

Article

Experimental Study on Permeation of Composite Grout with Multi-Particle-Size Distribution: Comparative Analysis with Nano-Silica Sol and Cement Grout

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Abstract: The low injectability and strong permeation of micro-fractures in argillaceous rock masses significantly impair the impermeabilization and reinforcement performance of conventional cement-based grouting materials. This study first develops a highly injectable and high-strength nano-silica sol-based composite grout. Then, the characteristics of silica sol, cement grout, and composite grout in argillaceous fractured rock masses are analyzed and compared. The permeation mechanism of the composite-grout grouting in these rock masses is preliminarily elucidated, and the grouting process is described in detail, showing its application prospects. The research results indicate the following: (1) The electrical conductivity and stone-formation rate of granular pulp can reflect the characteristics of pulp filtration. Silica sol is a grouting material with nanometer particles, and the stone rate and gel strength are weakly affected by rock mass infiltration. (2) A large amount of water cannot be combined into the gel network and separated during the cement slurry percolation process, resulting in a significant reduction in the stone rate and compressive strength of deep rock mass. The minimum stone rate decreased to 45.19%, and the minimum compressive strength decreased to 2.29 MPa. This reduces the sealing and reinforcement effect of cement grouting on deep rock masses. (3) Rock permeation primarily affects the compressive strength of the formed stones, with minimal impact on the stability and stone-formation rate of the composite grout. As permeability decreases, the position of rock permeation shifts closer to the rock surface, while the sealing of deeper rock masses is less affected, enabling the composite grout to achieve dual functions of superficial reinforcement and deep sealing. This study provides theoretical support for the practical application of composite-grout grouting in reinforcing argillaceous rock masses.

Keywords: argillaceous rock; micro-fractures; aluminous cement; silica sol; grouting technology



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1. Introduction

Argillaceous rock masses are extensively present in deep underground engineering projects across China. Due to their high content of clay minerals, these rock masses suffer from water-induced swelling, softening, and even disintegration, which severely compromises the safety and stability of underground structures such as coal mine tunnels, subway tunnels, etc. [1,2]. Grouting methods can be employed to enhance the physical and mechanical properties of the surrounding argillaceous rock masses [3,4]. For deep

argillaceous rock masses, the effectiveness of grout modification is closely related to the injectability of the grout material [5], as these masses are featured with multi-scale fractures distribution, micro-fractures development, with the presence of numerous millimeter-to-micrometer-to-nanometer scale fractures.

In terms of grout injectability, highly injectable chemical grouts are often restricted in their application due to their toxicity and heat generation [6]. Conventional cement-based grouting materials have micrometer-sized particles, poor injectability, and struggle to meet the demands for sealing and consolidating micro-cracks [7,8]. This gives nano grouts and nano–micro composite grouts significant technical advantages and application prospects in the control of argillaceous rock bodies via grouting. For example, ultra-fine cement, which is at the quasi-nano or sub-nano level, has high injectability in fine cracks and has received widespread attention. Huang [9] developed a new process for preparing wet-milled ultra-fine cement, with the largest particle size of the produced cement not exceeding 40 μm and the median particle size (50% content) being less than 10 μm , making it suitable for grouting in micro-cracked rock bodies. Chen [10] studied the long-term strength of ultra-fine cement grout cubes and concluded that ultra-fine cement is an effective hydraulic filling material for improving cement properties. Yao [11] studied the different grouting effects of ordinary cement grout and ultra-fine cement grout in sandy soils. Their results indicate that the modification and reinforcement effects of ultra-fine cement are superior to those of ordinary cement. Ghafar [12] investigated the rheological properties and permeation of cement-based grout materials, concluding that instantaneous variable-pressure grouting could significantly improve the diffusion of cementitious materials in fractures, although the dissipation of pressure pulses notably increases in fractures with small apertures. There has also been research on the grout permeation patterns of nanomaterials in fractured rock masses. Tani [13] studied the flow patterns of cement grout in one- and two-dimensional fractured rock bodies under constant flow, constant pressure, and constant energy grouting methods. However, the current widely used ultra-fine cement has a fineness of 800–1250 mesh, suitable for rock fractures with a width of $\geq 10 \mu\text{m}$, and thus the grouting sealing effect on the main water-conducting channels (0.3–5 μm) of micropores in argillaceous rock is not significant.

In the permeation of cementitious grouts, particle-based cementitious grouts consist of solid particles mixed with a liquid phase. During the grouting penetration process in rock-like porous media, if the solid particles are equal to or larger than the pore/fracture width of the porous medium, the grout is completely non-injectable; when solid particles are smaller yet close to the width of the pores/fractures of the porous medium, the skeletal network of the porous medium acts as a filter, leading to the accumulation and retention of solid particles on the surface and inside the porous medium, known as the permeation effect [14]. This effect is widely observed in the grouting permeation process in porous media such as sand or soil layers and plays a crucial role in the diffusion of particulate slurries, as well as in the sealing and reinforcement of rock bodies. However, studies have found [15,16] that significant permeation effects also occur during the grouting of particulate materials in fractured rock masses, loose coal bodies, cracked rock bodies, and micro-fractured rock bodies. The permeation effect of particulate grouts in cracks/fractured rock bodies causes phenomena such as filtration, retention, and blockage during the grouting process, significantly affecting the flow state of the grout in the rock body. This leads to the separation of solid particles and liquid phase in the particulate grout, causing an uneven distribution of grout particles in the direction of permeation, thus affecting the sealing and reinforcement effects of the grouting structure. The literature has indicated that there is a significant permeation effect during the grouting process with cement grout in micro-fractured rock bodies, with grout particles accumulating at the entrance of micro-pores

to form a “filter cake”, making it difficult for the grout to permeate evenly. As a result, the grouting range can hardly be managed, severely reducing the injectability of deep micro-pores. Therefore, the key to the reinforcement of multi-scale fractured clay rocks is the consolidation of micro-pores, and sealing and strengthening the matrix micro-pores are fundamental issues that cannot be avoided in controlling large deformations in argillaceous rocks [17]. Thus, a nano–microscale composite grout is needed to perform the gradient filling and consolidation of multi-scale porous fractures in argillaceous rock bodies.

