Research Article

The Influence of the Different Cementitious Material on Self-Healing of Microcracks in Shotcrete

Junru Zhang, Yi Dai, Jian Xu, Jimeng Feng, and Kaimeng Ma

School of Civil Engineering, Southwest Jiaotong University, Chengdu 610031, China

Correspondence should be addressed to Kaimeng Ma; mkm@my.swjtu.edu.cn

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Abstract

Due to a particular construction process, the shotcrete structure is affected by external load, material aging, and external temperature during use, with cracks inevitably appearing. Cracks are formed from microstate gradually, and thus controlling the development of microcracks in the early phase can effectively improve the strength and impermeability of shotcrete. In this study, the method of laboratory experiment and analysis is adopted to study the effect of ettringite on achieving the self-healing effect of shotcrete. The test results show that: (1) after encountering water, ettringite effectively plays a microexpansion effect to fill the pores, helping shotcrete achieve the effect of waterproofing and self-healing, which is very suitable for single-layer lining structures with water seepage. (2) The content of ettringite is inversely proportional to the change law of pore structure. When the content of ettringite increases, the porosity and harmful pores proportion have a significant decrease. (3) Fly ash and mineral powder with a mixing amount of about 30% will not affect the strength of the concrete, while prolonging the time of the effect of ettringite, will effectively improve the impermeability of the shotcrete.

1. Introduction

Shotcrete single shell-lining technology has obvious characteristics such as simple process, strong load-bearing capacity, good economic efficiency, and convenient maintenance [1–3]. With the continuous optimization and improvement of shotcrete construction technology and performance in recent years, the development of single shell-lining technology has been rapidly promoted and the technology has been applied in tunnels all over the world. However, because of no waterproof layer between the supporting layers of the single-shell lining, the waterproof property of the tunnel structure mainly depends on the characteristics of the shotcrete itself. Thus the problem of water leakage is still a significant issue in the academic and engineering fields for many years [4, 5].

The occurrence of cracks is the essential cause of water leakage in concrete, and the cracks can be divided into macro- and microcracks according to the size. For macroscopic cracks, postrepair technology is generally adopted, while concrete self-healing technology is considered for microscopic cracks. Concrete self-healing technology hitherto can be summarized as concrete self-healing, binder-based self-healing, microorganism-based self-healing, mineral additive-based self-healing, and ions chelating agent-based self-healing [6–12].

In the 19th century, some scholars accidentally discovered that the concrete specimens with cracks showed self-healing phenomenon, and the compressive strength after healing was improved compared with the 28-d compressive strength of concrete [13–15]. This phenomenon has a positive significance for concrete structures. After extensive researches, it is believed that calcium hydroxide [16], calcium silicate hydrate [17], and calcium carbonate [18] generated in cracks are the main products of self-healing. Unfortunately, the self-healing ability of concrete is limited, the self-healing is time-consuming, and the impermeability of concrete cannot be greatly improved only by self-healing [19].

The mechanism of binder-based self-healing is to fill and repair the cracks by the consolidation effect of the liquid binder. Usually, the liquid binder is enclosed in hollow glass...
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out and bonds the crack surface, achieving self-healing [24]. Microorganism-based self-healing is to use the metabolism of microorganisms to promote the production of calcium carbonate to achieve self-healing [25–28]. Among the four types of microbes: sulfur cycle [29], photosynthesis [30], anaerobic [31] and aerobic [32], the metabolism of anaerobic bacteria is relatively easy to control, and it can be induced to produce a large amount of calcium carbonate in a short time, and the self-healing effect for concrete is remarkable [33]. However, this kind of self-healing technology is difficult and costly, which makes it difficult to be widely promoted and applied.

The mineral additive-based self-healing is to mix mineral additives into concrete. The mineral additives attached to the surface of the crack chemically react with the infiltrated water, generating products to fill the cracks. Currently, commonly used mineral additives are divided into expansion additives [11, 34, 35], such as sulfate aluminate, calcium oxide, anhydrite, etc., and crystalline additives [36, 37], such as carbonate, active silica, t alc, etc.

