



# Effects of Different Ion Erosion on the Hydration Mechanism and Microstructure of Nano-Clay Single-Liquid Grouting Material

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## OPEN ACCESS

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### Specialty section:

This article was submitted to  
Interdisciplinary Physics,  
a section of the journal  
Frontiers in Physics

**Received:** 16 January 2022

**Accepted:** 23 February 2022

**Published:** 23 March 2022

### Citation:

Hong Z and Zuo J (2022) Effects of  
Different Ion Erosion on the Hydration  
Mechanism and Microstructure of  
Nano-Clay Single-Liquid  
Grouting Material.  
Front. Phys. 10:856062.  
doi: 10.3389/fphy.2022.856062

The effect of nano-clay (NC) on hydration and microstructure of grouting materials was investigated under different erosion conditions. Six different contents of NC specimens were prepared. This study investigated the effect of NC on the mechanical properties and microstructure of grouting materials under chloride ion erosion and standard curing conditions (SCCs), using ultrasonic pulse velocity (UPV), uniaxial compressive strength (UCS), Fourier transform infrared spectroscopy (FT-IR), and scanning electron microscopy (SEM). The experimental results demonstrated that the nano-core effect can promote the formation of the core reaction of grouting materials and accelerate the hydration process. With the NC increase, the hydration products of ettringite (Aft) and calcium silicate hydrate (C-S-H) also increases. Under chloride ion erosion, it was obtained that when NC was less than 2%, the UCS and UPV were improved. As the NC content is 2%, the hydration reaction is the most appropriate. However, under high humidity conditions, as the NC content is 1%, the amount and density of Aft increased and the formation of C-S-H gel enhanced. The hydration reaction inhibited, and the mechanical properties of grouting materials decreased when NC was further increased. It indicated that the complex underground engineering environment affected the hydration mechanism of nano-grouting materials.

**Keywords:** corrosion, ultrasonic pulse velocity, NC, hydration reaction, microstructure

## INTRODUCTION

There is an increasing demand for underground engineering in China, such as coal mines, subway repair, and tunnel reinforcement. Therefore, cement grouting materials are widely used in underground engineering to ensure the overall stability of the project [1, 2]. However, due to the complex conditions of the underground engineering, the existing cement grouting materials suffer several issues, such as low bearing capacity and easy cracking. Efforts have been made to overcome these shortcomings. Nanomaterials are unique in that they have many different chemical and physical properties, such as small size, surface, and quantum effects, compared with traditional materials [3, 4]. Therefore, compared with ordinary material particles, nanomaterial particles have higher catalytic activity and chemical activity. With the development of nanotechnology, more and more nanomaterials have partially replaced cement and have been widely used in the modification of

concrete materials, such as nano-clay [5], nano-graphene [6, 7], nano-TiO<sub>2</sub> [8], nano-SiO<sub>2</sub> [9], and carbon nanotubes (CNT) [10].

Liu et al. [11] showed that with an additional 1% nanoCaCO<sub>3</sub>, the strength was improved by 111 and 108% at 7 and 28 days by the cement mortar. Essawy et al. [12] showed that the strength of a cement specimen increased by 5% after adding 5 wt% nano TiO<sub>2</sub>. However, Hassan et al. [13] found that the compressive strength of 2% nano-TiO<sub>2</sub> changed a little, even presented a decreasing trend. Nazari et al. [14] studied the influence of nano-Al<sub>2</sub>O<sub>3</sub> on the compressive strength of concrete under different curing conditions, and the results showed that under saturated lime water and water curing conditions, the maximum dosage of nano-Al<sub>2</sub>O<sub>3</sub> was 2 and 1%, respectively.

The aforementioned analysis indicated that the properties of nanomaterials were unstable and needed to be further discussed [15–17]. Very few authors focused on the NC to increase the performance of grouting materials in complex environments, such as, ion erosion, and soaking water. In addition, the grouting material with small particle size required for small-scale damage caused by underground stress has not been reported. Therefore, the systematic research of the influence of NC on grouting materials with small particle sizes in complex underground engineering environments is the most important step.

This work aims to study the properties of nano-grouting reinforcement materials under different erosion conditions. Different erosion conditions and six different contents of NC samples were prepared, and the hydration mechanism of NC has been studied. The main preliminary results were obtained by microstructure experiments.