For sealing and reinforcing argillaceous fractured rock bodies, our research group developed a highly injectable and enhanced cross-scale, multi-particle-size-distribution composite grout using nano-silica sol as the main agent. The results show that the composite grout features a multi-level particle-size distribution ranging from 4.85 nm to 98.1 μm , providing a significant injectability advantage over traditional cement grout while maintaining high compressive strength [18–20]. Due to the nano–micro dual-scale multi-grain-size distribution characteristics of the composite grout, its adsorption, retention, and blocking permeation characteristics within the multi-scale fracture network of argillaceous rock bodies remain unclear. This understanding is particularly crucial for elucidating the permeation consolidation patterns of micro–nano grouts in fractured clay rocks.

Therefore, to study the permeation patterns and filtration characteristics of the composite grout in argillaceous fractured rock bodies and provide reference for grouting in coal mine tunnels and subway tunnels, this paper designs a grouting permeation experimental setup for such rock bodies. We conducted a comparative analysis of the changes in grout conductivity, stone-formation rate, and compressive strength under the influence of permeation for silica sol, cement grout, and composite grout, preliminarily elucidating the permeation mechanism of composite-grout grouting in these rock bodies. The research results indicate that: Rock permeation primarily affects the compressive strength of the formed stones, with minimal impact on the stability and stone-formation rate of the composite grout. As permeability decreases, the position of rock permeation shifts closer to the rock surface, while the sealing of deeper rock masses is less affected, enabling the composite grout to achieve dual functions of superficial reinforcement and deep sealing. The findings provide theoretical support for the practical application of composite-grout grouting in reinforcing argillaceous rock bodies in coal mine tunnels and subway tunnels.

2. Experimental Design

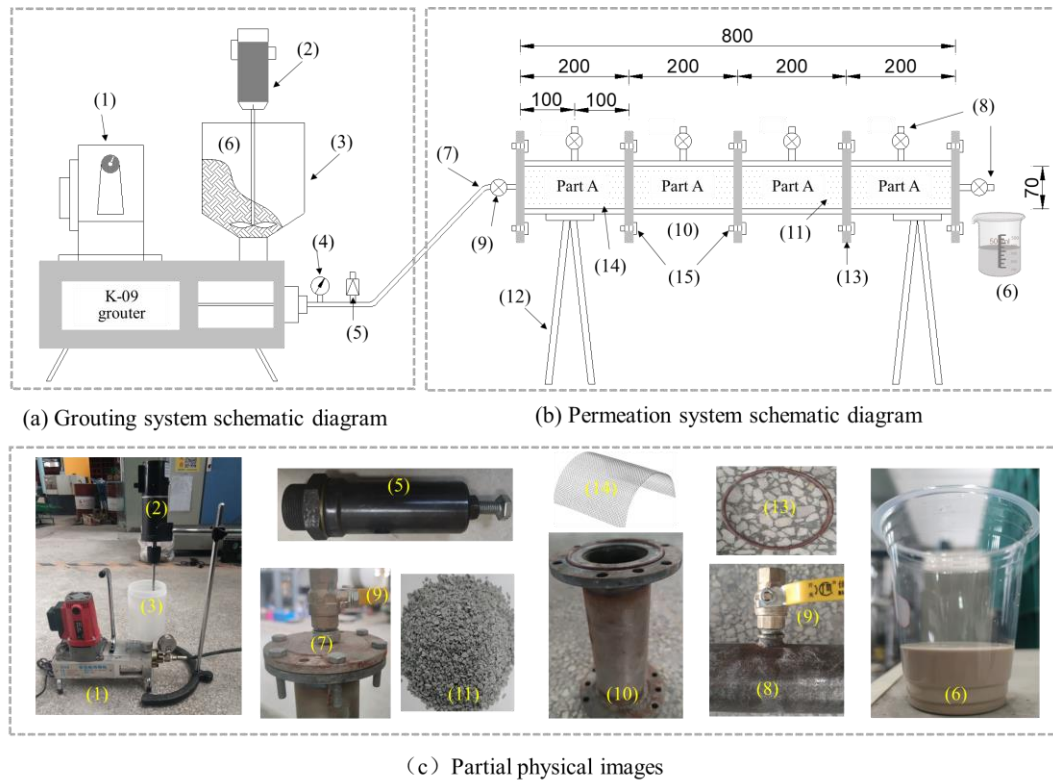
2.1. Experimental Equipment

To investigate the seepage behavior of composite grout in argillaceous fragmented rock masses, a grouting seepage experimental apparatus was designed. This apparatus is mainly composed of three parts: a grouting experimental system, a grouting seepage system, and a waste liquid collection and measurement system. The schematic diagram of the experimental setup is shown in Figure 1.

(1) Grouting Experimental System

The grouting experimental system consists of a constant flow grouting pump, a storage tank, a mixer, a pressure gauge, a pressure-relief valve, and high-pressure grouting pipes. During the experiment, the grout is thoroughly mixed in specific proportions and poured into the storage tank. The mixer ensures continuous high-speed stirring to maintain the grout’s stability and dispersibility. The grout enters the grouting pipeline by gravity and is then pressurized by the constant flow grouting pump to be injected into the grouting seepage system. The pressure gauge monitors the grouting pressure at the pump’s inlet, while the pressure-relief valve stabilizes the output pressure to protect the system. If the pressure gauge shows a value exceeding the upper limit and the relief valve

discharges a significant amount of grout, it indicates clogging in the seepage system, and the experiment is immediately halted. The output flow rate of the constant flow grouting pump is adjustable between 0 and 1.2 L/min, and the relief valve's opening pressure is set to 2 MPa. The storage tank is 25 cm high with an inner diameter of 18 cm, and it can hold up to 5 L of grout per batch.



(1) constant flow grouting pump; (2) mixer; (3) storage tank; (4) pressure gauge; (5) pressure relief valve; (6) grout; (7) grout inlet; (8) grout outlet; (9) transfer valve; (10) grouting steel pipe; (11) rock mass; (12) stand; (13) O-ring seal; (14) metal mesh; (15) M8 high-strength screws

Figure 1. Schematic and actual image of the grouting apparatus.

