

Article

Experimental Study on Performance of Modified Cement-Based Building Materials under High-Water-Pressure Surrounding Rock Environment

Jun Yao ^{1,2}, Di Feng ^{1,*} , Zhikui Wang ³ , Chengcheng Peng ¹, Yonggang Zhang ⁴ and Lei Han ⁴

¹ College of Civil and Transportation Engineering, Hohai University, Nanjing 210098, China

² College of Urban Construction and Transportation, Hefei University, Hefei 230601, China

³ China Railway Construction Underwater Shield Tunnel Engineering Laboratory, China Railway 14th Bureau Group Co., Ltd., Jinan 250101, China

⁴ Engineering Research Institute, China Construction Eighth Engineering Division Corp., Ltd., Shanghai 200122, China

* Correspondence: fengdi@hhu.edu.cn

Abstract: Traditional cement-based grouting materials have good reinforcement and anti-seepage effects on the surrounding rock under normal conditions, but the grouting effect is not ideal due to problems such as a long setting time, a low stone ratio, and poor crack resistance under high water pressure and in a dynamic water environment. In this study, we aimed to improve the physical properties, chemical properties, and microstructure of a cement-based slurry by forming a hydrogel through its chemical crosslinking with polyvinyl alcohol and boric acid as modifiers for the purpose of improving the permeability resistance of the surrounding rock grouting under high-water-pressure conditions, which can expand the function of traditional building materials. The grouting effect of the modified cementitious material on the surrounding rock was analyzed through indoor tests, the SEM testing of the performance of the modified slurry, the numerical calculation of the seepage field, and the application of the modified slurry in combination with the actual project to verify the water-plugging effect. The research findings demonstrate that (1) the additives boric acid and PVA can significantly speed up the slurry gel time, and the gel time can be controlled within 2–20 min to meet the specification requirements. (2) At a velocity of moving water > 1 m/s, the retention of the solidified modified slurry stone body reaches more than 80%. According to the SEM analysis, the structure of the solidified modified slurry stone body is dense and has good impermeability. (3) According to the numerical calculation analysis, the modified slurry can effectively change the seepage field of the surrounding rock and improve its seepage resistance. The water pressure outside the lining is reduced by 47%, 31%, and 22%, respectively, compared with no slurry, the pure cement slurry, and cement–water–glass grouting, and the indoor test and numerical simulation conclusions are consistent.

Keywords: cement-based material; polyvinyl alcohol; boric acid; impermeability



Citation: Yao, J.; Feng, D.; Wang, Z.; Peng, C.; Zhang, Y.; Han, L. Experimental Study on Performance of Modified Cement-Based Building Materials under High-Water-Pressure Surrounding Rock Environment. *Coatings* **2023**, *13*, 501. <https://doi.org/10.3390/coatings13030501>

Academic Editor: Valeria Vignali

Received: 3 February 2023

Revised: 18 February 2023

Accepted: 21 February 2023

Published: 24 February 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

With the rapid development of science and technology, building materials are increasingly widely used [1,2]. To increase permeability and protect the lining structure and the environment, the surrounding rock of the tunnel can be strengthened by grouting. Traditional grouting materials have good water-plugging and reinforcement effects in static environments, but the disadvantages of a slow setting time, dispersion resistance, and weak crack resistance of the traditional slurry will lead to a poor grouting effect in high-water-pressure and moving environments [3–6]. Therefore, an important research goal is to improve traditional cement-based grouting materials to meet the grouting requirements under high water pressure and in a dynamic water environment and to improve the application range of building materials.

The tunnel grouting material in the high-water-pressure surrounding rock environment needs to have good impermeability and injectability, and tunnel grouting materials have been studied by several researchers. Hua and Xie [7] conducted an indoor test to determine the fluidity, water barrier properties, and compressive strength of fly ash and a cement slurry and an engineering practice test to determine the grouting ratio. Zhang [8] analyzed the applicability and grouting effect of a single cement slurry, a double slurry composed of a cement slurry and water-glass slurry, and a fine cement slurry under different working conditions of karst tunnel curtain grouting in Gele Mountain, and the analysis showed that the double slurry grouting material composed of a cement slurry and water-glass slurry is more effective. Tian et al. [9] examined how fly ash, the water-reducing agent, and the water–cement ratio affected the grouting slurry’s flowability, setting time, and compressive strength. Through optimization, a grouting slurry with a high degree of compatibility was created. Li et al. [10] developed a new grouting material with a good grouting capacity, good water retention, and high early strength. The results show that the elastic modulus, grouting volume, and pressure of the material all have an impact on ground settlement, according to the application results of a cross-river shield tunnel grouting project. Through indoor tests, Peng et al. [11] examined the effects of the water-glass admixture, boehmite content, and powder ratio on the slurry’s performance. It was found that, compared with traditional materials, the double slurry has the advantages of a controlled setting time, high compressive strength, and environmental protection and is better used in river bottom tunnel grouting work. Zhang et al. [12] used bentonite and cement as base materials with a curing agent to obtain excellent flow, stability, and scouring resistance, which can be applied to meet engineering requirements in a moving water environment while being cost-effective and environmentally friendly. Zhang et al. [13] developed a grouting substance using cement, clay, meta-aluminate, and lignin. Indoor tests revealed that the substance has a quicker gel time, a lower exudation rate and volume shrinkage, a higher viscosity and anti-dispersion effect, and a better underwater grouting effect.

Through indoor tests, Zhu et al. [14] analyzed a slurry composed of cement, clay, and fly ash and tested its mechanical and rheological properties. The results show that the grouting material has good mechanical properties and impermeability. Liu et al. [15] prepared a kind of cement based on magnesium phosphate. The indoor test showed that GGBS significantly shortened the setting time, improved a certain amount of fluidity, produced a compact microstructure, and was environmentally friendly. Wan et al. [16] proposed water glass and bentonite as grouting materials and tested the mechanical properties and microscopic properties of the materials. The results indicate that the grouting materials have good viscosity. Wang et al. [17] studied the effect of PVA fibers on the mechanical properties and durability of rubber concrete through laboratory tests. The results show that PVA can significantly improve the impermeability and durability of rubber concrete. Zhang et al. [18] prepared a new type of double-fluid grouting material and analyzed the setting time, expansion rate, and mechanical strength characteristics of the grouting material through laboratory tests to meet the requirements of the grouting environment. Sun et al. [19] analyzed the influence of different proportions of organic materials such as fly ash, clay, waterborne polyurethane, and epoxy resin on the grouting performance of a cement slurry through a single-factor test, orthogonal test, and organic compound modification test. The results indicate that the addition ratio of clay and fly ash has a strong influence on the strength and stone ratio of the cement slurry.

Through indoor tests, Liu et al. [20] researched the effect of the PVA content on the performance of fly-ash-based cement grouting materials. It had a significant effect on the mechanical properties of the grouting material and could effectively improve the rock mass’ hydraulic coupling characteristics. The impermeability of PVA to the grouting material was markedly improved, and it increased with increasing amounts of PVA content. Lu et al. [21] proposed porous sand, PVA, cement, and rubber grouting materials. The density, consistency, fluidity, exudation rate, consolidation shrinkage rate, setting time, and

unconfined compressive strength of the slurry were tested in the laboratory. The results showed that the grouting material has good toughness and high strength.

In order to design grouting materials, many researchers have combined different grouting projects with their findings, obtained specific results based on the performance of cement bases, and added modified materials to the pure cement slurry to achieve the desired grouting anti-seepage and reinforcement effects under various working conditions.

