Original Article

Experimental study on properties of a new type of grouting material for the reinforcement of fractured seam floor

Wenquan Zhang\textsuperscript{a,b}, Xianxiang Zhu\textsuperscript{a,b,∗}, Shuanxiang Xu\textsuperscript{c}, Zaiyong Wang\textsuperscript{a,b}, Wei Li\textsuperscript{a,b}

\textsuperscript{a} College of Mining and Safety Engineering, Shandong University of Science and Technology, Qingdao 266590, China
\textsuperscript{b} State Key Laboratory of Mine Disaster Prevention and Control (Cultivation), Shandong University of Science and Technology, Qingdao 266590, China
\textsuperscript{c} Shandong New Dragon Energy Co. Ltd, Heze 274000, China

Abstract

In this paper, a grouting material with low cost and high density was proposed for the reinforcement of large-scale floor cracks. The component screening test, mechanical property test, rheological properties test, and impermeability test were conducted to obtain the strength, rheological properties, and permeability of the new grouting materials. In order to fully understand the physicochemical properties of the new grouting material, a total of 12 sets of test pieces were produced using cement, clay, and fly ash as the main body, and foaming agent as the auxiliary material. Each set of the test pieces had different proportions of ingredients, pores conditions, and auxiliary chemical materials (water reducing agents, defoamers). The test results showed that: (1) The optimal proportion of ingredients for the new grouting material (including 1% foaming agent) was: 40% of cement, 30% of clay, and 30% of fly ash. (2) The optimal amount of fly ash for the new grouting material was 30% and the optimal foaming amount for the new grouting material was 1%. The impermeability of the grouting material was 0.7 MPa, which reached Level P6. The new grouting material was suitable for the HB rheology model. (3) The pores were uniformly distributed inside the solidified body of the new grouting material. In the later stage, the strength of the solidified body was stable, and the flow loss was reduced. At present, the corresponding proportion of ingredients and the performance parameters of the new grouting material were tested in the laboratory. In the future, it is necessary to further determine the effect of the grouting material in the reinforcement of the floor crack of the coal seam and to improve the proportion of ingredients for the grouting material in the mine sites.

© 2019 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

At present, due to the fracture of the coal mine floor [1], the activation and expansion of the floor in the mining activities cause the communication of the floor pressure water [2,3].
As a result, the disasters such as water inrush and the casualties occur frequently, which seriously affects the safety of coal mine production [4]. The grouting reinforcement of the mine floor [5,6], the reconstruction of the confined aquifer to the water-repellent layer [7], and the improvement of the water-blocking capacity of rock layer is one of the important measures to ensure the safe mining over the pressure water in the coal mine floor [8]. However, at this stage, there is a huge demand on the grouting materials for the fractures of the mine floor, but some polymer grouting materials are expensive. Thus the production cost of mining enterprises continues to increase. Meanwhile, there is a yearly increase of the large-scale solid wastes, which affects people's production and living environment [9]. For instance, fly ash generated by the coal burning in thermal power plants [10,11], slag and ore powder produced in metal mines [12], and steel slag produced by steel-making enterprises have caused great harm to the surrounding environment [13]. Therefore, the recycling utilization of solid waste from industrial and mining enterprises to develop new grouting materials suitable for filling floor cracks has great significance to reduce the cost of coal mining enterprises, improve the utilization efficiency of solid waste products, and improve people's production and living environment [14–16].

Over the years, with the development of floor crack grouting reinforcement technology, there are more and more kinds of grouting materials, and various new grouting materials are constantly emerging [24–26]. Grouting materials are mainly divided into two categories: cement-based grout and chemical grout, as shown in Tables 1 and 2.