The ions chelating agent-based self-healing is to use ions chelating agent to promote the formation of crystalline products in the cracks to realize the self-healing of cracks. It has been used in hydraulic concrete, tunnels and subway segments [38–40].

It is obvious that the applicable environments of different concrete microcrack self-healing technologies are different, and they are mainly applied to cast-in-place concrete structures, while the self-healing technology of shotcrete is rarely studied. Also, because of different construction techniques between shotcrete and cast-in-place concrete, their mix ratio, raw materials, admixtures, and water-cement ratio are quite different, and the existing self-healing technology cannot be directly applied to shotcrete. It is particularly vital to conduct research on shotcrete self-healing materials in contact with water.

Ettringite, as one of the important hydration products of cement, has been extensively researched. After the concrete is formed for a long time, delayed ettringite (DEF) may be generated, which has a great impact on its pore structure. On one hand, delayed ettringite will swell with water and generate stress in the hardened paste of the cementitious substrate, causing more microcracks, which is an important factor in the later cracking of concrete [41–43], and on the other hand, delayed ettringite is conducive to the shrinkage compensation and early strength and rapid hardening of concrete, so delayed ettringite shows unique duality for concrete structures [44–46]. In order to effectively suppress the effect of delayed ettringite on the expansion and cracking of concrete structures and give full play to its advantages, related studies have shown that mixing 15%–20% of fly ash and 5% slag in cement can control the adverse effects of delayed ettringite expansion and cracking [47, 48], so as to use its expansibility to fill the pores and realize the self-healing of concrete microcracks. Besides, related documents [49–51] show that admixtures such as silica fume, fly ash, and slag powder can also control the pore characteristics of concrete at the microscopic scale so that the impermeability of concrete can be further optimized.

In summary, composite cementitious materials with a certain mix ratio can effectively suppress the adverse effects of delayed ettringite, control microscopic pore characteristics, and use the delayed ettringite expansion to realize the self-healing of shotcrete micro-cracks. Therefore, composite cementitious materials can be used as a self-healing material for micro-cracks in shotcrete. It is very necessary to study the pore characteristics and performance of shotcrete based on composite cementitious materials. But the references are all focused on the casting concrete, rather than the shotcrete. Due to the different procedures, pores and cracks are more likely to occur in shotcrete. In terms of the underground engineering with shotcrete as the permanent single-layer lining, there are higher requirements for impermeability. In this study, three admixtures of silica fume, fly ash, and mineral powder are added to modify the cement to obtain composite cementitious materials. The indoor nuclear magnetic test and X-ray Diffraction (XRD) test methods are used to evaluate the mechanical properties of shotcrete based on composite cementitious materials and to research the pore structure so as to verify its microcrack self-healing ability, to optimize the mix ratio of composite cementitious materials, and to improve its performance. It provides a new idea for the microcrack self-healing technology of shotcrete single shell lining, which has a high academic and engineering value.

2. Materials and Methods

2.1. Raw Materials. The details of the material used in the test are as follows: cement of class P.O 42.5R was used for the shotcrete, the specific surface area of which was 354 m²/kg, and the strength of cement mortar on day 28th was 43.1 MPa. The fly ash was selected from Grade I fly ash, produced by Chengdu Boilei Fly Ash Comprehensive Development Co., Ltd., with a water requirement ratio of 88%, a moisture content of 0.5%, and a fineness of 5.5%. The mineral powder was S105 grade slag powder from Aoping Cement Plant in Pengzhou City, Sichuan Province, with a moisture content of 0.7%, a specific surface area of 450–500 m²/kg, a fluidity ratio of 95%, and a 28-day activity index of 45%. The adopted silica fume was produced by Southeast Star Technology Co., Ltd., model 92U. Clean tap water was used in the test, which did not contain harmful impurities that affect the condensation and hardening of the cement. TK-J accelerating agent from China Railway Yanfeng Chengdu Technology Co., Ltd. was selected for the test. The water reducing agent is NOF-AS type polycarboxylic acid superplasticizer produced by Shandong Huawei Yinkai Building Material Technology Co., Ltd.