However, there are still some issues within the current literature, such as the slurry's low stone solidification retention ratio, low compressive resistance, and insufficient crack resistance, which will result in a poor water-plugging effect when it is exposed to high water pressure or a moving water environment. In recent years, polyvinyl alcohol and boric acid have become increasingly applied modified materials, which are used to rapidly induce gelation via chemical crosslinking at certain concentrations. This mechanism improves the properties of cement-based materials so as to meet the grouting requirements under high water pressure and in moving water environments. In this study, an indoor test was performed to examine the effects of parameters such as the water–cement ratio, the concentration of polyvinyl alcohol, and the concentration of boric acid on the properties of the slurry setting time, stone solidification retention ratio, and compressibility in a moving water environment against the backdrop of the surrounding rock under high water pressure. Combined with scanning electron microscopy, the microstructural characteristics of the modified material's stone body were analyzed to verify whether the modified slurry achieved design expectations. Finally, the water-plugging effect of the cement–polyvinyl alcohol–boric acid slurry was examined by numerical calculations using a real-world engineering application as an example, and the consistency between the results of the indoor test and the numerical calculation was verified.

The main purpose of this work was to analyze the liquid properties of the grouting material, the properties of the stone body, and the water-plugging properties of the whole grouting ring after grouting through laboratory tests and numerical simulations. Further, tests were performed to verify whether the modified cement-based materials can meet the requirements of the surrounding rock grouting in a high-water-pressure environment from the characteristics of the liquid and solid material and the engineering application process in three stages. The results of this study can provide a comprehensive understanding of modified grouting materials in engineering practice.

2. Basic Performance Study of Single Cement Slurry

The primary component of composite grouting materials is the single cement slurry, which is enhanced by modified materials to meet the needs of various engineering environments, including requirements for grouting fluid impermeability and injectability [22]. As a result, the performance of the composite grouting material is directly influenced by the fundamental performance of the single cement slurry, and the following indoor test study was conducted to determine this fundamental performance.

2.1. Test Materials and Procedure

Since the water–cement ratio affects the primary characteristics of the common cement slurry, the pure cement slurry is primarily composed of silicate cement with different water–cement ratios (W/C). The pure cement slurry was prepared with five different water–cement ratios: 0.5:1 (50 g water, 100 g cement), 0.8:1 (80 g water, 100 g cement), 1:1 (100 g water, 100 g cement), 1.5:1 (150 g water, 100 g cement), and 2:1 (200 g water, 100 g cement). Each group of material tests was conducted three times, and the data in the figures in the manuscript are the average values of the three groups of tests.

Figure 1 shows the precise results from a rotary viscometer (Shanghai Jinglai Electronic Technology Development Co., Ltd., Shanghai, China) used to measure the viscosity of the cement slurry at various water–cement ratios. A viscometer (Shanghai Leiyun Test Instrument Manufacturing Co., Ltd., Shanghai, China) was used to determine the initial and final setting times of the cement slurry at various water–cement ratios, and the precise

results are displayed in Figure 2. For standard curing, the cement slurry was formed into cubic specimens. Uniaxial compressive strength tests were then carried out at 3 d, 7 d, 14 d, and 28 d [23]. The results are shown in Figure 3. To calculate the stone solidification ratio, 100 mL of each type of slurry with one of the five water–cement ratios was placed in a measuring cylinder and left for 3 h. The liquid level was then read and recorded.

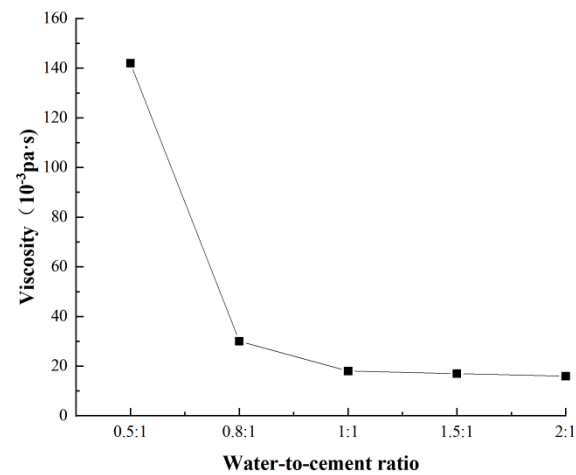


Figure 1. The influence of the water–cement ratio on the viscosity of the slurry.

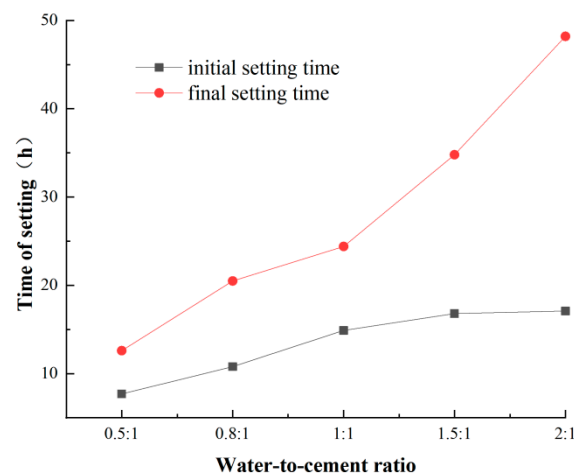


Figure 2. The influence of the water–cement ratio on the slurry setting time.

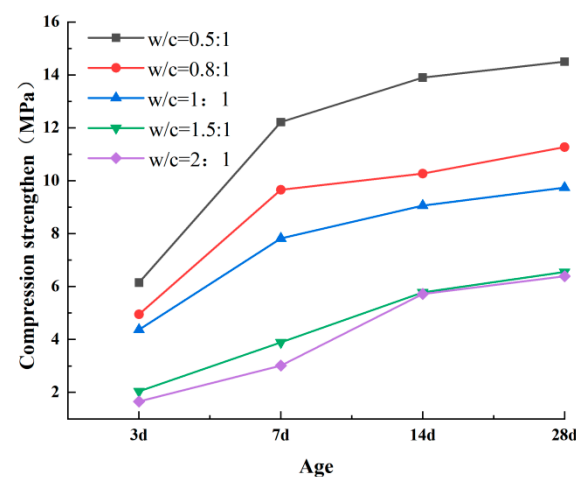


Figure 3. Compressive strength of the solidified slurry stone body.

Since the groundwater has a certain flow rate under the effect of high water pressure, the retention ratio of the stone body solidification of the slurry in a static water environment and a moving water environment after grouting must be taken into account in order to simulate the actual grouting environment. Cement slurries were prepared with water–cement ratios of 0.5:1, 1:1, and 2:1. After the initial setting of the material, it was placed on inorganic glass and in a homemade inorganic glass sink with a flow rate of 0.2, 0.4, 0.6, 0.8, 1.0, or 1.2 (m/s). The stone solidification retention ratio of the slurry was measured after 30 min in static water and moving water. The test primarily analyzed the water–cement ratio and water velocity on the slurry, combined with the anti-dispersion impact, and the test results are shown in Figures 4 and 5.

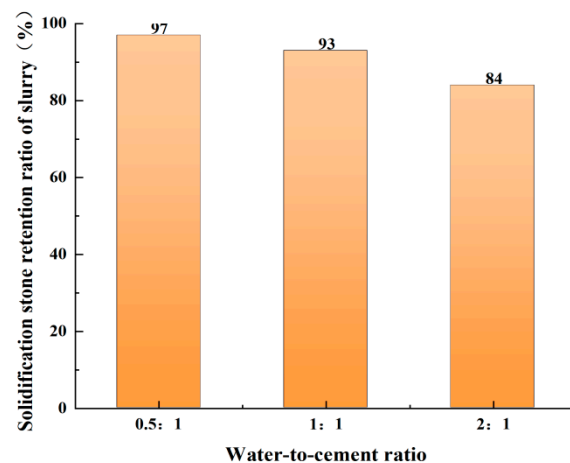


Figure 4. Stone solidification retention ratio of slurry in static environment.

