Study on mechanical properties and microstructure of the new grouting material

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Abstract. The new grouting material with advantages of early strength, strong liquidity, better expansibility and environmental protection can be applied to underground structure engineering. The effects of different w/b ratios, curing ages, limes and SiO₂ on the compressive strength of the new grouting material were investigated. By SEM and TGA-DSC analysis, its microscopic morphology and hydration products are explored. The results show that the early strength of the new grouting material develops rapidly, and the 3d compressive strength can reach 80% of the 28d compressive strength. Under the condition that the w/b ratio is 1.0, the compressive strength increases with CaO content in lime increasing. The addition of micron-SiO₂ can improve compressive strength by about 5% when the formulation is reasonable. The main hydration products of SEM-EDS are needle-like ettringite, spherical aluminum gel and amorphous C-S-H(C-A-S-H) gel, corresponding to three endothermic peaks appearing in TGA-DSC at around 90℃, 230℃ and 660℃, respectively.

1. Introduction
Nowadays, with rapid accelerated urbanization, underground space utilization is increasing and the construction of underground structure engineering is expanding, inseparable from grouting materials. At present, the grouting materials commonly used are micro-fine cement grouting materials [1-2], cement-water glass grouting materials [3] and cement-fly ash grouting materials [4-6]. However, for complex strata, cement-based grouting material has low early strength, easy delamination and poor water corrosive resistance, which cannot meet the requirements of underground construction. Therefore, it is especially necessary to develop new grouting materials with excellent performance.

The new grouting material is modified and developed on the basis of high-water and quick-setting material, consisting of material A (sulphoaluminate cement + additive AA) and material B (gypsum, lime + additive BB). In recent years, along with the wide application of grouting materials, many scholars have conducted their research on mechanical properties and microstructure of them. Xie Hui [7] pointed out the main minerals of high water material are sulphoaluminate and gypsum; Peng Meixun et al [8-9] studied the influence of various components on compressive strength and coagulation properties of material with different formulations and curing conditions. Xia Junwu [10] proposed the hydration mechanism of high-water and quick-setting material by SEM tests combined with analysis of compressive strength and hydration process. Frank et al [11-12] explored the effects of the calcium sulfate on the hydration reaction of calcium sulphoaluminate by calorimetry,
thermogravimetric analysis and nuclear magnetic resonance. He Tao [13] studied that different pH values will affect the microstructure of the grouting material and thus material exhibits different strength characteristics. In this paper, the effect mechanism on compressive strength of the new grouting material is studied. Besides, the hydration products of each stage are explored by SEM and TGA-DSC tests. In addition, the relationship between microstructure and strength properties is analysed, providing a basis for the development of grouting materials and their application in engineering.

2. Materials and experimental works

2.1. Raw materials

The raw materials used in the new grouting material include: (1) Material A: sulfoaluminate cement CSA; additive AA. (2) Material B: gypsum; three kinds of lime (L1, L2 and L3), wherein L3 is pure calcium oxide; additive BB. (3) Modified SiO2 (S1and S2): S1 is micron-SiO2; S2 is vapor-phase hydrophilic nano-SiO2. Table 1 shows the chemical composition of CSA, gypsum, L1 and L2.

| Samples | Mass fraction/% |
|---------|----------------|
| CSA     | CaO 36.76  Al2O3 33.66  SiO2 7.41  SO3 9.00  Fe2O3 2.43  MgO 0.92  K2O 0.29  SrO 0.08  CO3 3.65  Others 1.82 |
| Gypsum  | 36.33 0.17 1.07 45.48 0.04 2.85 0.04 0.27 13.67 0.02 |
| L1      | 69.06 0.85 1.62 0.44 0.23 0.82 0.03 0.03 26.84 0.14 |
| L2      | 88.12 0.49 1.15 0.15 0.13 9.87 0.02 0.06 0.00 0.02 |

2.2. Mix formulations and preparation

Referring to the optimum gypsum-lime content [10], the new grouting material experiment adopted the ratio of CSA:AA:Gypsum:Lime:BB=1:0.1:0.8:0.2:0.1. And SiO2 replaces 5% sulfoaluminate cement by mass in the modified groups. The test considered the influence of three w/b ratios (1.0, 1.5, and 2.0 corresponding to W1, W2, and W3 respectively), three types of lime (L1, L2 and L3), two types of SiO2 (S1 and S2) on the material, with 27 groups in total. And the performance of material at different ages (5h, 1d, 3d, 7d, 14d and 28d) were tested. The way of naming in this study is shown by an example: W1L2S1 indicates that the w/b ratio, type of lime and SiO2 of the material are 1.0, L2 and S1 respectively.