The gradation distribution of coarse and fine aggregates is shown in Tables 1 and 2, and the coarse and fine aggregates used in the test are shown in Figures 1 and 2.

2.2. Mix Design. Shotcrete single shell lining, as a permanent supporting structure, in addition to ensuring strength and
durability, also needs to have the characteristics, such as low percentage of rebound, low dust concentration, and good pressure delivery, to meet the demands of working performance, which makes the design of the shotcrete mix ratio very critical. In the design phase of the mix ratio, water-binder ratio, sand ratio, unit water consumption, mineral admixtures, and additives and other indicators should be paid enough attention.

To meet the requirement of using shotcrete single shell lining as a permanent support structure, sufficient strength and good durability should be attached. Therefore, the shotcrete with the strength of C30 or above is generally chosen for the design. In this study, C30 shotcrete was used as the test benchmark.

According to engineering experience and the results of the trail [52], the main parameters of C30 shotcrete were determined as follows: water-binder ratio of 0.42, sand ratio of 52%, accelerating agent 3%, and water reducing agent 0.9%.

Standard mix ratios for one cubic meter in the test were as follows: cement 414 kg, silica fume 36 kg, fine aggregate 864 kg, coarse aggregate 796 kg, water 190 kg, water reducing agent 4 kg, accelerating agent 13.5 kg. Under the condition that the quality of the total cementitious material remained unchanged, the ratio of each component in the cementitious material was adjusted. A total of 7 mix ratios were configured in the experiment. See Table 3 for details.

where, N1 is the standard mix ratio, N2–N4 are only mixed with mineral powder at the ratios of 10%, 20%, and 30%, and N5–N7 are only mixed with fly ash at the ratios of 10%, 20%, and 30%.

2.3. Shotcrete Samples Preparation

2.3.1. Weigh and Mix. The amount of cementitious material, water, coarse and fine aggregate, and water reducing agent required for each concrete mix according to the design mix ratio was accurately calculated and mixed at the concrete mixing station.
2.3.2. Spray Operation. The large slab test mold was placed in the special plant area for shotcrete test at an inclination angle of 80°. The mixed concrete was loaded into the sprayer, and the large slab test mold was sprayed by the high-pressure wind. The continuity of the material loading must be ensured. The nozzle was perpendicular to the sprayed surface and kept a distance of 1.5 m. When spraying, several large slabs were sprayed by layer till the slabs were filled with shotcrete. To cut the test specimen easily, the spray surface should be as flat as possible.

2.3.3. Specimen Processing. The shotcrete slab was cured in a humid environment for one day and then demoulded and moved to a standard curing room for curing. On the 7th day, the shotcrete slab was cut and processed into 100 × 100 × 100 mm and 85 × 85 × 85 mm specimens. During the process, the defective parts of the shotcrete should be avoided to make the test results more accurate. The process is shown in Figure 3.

3. Testing Methods

3.1. Compressive Strength Test. The concrete strength test value is related to the size of the specimen, the hoop effect, and the loading speed, which will affect the final test result. The test piece should be a cube of 100 mm × 100 mm × 100 mm, and 3 specimens shall be tested for each group of mixture ratios. The measured value shall be based on the arithmetic mean of the test results of the 3 specimens, with an accuracy of 0.1 MPa. If the difference between the minimum or maximum of the three measured values exceeds 15% of the intermediate value, the intermediate value is taken as the measured value. The final compressive strength value is multiplied by the size conversion factor of 0.95. There is frictional contact between the testing machine and the end surface of the test piece, and the loading speed is 0.7 MPa/s. The compressive strength of the test piece is calculated as follows:

\[
f_{cu} = \frac{F}{A},
\]

where: \(F\)—Failure load (N); \(A\)—Pressure area (mm²); \(f_{cu}\)—Compressive strength of test piece, accurate to 0.1 MPa.