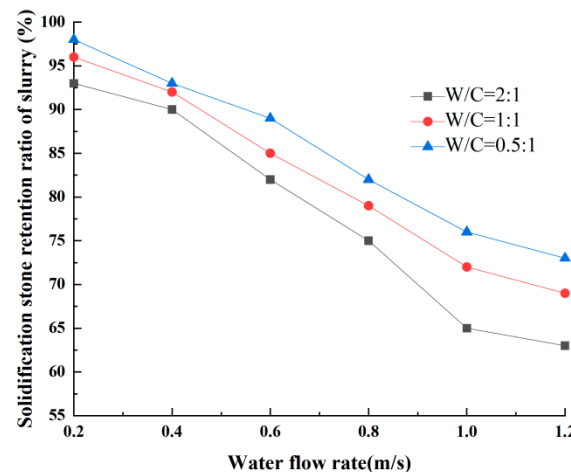


Figure 5. Stone solidification retention ratio of slurry in moving water environment.

2.2. Analysis of Experimental Results

According to Figure 1, as the water–cement ratio rises, the concentration of a single cement slurry decreases. The viscosity of the cement slurry decreases significantly from 140×10^{-3} to about 40×10^{-3} , or by about 70%, when the water–cement ratio is between 0.5 and 1.0. When the water–cement ratio is greater than 1, the viscosity of the slurry tends to reach a plateau and hardly change. The change is primarily caused by the relatively high water–cement ratio, which causes a complete reaction of cement hydration and prevents the viscosity from rising as the water ratio rises.

The water–cement ratio has a greater impact on the setting time of the pure cement paste, as shown in Figure 2. The initial setting time increases from 7 h to around 15 h as the water–cement ratio rises, and the final setting time rises as well. The initial to final setting

time interval of the pure cement slurry varies with the water–cement ratio; for example, for a water–cement ratio of 0.5, the interval is approximately 5 h, whereas for a water–cement ratio of 2.0, the interval is approximately 30 h. This difference is primarily due to the higher cement content, which causes the slurry to set faster.

The solidification strength of the pure cement slurry is also influenced by the water–cement ratio, as shown in Figure 3, and the greater the compressive strength at the same age, the smaller the water–cement ratio. The strength growth is faster for the four water–cement ratios from 3 d to 7 d, and the solidification strength increases gradually after 7 d. The solidification strength of the cement slurry varies significantly depending on the water–cement ratio; for example, the solidification strength of a water–cement ratio of 0.5 is approximately 15 MPa, while that of a water–cement ratio of 2 is only approximately 6 MPa, a difference of approximately 2.5 times [24]. The solidification ratio of the pure cement slurry, which can reach about 99% with a high solidification ratio for all five water–cement ratios, is essentially unaffected by the water–cement ratio.

Figure 4 shows that the slurry with a water–cement ratio of 0.5 had the highest combined retention ratio of 97%, and the slurry with a water–cement ratio of 2 had the lowest combined retention ratio of 84% after being placed in still water for 30 min after the initial setting. This shows that the slurry with a high cement content had a better cementing effect in still water. Following the initial slurry setting with various water–cement ratios, Figure 5 illustrates the retention ratio of slurry stone solidification in moving water at various water velocities. As can be seen in the figure, the retention ratio of stone solidification decreases with the increasing moving water flow velocity and increases with the decreasing water–cement ratio at the same flow velocity. The stone solidification retention ratio for each water–cement ratio at a 1.2 m/s flow velocity is only 60%–70% of the stone solidification retention ratio at a 0.2 m/s flow velocity according to this law, which states that the slurry needs to have a certain carrier dispersion to ensure the grouting effect in the moving water environment. The grouting fluid should have better anti-dispersion properties under high-water-pressure conditions because the slurry is easily dispersed in the moving water environment compared to the static water environment.

3. Basic Performance Study of Cement–Polyvinyl Alcohol–Boric Acid Slurry

The pure cement slurry has good viscosity and a high ratio of solidified stone formation, but it also has a long setting time, numerous brittle material pores in the formed stone body, a low ratio of stone retention under high water pressure, and insufficient durability. Under high water pressure and with enhanced permeability, the pores of the solidified slurry stone body will further open up and form cracks, which will greatly reduce the water-plugging effect and prevent the expected grouting effect from occurring [25–27]. The use of the polyvinyl alcohol and cement slurry mixture, owing to the polyvinyl alcohol hydrogel's anti-cracking properties, enhances the performance of the grouting solution to achieve the expected effect of grouting. This improves the cement slurry setting time, improves the crack resistance of the grouted stone body, and enhances the durability of the grouting material [28,29].

3.1. Effect of Polyvinyl Alcohol Concentration on Gelation Time

Polyvinyl alcohol, or PVA, is a type of polymer with good water solubility that deforms well and has good toughness once it has gelled into a film. The PVA solution and cement liquid mix well, creating a gel film with good plasticity that also protects the cement from corrosion and increases the durability and crack resistance of the stone body [30–32].

Polyvinyl alcohol is insoluble in water at room temperature. Therefore, in this test, in order to dissolve it in water, it was heated and stirred with a magnetic stirrer. The temperature was set at 80 °C, and the solution was stirred for twenty hours. Different concentrations of the PVA solution and cement slurry volumes were mixed to configure PVA aqueous solutions with concentrations of 1%, 2%, 3%, 4%, and 5%, and the volume ratio of cement to PVA solution was 4:1. The inverted cup method was used to measure the

water–cement ratio of the PVA solution with various concentrations and the time it took for the double-slurry gel to form. The specific results are shown in Table 1.

Table 1. Gel times of double slurries with different concentrations and water–cement ratios.

Concentration	W/C				
	0.5:1	0.75:1	1:1	1.5:1	
1%	189	654	1108	1598	
2%	174	612	1097	1574	
3%	154	563	1006	1528	
4%	121	487	987	1503	
5%	97	425	945	1458	

Table 1 shows that the gel time of the cement–polyvinyl alcohol slurry ranges from 97 to 1458 s at various water–cement ratios and polyvinyl alcohol concentrations, all within a half-hour, which essentially satisfies the requirements for the gel time of the grouting material in grouting construction. The gel time decreased by up to 50% with an increase in the polyvinyl alcohol concentration at the same water–cement ratio, indicating that the polyvinyl alcohol concentration has a greater influence on the gel time. At the same polyvinyl alcohol concentration, the gel time increases with a higher water–cement ratio, in line with the law of change of the pure cement slurry.

3.2. Effect of Boric Acid on Cement–Polyvinyl Alcohol Slurry Properties

The cement–polyvinyl alcohol slurry was mixed with a boric acid solution to speed up the gelation process. As a type of chemical crosslinking agent for polyvinyl alcohol, boric acid is very sensitive to a PVA aqueous solution and can shorten the time it takes for the solution to gel and turn into a hydrogel. This meets the requirement for a slurry's controllable setting time under high water pressure.

In order to easily analyze the influence law of boric acid on the gel time of the cement–polyvinyl alcohol slurry, a 5% PVA solution concentration was used, with the ratio of the cement solution volume to the PVA solution volume = 4:1, and the boric acid–polyvinyl alcohol ratios were taken as 0.05, 0.1, 0.15, and 0.2. The gel times of different slurries were measured by the inverted cup method. At the same time, compressive tests were conducted on the solidified stone bodies at the age of 3 d for different slurries. The results obtained are shown in Figures 6 and 7.