## MATERIAL AND SPECIMEN PREPARATION

### Raw Materials

The experimental materials used were sulphoaluminate cement clinker (CSA) and anhydrite, purchased from Shandong Cement Co., Ltd. and Xian Anhydrite Plant, respectively. The composition of sulphoaluminate cement clinker was tested by XRF to be 11.51% SiO<sub>2</sub>, 43.59% CaO, 2.10% Fe<sub>2</sub>O<sub>3</sub>, 29.96% Al<sub>2</sub>O<sub>3</sub>, 8.06% SO<sub>3</sub> and 2.12% MgO. And the composition of anhydrite was tested by XRF to be 3.50% SiO<sub>2</sub>, 49.80% CaO, 0.51% Fe<sub>2</sub>O<sub>3</sub>, 1.13% Al<sub>2</sub>O<sub>3</sub>, 41.23% SO<sub>3</sub> and 3.16% MgO. At the same time, compound admixture and nano-clay materials were also added to the grouting reinforcement materials. Nano-clay was purchased from Hebei Trading Co., LTD. Nano-clay was classified as nano-clay with a powdery appearance and white color. The composition of the nano-clay was tested by XRF to be 75.95% SiO<sub>2</sub>, 2.19% CaO, 1.70% Fe<sub>2</sub>O<sub>3</sub>, 4.31% Al<sub>2</sub>O<sub>3</sub>, 41.23% SO<sub>3</sub>, 0.68% MgO, and 0.76 Na<sub>2</sub>O.

### Specimen Preparation

The mixed proportion (CSA cement clinker:anhydrite:compound additives is 80, 20, and 3%) was fixed. The content of NC was added at 0, 1, 2, 3, 5, and 7 wt% for a fixed W/C of 1.0. The specimens were 50\*100 mm (diameter\*height), the specimens were solidified and placed in a solution of chloride ions, the chloride ion solution was prepared with NaCl, and 5% chloride ion solution was prepared

**TABLE 1** | Mechanical properties with NC content under different conditions.

Compressive strength (MPa)	NC content (%)					
	0	1	2	3	5	7
Chloride ion erosion	6.43	8.64	7.69	6.59	6.04	6.14
Increment (%)	0	34.4	19.6	2.50	-6.10	-4.51
SCC	5.86	8.50	6.86	5.49	5.26	5.56
Increment (%)	0	45.1	17.1	-6.31	-10.2	-5.11

according to the test requirements, and other parts of specimens were cured under standard curing conditions. The compressive strength and ultrasonic pulse velocity were tested using the system of GCTS RTR-1000 rapid triaxial rock testing. The FT-IR was measured by using a Nicolet iS10 FT-IR spectrometer, and the range was from 400 to 4,000 cm<sup>-1</sup>. SEM analysis was carried out using a Hitachi SU8010 Japan system.

## EXPERIMENTAL METHOD

### Ultrasonic Pulse Velocity Measurement

The measurement UPV was used to test the wave velocities of specimen P wave and S waves, and the coupling agent was honey. Then the wave velocities were measured under different corrosion times. The wave velocities at every angle were taken as the average of three measurements.

### Uniaxial Compression Test

The compressive strength of the specimens was tested by using a GCTS RTR-1000 Rapid Triaxial Rock Testing System. The compressive strength was tested at various curing times of 7 d, 28 d, and 60 d, respectively. For each test, a mean value of three pastes was used.

### Fourier Transform Infrared Spectroscopy

The mineral composition and hydration products of grout materials were analyzed by Fourier transform infrared spectroscopy (FT-IR). The Nicolet iS10 FT-IR spectrometer was used to collect the test results, with a measurement range of 400–4,000 cm<sup>-1</sup>.