The test process is shown in Figure 4.

3.2. Nuclear Magnetic Resonance Analysis

3.2.1. Test Principle. Shotcrete is a kind of porous material, and its internal pore structure, such as porosity and pore size distribution, can be obtained through nuclear magnetic resonance (NMR) test results. Low-field nuclear magnetic resonance technology was used in this experiment to test the transverse relaxation time \(T_2\) of the water in the pores of the shotcrete test block. Carr–Purcell–Meiboom–Gill (CPMG) spin-echo pulse sequence was adopted to obtain relatively accurate test results with less interference.

For the water in the pores, there are three different lateral relaxation mechanisms: ① free relaxation, ② surface relaxation, and ③ diffusion relaxation. When the magnetic field is uniform, short return interval is used and the pores contain only water, and the free relaxation and diffusion relaxation are very small compared with the surface relaxation, and the \(T_2\) relaxation of the medium is determined by the surface relaxation. The surface relaxation is closely related to the pore structure [53, 54], as in the following formula.

\[
\frac{1}{T_2} \approx \frac{1}{T_{2Surface}} = \rho_2 \left(\frac{S}{V}\right)_{Pore},
\]

where: \(\rho_2\) is the surface relaxation rate of \(T_2\); \(S/V)\)_{Pore} is the specific surface area of the pore; \(S\) is the pore surface area (\(\mu m^2\)); \(V\) is the pore volume (\(\mu m^3\)).

The NMR \(T_2\) spectrum distribution can reflect the pore structure of the sample. The position of the peak is related to...
the pore size, and the area of the peak is related to the number of the corresponding pore size. A smaller $T_2$ value corresponds to a smaller pore group and vice versa.

The self-healing performance was studied in this work, so the concept of pores can be understood as a collection of macro- and microcracks. Porosity can be regarded as the percentage of the total volume of pores to the volume of the concrete test block. From a macro perspective, it can describe the density of the test block, while from a microscopic point of view, it can reflect the development of microcracks. There have been hitherto few research reports on quantitative testing of the surface relaxation strength of shotcrete. Valckenborg et al. [55] estimated that the surface relaxation strength of cement after long-term hydration is 3–4.3 μm/s. Muller et al. [56] found that the surface relaxation strength of the synthetic CSH gel was 3.73 μm/s at 20 MHz. Therefore, the surface relaxation strength of shotcrete mixed with fly ash was taken as $\approx 4 \text{ μm/s}$ for the calculation.

To test the pore-size distribution in the fly ash shotcrete test block, assuming that the pores in the test block are cylindrical, the relationship between the pore radius and the transverse relaxation time is shown in the equation below.

$$r = 2p_1^2 T_2,$$

where: $r$ is the radius of the cylindrical pore (μm). It can be seen that the $T_2$ spectrum distribution reflects the pore size and distribution of the medium. The pore size is related to the position of the spectrum peak, and the number of pores corresponding to the pore size is related to the peak area.

For concrete mixed with iron-containing mineral admixtures, due to the influence of paramagnetic substances, the accuracy of the final test results will be affected. To reduce its influence, by comparing the porosity test results of the nuclear magnetic method and the weighing method, it can be seen that when the resonance frequencies were 2 MHz, 12 MHz, and 23 MHz during the test, the results at the frequency of 12 MHz was the closest to the test result of the weighing method. It can be seen that when performing nuclear magnetic resonance on a short-relaxed sample such as a cement concrete sample, the resonance frequency should be at about 12 MHz, which can not only greatly shorten the sampling time, but also increase the signal-to-noise ratio of the test piece. When the sample contains paramagnetic substances, its sensitivity is relatively low when subjected to a frequency of 12 MHz [57].