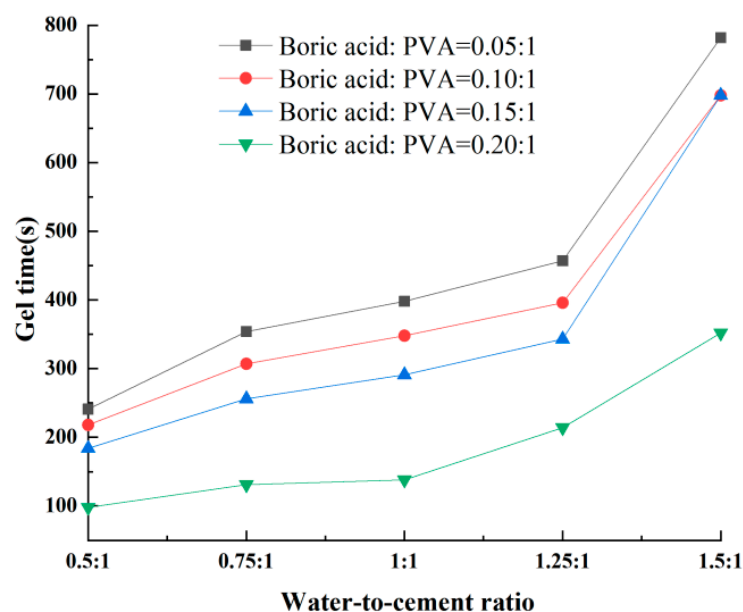


Figure 6. The influence of the water–cement ratio and boric acid on the slurry setting time.

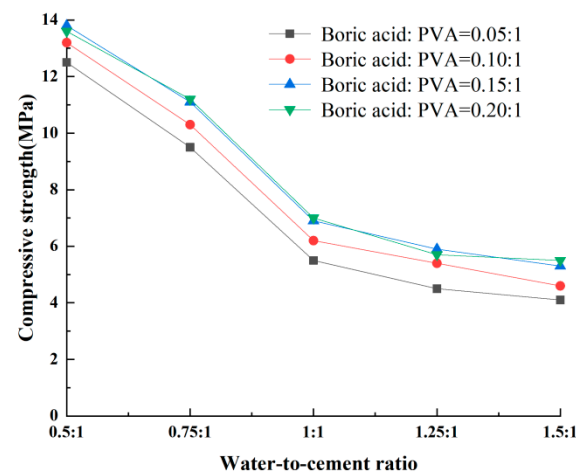


Figure 7. The influence of the water–cement ratio and boric acid on compressive strength.

As can be seen from Figure 6, when the ratio of boric acid to polyvinyl alcohol is less than 0.15, with an increase in the ratio, the time needed for the cement–polyvinyl alcohol slurry to gel is significantly shortened. PVA is very sensitive to boric acid, and a gel is formed between them through chemical crosslinking to accelerate the setting of the cement slurry. It can be seen from Figure 7 that both the water–cement ratio and boric acid ratio affect the compressive strength of the stone body. At the same water–cement ratio, the compressive strength increases with the increase in the boric acid ratio. When the boric acid ratio is higher than 0.15, the compressive strength increases slowly. BA ionizes $B(OH)_4$ in water, and $B(OH)_4$ crosslinks with the hydroxyl group on the PVA molecular chain to form a stable six-membered ring structure. Due to chemical crosslinking between boric acid and PVA, the compressive strength increases. The reaction process is shown in Figure 8.

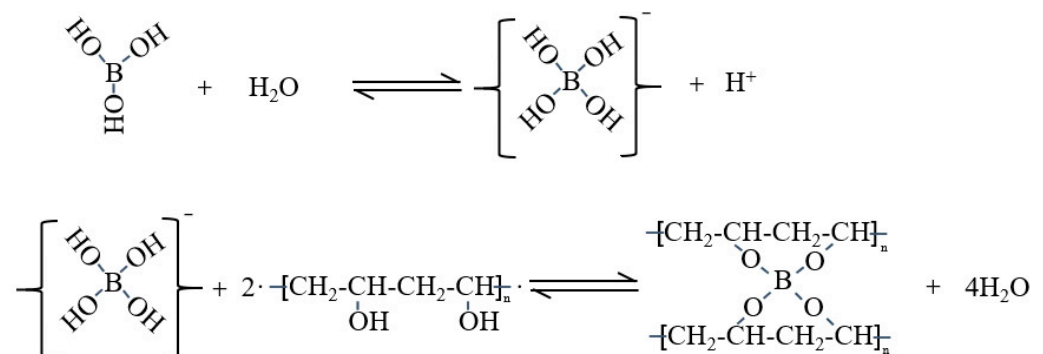


Figure 8. Reaction process of BA and PVA.

3.3. Effect of Polyvinyl Alcohol Concentration on Stone Formation Ratio

A cement solution with a water–cement ratio of 1:1 was mixed with 1%, 2%, 3%, 4%, and 5% polyvinyl alcohol solutions to form five cement–polyvinyl alcohol solutions with a volume ratio of cement solution to PVA solution of 4:1. In order to calculate the stone solidification ratio, 100 mL of each of the five water–cement ratio slurry mixtures was placed in a measuring cylinder. After three hours' rest, the liquid height was read and recorded. The overall stone solidification ratio is high, almost 100%. Figure 9 displays the results of measuring five solutions on a rotational viscometer to determine the viscosity of various slurries. From this figure, it is illustrated that the slurry viscosity generally increases with the concentration, but at concentrations greater than 3%, this growth is constrained. This is primarily due to the spatial grid structure that the solubilizer has created in the slurry, which no longer increases with the concentration.

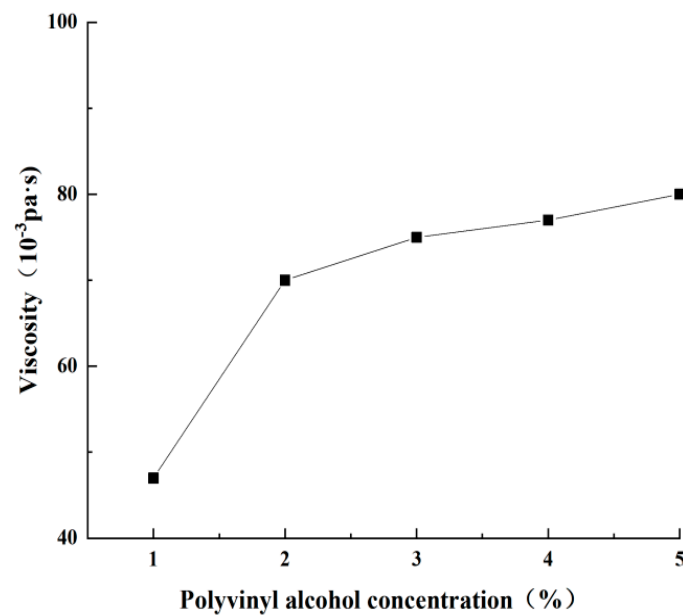


Figure 9. Effect of polyvinyl alcohol concentration on the slurry viscosity.