### Scanning Electron Microscopy

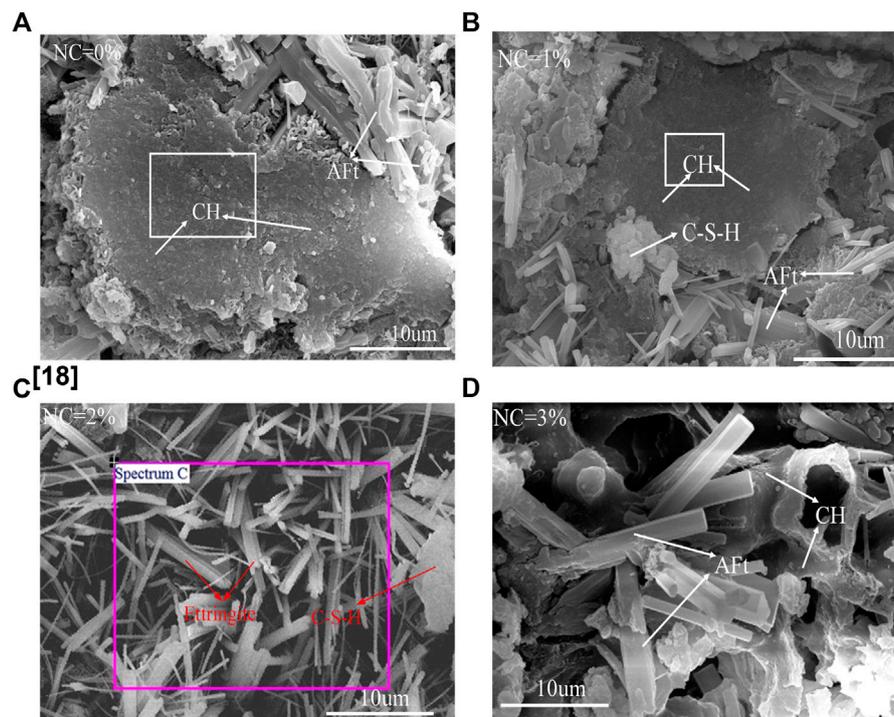
The microstructure of hydration products was studied by scanning electron microscopy (SEM). SEM uses the Hitachi SU8020 test system, in which the working voltage of the SEM method was set as 15 kV and the working distance 12.5 mm.

## RESULTS AND DISCUSSION

### Ultrasonic Pulse Velocity and Uniaxial Compressive Strength Analysis

The curves of ultrasonic pulse velocity (UPV) and uniaxial compressive strength (UCS) under different ion erosions were evaluated. As shown in **Table 1**, it indicates that the influence of NC on the cement material is greatly affected by the different curing environments. Under chloride ion erosion, the UCS





**FIGURE 2** | SEM image of hydrated specimens in chloride ion solution for 7d.

The main reason is that the crystal core centered on NC was formed, which can make the loose gel product become the network structure with nanoparticles as the core; this accelerated the formation of Aft and C-S-H gel. When the nano-grouting material was soaked in chloride ion erosion, due to the complex erosion conditions, more NC (NC = 2.0%) was needed to give full play to its nano-effect. However, as more NC was added, the nano-core effect decreased, the hydration process was limited, and the peak weakened. It showed calcite with a double energy band at  $1,483$  and  $1667\text{ cm}^{-1}$  of  $(\text{CO}_3)^{2-}$ . The strongest vibration occurred at  $3,430\text{ cm}^{-1}$  and  $3,634\text{ cm}^{-1}$ , and it is presented by the O-H [18] bond of CH. The existence of the substances produced in the hydration process was verified by FT-IR analysis, which provided the basis for SEM analysis.

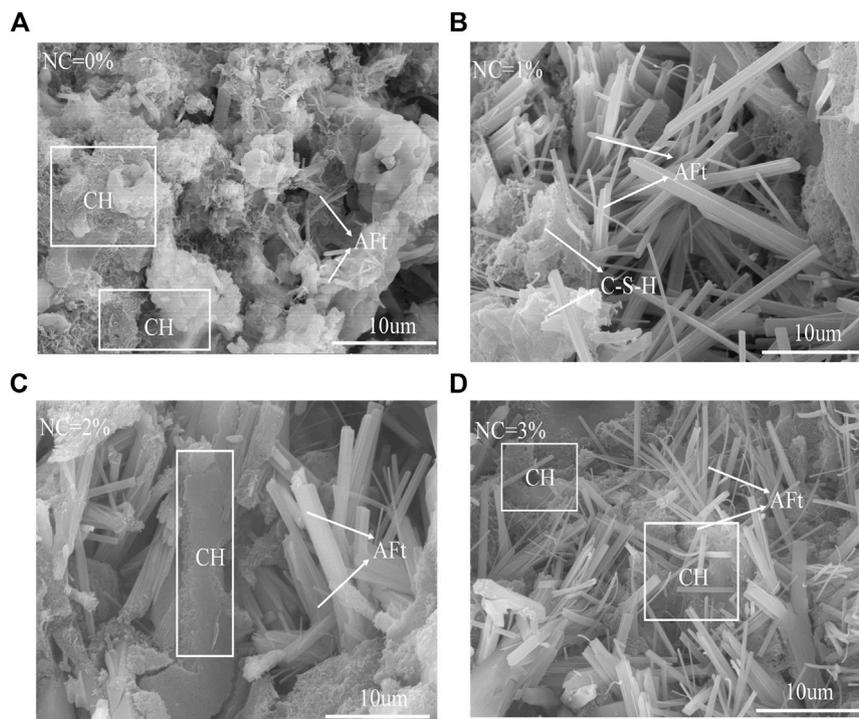
### Scanning Electron Microscopy Micrographs Analysis of Ion Erosion Conditions