3.2.2. Test Procedure. In the research process of porosity and pore size distribution, we cooperated with Shanghai Niumai Electronic Technology Co., Ltd. to rent the MacroMR12-150H-I nuclear magnetic resonance imaging analyzer produced by the company to conduct experiments and analyze the results. The basic parameters of the test equipment were set to resonance frequency 12.798 MHz, used to collect $T_2$, the temperature of the magnet was controlled at 31.99–32.01°C, and the diameter of the coil, which was 150 mm. The field test process is shown in Figure 5.

3.3. X-Ray Diffraction Analyses

3.3.1. Test Principle. The Rietveld full-spectrum fitting method is an analytical method for XRD diffraction test of powdered samples. The basic principle is that the polycrystalline diffraction in the three-dimensional space is compressed into one dimension, and the directionality of each crystal plane index is lost. The overlap of diffraction peaks blurs the distribution curve of the diffraction intensity of the crystal plane and loses the structural information hidden in the powder diffraction pattern. However, the position of the diffraction lines of different phases will not change, and the intensity of the diffraction lines is mainly determined by factors such as the percentage of the phase in the mixture, and the scaling factor is just a reflection of this intensity change. Rietveld quantitative analysis is based on the relationship between the scale factor and the reference intensity ratio so as to deduce the relationship between the relative content of the phase and the scale factor [58, 59].

3.3.2. Test Procedure. Since the sample for the XRD test is required to be in powder form with a mass of about 0.2 g, it is necessary to break and grind the shotcrete test block. Therefore, first, the sample is processed manually, a small sample from the test block is knocked under curing and numbered (in block), then a hammer and grinding bowl are used to grind (in granular), and finally, it is put into a ball mill to grind into powder. After drying, the test samples are
prepared, numbered for testing, and the XRD test process is shown in Figure 6.

3.3.3. Calibration Process. The XRD calibration results of 4 kinds of cementitious materials are shown in Figure 7.

According to the test results, a calibration result can be obtained, as shown in Table 4. Fly ash is mainly amorphous, but the crystalline substances are consistent with 70.05% mullite and 29.95% quartz. The cement used in the test consists of 16.85% calcite, 55.63% tricalcium silicate, 3.87% quartz, 3.11% corundum, 3.65% plaster, 4.70% perovskite, and 12.19% borax pentahydrate. Silica fume is amorphous. Mineral powder is made up of 90.78% calcite, 7.86% dolomite, and 1.36% quartz.

4. Result and Discussion

4.1. Compressive Strength Analysis. The shotcrete cube compressive strength test was carried out in accordance with the "Cement Concrete Cube Compressive Strength Test Method" (T0553-2005). The shotcrete specimens with the age of 28 days were tested, and the test results are shown in Table 5.

From the data in Table 4 we can get: (1) the 28 d compressive strength of the shotcrete with 7 different mix ratios, all reaching the C30 strength standard 30 MPa, required by “Design Code of Concrete Structures” (GB50010-2010), some of which got sufficient strength potential. In terms of the compressive strength, all the specimens met the requirements; (2) with the same mixing content, the compressive strength of the specimens only mixed with mineral powder was higher than that of the specimens only mixed with fly ash. As the content of single active mineral admixture increased, the compressive strength of concrete decreased, indicating that the increase of single active mineral admixture will cause the compression strength of the test block to decrease.

4.2. Nuclear Magnetic Resonance Analysis

4.2.1. Test Results. According to the low-field nuclear magnetic resonance test mentioned above, the shotcrete blocks made of 7 mix ratios N1 to N7 were tested, and the test results of 7 d, 14 d, 28 d, 56 d, and 92 d were obtained.