In the use of industrial and mining enterprises to prepare grouting materials for solid waste, domestic and foreign scholars have also carried out a large number of research [11,27,28]. On the basis of making full use of coal mine waste coal gangue, Wang et al. [29,30] developed a new type of inorganic grouting material suitable for aquifer rebuilding, which provides reference for the exploitation of pressurized underwater coal mines; Guo [31] started the research on the slag micro-powder grouting material slurry by orthogonal test from the water-discharging rate and fluidity of grouting material, and realized the diversification of grouting materials. At this stage, the research on grouting materials with fly ash as the main body is also numerous, Sun [32] analyzed the influences of solid mass concentration, fine gangue ratio and fly ash content on workability and strength of slurry backfill materials. It was concluded that when the fly ash content was 15.67% of the total mass, fly ash had stronger activity, which could promote the early formation of calcium silicate gel and improve the agglomeration formation strength of hydrated calcium silicate gel. In view of the performance of renewable concrete, Bui [33] found that the mix ratio of 5% PSA, 10% SF, 15% MK and 15% FA recycled concrete (RAC) and 100% coarse recycled concrete aggregate (RCA) was the highest; Wan et al. [34] analyzed the influence of fly ash content on the impermeability of cement sodium silicate slurry in view of the seepage problems in water conservancy and geotechnical engineering. Through field tests, it was concluded that fly ash content at 25% could meet the requirements of the code. However, in terms of grouting materials for cracks in coal mine floor, there are few relevant scholars studying them, focusing only on the uniaxial compressive strength, water-cement ratio and setting time of materials. Insufficient attention has been paid to the degree of filling compactness of grouting cracks and the bonding force with rock wall, and less attention has been paid to the slurry flow characteristics in the grouting process.

Thus, in the grouting engineering design, the grouting materials should be selected depending on the actual situation and comprehensive consideration of various factors. The traditional grouting materials have a certain degree of deficiencies. Meanwhile, people generally use Cement numbered 32.5, such as cement, etc., to fill the floor cracks. The grouting material only needs to fill the cracks and strengthen the impermeability of the grouting consolidation, while the strength requirement is low. The use of cement as the grounding material greatly increases the production cost.

In order to address the above problems, in this paper, a new type of grouting material was developed for the grouting reinforcement of the fractured floor of the coal mines using the fly ash from coal-fired thermal power plants as the raw material, the cement and clay as the addition material, the foaming agent and water-reduction agent for the performance enhancement as the supplemented material. The development of the new grouting material was based on the consideration of the cost of grouting materials, the recycling utilization of solid waste from industrial and mining enterprises, the improvement on the adhesion of the grouting material, and the safety of grouting engineering. The physicochemical properties of the new materials were studied using mechanical experiment, rheological experiment, impermeability test and microscopic analysis. From the perspective of performance and cost, the developed grouting material in this paper was compared with other grouting materials. This study provided an alternative selection of the grouting material for the sealing and reinforcement of the fractured floor in coal mines.

2. Preparation of experiment

2.1. Objectives of research and development

In the analysis on the cement-fly ash-clay grouting material system, the key consideration was the balance between the amount of solid waste in the grouting material and the performance of the material. Especially, the requirements of the fracture in the coal mine floor on the performance of the grouting material need to be considered. The requirements included that the final compressive strength of the material should be larger than the hydrostatic pressure of the pre-surge water, the grouting consolidation should have high impermeability, and the compactness of the filling should be high. When all the above requirements are satisfied, the proportion of solid waste products in the grouting material should be increased.

2.2. Analysis on experimental component

2.2.1. Fly ash

The fly ash used was the Grade I fly ash produced in a power plant in Shandong. The density of fly ash was tested to be
Table 1 – Characteristics of several cement-based grout [17–19].

<table>
<thead>
<tr>
<th>Name</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Clay-concrete slip</td>
<td>Good stability, abundant material source and low cost</td>
<td>Low strength, poor adhesion and uncontrollable solidification time</td>
</tr>
<tr>
<td>Cement-water glass</td>
<td>Rich source, short setting time and high initial strength</td>
<td>Easy segregation, difficult to control the solidification time, poor diffusion</td>
</tr>
<tr>
<td>Cement and flying ash grout</td>
<td>Good stability, high injectability and low cost</td>
<td>The early stage of consolidation has low strength and poor adhesion</td>
</tr>
</tbody>
</table>

Table 2 – Characteristics of several chemical grout [20–23].

<table>
<thead>
<tr>
<th>Name</th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
</thead>
<tbody>
<tr>
<td>Epoxy resin</td>
<td>High compressive strength, strong adhesion, acid and alkali resistance</td>
<td>High viscosity, not resistant to moisture, long curing time</td>
</tr>
<tr>
<td>Unsaturated polyester</td>
<td>Low viscosity and high strength</td>
<td>Curing volume shrinkage, high temperature, odor, flammable</td>
</tr>
<tr>
<td>Urea formaldehyde resin</td>
<td>Low viscosity and high curing strength</td>
<td>After curing, it has high brittleness, free formaldehyde in the slurry, certain toxicity and short storage period</td>
</tr>
<tr>
<td>Polyurethane (pu)</td>
<td>Low viscosity, good permeability, high strength, high comprehensive performance</td>
<td>Flammable, high reaction temperature</td>
</tr>
</tbody>
</table>

Table 3 – Chemical composition of fly ash (unit:%).