Figure 2 shows the SEM micrographs of the chloride ion solution for 7d. It is clearly observed that NC promoted the formation of Aft and C-S-H hydration products and improved the corrosion resistance of grouting materials. It can be seen from Fig. (a) and (b) that Aft is wrapped by CH and cannot develop well, and it shows that when the NC content is small, the hydration of grouting materials cannot be well stimulated. As the NC content increased, especially when the NC content is 2%, during the hydration process of grouting materials, more Aft was formed, CH was consumed, and C-S-H gel was increased.

The hydration reaction of grouting material reflects the mechanical properties. The mechanical properties of grouting materials can be improved with the increase in the ettringite content and the increase in C-S-H production. Therefore, the mechanical properties of grouting materials improved. However, as NC was more than 2%, for example, if the NC content was 3%, the Aft became coarse and rod-shaped, and the amount and density of Aft decreased obviously; meanwhile, CH consumption was reduced, C-S-H gel formation was blocked, and the hydration products had larger pores. It showed that more NC (more than 2%) inhibits the hydration process of grouting material.

### Scanning Electron Microscopy Micrographs Analysis of Humidity Curing

Figure 3 shows a SEM micrograph for humidity curing 7d under different NC contents. As the NC is more than 1%, as shown in images (c) and (d), it is noticed that the hydration products of Aft and C-S-H were inhibited, the amount and the density of Aft decreased, and the morphology became finer and shorter compared to those less than 1% NC. Meanwhile, the C-S-H gels were limited; the C-S-H gel with a granular and short fibrous shape did not overlap between the gels. Especially, as the NC is more than 2%, the flake CH obviously increased, the Aft showed a concentrated development, the “coarse-rod flowers state” disappeared, and the Aft was wrapped in flake products. Because C-S-H gels can fill pores in cement, less C-S-H gels were found, and as a result, the microstructural compactness dropped. It indicated that too much NC (more than 1%) inhibited



**FIGURE 3** | SEM images of microstructure of relative humidity is 90% for curing 7d.

the hydration process, and the hydration products were also restricted. The distribution of microstructure was bound to affect the mechanical properties of the cement grouting material.

The hydration process and products of grouting material affected the mechanical properties; the amount and density of AFt and the filling effect of C-S-H gel determined the mechanical properties of grouting material. When the grouting material was in the chloride ion erosion environment, NC was 2%, hydration reaction was adequate, and mechanical properties and erosion resistance were the best. When the grouting material was in a high humidity condition, NC was 1%, and the hydration process and mechanical properties were the best. This was consistent with the results of the FT-IR analysis.

## CONCLUSION

The study investigated the effect of NC on hydration and microstructure of grouting materials under different ion erosions. The conclusions were drawn as follows: that under the chloride ion erosion, as NC was less than 2%, the UCS and UPV improved; NC accelerated the hydration process, resulting in the hydration products of AFt and C-S-H well developed; however, the hydration effect of NC varied greatly under different environments. The density and the morphology of AFt were increased, CH was exhausted, the C-S-H was formed during the hydration reaction, and the microstructural compactness was improved. Under chloride ion erosion and high humidity conditions, NC hydration reaction was the best when NC is 2

and 1%, respectively. However, with the increase in NC, the nano-core effect was inhibited, the morphology of AFt became thinner and shorter, and the C-S-H gel was restricted. In the future, facing the complex underground environment, the research and development of grouting materials with better adaptability will play an important role in China's underground engineering.

## DATA AVAILABILITY STATEMENT

The original contributions presented in the study are included in the article/Supplementary Material, further inquiries can be directed to the corresponding author.

## AUTHOR CONTRIBUTIONS

ZH wrote the manuscript, and JZ revised the manuscript.

## FUNDING

This study was financially supported by the Outstanding Young Scientist of Beijing (BJJWZYJH01201911413037), the Science and Technology Project of Henan Province (222102320004), the Fund Project for Improving Young Teachers' Scientific Research Ability of the School of Civil Engineering, Henan Polytechnic University, and the Doctoral Fund of Henan Polytechnic University.

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