The low-field nuclear magnetic resonance used in this study is mainly to measure the transverse relaxation time $T_2$.
by means of a CPMG spin-echo pulse sequence with the
principle mentioned in Section 3.2.1. The relaxation rate of a
porous fluid is closely related to its inherent properties. It is
known that the $T_2$ spectrum reflects the size and the dis-
tribution of the pore. The pore size is related to the $T_2$ value,
and the number of pores corresponding to the pore size is
related to the peak area.

At present, there are few reports on the quantitative
measurement of the surface relaxation strength of composite
cementitious materials. However, due to the different
components and microstructures of the materials, the sur-
face relaxation strength test values of other materials cannot
be directly applied. Therefore, in the early stage of the
nuclear magnetic resonance test, a set of mercury-intrusion

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**Figure 7:** XRD calibration results of 4 kinds of cementitious materials (a) XRD calibration results of fly ash (b) XRD calibration results of cement (c) XRD calibration results of silica fume (d) XRD calibration results of mineral powder.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fly ash</th>
<th>Cement</th>
<th>Silica fume</th>
<th>Mineral powder</th>
</tr>
</thead>
<tbody>
<tr>
<td>Result</td>
<td>Mainly amorphous, among crystalline substances:</td>
<td>Calcite (16.85%) Tricalcium silicate (55.63%)</td>
<td>Quartz (29.95%) Calcite (90.78%) Dolomite (7.86%)</td>
<td>Silica fume</td>
</tr>
<tr>
<td></td>
<td>Mullite (70.05%)</td>
<td>Quartz (3.87%) Corundum (3.11%) Plaster (3.65%)</td>
<td>Perovskite (4.70%) Borax Pentahydrate (12.19%)</td>
<td></td>
</tr>
</tbody>
</table>

<p>| Table 5: Test results of compressive strength of C30 shotcrete. |
|---------------------------------|--------------------|--------------------|--------------------|--------------------|</p>
<table>
<thead>
<tr>
<th>Number</th>
<th>Proportioning type</th>
<th>Measured value (kN)</th>
<th>Measured value (kN)</th>
<th>Measured value (kN)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N1</td>
<td>JZ</td>
<td>427.09</td>
<td>431.53</td>
<td>403.8</td>
<td>40.0</td>
</tr>
<tr>
<td>N2</td>
<td>F10</td>
<td>424.61</td>
<td>531.08</td>
<td>485.00</td>
<td>45.6</td>
</tr>
<tr>
<td>N3</td>
<td>F20</td>
<td>347.92</td>
<td>301.87</td>
<td>406.49</td>
<td>33.1</td>
</tr>
<tr>
<td>N4</td>
<td>F30</td>
<td>382.79</td>
<td>395.66</td>
<td>402.72</td>
<td>37.4</td>
</tr>
<tr>
<td>N5</td>
<td>K10</td>
<td>387.63</td>
<td>417.34</td>
<td>572.89</td>
<td>39.6</td>
</tr>
<tr>
<td>N6</td>
<td>K20</td>
<td>407.59</td>
<td>458.15</td>
<td>381.51</td>
<td>39.5</td>
</tr>
<tr>
<td>N7</td>
<td>K30</td>
<td>434.76</td>
<td>382.30</td>
<td>365.81</td>
<td>37.5</td>
</tr>
</tbody>
</table>
Figure 8: Continued.
experiments were carried out, and the pore-size distribution range of the microscopic pores of the composite cementitious material was initially obtained. Then, it can be deduced that the surface relaxation strength of the hardened slurry of the composite cementitious material varies in the range of $10 \mu m/s \sim 50 \mu m/s$, and the intermediate value $\rho_2 = 30 \mu m/s$ is taken in this study.

The $T_2$ relaxation spectrum can be obtained by the nuclear magnetic resonance imaging analyzer, as shown in Figure 8.