3.4. Cement–Polyvinyl Alcohol Slurry’s Moving Water Retention Ratio

A cement solution with a water–cement ratio of 1:1 was mixed with polyvinyl alcohol solutions with concentrations of 1%, 2%, 3%, 4%, and 5%. The ratio of the cement liquid volume to polyvinyl alcohol solution volume was 4:1, creating five different cement–polyvinyl alcohol solutions. In order to measure the retention ratio of solidified slurry stones after 30 min and analyze the slurry’s binding resistance to dispersion, the materials were first placed on inorganic glass and then placed in hydrostatic water and a homemade water tank with a specific flow rate. The results are shown in Figure 10.

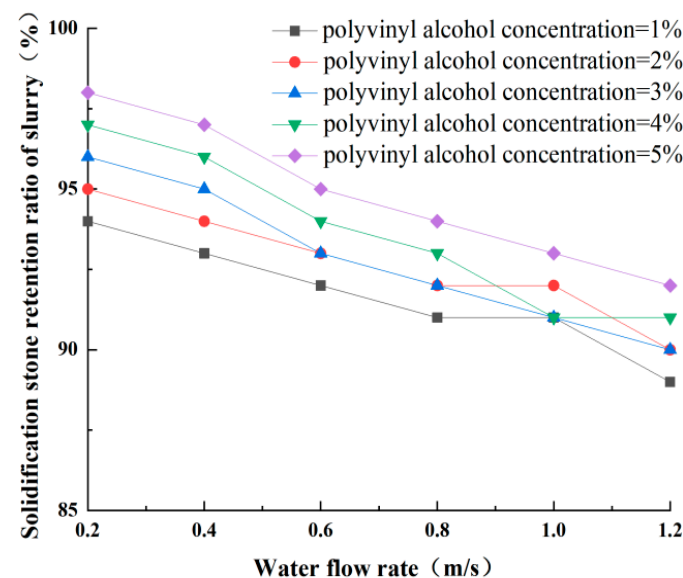


Figure 10. Effect of water flow rate on slurry solidification ratio.

Figure 10 demonstrates that the influence of different polyvinyl alcohol concentrations on the slurry’s moving water retention rate is less, but the higher polyvinyl alcohol concentration results in a higher stone solidification retention ratio. In addition, the retention of the cement–polyvinyl alcohol slurry solidification ratio is higher in a moving water environment. This is primarily because the higher the polyvinyl alcohol concentration, the

greater the gel formation and the higher viscosity of the slurry, which results in a higher retention ratio in the moving water environment.

3.5. Scanning Electron Microscope Analysis

Information on the solidified cement slurry and cement–polyvinyl alcohol slurry stones was obtained, as shown in Table 2, and a scanning electron microscopy test was carried out to observe the crack characteristics of both solidified slurry stones from a microscopic perspective. This was carried out to confirm that the crack resistance of cement–polyvinyl alcohol slurry nodules was improved [33]. A cold field-emission scanning electron microscope, model SU8010 from Hitachi, Japan, was used for the test. In order to conduct the test, samples from two solidified slurry stone bodies were first taken and pasted on conductive tape. The specimens were then placed in the apparatus for vacuum treatment and gold spraying. Finally, the specimens were scanned under a microscope to see the microscopic cracks.

Table 2. Preparation of slurry for electron microscope scanning.

No.	Slurry Type	Water–Cement Ratio	Additive Volume Ratio	External Additive Concentration	Age
A01	Cement slurry	1:1	/	/	3 d
A02	Cement–polyvinyl alcohol	1:1	4:1	5%	3 d

As seen in Figure 11a,b, the solidified cement slurry stones have more pores, which are randomly distributed throughout the stones. The porous and brittle nature of cement-based materials causes them to further develop when exposed to high water pressure, resulting in larger pores and the formation of fissures, which reduce the slurry stone body's bearing capacity and durability and interferes with the grouting effect.

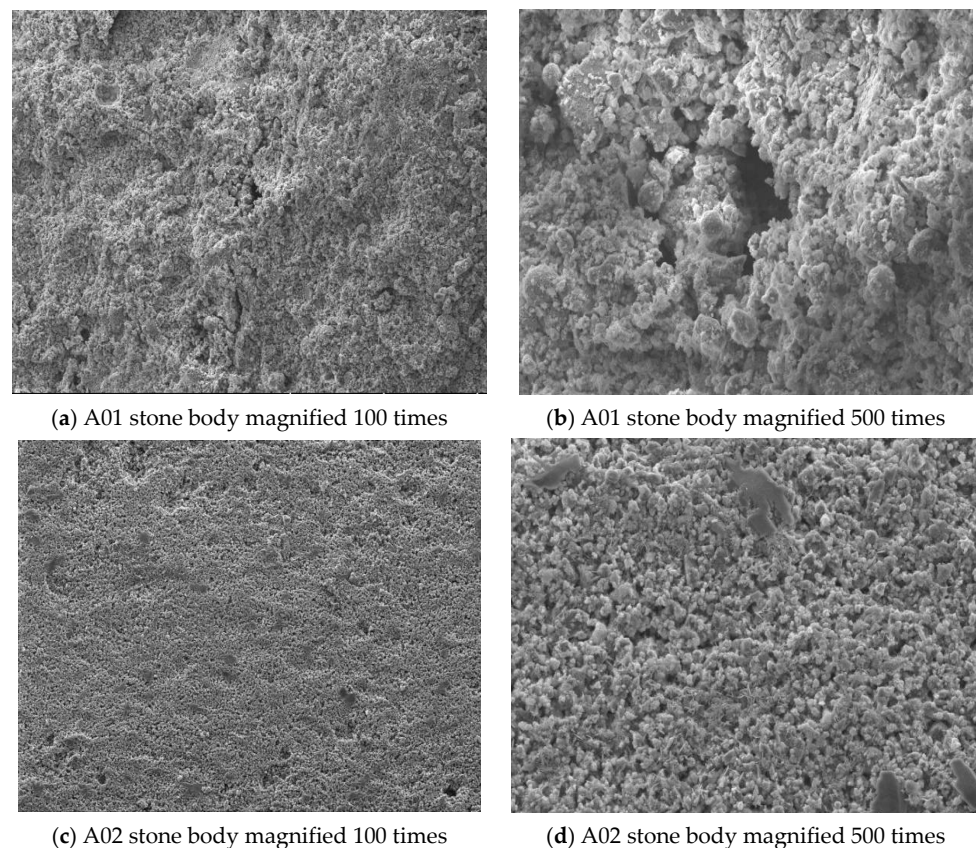


Figure 11. Scanning electron microscopy images of stone body.

The dense structure of the cement–polyvinyl alcohol slurry stone body in Figure 11c,d suggests that polyvinyl alcohol has some effect on the slurry stone body’s ability to resist cracking. The solidified cement–polyvinyl alcohol slurry stone body has weak permeability and high compressive strength due to the microscopic characteristics of the slurry stone body combined with compressive strength characteristics, which meets the requirement for the water plugging of the surrounding rock grouting under high water pressure. Compared to the conventional cement slurry and cement–water–glass slurry, it is more appropriate for grouting requirements under high water pressure.

4. Project Application

The study area is located in +900 m of Qiandao Lake water diversion tunnel K22 in Hangzhou. This site has an upper rock layer of 100 m and IV~V surrounding rock, and its permeability coefficient indicates strong permeability. The groundwater level is at ground level, and the tunnel’s central position head is 100 m. In order to prevent the excessive discharge of groundwater during tunnel construction, slurry plugging is applied to the surrounding rock [34–36]. The slurry ring thickness and slurry ring permeability coefficient are variables. The inner chamber of the cave is simplified as a circle, the equivalent inner diameter of the lining is 6.7 m, the equivalent outer diameter is 8.4 m, the lining permeability coefficient is 1.5×10^{-6} m/s, and the equivalent lining thickness is 0.85 m.