<table>
<thead>
<tr>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>Ignition loss</th>
<th>MgO</th>
<th>SiO₂</th>
<th>SO₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>25.67</td>
<td>4.16</td>
<td>4.87</td>
<td>8.75</td>
<td>1.56</td>
<td>54.14</td>
<td>0.85</td>
</tr>
</tbody>
</table>

Table 4 – Fundamental properties of fly ash used.

<table>
<thead>
<tr>
<th>Density (g/cm³)</th>
<th>Bulk density (g/cm³)</th>
<th>Specific surface area (cm²/g)</th>
<th>45 μm square hole sieve residue (%)</th>
<th>Water demand ratio (%)</th>
<th>28d compressive strength ratio %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.07–2.40</td>
<td>1.0–1.3</td>
<td>1500–5000</td>
<td>≤12</td>
<td>≤95</td>
<td>37–85</td>
</tr>
</tbody>
</table>

1.07–2.40 g/cm³. The color of the fly ash was grayish white. The fundamental properties of fly ash used are shown in Tables 3 and 4.

From Table 3, the chemical composition of fly ash has the following characteristics: (1) The content of SiO₂ is about 54.14%, and the content of CaO is small, indicating that the main ingredient is quartz and the activity of the material is weak. (2) The content of Al₂O₃ is relatively high. The content of Al₂O₃ accounts for 25.67%, indicating that the components of fly ash are relatively stable and the content of the active minerals is low. (3) The alkalinity is low. The ratio of fly ash (CaO + MaO)/(SiO₂) is low, indicating it is a low-alkaline mineral.

2.2.2. Clay

The clay used in the experiment was provided by a mine in Shandong Province with a density of about 1.40 g/cm³. The color of the clay was dark red. The basic properties of clay are shown in Tables 5 and 6. The clay was mainly composed of SiO₂, Al₂O₃, and a small amount of Fe₂O₃.

2.2.3. Other materials

Ordinary silicate cement, a hydraulic cementitious material, was made of silicate cement clinker, 5–20% mixed material, and appropriate amount of gypsum. The amount of the mixed material was based on the weight percentage. The weight percentage of the active mixed material should not exceed 15%, which was allowed to be substituted with no more than 5% of the kiln or no more than 10% of the inactive mixed material. The weight percentage of the inactive mixed material should not exceed 10%. The used cement numbered 32.5 was the cement produced by Shanshui Cement Plant. The chemical composition and Fundamental properties of the cement are shown in Tables 7 and 8. In addition, in the experiment, a small amount of conventional foaming agent and water reducing agent were also added, whose physicochemical properties were not explained in this paper.

2.3. Experimental method

The ordinary cement, fly ash, and clay were mixed in a certain ratio and the foaming agent was prepared. After the foam was stabilized, the two liquids were mixed and stirred uniformly to obtain a new grouting material. The grouting consolidation was cured for 1 d, 7 d, and 28 d. Meanwhile, the performance tests including the physical and mechanical properties, impermeability, and microscopic analysis were conducted.
Table 5 – Chemical composition of clay (unit%).

<table>
<thead>
<tr>
<th></th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>Fe₂O₃</th>
<th>Impurities</th>
<th>MgO</th>
<th>SiO₂</th>
<th>K₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>35.38</td>
<td>1.96</td>
<td>2.04</td>
<td>8.34</td>
<td>0.34</td>
<td>49.86</td>
<td>2.08</td>
</tr>
</tbody>
</table>

Table 6 – Fundamental properties of clay used.

<table>
<thead>
<tr>
<th>Moisture content (%)</th>
<th>Proportion</th>
<th>Density (g/cm³)</th>
<th>Pore ratio</th>
<th>Plastic limit (%)</th>
<th>Liquid limit (%)</th>
<th>Plastic limit index (%)</th>
<th>Liquid limit index (%)</th>
<th>Undrained shear strength index</th>
<th>Cohesion (KPa)</th>
<th>Internal friction angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>74.1</td>
<td>2.72</td>
<td>1.40</td>
<td>2.07</td>
<td>28.4</td>
<td>55.5</td>
<td>27.1</td>
<td>1.68</td>
<td>17</td>
<td>18</td>
<td></td>
</tr>
</tbody>
</table>

Table 7 – Chemical and mineral composition of cement (unit%).