(2) Grouting Seepage System

The seepage system consists of a support frame, a grouting end, four sections of assembled steel pipes, an outlet end, and a one-way valve. The steel pipes have an inner diameter of 70 mm and a total length of 800 mm, with each section measuring 200 mm in length. The sections are labeled as A (0–200 mm), B (200–400 mm), C (400–600 mm), and D (600–800 mm). Liquid sampling ports are located in the middle of each steel pipe, allowing for the measurement of grout properties at different times and locations. The steel pipes are connected using M8 high-strength bolts and placed on the support frame. To ensure system sealing, O-ring rubber gaskets are placed between the flanges at the grouting and outlet ends, as well as between the sections of steel pipes. Waterproof gaskets are also installed at the connections between the grouting pipes and the seepage system, and between the one-way valve and the steel pipes. Screens are placed at the grouting end, outlet end, and liquid sampling ports to prevent unmixed cement from entering the seepage system and to block the escape of rock particles. Additionally, a layer of plastic film adhered with petroleum jelly is attached to the inner walls of the steel pipes, making it easier to extract the grout–rock cemented body for mechanical testing after the grout has solidified.

(3) Measurement System

To characterize the properties of the grout under different test conditions, beakers are placed at each opening of the permeation system to collect the outflowing grout. The measuring instruments include an electronic scale, a stopwatch, a conductivity meter, and a press.

2.2. Experimental Materials

(1) Rock Materials

The argillaceous rock body was taken from the roof surrounding rock of the 24,100 working-face roadway in a mine. The natural moisture content of the experimental rock body was tested at 3.19% and the saturated moisture content (porosity) was tested at 7.05% using the vacuum saturation method. The rock fragments formed by crushing had three ranges of particle sizes—① 5–10 mm, ② 2–5 mm, and ③ 0.5–2 mm—and the porosities were tested at 0.44, 0.38, and 0.31, respectively.

(2) Grouting Materials

The grouting materials include silica sol, cement grout, and composite grout. The parameters for each are as follows:

① Silica sol: The experimental silica sol used is a common commercial product provided by Shandong Kehan Silicon Source New Materials Co., Ltd., Linyi, China, with an average particle size of 9.6 nm, a silica concentration of 30%, a pH value of about 9.55, and a density of 1.2 g/cm³. The parameters are shown in Table 1. The coagulant used is a homemade 10% NaCl solution, with a volume ratio of silica sol to coagulant of 6:1.

Table 1. Silica-sol parameters.

Appearance	pH	Density/(g/m ³)	Viscosity/mPa·s	Average Particle Size/nm	SiO ₂ Concentration/%	Na ₂ O Concentration/%
Light blue, transparent	9.55	1.203	≤5	9.6	30.18	0.31

② Cement grout: The cement used for the experiment is commercially available 425# Portland cement (P.O42.5R Portland cement produced by Xuzhou Zhonglian Concrete Co., Ltd., Xuzhou, China). Physical testing (see Table 2) shows that the main components are tricalcium silicate, dicalcium silicate, and tricalcium aluminate. During the experiment, the water/cement ratio of the cement grout was set at 2:1. Particle-size testing shows (see Figure 2) that the D50 of the cement grout is 11.53 μm, and D95 is 52.25 μm.

Table 2. Main chemical components of Portland cement.

CaO	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	SO ₃	R ₂ O	Others
64.02	20.94	4.85	3.44	1.7	1.88	0.50	2.67

③ Composite grout: The composite grout is based on a previously researched optimal ratio [18], consisting of silica sol, aluminate cement, coagulant, and MgO. The cement accounts for 50% of the weight (the same weight ratio with silica sol), the water/cement ratio is 0.6, the coagulant proportion is 0.5%, and the MgO proportion is 0.6%. The aluminate cement is provided by Zhengzhou Jianai Special Aluminates Co., Ltd., Zhengzhou, China, and magnesium oxide is supplied by Tianjin Zhiyuan Chemical Reagent Co., Ltd., Tianjin, China. The silica sol and coagulant are provided by the previously mentioned companies in ① and ②. The main chemical components of the aluminate cement used in the composite

grout are detailed in the accompanying Table 3. The composite grout features nano–micro dual-scale particle-size-distribution characteristics, with a nano-level median-particle-size D50 of 42.13 nm, and a micro-level median-particle-size D50 of 10.32 μm . The grout solidification rate is $\geq 97.5\%$, the 28-day volume shrinkage rate is $\leq 0.5\%$, the 7-day compressive strength is 13.67 MPa, and the 28-day compressive strength is 14.5 MPa.

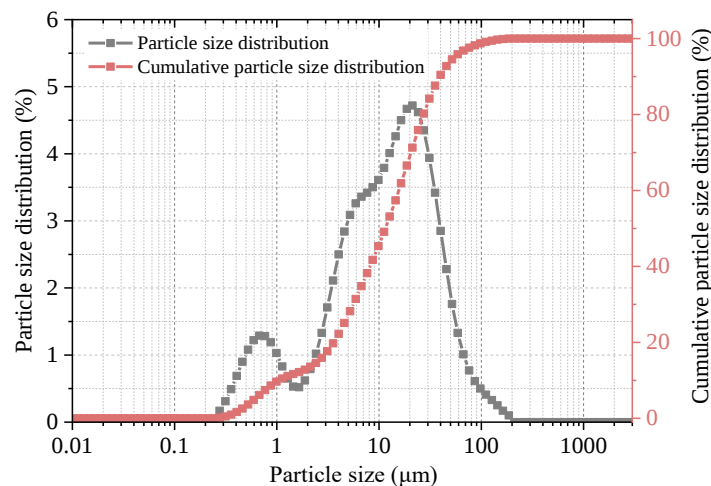


Figure 2. Particle-size distribution chart of the cement.

Table 3. Main chemical components of aluminate cement.

SiO ₂	CaO	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	K ₂ O	Na ₂ O	LOI
5.01	36.1	52.24	1.71	0.61	0.2	0.25	0.21

2.3. Experimental Steps

- (1) The grouting end was connected to the steel tube, and single-way valves were installed on each segment. The inner walls of each steel tube were coated with a layer of Vaseline, followed by a thin plastic film that was also coated with Vaseline to ensure a smooth surface and prevent leakage. M8 high-strength screws were used to connect the four segmented grouting tubes. Rock fragments were evenly filled into the grouting tubes from a fixed height in layers and compacted thoroughly; then, the discharge end cap was installed, and the permeation apparatus was placed on a stand.
- (2) The high-pressure grouting pipe was connected to a constant-flow grouting pump, a pressure-relief valve, a grout storage barrel, and the grouting permeation system. The specifically proportioned grout material (silica gel, cement grout, composite grout) was poured into the storage barrel, and the grout was continuously stirred using a mixer. The grouting pump's flow rate was set to 800 mL/min, and the grouting pipe valve along with the grouting pump were opened to start the permeation grouting experiment. Once the grout began flowing out steadily from the discharge end, the grouting pump was stopped every 10 s (at permeation times of 10 s, 20 s, 30 s, 40 s, and 50 s), and the single-way valves on each steel tube were opened to collect the grout flowing out at different depths (100 mm, 300 mm, 500 mm, and 700 mm).
- (3) The grouting was stopped when the total grout volume reached 3 L, the grouting time reached 1 min, or when the pressure gauge indicated an over-limit value and a significant amount of grout leaked through the pressure-relief valve. After each grouting experiment, the grouting pipelines were cleaned with water.