The tunnel excavation and grouting process was simulated using a two-dimensional seepage–stress coupling model created with the aid of the ABAQUS software. The model takes into account a hole influence range of 10 times its own diameter, and the model is designed to be 84 m wide and 130 m high. Horizontal displacement constraints are set on the model’s left and right sides, while vertical displacement constraints are set at the bottom. Position heads are set at the left and right boundaries, while boundary heads are set at the top and bottom, and the top of the model is impermeable. The inner surface of the liner is a permeable surface, and the water pressure is set to 0. Four calculation conditions were established, as shown in Table 3, in order to analyze the impact of cement–polyvinyl alcohol–boric acid slurry injection, and Figure 11 depicts the seepage field’s post-injection pore pressure cloud.

Table 3. Information of four working conditions and water pressure outside the liner.

Working Condition	Slurry Type	Slurry Ring Permeability Coefficient (m/s)	Water Pressure Outside the Liner (MPa)
Case 1	No grouting	1.0×10^{-5}	0.78
Case 2	Cement slurry	6.0×10^{-7} [37,38]	0.61
Case 3	Cement + water glass	1.8×10^{-7} [39,40]	0.54
Case 4	Cement + polyvinyl alcohol + boric acid	1.0×10^{-7} [41]	0.42

As seen in Figure 12a, when a tunnel is surrounded by rock without grout, the pore pressure cloud has the shape of an inverted funnel. The groundwater enters the tunnel after excavation, its level drops significantly, and the water pressure outside the lining is great. Excavation has a great influence on the seepage field. Figure 12d shows that after the injection of the cement–polyvinyl alcohol–boric acid slurry, the inverted funnel range of the pore pressure cloud decreases, and the drop in the groundwater level is smaller, which shows that tunnel excavation after grouting has little influence on the seepage field. This means that grouting has had a good effect on water plugging and achieved the expected plugging effect. When compared to Figure 12a, the pore pressure cloud diagram’s inverted funnel shape is improved in Figure 12c,d, suggesting that grouting has a stronger anti-seepage effect. However, the anti-seepage effect varies because the grouting materials have different anti-seepage effects, and cement-based slurry stones are brittle materials that are vulnerable to cracking and have a minimal anti-seepage effect when subjected to external water pressure. Due to the function of the modifiers, the anti-seepage effect of the cement–polyvinyl alcohol slurry is strengthened.

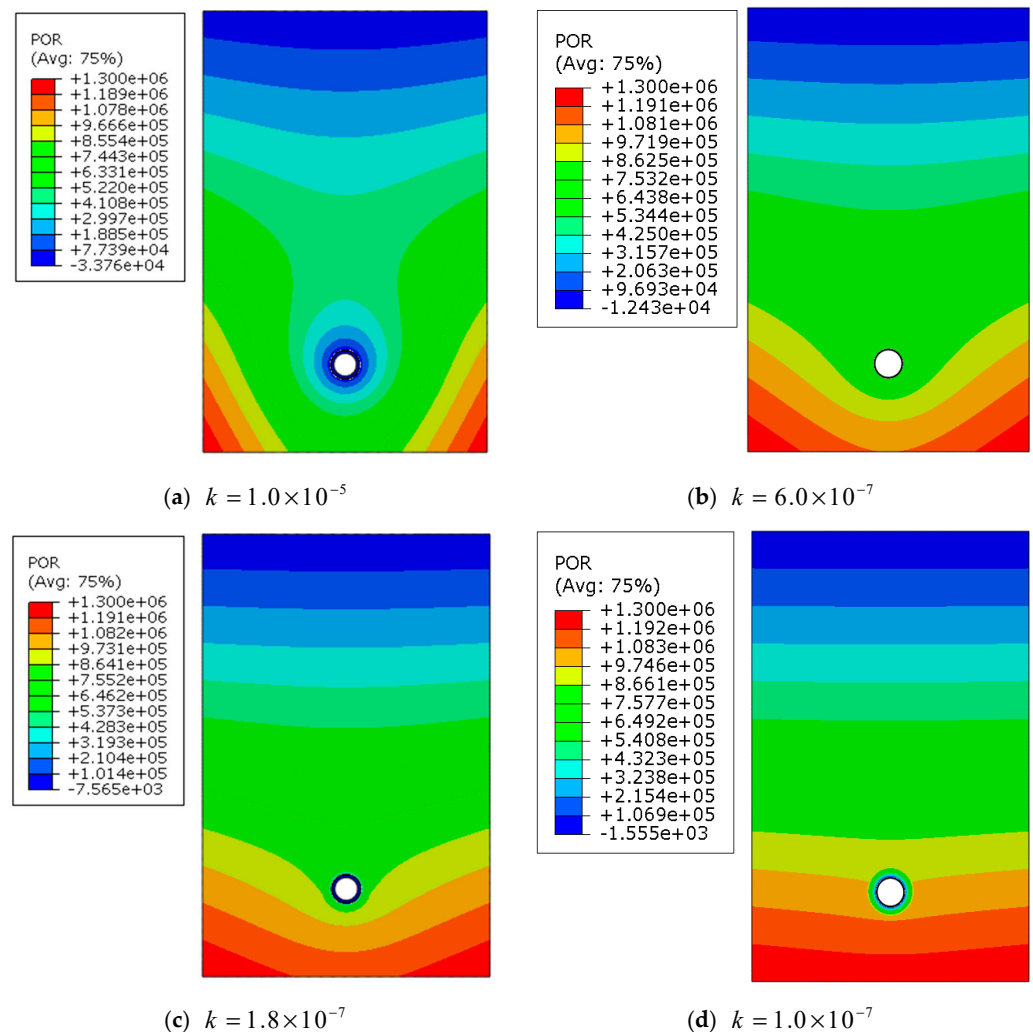


Figure 12. Pore pressure distribution clouds of the surrounding rock for the four working conditions.

According to Table 3, which displays the external water pressure of the lining under the four grouting conditions, the external water pressure of the lining starts to decrease once the permeability of the grouting ring is reduced, and it can withstand the external water pressure. In comparison to the first three working conditions, the external water pressure after the injection of cement–polyvinyl alcohol–boric acid grouting was reduced by 47%, 31%, and 22% after grouting with cement, polyvinyl alcohol, and boric acid, which perfectly demonstrates the improvement effect of the polyvinyl alcohol and boric acid modifiers. After grouting, a good water-plugging effect is achieved, which can reduce the water pressure outside the lining and reduce the discharge of groundwater.

5. Discussion

This study's findings indicate that when conventional grouting materials are used to seal off high water pressure around rocks, the grout's poor grouting performance and low retention ratio in a moving water environment endanger the tunnel's structural safety. As shown in Figures 6, 7, 10 and 11, the polyvinyl alcohol–boric acid–cement slurry controls the gel time through a modified concentration and volume ratio, a high retention ratio in moving water environments, and the good anti-seepage effect of the dense structure of the rock mass, and it had better grouting and water-plugging effects in an actual project of a water diversion tunnel, as depicted in Figure 12.

In this study, the laboratory test was mainly conducted to study the physical and mechanical properties of modified cement-based materials. To persuasively assess the

grouting effect of the grouting fluid on the surrounding rock, differences in the strength and permeability of the surrounding rock before and after grouting were tested by on-site sampling, and the reinforcement and water-blocking effects of the modified grouting fluid were analyzed. In the numerical calculation, for simplicity, only the influence of the grouting ring's permeability coefficient on the seepage field was considered, and the external water pressure of the lining was calculated. In situ rock sampling was not carried out for the test, nor were numerical calculation results compared. These optimal steps should be carried out in the future.