### 4.2.2. Pore Analysis

The porosity distribution inside the test block was obtained through data inversion. Since the initial pores might be affected by the mixing or spraying process, the change rate of porosity was mainly concerned with the analysis of the self-healing ability, as shown in Figure 9.

The pore-change law can be divided into three parts, 7 to 14 days is the pore reduction stage, 14 to 28 days is the stable stage, and after 28 days is the lag stage. In the reduction stage, the porosity of the shotcrete of each mix ratio decreased. At this time, the hydration reaction occurred inside the shotcrete, which produced ettringite and microexpands to fill the pores. In the early 28 days, when the amount of mineral powder and fly ash was small (N2 and N5), the porosity of the group was smaller than that of the N1. When the dosage was large (N3, N4, N6, N7), the porosity of the group was greater than that of the N1. The addition of the cementitious material at this time is not effective to control the porosity. After 28 days, except the N1, the porosity of the samples with cementitious materials decreased to a certain extent. In the stable stage, the porosity change of the other groups except N1 tended to stabilize, while the porosity of the N1 group continued to decrease. At this moment, adding mineral powder and fly ash can effectively delay the production of ettringite. In the lag phase, it can be seen that the porosity of test blocks has increased except for N4, N6, and N7 (marked by the solid line in the figure), especially N1 increased more. At this moment, the growth of ettringite in shotcrete without adding mineral powder and fly ash was limited in the later stage, and the porosity of the three groups of N4, N6, and N7 further decreased, which made better use of the expansion effect of ettringite to make the shotcrete with microcracks achieve a certain self-healing effect.

Academician Wu Zhongwei roughly classified the pore size in the concrete [60]. The pores with a radius of $0–0.025 \mu m$ can be regarded as harmless pores. The pores with a radius of $0.025–0.25 \mu m$ are considered less harmful and harmful pores, respectively. Pores with a radius of $\sim 0.25 \mu m$ are hazardous pores. Statistics of the pore volume ratios in the 3-pore size ranges at each age of all the mix ratios, and the following results are obtained. See Table 6 for details. The harmful pores and hazardous pores are sorted as shown in Figure 10.
There are also three stages in the change law of harmful pores. Between days 7 and 14 is the growth stage, 14 to 28 days is the stable stage, and after 28 days is the decline stage.

4.3. X-Ray Diffraction Analyses. The ettringite is generated by the following three steps:

\[ \text{AlO}_2^- + 2\text{OH}^- + 2\text{H}_2\text{O} = [\text{Al(OH)}_6]^3^- \],

(4)

\[ 2[\text{Al(OH)}_6]^3^- + 6\text{Ca}^{2+} + 24\text{H}_2\text{O} = [\text{Ca}_6[\text{Al(OH)}_6]^2 \cdot 24\text{H}_2\text{O}]^{6+} \],

(5)

\[ [\text{Ca}_6[\text{Al(OH)}_6]^2 \cdot 24\text{H}_2\text{O}]^{6+} + 3\text{SO}_4^{2-} + 2\text{H}_2\text{O} = [\text{Ca}_6[\text{Al(OH)}_6]^2 \cdot 24\text{H}_2\text{O}](\text{SO}_4^{2-})_2\text{H}_2\text{O} \].

(6)
Since both N4 and N7 had good effects as mentioned in Section 4.2, XRD analyses were conducted on the specimens of N1, N4, and N7. According to the results of XRD tests and referring to the calibration XRD analysis test results, combined with the formula for the formation of ettringite, the result can be deduced that it is OH$^-\hspace{1cm}$ and SO$_4^{2-}$ that mainly affected the balance of the reaction. Calcium hydroxide and ettringite are largely discussed in this section. See Table 7 for details.

Comparing the content of ettringite and the porosity from Section 4.2 as shown in Figure 11, it is clear that the variation of ettringite content can also be divided into three phases, and the change of porosity can be deduced by the content of ettringite. With the increase of the ettringite content, the porosity decreased marginally, while the ettringite content of N1 showed a decline after 28 days, with the corresponding porosity climbing accordingly, even though the participation of fly ash and mineral powder can enhance the generation of ettringite, sustaining the hydration of concrete.