- (4) After each grouting operation, the electrical conductivity and the stone-formation rate of the outflowing grout were measured. Additionally, the setting time for some of the samples was measured.
- (5) After the grouting process had completed and 24 h had elapsed, the permeation experiment apparatus was disassembled section by section, and the grouted material cemented rock composites (hereafter referred to as grout–rock cemented bodies) were placed in a curing chamber with constant temperature and humidity. The samples were maintained in a standard curing environment of 20 °C temperature and >95% relative humidity for 7 days. Afterwards, each section was cut into two pieces and subjected to uniaxial compressive strength tests. Each section was tested twice to obtain the average value, which was used as the compressive strength for that section.
- (6) Following the above procedures, the permeation and consolidation patterns of three different grout materials (silica gel, cement grout, and composite grout) were tested within three ranges of rock fragment sizes (0.5–2 mm, 2–5 mm, and 5–10 mm).

3. Experimental Results

3.1. Flow and Permeation Characteristics of Silica-Gel Grouting

(1) Change in Electrical Conductivity

To maintain the long-term stability of silica gel, trace amounts of metal cations such as Na^+ or K^+ are often added during production. These cations help stabilize the charge balance between silica-gel clusters, preventing agglomeration through electrostatic repulsion and ensuring excellent dispersion. During the grouting process, the high surface free energy between rock interfaces and nano-sized silica-gel particles causes some silica-gel nanoparticles near the rock surface to be adsorbed, increasing the concentration of the conductive solution within the gel. By measuring the electrical conductivity of the outflowing grout under various grouting conditions, the degree of adsorption and filtration loss of silica gel during permeation can be assessed. Figure 3 illustrates the changes in electrical conductivity of silica gel under permeation conditions across three different rock fragment sizes. The conductivity increases with the depth of grout permeation, the duration of permeation, and the decrease in rock fragment size, though these increases are modest. Overall, the changes in the conductivity of silica gel are minimal, and it is less affected by permeation. In terms of the impact on the permeation of silica gel, the order is rock fragment size > permeation depth > permeation time. This occurs because silica gel, as a nano-particle grouting material, experiences less impact on its flow under constant fracture levels. As the rock fragment size decreases, the increased surface area results in a larger adsorption area for the silica gel, leading to a relatively greater amount of particle filtration loss.

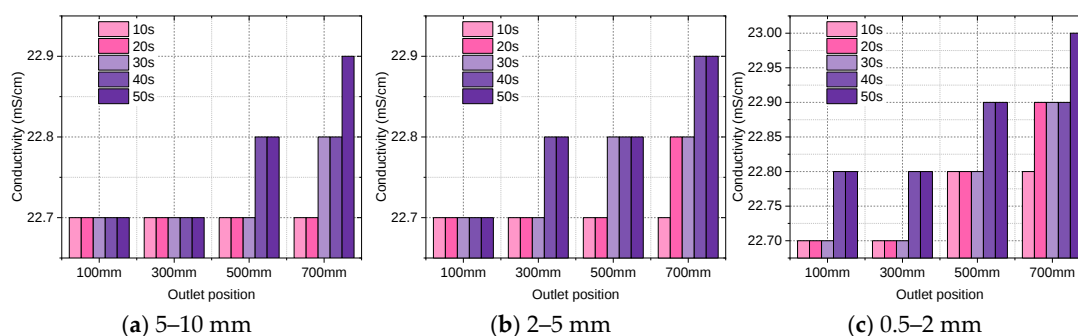


Figure 3. Change in electrical conductivity after silica-gel permeation.

(2) Change in Stone-Formation Rate

The permeation effect of the rock body on the grout can also be reflected in the stone-formation rate of the grout: the greater the filtration of solid particles, the less the amount of solidified gel. Figure 4 shows the change in stone-formation rate of silica gel after permeation through 0.5–2 mm rock fragments (data for 5–10 mm and 2–5 mm fragments are not provided due to minimal changes). The stone-formation rate decreases with increasing permeation depth and duration. For a permeation depth of 100 mm and a duration of 10 s, the stone-formation rate of silica gel is 98.5%; at a permeation depth of 700 mm and a duration of 50 s, the rate is 97.1%—a decrease of 1.4%. Notably, when the ratio of silica gel to coagulant is 6:1, the stone-formation rate is 100% [21], and conductivity tests indicate that permeation has a minimal impact on silica gel. However, the stone-formation rate shows a reduction after permeation. This suggests that during the grouting process of silica gel, in addition to the effect of permeation, the fractured rock body also absorbs some of the water from the silica gel, and the longer the permeation distance and duration, the greater the amount of water absorbed. The post-permeation silica gel, lacking this portion of bound water, thus experiences a loss in volume and weight, leading to a decrease in stone-formation rate.

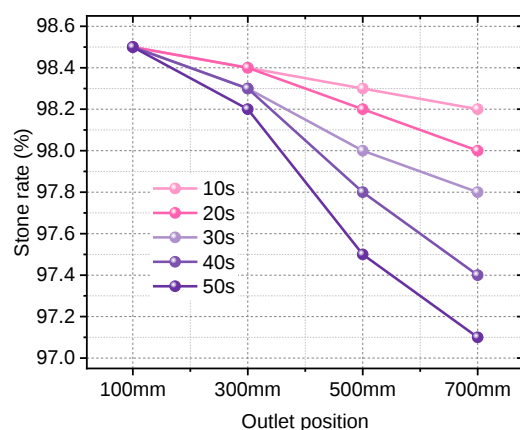


Figure 4. Stone-formation rate of silica gel after permeation through 0.5–2 mm rock fragments.