In different engineering contexts, the requirements for the physical properties and mechanical properties of the grouting fluid vary greatly [42–44]. Therefore, the grouting solution should be designed with modified materials according to the project needs, and if possible, intelligent machine technology should be combined with grouting technology to improve the grouting effect. In the near future, grouting technology may have broader applications, such as the landslide management of slopes and other projects, giving full play to the role of grouting material reinforcement and seepage resistance [45].

6. Conclusions

In this study, traditional building materials were improved to meet the requirements of the surrounding rock grouting under high water pressure and in a dynamic water environment. Through indoor tests, SEM tests, and numerical simulation methods, the following main conclusions are obtained.

The physical and mechanical characteristics of a single cement slurry exhibit a certain degree of injectability, a high stone ratio, high compressive strength, and high viscosity. The water–cement ratio has a greater effect on a single slurry; the smaller the ratio, the quicker the slurry initially and finally sets, and the higher the annual retention ratio of stones in a moving water environment.

The performance of cement-based materials for grouting is enhanced by polyvinyl alcohol and boric acid. By chemically crosslinking polyvinyl alcohol and boric acid to create a polymer–cement glue, the gel time of the cement-based slurry is shortened, indicating that the gel time can be adjusted by modifying the polyvinyl alcohol concentration and boric acid content. The formation of the cement gel increases the density of the slurry stone structure, and SEM verification suggests that the stone body will be more effectively sealed in the surrounding rock and will perform better in increasing seepage resistance.

The seepage flow field's numerical calculation demonstrates that the cement-glue-modified material has a better water-plugging effect. The low permeability of the grouting ring protects the tunnel's idyllic surroundings by reducing groundwater seepage, lowering water pressure outside the lining, and preventing groundwater levels from dropping.

Author Contributions: Data curation, D.F.; numerical calculation, J.Y. and C.P.; experiment, J.Y., C.P. and Z.W.; project administration, Y.Z. and L.H.; writing—original draft, J.Y.; writing—review and editing, D.F. All authors have read and agreed to the published version of the manuscript.

Funding: Key Project of Natural Science Research Project of Higher Education Institutions in Anhui Province (Grant No. KJ2019A0822); National Natural Science Foundation of China (Grant No. 52179100).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data used to support the findings of this study are available from the corresponding author upon request.

Acknowledgments: The authors wish to thank JLL for advice on the experimental design.

Conflicts of Interest: No potential conflicts of interest were reported by the authors.

References

1. Assaad, J.J.; Gerges, N. Styrene-butadiene rubber modified cementitious grouts for embedding anchors in humid environments. *Tunn. Undergr. Space Technol.* **2018**, *84*, 317–325. [\[CrossRef\]](#)
2. Han, X.L.; Chen, X.M.; Jiao, H.Z.; Sun, G.D.; Dong, T.F. Research status and prospect of polymer-cement grouting materials. *Bull. Chin. Ceram. Soc.* **2018**, *37*, 2457–2462. [\[CrossRef\]](#)
3. Corson, L.; Reid, C.; Lunn, R.J.; El Mountassir, G.; Henderson, A.E.; Henderson, K.; Pagano, A.G.; Kremer, Y. Field validation of a detectable, magnetic, cementitious grout for rock fracture grouting. *Int. J. Rock Mech. Min. Sci.* **2021**, *145*, 104853. [\[CrossRef\]](#)
4. De la Varga, I.; Spragg, R.P.; Muñoz, J.F.; Helsel, M.A.; Graybeal, B.A. Cracking, bond, and durability performance of internally cured cementitious grouts for prefabricated bridge element connections. *Sustainability* **2018**, *10*, 3881. [\[CrossRef\]](#)
5. Li, X.; Cao, L.; Zhao, X. Assessment of potential impact of tunneling on the groundwater in Epi-Fissure-Karst-Zone and ecological environment. *Environ. Earth Sci.* **2011**, *66*, 967–976. [\[CrossRef\]](#)
6. Xie, X.-C.; Ceccato, F.; Zhou, M.-L.; Zhang, D.-M. Hydro-mechanical behaviour of soils during water-soil gushing in shield tunnels using MPM. *Comput. Geotech.* **2022**, *145*, 104688. [\[CrossRef\]](#)
7. Hua, X.Z.; Xie, G.X. Research on grouting material for bolt and grouting reinforcement of soft rock tunnel and its application. *Rock Soil Mech.* **2004**, *25*, 1462–1466.
8. Zhang, X.D. Study of Material for Curtain Grouting in Karst Tunnel. *Undergr. Space Eng.* **2005**, *3*, 432–434.
9. Tian, K.; Ding, Q.J.; Chen, Y.Q.; Luo, J. Optimal design of high volume fly ash simultaneous grouting material for shield tunnel. *Tunnel Constr.* **2007**, *27*, 26–29.
10. Xiao, L.; Zhang, Q.H.; Zhao, T.S.; Yang, J.L.; Yang, G.H. Study on mortar material of tail void grouting in slurry shield tunnel. *Chin. J. Undergr. Space Eng.* **2011**, *7*, 59–64. [\[CrossRef\]](#)
11. Liu, P.; Yan, C.; Sun, G.; Xi, L.; Liu, J. Experimental study on performance of grouting material for repairing surrounding rock in river intake tunne. *Geotech. Investig. Surv.* **2016**, *44*, 11–15+44.
12. Zhang, C.; Fu, J.; Yang, J.; Ou, X.; Ye, X.; Zhang, Y. Formulation and performance of grouting materials for underwater shield tunnel construction in karst ground. *Constr. Build. Mater.* **2018**, *187*, 327–338. [\[CrossRef\]](#)
13. Zhang, C.; Yang, J.; Fu, J.; Ou, X.; Xie, Y.; Liang, X. Performance evaluation of modified cement-sodium silicate grouting material for prereinforcing loose deposit tunnels. *J. Mater. Civ. Eng.* **2019**, *31*, 06019003. [\[CrossRef\]](#)
14. Zhang, W.; Zhu, X.; Xu, S.; Wang, Z.; Li, W. Experimental study on properties of a new type of grouting material for the reinforcement of fractured seam floor. *J. Mater. Res. Technol.* **2019**, *8*, 5271–5282. [\[CrossRef\]](#)
15. Liu, Y.; Chen, B. Research on the preparation and properties of a novel grouting material based on magnesium phosphate cement. *Constr. Build. Mater.* **2019**, *214*, 516–526. [\[CrossRef\]](#)
16. Wan, Y.; Zhu, Z.; Song, L.; Song, S.; Zhang, J.; Gu, X.; Xu, X. Study on temporary filling material of synchronous grouting in the middle of shield. *Constr. Build. Mater.* **2020**, *273*, 121681. [\[CrossRef\]](#)
17. Wang, J.; Dai, Q.; Si, R.; Guo, S. Investigation of properties and performances of Polyvinyl Alcohol (PVA) fiber-reinforced rubber concrete. *Constr. Build. Mater.* **2018**, *193*, 631–642. [\[CrossRef\]](#)
18. Zhang, J.; Guan, X.; Li, H.; Liu, X. Performance and hydration study of ultra-fine sulfoaluminate cement-based double liquid grouting material. *Constr. Build. Mater.* **2017**, *132*, 262–270. [\[CrossRef\]](#)
19. Sun, Y.; Zhang, P.; Yan, W.; Wu, J.; Yan, F. Grouting Material Development and Dynamic Grouting Test of Broken Rock Mass. *J. Mater. Civ. Eng.* **2022**, *34*, 04022072. [\[CrossRef\]](#)
20. Liu, B.; Yin, L.; Chen, J.; Li, M.; Tang, D.; Zhang, Y. Experimental study on the influence of PVA content on the performance of grouting material in deep stope. *Geofluids* **2021**, *2021*, 6684754. [\[CrossRef\]](#)
21. Lu, Y.; Li, C.; Zhang, X.; Huang, X.; Zhao, Z. A Workability Characterization of Innovative Rubber Concrete as a Grouting Material. *Materials* **2022**, *15*, 5319. [\[CrossRef\]](#) [\[PubMed\]](#)
22. Yang, Q.; Geng, P.; Wang, J.; Chen, P.; He, C. Research of asphalt-cement materials used for shield tunnel backfill grouting and effect on anti-seismic performance of tunnels. *Constr. Build. Mater.* **2021**, *318*, 125866. [\[CrossRef\]](#)
23. Le, H.; Sun, S. Effect of grouting materials and inclination angle of preexisting flaw on uniaxial compressive strength and failure mode of rock-like specimens. *Rock Soil Mech.* **2018**, *39*, 211–219. [\[CrossRef\]](#)
24. Ma, S.; Ma, D. Grouting Material for broken surrounding rock and its mechanical properties of grouting reinforcement. *Geotech. Geol. Eng.* **2021**, *39*, 3785–3793. [\[CrossRef\]](#)
25. Le, H.; Sun, S.; Wei, J. Influence of Types of Grouting Materials on Compressive Strength and Crack Behavior of Rocklike Specimens with Single Grout-Infilled Flaw under Axial Loads. *J. Mater. Civ. Eng.* **2019**, *31*, 06018022. [\[CrossRef\]](#)
26. Zhu, C.; Zhang, J.; Peng, J.; Cao, W.; Liu, J. Physical and mechanical properties of gypsum-based composites reinforced with PVA and PP fibers. *Constr. Build. Mater.* **2018**, *163*, 695–705. [\[CrossRef\]](#)
27. Zhang, B.; Gao, F.; Zhang, X.; Zhou, Y.; Hu, B.; Song, H. Modified cement-sodium silicate material and grouting technology for repairing underground concrete structure cracks. *Arab. J. Geosci.* **2019**, *12*, 680. [\[CrossRef\]](#)
28. Duque-Ossa, L.; Ruiz-Pulido, G.; Medina, D. Triborheological study under physiological conditions of PVA hydrogel/HA lubricant as synthetic system for soft tissue replacement. *Polymers* **2021**, *13*, 746. [\[CrossRef\]](#)
29. Yuan, Z.; Zhang, C.; Xia, C.; Wu, L.; Yu, Z.; Li, Z. Flexural properties of PVA fiber reinforced high ductility cementitious composites containing calcium carbonate whisker. *Constr. Build. Mater.* **2021**, *300*, 124329. [\[CrossRef\]](#)

