason that the water absorption rate of SAP selected in the experiment is higher than that of TD-1. The water holding capacity of SAP is stronger than that of TD-1, which also leads to the reason that the internal porosity of concrete mixed with SAP is greater than that of concrete mixed with TD-1.

6.4 Compressive Strength of Concrete

The compressive strength values of concrete at different ages are shown in Fig.5.

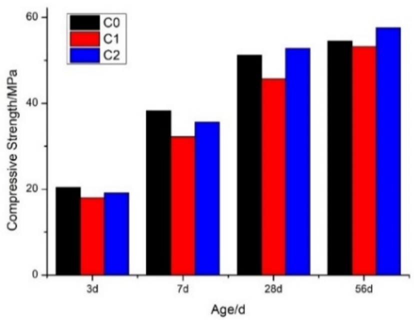

Fig. 5. Compressive strength values of concrete at different ages.

It can be seen from Fig.5 that the early strength of concrete decreased to different degrees after adding SAP and TD-1 internal curing agent to ordinary concrete. Compared with ordinary concrete, the 3d and 28d compressive strength of concrete decreased by 11.8 % and 15.9 % respectively after adding SAP. After adding TD-1, the 3d and 7d compressive strength of concrete decreased by 6.4 % and 7.0 % respectively. However, the effect of adding SAP and TD-1 on the later strength of concrete is obviously different. After adding SAP, the compressive strength of concrete at 28 d and 56 d decreased by 10.7 % and 2.3 % respectively, while after adding TD-1, the compressive strength of concrete at 28 d and 56 d increased by 3.1 % and 5.7 % respectively. After adding internal curing agent into concrete, on the one hand, the hydration of concrete is more sufficient, and the holes generated by the release of water adsorbed by the internal curing agent will also have a negative impact on the concrete structure, resulting in a decrease in the compressive strength of concrete [9]. The high water absorption material in the early strength internal curing agent TD-1 occupies the hole of the powder quartz. The high water absorption material will not increase too many pores after releasing water, which basically ensures the compactness of the concrete. Therefore, after adding the early strength internal curing agent TD-1, the later strength of the concrete is improved.

6.5 Cracking Resistance of Concrete

The crack resistance of concrete was tested 24 hours after concrete molding. The test results are shown in Table 2.

Table 2. Concrete cracking index.

No.	The average cracking area of each crack/(mm^2)	Number of cracks per unit area/(Number/m^2)	Total cracking area per unit area/(mm^2/m^2)	Total crack length/(mm)	Maximum crack width/(mm)
C0	9	35	216	657	0.59
C1	5	16	121	304	0.32
C2	4	11	92	236	0.28

It can be seen from Table 2 that there are 35 cracks per square meter in ordinary concrete within 24 hours, the total length of cracks reaches 657 mm, and the maximum crack width is 0.59 mm. After the incorporation of commercially available SAP and self-made TD-1 internal curing agent, the cracking of concrete was significantly improved. The number of cracks per unit area was reduced to 16 and 11, respectively. The total length of cracks was reduced to 304 mm and 236 mm, and the maximum crack width was reduced to 0.32 mm and 0.28 mm. Internal curing agent can effectively inhibit the generation of concrete cracks. This is because under the action of forced blowing and crack inducer, the water loss on the surface of ordinary concrete is very fast, which leads to dry shrinkage cracks in concrete soon. After adding internal curing agent, the high molecular polymer absorbing enough water is evenly distributed in concrete, including the surface of concrete. With the decrease of humidity on the surface of concrete, the water release rate of high molecular polymer on the surface gradually decreases, which inhibits the evaporation of water on the surface of concrete. The high molecular polymer inside concrete still contains more water. With the progress of concrete hydration reaction, it can be released slowly, which plays a role in fully curing concrete and reducing the generation of concrete cracks.

6.6 Pore Structure Evolution

According to the MIP test results, the characteristic parameters of pore structure of concrete at 56d age are shown in Table 3.

Table 3. Characteristic parameters of concrete pore structure

No.	Porosity/%	Average pore size/nm	Most probable pore size/nm	Pore size distribution/（mL/g）			
				3-10nm	10-100nm	100-1000nm	＞1000nm
A0	10.23	18.82	18.1	0.0067	0.0198	0.0051	0.0088
A1	13.84	16.11	17.3	0.0142	0.0212	0.0083	0.0124
A2	12.15	15.74	16.5	0.0092	0.0231	0.0055	0.0078

It can be seen from Table 3 that when the internal curing agent is mixed with concrete, the porosity of concrete increases slightly. The porosity of concrete mixed with commercial SAP increases by 35.3 %, and the porosity of concrete mixed with TD-1 internal curing agent increases by 18.8 %. This is mainly due to the release of water from the super absorbent resin, leaving a gap, increasing the porosity of the concrete. Because the TD-1 internal curing agent contains powder quartz particles as the support, the porosity increases slightly, and the compactness of the concrete is basically maintained.