3.2. Flow and Permeation Characteristics of Cement Grout

(1) Change in Electrical Conductivity

Figure 5 illustrates the change in electrical conductivity of cement grout under different permeation conditions. The test results demonstrate that cement grout's electrical conductivity is significantly influenced by rock permeation. For example, with rock fragments with a size of 5–10 mm, a permeation depth of 100 mm, and a duration of 10 s, the conductivity measures 12.76 mS/cm. When the rock fragment size reduces to 0.5–2 mm, the permeation depth increases to 700 mm, the duration extends to 50 s, and the conductivity escalates to 16.12 mS/cm, which is an increase of 4.26 mS/cm or 35.92% from an original 11.86 mS/cm. For a consistent rock fragment size of 5–10 mm and a permeation depth of 100 mm, increasing the duration to 50 s raises the conductivity to 12.29 mS/cm. If the depth extends to 700 mm with the same duration, the conductivity further increases to 14.16 mS/cm. With a fixed depth of 500 mm, the conductivity starts at 12.87 mS/cm for a 10 s duration and rises to 13.86 mS/cm when the duration extends to 50 s. For smaller rock fragments sized 0.5–2 mm under the same conditions, the conductivity reaches 15.22 mS/cm.

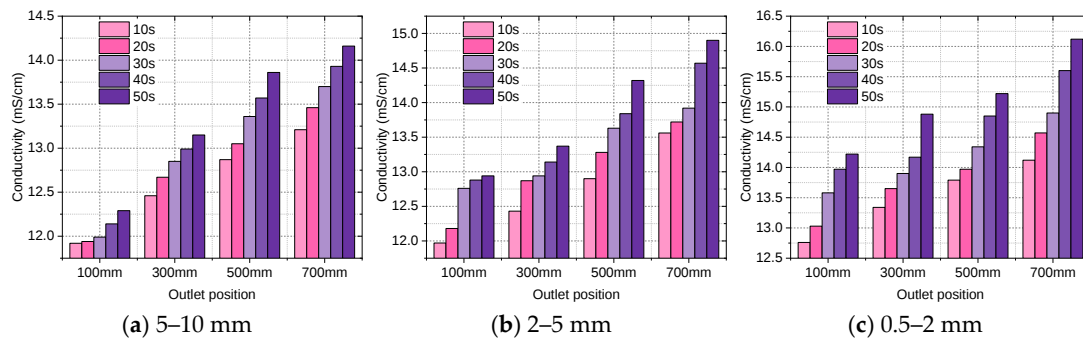


Figure 5. Changes in electrical conductivity after cement-grout permeation.

Overall, during the permeation process, the conductivity of cement grout increases with the depth and duration, as well as with decreasing rock fragment size. The impact of rock fragment size and permeation depth on conductivity changes is more pronounced than on permeation time. This is primarily because conductivity in the system occurs through ion transport in the liquid phase of the cement grout [22], while the solid-phase cement particles are non-conductive (or have a very low conductivity). During the permeation process of the cement grout with the rock body, the solid-phase particles in the cement grout are extensively filtered out by the rock fractures, while the liquid phase is less affected. As a result, in the filtered cement grout, the concentration of cement particles decreases. Thus, the concentration of the conductive medium per unit distance/volume increases, enhancing the conductivity of the grout material, manifested by increased conductivity values. Additionally, as the permeation depth and duration increase, the probability of larger particles being filtered by the rock skeleton also increases, leading to greater pore clogging and thus more pronounced permeation; also, as rock fragment size decreases, the available pore space in the skeletal network diminishes, allowing less passage for cement particles, thereby increasing the amount of grout material filtered and overall increasing the system's conductivity.

(2) Change in Stone-Formation Rate

Figure 6 shows the variation in the stone-formation rate of cement grout under different permeation conditions. Under the influence of permeation, the stone-formation rate of the cement grout decreases. For rock fragments with a size of 5–10 mm, at a permeation depth of 100 mm and a permeation time of 10 s, the stone-formation rate of the cement grout is 81.54%—a decrease of only 1.58% (a reduction rate of 1.9%) from the initial rate of 83.12%. However, when the rock fragment size is 0.5–2 mm, the permeation depth is 700 mm, and the permeation time is 50 s, the stone-formation rate of the cement grout drops to 45.19%—a reduction of 37.93% (a reduction rate of 45.63%) from the initial rate. This significant decrease is due to a large amount of cement particles being filtered within the rock fractures, reducing the amount of skeleton available for hydration products to adhere to during the cement solidification process, which hinders the hydration process. A large amount of water cannot be integrated into the gel network and bleeds out (as seen in Figure 7), ultimately resulting in a significant reduction in the stone-formation rate of the cement bodies. Moreover, the farther the permeation distance, the longer the permeation time, and the smaller the rock fragment size, the lower the stone-formation rate of the cement. These results indicate that the permeation effect of the rock body on the cement grout is exceptionally prominent, with the lowest stone-formation rate dropping to 45.19%, which significantly affects the sealing effectiveness of the cement grout on fractured rock bodies.

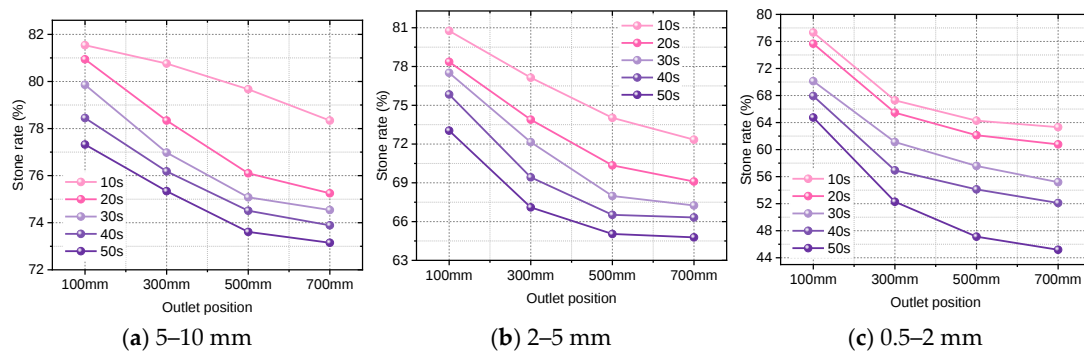


Figure 6. Variation patterns of cement slurry-filtrate precipitation rate.



Figure 7. Severe dehydration of cement permeate samples.