30. Jiang, H.; Qiu, X. Performance assessment of a newly developed and highly stable grouting material for a completely weathered granite dam foundation. *Constr. Build. Mater.* **2021**, *299*, 123956. [\[CrossRef\]](#)
31. Pei, J.; Cai, J.; Zou, D.; Zhang, J.; Li, R.; Chen, X.; Jin, L. Design and performance validation of high-performance cement paste as a grouting material for semi-flexible pavement. *Constr. Build. Mater.* **2016**, *126*, 206–217. [\[CrossRef\]](#)
32. Zhang, P.; Su, Y.-L.; Fan, J.-J.; Feng, H.; Shao, J.; Guo, H.; Gao, D.-Y.; Sheikh, S.A. Experimental research on the mechanical behavior of grouted sleeves with fiber-reinforced grouting material under cyclic loading. *Structures* **2021**, *34*, 2189–2204. [\[CrossRef\]](#)
33. Xiao, C.; Zhang, Y. Structural investigation of poly(vinyl alcohol) fibers under axial compressional deformation. *Acta Polym. Sin.* **2002**, *18*, 791–794. [\[CrossRef\]](#)
34. Li, J.-F.; Liu, Y.-T.; Li, S.-J.; Song, Y. Experimental investigation of synchronous grouting material prepared with different mineral admixtures. *Materials* **2022**, *15*, 1260. [\[CrossRef\]](#)
35. Liu, D.; Xu, Q.; Tang, Y.; Jian, Y. Prediction of water inrush in long-lasting shutdown karst tunnels based on the HGWO-SVR model. *IEEE Access* **2020**, *9*, 6368–6378. [\[CrossRef\]](#)
36. Li, Z.; Li, S.; Liu, R.; Jiang, Y.; Zhang, Q.; Yang, L.; Sha, F.; Chen, B.; Wang, H. Model tests on grouting reinforcement of water-rich broken rock mass. *Chin. J. Geotech. Eng.* **2016**, *37*, 1937–1946. [\[CrossRef\]](#)
37. He, Z.; Shen, A.; Guo, Y.; Lyu, Z.; Li, D.; Qin, X.; Zhao, M.; Wang, Z. Cement-based materials modified with superabsorbent polymers: A review. *Constr. Build. Mater.* **2019**, *225*, 569–590. [\[CrossRef\]](#)
38. Snoeck, D.; Steuperaert, S.; Van Tittelboom, K.; Dubrue, P.; De Belie, N. Visualization of water penetration in cementitious materials with superabsorbent polymers by means of neutron radiography. *Cem. Concr. Res.* **2012**, *42*, 1113–1121. [\[CrossRef\]](#)
39. Zhou, Y.; Wang, G.H.; Yuan, Y.F. Basic Properties and Engineering Application of Bentonite-Cement-Water Glass Grouting. *KSCE J. Civ. Eng.* **2020**, *24*, 2742–2750. [\[CrossRef\]](#)
40. Kazemian, S.; Prasad, A.; Huat, B.B.K.; Bazaz, J.B.; Aziz, F.N.A.A.; Ali, T.A.M. Influence of cement-sodium silicate grout admixed with calcium chloride and kaolinite on sapric peat. *J. Civ. Eng. Manag.* **2011**, *17*, 309–318. [\[CrossRef\]](#)
41. Zheng, K.; Xuan, D.; Li, J. Study on Fluid–Solid Characteristics of Grouting Filling Similar-Simulation Materials. *Minerals* **2022**, *12*, 502. [\[CrossRef\]](#)
42. Jiang, Y.; Xu, Z.; Geng, D.; Dong, J.; Liao, Y. Optimization of grouting material for shield tunnel antifloating in full-face rock stratum in nanchang metro construction in China. *Int. J. Géoméch.* **2022**, *22*, 04022009. [\[CrossRef\]](#)
43. Wang, S.; Wang, J.-F.; Yuan, C.-P.; Chen, L.-Y.; Xu, S.-T.; Guo, K.-B. Development of the nano-composite cement: Application in regulating grouting in complex ground conditions. *J. Mt. Sci.* **2018**, *15*, 1572–1584. [\[CrossRef\]](#)
44. Wang, C.; Zhang, D.; Chen, H.; Zhang, H.; Xiao, X.; Liu, Z. Preparation and properties of silicon-modified epoxy grouting material for repairing microcracks. *J. Mater. Civ. Eng.* **2022**, *34*, 04021479. [\[CrossRef\]](#)
45. Chang, Z.; Huang, F.; Huang, J.; Jiang, S.-H.; Zhou, C.; Zhu, L. Experimental study of the failure mode and mechanism of loess fill slopes induced by rainfall. *Eng. Geol.* **2021**, *280*, 105941. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.