After adding internal curing agent to concrete, the pore size distribution of concrete is more uniform, and the average pore size and the most probable pore size are reduced. This is because the internal curing water will be connected with the capillary pore network inside the slurry, the internal humidity of the concrete is more uniform, the hydration reaction is more sufficient, the pore structure inside the slurry is effectively refined, and the average pore size and the most probable pore size of the pores inside the slurry are significantly reduced, which makes up for the adverse effects of the increase of porosity on the concrete. According to the classification standard of Kumar [10], the pores of 3 ~ 10 nm are gel pores, the pores of 10 ~ 100 nm are small capillary pores, the pores of 100 ~ 1000 nm are large capillary pores, and the pores above 1000 nm are pores. From table 3, it can be seen that after adding SAP and TD-1 internal curing agent to concrete, the gel pores and small capillary pores of concrete increase greatly, while the large capillary pores are not much different. For pores with a pore size greater than 1000 nm, after adding SAP, the pores of concrete increase, while after adding TD-1, the pores of concrete decrease. This also shows that after adding SAP to concrete, the number of harmful pores of concrete increases, resulting in a decrease in the compressive strength of concrete. After adding TD-1, the harmful pores of concrete decrease and the compressive strength of concrete is improved.

7 Engineering Application

The pilot project is located in the south side wall of the negative first floor of the fourth construction section of Sino-German Industrial Park Station of Qingdao Metro Line 6. The design adopts C45 concrete. On the basis of the mix ratio of ordinary C45 concrete, 1.65 kg of TD-1 concrete internal curing agent is added to each cubic meter of concrete, and a total of 160m3 wall is poured. At the same time, it is compared with the 220m3 wall poured with ordinary C45 concrete without internal curing agent.

After on-site testing, after adding TD-1, the concrete mold temperature is about 21 °C. After pouring for 30 h, the maximum temperature of the concrete center is 61 °C, and the temperature control results are basically consistent with expectations. Continuous observation within 4 months after pouring showed that the concrete surface was good and the concrete cracks were significantly improved.

8 Conclusion

(1) High strength concrete internal curing agent TD-1 was prepared by monomer polymerization with porous powder quartz as carrier.

(2) Compared with the reference concrete, the internal curing agent TD-1 can reduce the water evaporation rate on the surface of the concrete, reduce the hydration heat release rate, and reduce the cumulative heat release of the concrete by 11.1 % within 72 h.

(3) Compared with the reference concrete, after adding TD-1 internal curing agent, the porosity of the concrete increased by 18.8 %, and the early strength decreased slightly, but the concrete hydration was more sufficient, the pore size distribution was more uniform, the later strength was improved, and the 56 d compressive strength of the concrete increased by 5.7 %.

(4) Engineering application shows that TD-1 internal curing agent has good ability to inhibit concrete cracking.

References

1. Wang R, Wang W, Wang Y, Tian Q and Li L (2021) Standard interpretation of JC/T 2551-2019 Superabsorbent polymer for internal curing of concrete. NEW BUILDING MATERIALS, 48(12): 59-62.
2. Zhang Y, Song X and Duan Z (2021) Advances in the Study of Super Absorbent Polymers for Internal Curing of Concrete. FLY ASH COMPR EHENSIVE UTILIZATION, 35(05): 73-77. DOI: 10.19860/j.cnki.issn1005-8249.2021.05.013.
3. Liu W, Zhang Y, Li Z, Zhao F and Wang T (2022) Growth mechanism of the compressive strength of expanded perlite internal curing concrete and establishment of mathematical model. Acta Materiae Compositae Sinica, 39(11): 5423-5435. DOI: 10.13801/j.cnki.fhclxb.20210930.001.
4. Du Y and Li S (2022) Analysis of autogenous shrinkage and pore structure of cement mortar with low-activity slag as internal curing material. Hydro-Science and Engineering, (3): 136-

144.

5. Wang X, Liu W, Wu Z, Guo C, Fan W and Yang X (2021) Synthesis and characterization evaluation of YJ concrete internal curing compounds. NEW BUILDING MATERIALS,48(05):34-37.
6. Guo R, Wang X, Lei L, Xiong L and Zhao R (2020) Preparation and properties of a starch grafted acrylic acid and acrylamide internal curing agent. NEW BUILDING MATERIALS, 47(10):81-84.
7. Yu Y, Wang X and Deng F (2021) Effect of super- absorbent polymer on the plastic- shrinkage cracking of high- strength concrete. Concrete, (03): 27-30+34.
8. Xie B, Xu W, Zhang J, Wu L, Zhou W, Xia F and Zhou J (2021) C50 low temperature rise and low shrinkage marine mass concrete research and application of crack resistance. Concrete, (09):98-101+105.
9. LI X, Xu J, Jiang D, Lv Y, He C, Zhang C and Fu Q (2021) Effect of Internal Curing of SAP on Properties of Alkali-Activated Slag Cementitious Materials. BULLETIN OF THE CHINESE CE R AMIC SOCIETY,40(10): 3435-3441. DOI: 10.16552/j.cnki.issn1001-1625.20210805.001.
10. Kumar R and Bhattachar B (2003) Study on some factors affecting the results in the use of MIP method in concrete research. Cement and Concrete Research, 33(3): 417-424.