From the curve in Figure 6a, for instance, when the permeation time is 10 s, the curve exhibits a near-linear decrease (slightly concave), indicating a uniform rate of decrease in stone formation across the entire experimental segment and a low level of permeation without significant clogging. When the permeation time is between 20 and 50 s, a distinct inflection point appears at 500 mm, suggesting significant permeation clogging between 300 and 500 mm. Moreover, as permeation time increases and rock fragment size decreases, the permeation site gradually shifts towards the inlet, indicating increasingly apparent shallow rock-body permeation. In practical engineering applications, as the openness of rock fractures decreases, the location of permeation gradually shifts towards the surface. Increased shallow permeation significantly impacts the stone-formation rate of cement grout injected into deeper sections, ultimately resulting in effective shallow reinforcement and sealing but significantly reduced effectiveness in deeper sections. This substantially diminishes the sealing and reinforcement effects of cement grouting on deep rock formations.

3.3. Flow and Permeation Characteristics of Modified Composite-Grout Materials

(1) Change in Electrical Conductivity

Figure 8 displays the variation in electrical conductivity of composite-grout materials under different permeation conditions. According to conductivity test results, there is some permeation during the grouting process of the composite materials, similar to that of cement paste. The conductivity of the composite grout increases with the depth of permeation, duration of permeation, and decrease in rock fragment size, with the impact of rock fragment size and permeation depth on the conductivity change during the permeation process being more significant than the duration of permeation. However, the change in conductivity due to permeation is significantly weaker than that in cement paste. For example, when the rock fragment size is 5–10 mm, the permeation depth is 100 mm, and the permeation duration is 10 s, the conductivity of the composite grout is 3.49 mS/cm. When the rock fragment size is 0.5–2 mm, the permeation depth is 700 mm, and the permeation

duration is 50 s, the conductivity is 3.68 mS/cm, which is an increase of 0.2 mS/cm (or 5.75%) from the original conductivity of 3.48 mS/cm. This is because the composite grout contains particles in the nano- to micro-meter size ranges, predominantly nano-sized particles. As indicated by the test results in Section 3.1, the permeation effect on nano-sized silicate gel particles is low. Therefore, the permeation of the composite grout mainly occurs at the level of micro-sized particles, i.e., the cement particles. Since the conductivity of silicate gel is higher than that of aluminate cement and silicate gel is the main component (comprising more than 50%) of the composite grout, the conductivity of the composite grout is primarily controlled by the silicate gel. Thus, the loss of cement particles through filtration has a less significant impact on the overall conductivity compared to cement paste. This phenomenon is also reflected in the grout's gelation time. After the experiment, the gelation time of some filtered liquid was tested and found to be extended, which is because large cement particles are filtered by the rock fractures, reducing the skeleton available for hydration products to adhere to during the solidification process. Consequently, the solidification is delayed, leading to a longer setting time for the composite grout. The more pronounced the permeation, the longer the gelation time, aligning with the observed conductivity results.

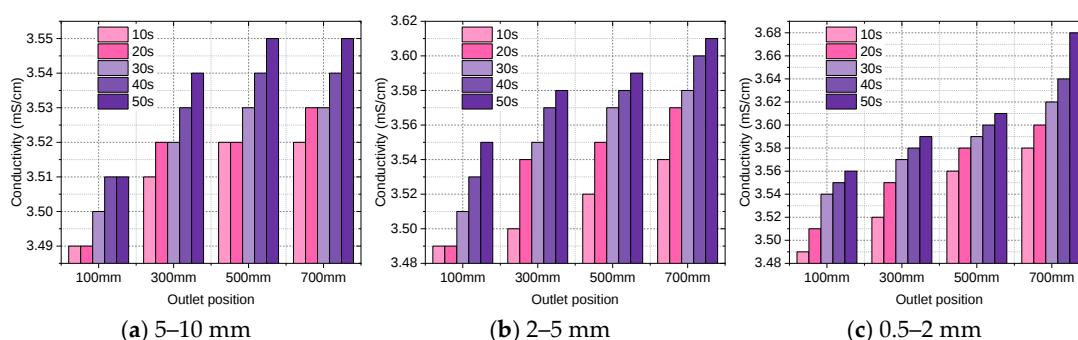


Figure 8. The change in electrical conductivity after the permeation of composite-grout materials.

(2) Change in Stone-Formation Rate

Figure 9 illustrates the variation in stone-formation rate of composite-grout materials under different permeation conditions. Under the effect of permeation, there is a slight decrease in the stone-formation rate of composite grout. When the rock fragment size is 5–10 mm, the permeation depth is 100 mm, and the permeation duration is 10 s, the stone-formation rate of the composite grout is 96.24%—a decrease of only 0.16% (or 0.166%) from the initial rate of 96.4%. When the rock fragment size is 0.5–2 mm, the permeation depth is 700 mm, and the permeation duration is 50 s, the stone-formation rate is 90.16%—a decrease of 6.24% (or 6.47%) from the initial rate. This is significantly higher compared to cement paste. Although large cement particles are filtered by the rock, the permeation has little impact on the nano-sized silicate gel particles. Therefore, after permeation, the silicate gel can form a volume- and mass-stable solid gel to compensate for the loss of cement particles, thereby minimizing the overall impact of permeation on the stone-formation rate of the composite grout. As a result, the overall stone-formation rate of composite grout is less affected by permeation compared to cement paste, with smaller variations in stone-formation rate.

In terms of permeation location, as the size of rock fragments decreases, there is a significant change in the curve shape of the rate of stone formation: it changes from a concave shape for 5–10 mm to a linear shape for 2–5 mm, and finally to a concave shape for 0.5–2 mm. This indicates a significant shift in the primary permeation site. The location with the highest decrease rate in stone formation corresponds to the main permeation

site. For 5–10 mm fragments, the main permeation site is between 500 and 700 mm; for 2–5 mm, it is primarily between 300 and 500 mm; and for 0.5–2 mm, it is mainly between 100 and 300 mm. This demonstrates that as the permeability of the rock body decreases, the permeation site moves closer to the rock layer surface, similar to the permeation pattern observed with cement paste. However, a key distinction is that, because the main component of the composite grout—silicate gel—is less affected by permeation, even as the permeation intensifies and moves closer to the shallow layers of the rock body, the rate of stone formation in the deeper grout remains largely unaffected. Consequently, the impact of permeation on the sealing capability of the composite grout in deeper rock formations is minimal.