Although the actual porosity of N1 is comparable to that of N4 and is significantly lower than that of N7, it contains harmless pores with a pore radius between 0 and 0.025 μm, which does not contribute to the leakage of concrete. The distribution of harmful pores is shown in Figure 10. It can be seen that the addition of fly ash and mineral powder can obviously reduce the harmful pores in the specimen, especially after 28 days, the delayed production of ettringite effectively reduced the harmful pores.

5. Conclusions

(1) Utilizing the characteristics of ettringite, that it can play a microexpansion effect to fill the pores when countering water, can help shotcrete gratifying the requirement of self-healing and waterproof, which can be applied in single shell lining structures with water seepage.

(2) The content of ettringite is inversely proportional to the change law of pore structure. When the content of ettringite increases, the porosity and the pores proportion of harmful decreases significantly. The addition of cementitious materials can effectively prolong the hydration of concrete. When the pore water is reduced to a certain amount, the ettringite will not increase any more, reducing the influence of ettringite expansion on the concrete structure. Thus, controlling the proportion of ettringite can achieve the requirement of waterproofing.

(3) Fly ash and mineral powder with a mixing amount of about 30% will not affect the strength of the concrete, while prolonging the time of the effect of ettringite, effectively improving the impermeability of the shotcrete.

(4) Since the process of shotcrete is relatively complicated and there still are a few deficiencies in the tests, the technology of self-healing needs further research. Adapting the proportion of cementitious material and testing the internal structure of shotcrete by nuclear magnetic methods are mainly discussed in this study, which can provide ideas and information for other similar researches.

### Table 7: Specimens’ XRD analyses results with different ratios and ages.

<table>
<thead>
<tr>
<th>Age (d)</th>
<th>N1</th>
<th>N4</th>
<th>N7</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>Calcium hydroxide (2.55%)</td>
<td>Calcium hydroxide (1.86%)</td>
<td>Calcium hydroxide (1.76%)</td>
</tr>
<tr>
<td></td>
<td>Ettringite (1.01%)</td>
<td>Ettringite (3.57%)</td>
<td>Ettringite (1.64%)</td>
</tr>
<tr>
<td>14</td>
<td>Calcium hydroxide (2.21%)</td>
<td>Calcium hydroxide (2.82%)</td>
<td>Calcium hydroxide (2.30%)</td>
</tr>
<tr>
<td></td>
<td>Ettringite (4.32%)</td>
<td>Ettringite (2.86%)</td>
<td>Ettringite (4.32%)</td>
</tr>
<tr>
<td>28</td>
<td>Calcium hydroxide (3.69%)</td>
<td>Calcium hydroxide (3.35%)</td>
<td>Calcium hydroxide (3.94%)</td>
</tr>
<tr>
<td></td>
<td>Ettringite (4.76%)</td>
<td>Ettringite (3.85%)</td>
<td>Ettringite (4.14%)</td>
</tr>
<tr>
<td>56</td>
<td>Calcium hydroxide (2.78%)</td>
<td>Calcium hydroxide (2.67%)</td>
<td>Calcium hydroxide (2.83%)</td>
</tr>
<tr>
<td></td>
<td>Ettringite (4.10%)</td>
<td>Ettringite (2.04%)</td>
<td>Ettringite (2.93%)</td>
</tr>
<tr>
<td>92</td>
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<td>Calcium hydroxide (2.12%)</td>
<td>Calcium hydroxide (3.49%)</td>
</tr>
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<td>Ettringite (3.86%)</td>
<td>Ettringite (4.11%)</td>
</tr>
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</table>

**Figure 11: Variation chart of ettringite content.**
Data Availability
The experimental data used to support the observations of this study are included in the article.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

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