The new grouting slurry is prepared by mixing slurry A and slurry B in an equal proportion. For the modified groups where nano-SiO2 (S2) is added, S2 is first dispersed into water by an ultrasonic disperser to obtain the part one of slurry A. The preparation process is shown in Figure 1.

**Figure 1. The preparation process of the new grouting material: (a) without SiO2 addition and with addition of S1; (b) with addition of S2.**

2.3. Test methods

The mixing slurry was poured into a 40 mm×40 mm×160 mm triple test mould, and then the demoulding samples wrapped in plastic film were cured in a standard curing room (temperature 20±2°C, relative humidity 95±5%) until the predetermined age.

Compressive strength test: Referring to GB/T17671-1999 [14], the compressive strength of samples was tested by a full dynamic cement strength testing machine with the loading speed 2400N/s.
SEM: Small material pieces cured to specified age were immersed in absolute ethanol for 7 days, and then dried at 60 °C. The prepared SEM samples are tested by the scanning electron microscope of American FEI Company (Model Quanta 250) and its accessories Energy Dispersive Spectrometer.

TGA-DSC: The dried pieces described before were ground to a powder less than 200 mesh by a mortar. The obtained samples were heated from room temperature to 1000 °C with the heating rate of 5 °C/min by a synchronous thermal analyser (model STA449F5), using a nitrogen atmosphere.

3. Test results and discussion

3.1. Compressive strength
The compressive strength of the material with different formulations was obtained, shown in Figure 2.

3.1.1. Effect of w/b ratio on strength. Figure 2 indicates that the compressive strength decreases with increasing w/b ratio, mainly because the increase of water reduces the collision between material particles and increases the pore water content, affecting the development of compressive strength. Table 2 shows the influence of the increasing w/b ratio on the reduction of strength. With the w/b ratio increasing by 0.5(from W1 to W2, from W2 to W3), the 28d compressive strength declined by 27.54-67.64%. For the groups without addition of SiO2 and with addition of micron-SiO2(S1), the effect of increasing w/b ratio on the reduction of compressive strength increases with the increasing CaO content in lime, because the low water consumption feature of CaO results in more free water in the material, thereby causing more reduction of compressive strength. For the groups with addition of nano-SiO2 (S2), the influence of increasing w/b ratio on the reduction of compressive strength has no obvious relationship with the CaO content. The w/b ratio increases by 0.5 and the strength reduces by about 48%.

| Material | L1  | L2  | L3  |
|----------|-----|-----|-----|
|          | W1→W2 | W2→W3 | W1→W2 | W2→W3 | W1→W2 | W2→W3 |
| no SiO2  | 40.36% | 27.54% | 42.93% | 33.61% | 46.84% | 45.15% |
| S1       | 40.97% | 32.05% | 44.23% | 42.77% | 49.11% | 67.64% |
| S2       | 46.31% | 51.63% | 43.17% | 49.87% | 45.39% | 50.41% |

3.1.2. Effect of curing age on strength. The compressive strength of the new grouting material develops rapidly, and the compressive strength of the superior group can reach 8-10 MPa curing for 5 h. However, the development of compressive strength in the early age 5h is greatly affected by the w/b ratio: when the w/b ratio is 1.0, 1.5 and 2.0, the 5h compressive strength accounts for 62%, 53%, 30% of the 28d compressive strength, respectively. The smaller the ratio is, the faster the 5h compressive strength grows. The compressive strength at 1d, 3d and 7d age can reach about 70%, 80% and 90% of that at 28d age, respectively, which shows great early strength characteristics. In Figure 2, the compressive strength of material with different mix formulations enhances with curing time increasing, and the compressive strength develops rapidly in the early age(0~7d), tending to be flat until 28d.

3.1.3. Effect of types of lime on strength. Figure 2(a) and (b) shows that compressive strength grows with increasing CaO content in lime at a w/b ratio of 1.0, for samples without addition of SiO2 and with addition of S1. The compressive strength of material using L2 and L3 is 4.61% and 10.90% higher than that of L1. This is because the increasing CaO content adds the alkalinity of slurry, which is beneficial for the formation of ettringite and higher compressive strength. When the w/b ratio increases to 2.0, low water consumption feature has a greater influence on the strength than the alkalinity of increasing CaO content, lowering the compressive strength of the new grouting material. The different types of lime have little effect on the compressive strength of groups with addition of S2, seen from Figure 2(c). Comparing the influence of three types of lime on the compressive strength, lime L2 is the best.
3.1.4. Effect of types of SiO₂ on strength. It can be seen from Figure 3 that under the condition of the w/b ratio 1.0, the addition of micron-SiO₂ (S1) can increase the compressive strength by about 5% on average, comparing with the group without SiO₂ addition. The reason is that micron-SiO₂ increases the content of SiO₂, which is advantageous to form CSH gel and improve the compressive strength. However, the material with nano-SiO₂ shows about 18% lower compressive strength than that without SiO₂. Because nano-SiO₂ has high activity and it can quickly wrap other materials to hinder the reaction between components after added, which is not conducive to the formation of ettringite, resulting in loose structure and lower strength. Therefore, in the application of the new grouting material, it is considered to add micron-SiO₂ in order to increase the compressive strength.