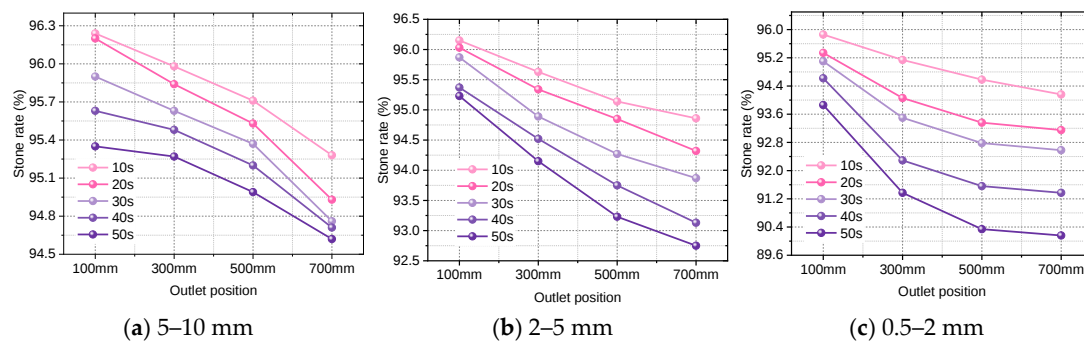


Figure 9. Variation in the rate of stone formation after the permeation of composite-grout materials.

3.4. Effects of Three Grout Materials on Reinforcement of Argillaceous Fractured Rock Bodies

The results of the compressive strength tests for grout–rock cemented bodies, using three different grout materials after grouting permeation and solidification, are detailed in Figure 10. Figure 10a shows that for silicate gel-grouted rock bodies, compressive strength fluctuates minimally across sections, suggesting that silicate gel permeation slightly impacts the strength of these bodies. The compressive strength increases as rock fragment size decreases, with increments of about 0.24 MPa for 5–10 mm, 0.36 MPa for 2–5 mm, and 0.45 MPa for 0.5–2 mm fragments. Figure 10b illustrates that the compressive strength of cement-grouted bodies significantly declines due to rock permeation, with varying trends across sections. For example, with 5–10 mm fragments, section A records a strength of 5.98 MPa, dropping to 5.36 MPa in section B and further to 4.43 MPa in section D. As rock fragment size decreases, the compressive strength in section A increases (from 5.98 MPa at 5–10 mm to 7.24 MPa at 0.5–2 mm), while the strengths in sections B, C, and D gradually decrease (for instance, from 4.43 MPa at 5–10 mm to 2.29 MPa at 0.5–2 mm in section D). The difference in strength between sections A and B also widens (from 0.62 MPa at 5–10 mm to 3.69 MPa at 0.5–2 mm). This is because, with rock fragment sizes of 5–10 mm, the permeation of the grout is comparatively minor, and fewer cement particles accumulate at the surface, leading to a relatively uniform distribution of cement particle concentration. Therefore, the compressive strength in section A for this size range is lower compared to other rock fragment sizes, and the decrease in compressive strength from section A to D is less pronounced. As the rock fragment size decreases, the permeation-retention amount of cement particles at shallow depths increases; thus, the compressive strength in section A gradually increases and the strengths in the later sections decrease, resulting in a larger difference between sections A and B. Furthermore, the greater the permeation, the higher the strength in section A and the lower the strengths in sections B, C, and D, with an increasing difference between sections A and B.

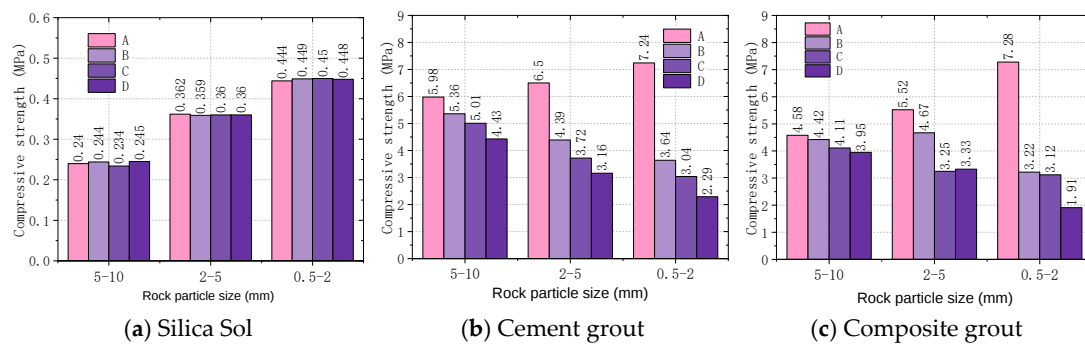


Figure 10. Compressive strength of three grouting types.

As shown in Figure 10c, the compressive strength of the grouted composite material is influenced by rock permeation similarly to cement paste, but with more pronounced effects. When rock fragments are 5–10 mm, the material's strength is lower than that of cement paste, with compressive strength decreasing slightly from 4.58 MPa in section A to 3.95 MPa in section D—a reduction of only 0.62 MPa. For rock fragments of 2–5 mm, the strengths in sections A (5.52 MPa) and B (4.67 MPa) are significantly higher than in sections C and D, suggesting an accumulation of larger cement particles in these sections. With rock fragment sizes of 0.5–2 mm, the strength peaks at 7.28 MPa in section A and decreases markedly in sections B, C, and D, indicating a shift in permeation towards section A, consistent with previous stone-formation-rate tests. As rock permeability decreases, permeation shifts closer to the rock layer surface. In highly porous and permeable rock layers, the strength of the grouted composite material in argillaceous fractured rock bodies is lower, with minimal proactive reinforcement. Conversely, in areas with lower permeability, the surface reinforcement by the composite material is more significant. This process indicates that the multi-scale and multi-grain-size composite material provides both shallow reinforcement and deep closure effects, with the grouting structure maintaining stable closure.

4. Discussion

4.1. Adaptability and Comparison of Composite Grout to Rock Body Permeation Characteristics

According to this study, there is an optimal porosity for rock body permeation; exceeding this porosity significantly reduces or increases the permeation phenomenon. If the particle size is much smaller than this porosity, it is unaffected or minimally affected. Within the experimental range, the permeability of the rock body is insufficient to cause the significant permeation of silica sol. Cement-based particulate grouting materials with larger particle sizes, such as PO 42.5 cement, whose D₉₅ is 52.25 μm , are mainly capable of injecting and sealing rock fractures larger than 0.157 mm, with poor injectability. At the level of permeation, permeation significantly impacts the larger cement particles of micron size. Cement and large cement particles in the composite grout are filtered by the rock pore skeleton, reducing the rock's stone-formation rate and sealing effect. This aspect enhances the reinforcement effect at the surface due to the accumulation of more cement filling the superficial areas, while the reinforcement and sealing effects at deeper levels are greatly reduced due to lower cement content and stone-formation rates, leading to a decrease in the sealing coverage of the grouted area.