Figure 2. Compressive strength curves of the material with different formulations at different curing ages: (a) without SiO₂ addition; (b) with addition of S1; (c) with the addition of S2.

3.2. SEM analysis
The new grouting material of W2L1-28d was analysed by SEM-EDS, as shown in Figure 4.
It can be seen from Figure 4(a) that the microscopic morphology is mainly cluster-like and needle-shaped. The clusters correspond to all or part of Ca, O, Al and Si element in Figure 4(b), and it can be conjectured to be aluminum gel and C-S-H (C-A-S-H) gel considering hydration reaction of the material. Figure 4(c) gives the EDS result of needle-like area, showing the main elements are Ca, S, O, and Al. And the corresponding hydration product is ettringite.

Figure 5 shows the SEM images of the material with different formulations at different curing ages. A large number of needle-like and prismatic ettringite, spherical aluminum gel and amorphous C-S-H (C-A-S-H) gel are observed. Compared with Figure 5(a), the ettringite crystal becomes more slender as the w/b ratio increases (Figure 5(b)), leading to a decline strength, which is consistent with the result of the previous compressive test. The number of ettringite at 28d age (Figure 5(c)) is obviously more than that of 7d. As curing age grows, the hydrated product ettringite develops continuously and the structure becomes denser. The gel phase of W2L3-7d (Figure 5(d)) is more than that of W2L1-7d, with the increasing content of CaO in lime the gel phase grows, enhancing the strength. Figure 5(e) indicates that addition of S1 increases the formation of the gel phase which is advantageous to improve the strength. Figure 5(f) is the SEM image of the material with a poor result in compressive test. It can be found that the hydrated product ettringite is very slender, without a tight connection, and the microstructure is very loose, corresponding to the low compressive strength. Combined with the results of compressive strength and SEM image analysis, different w/b ratios, curing ages, the types of lime and SiO₂ mainly affect the hydration products and microstructure of the new grouting material. With the number of hydration products gel phase and ettringite increasing, the microstructure becomes denser and the macroscopic mechanical properties of the material are correspondingly better.
3.3. TGA-DSC analysis

The new grouting material with representative proportions and curing ages was analysed in order to obtain the TG-DTG and DSC curves, as shown in Figure 6. Figure 6(a) shows the temperature peaks of different types of the materials appear in the three areas of 86.5–96.0°C, 228.5–237.7°C, and 651.0–667.0°C respectively. The endothermic peaks appearing in the DSC curves (Figure 6(b)) are obviously consistent with that in Figure 6(a). The endothermic peak of ettringite hydrolysis and aluminum gel dehydration occurs around 90 °C, 230 °C, and the endothermic peak of 650 °C corresponds to the dehydration of C-S-H (or C-A-S-H) gel. In summary, it can be seen that the hydration products of the new grouting material mainly include ettringite, aluminum gel and hydrated calcium silicate gel, which are consistent with the SEM analysis results.

4. Conclusions

According to the compressive strength test, SEM and TGA-DSC analysis, the conclusions are as follows:

1. The compressive strength of the new grouting material decreases with increasing w/b ratio. The w/b ratio increases by 0.5 and the 28d compressive strength declines by 27.54-67.64%. The w/b ratio ranging from 1.0-2.0 is suitable for underground construction.

2. The new grouting material has great early strength, and the 3d compressive strength can reach about 80% of that at age of 28d. The early strength increases rapidly, and the compressive strength curves tend to be flat until 28d.

3. In the case of relatively small w/b ratio, the compressive strength of the new grouting material increases with the increasing CaO content in lime. The addition of micro-SiO2 is beneficial for the
formation of C-S-H gel, and adding appropriate content of micro-SiO$_2$ can be applied to grouting engineering underground to enhance the strength.

(4) The results of SEM-EDS are consistent with TGA-DSC. The main hydration products of the new grouting material are ettringite, aluminum gel and hydrated calcium silicate gel. With the number of hydration product gel phase and ettringite increasing, the microstructure becomes denser and the macroscopic mechanical properties of the material are correspondingly better.

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