The composite grout exhibits a multi-level particle-size distribution ranging from 4.85 nm to 98.1 μm , and given that silica sol constitutes the majority within the composite (comprising about 55.56% by weight and approximately 64.1% by volume in a mixture with 50% cement and a water/cement ratio of 0.6), it is well-suited for sealing smaller-scale fractures with strong injectability. At the permeation level, during the grouting process of the multi-particle-size composite grout, larger cement particles are filtered out at micro-

fractures (similar to the filtration of cement grout), allowing the smaller-particle-size grout, devoid of large particles, to penetrate into deeper micro-fractures. This process continues with permeation acting progressively, enabling even smaller grout sizes to enter smaller fractures (akin to soil filtering and purifying suspended liquid waste), hence allowing the composite grout to infiltrate fractures significantly smaller than those accessible to cement grout. Measuring by the smallest sealing size of silica sol, the minimum fracture size injectable by the composite grout can be as low as 20 nm [23]. After permeation accumulation, a stone formed mainly from cement particles, which has high strength, can reinforce the surrounding fractured rock. Meanwhile, the smaller particles that penetrate into the micro-fractures, primarily consisting of silica sol, form a gel with lower strength but higher sealing properties. The interaction between the grout and the fractured rock body acts as reverse precipitation; the more pronounced the permeation, the greater the accumulation of cement particles at shallow fractures, and the smaller the fracture sizes into which silica sol particles are injected, resulting in more pronounced shallow rock reinforcement and more thorough deep sealing. The stronger the rock body permeation phenomenon, the more apparent the effects of this process.

4.2. Grouting Technology and Application Prospects

In the construction process, applying composite grout is straightforward. This material can be easily used with conventional single-fluid grouting pumps and requires only the basic mixing and stirring of the materials. In areas with small-aperture fracture development, such as deep micro-cracks, the grout can be mixed and used independently. In scenarios with multi-scale fracture development, such as deep fractured rock mass tunnels, it is necessary to use the composite grout in conjunction with aluminate cement for combined deep and shallow grouting. After sealing large macroscopic fractures with aluminate cement grout, it is crucial to use composite grout for secondary grouting. Special attention is needed as composite grout must not be mixed with Portland cement grout. The latter significantly accelerates the gelling process of the composite grout, reducing both the gelling time and overall construction period, thereby drastically shortening the intended construction schedule.

In terms of application prospects, we can propose several reasonable scenarios for the use of this material. Originally developed for the characteristics of argillaceous fracture soft rocks, its applicability for the impermeabilization and reinforcement of such rocks is discussed in Section 4.1. Additionally, we have identified significant potential for its use in other tunneling applications: (1) Pre-grouting for water sealing and reinforcement in tunneling. By injecting the composite grout in advance, the initial fractures in the rock mass can be sealed and reinforced, enhancing its impermeability and strength, thus preventing the occurrence of water-conductive continuous fractures. (2) Grouting for the impermeabilization and reinforcement of fractured small coal pillars. The fracture-size distribution in coal pillars also typically varies from larger at the edges to smaller in the middle; thus, the composite grout can replace cement grout to seal and reinforce coal pillars. In addition to shielding against wastewater and gases, it also improves the strength of the coal pillars, with better results than those achieved with cement grout. (3) Extensive permeation phenomena also exist in engineering projects outside coal mine tunnels, such as the solidification of sandy soils and the strengthening of soft soils. The permeation effect in sandy soil is more significant than in rock; thus, the reinforcement and impermeabilization effects of the composite grout are more pronounced. (4) Another potential application is in hydraulic engineering, particularly in the impermeabilization and reinforcement of earth and rock dams. Dams often develop through-going cracks due to various reasons, leading to leakage, and conventional cement grout generally shows low effectiveness in grouting

for impermeabilization and reinforcement. Composite grout can also perform well in the sandy soils of earth and rock dams under permeation conditions because the consolidated bodies provide both sealing and reinforcement. This offers better water blocking than cement grout and stronger reinforcement than silica sol.

5. Conclusions

- (1) Conductivity can be achieved through ion transport in a granular gel system, and the percolation characteristics of slurry can be reflected through the conductivity and stone rate of percolation slurry. Silica sol is a grouting material with nanometer particles. Under the condition that the fracture level remains unchanged, the seepage depth and time have little influence on the slurry flow and particle loss, and the stone rate and gel strength are weakly affected by the rock mass seepage.
- (2) Cement grout is significantly affected by rock permeation. With the increase in infiltration depth and infiltration time, the sedimentation amount of large particles in the cement slurry filtered by the rock skeleton increases, and the pore blockage becomes larger. As the degree of rock fragmentation decreases, the extent of superficial permeation increases, leading to a notable reduction in the deep-rock stone-formation rate and compressive strength. The minimum stone-formation rate is reduced to 45.19%, and the minimum compressive strength is reduced to 2.29 MPa, substantially diminishing the sealing and reinforcement effects of cement grouting on deep rock bodies.
- (3) The impact of rock permeation on composite grout with nano–micro and multi-particle-size distribution primarily affects the compressive strength of the formed stones, while the stability and stone-formation rate of the grout are less influenced. With decreasing permeability, the location of rock permeation moves closer to the rock surface, and the sealing of deeper rock bodies is less affected. Therefore, the composite grout can not only achieve shallow reinforcement but also realizes deep sealing.
- (4) Composite-grout material can be easily used with conventional single-fluid grouting pumps and requires only the basic mixing and stirring of the materials. In areas with small-aperture fracture development, such as deep micro-cracks, the grout can be mixed and used independently. In scenarios with multi-scale fracture development, such as deep fractured rock-mass tunnels, it is necessary to use the composite grout in conjunction with aluminate cement for combined deep and shallow grouting.
- (5) Future research recommendations: The interaction mechanism between the gelation of silica-sol composite slurry and mudstone mudification in water-rich environments still needs to be revealed. There is still potential for optimizing the grouting performance of composite-grout materials. The industrial testing and promotion of silica-sol slurry materials still need strengthening.

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