<table>
<thead>
<tr>
<th></th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>SO₃</th>
<th>MgO</th>
<th>R₂O</th>
<th>other</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>22.56</td>
<td>5.26</td>
<td>2.96</td>
<td>64.73</td>
<td>0.72</td>
<td>1.93</td>
<td>1.01</td>
<td>0.83</td>
</tr>
</tbody>
</table>

Table 8 – Fundamental properties of cement used.

<table>
<thead>
<tr>
<th>Setting times (min)</th>
<th>Compressive strength (MPa)</th>
<th>0.08 mm square hole sieve residue (%)</th>
<th>Autoclave expansion (%)</th>
<th>Ignition loss (%)</th>
<th>Specific gravity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>Final</td>
<td>3d 28d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2h 30 min</td>
<td>4h 35 min</td>
<td>10 32.5</td>
<td>≤4</td>
<td>0.01</td>
<td>2.05</td>
</tr>
</tbody>
</table>

Table 9 – Test material allocation ratio scheme.

<table>
<thead>
<tr>
<th>Group</th>
<th>The serial number</th>
<th>Cement (elastic adjustment) (%)</th>
<th>The clay (%)</th>
<th>The fly ash (%)</th>
<th>Foaming agent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>A</td>
<td>35</td>
<td>45</td>
<td>20</td>
<td>0/1/2</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>35</td>
<td>35</td>
<td>30</td>
<td>0/1/2</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>35</td>
<td>25</td>
<td>40</td>
<td>0/1/2</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>40</td>
<td>40</td>
<td>20</td>
<td>0/1/2</td>
</tr>
<tr>
<td>II</td>
<td>E</td>
<td>40</td>
<td>30</td>
<td>30</td>
<td>0/1/2</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>40</td>
<td>20</td>
<td>40</td>
<td>0/1/2</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>45</td>
<td>35</td>
<td>20</td>
<td>0/1/2</td>
</tr>
<tr>
<td>III</td>
<td>H</td>
<td>45</td>
<td>25</td>
<td>30</td>
<td>0/1/2</td>
</tr>
<tr>
<td></td>
<td>I</td>
<td>45</td>
<td>15</td>
<td>40</td>
<td>0/1/2</td>
</tr>
<tr>
<td></td>
<td>J</td>
<td>35</td>
<td>65</td>
<td>0</td>
<td>0/1/2</td>
</tr>
<tr>
<td>IV</td>
<td>K</td>
<td>40</td>
<td>60</td>
<td>0</td>
<td>0/1/2</td>
</tr>
<tr>
<td></td>
<td>L</td>
<td>45</td>
<td>55</td>
<td>0</td>
<td>0/1/2</td>
</tr>
</tbody>
</table>

3. Experiment procedures

On the basis of satisfying the physicochemical properties of the new grouting materials, the portion of the used solid waste was maximized, while the amount of the used cement was the lowest. Then the optimal proportions of the components for the new grouting material were obtained to satisfy the both the economic and performance requirements. Considering the influencing factors to be studied, a total of 4 large groups and 12 groups of materials were designed, and the components were related to each other to control a single variable. The first 3 groups were used to investigate the influence of contents of fly ash, clay content and foaming agent on the physicochemical properties of the grouting material. The cement content is adjusted proportionally with the addition of foaming agent, which is not reflected in the table, while the last 3 groups were used as control. In the experiment, the water-cement ratio was 1:2. The component ratio of the materials is shown in Table 9 and the experimental process is shown in Fig. 1.

4. Experimental results and analysis

4.1. Compressive strength characteristics of new grouting materials at different ratios

First the required raw materials were weighed and added to the stirrer in proper order. The raw materials were stirred at low speed for 60 s, and then the foam was added. The solution was stirred at high speed for 60 s and then manually stirred for a few times. Then the solution was poured into the prepared test mole with the size of 70 mm × 70 mm × 70 mm. The excess solution was erased and the serial number was marked with a black marker. Then the test block was put into the curing box for the curing periods of 1 d, 7 d, and 28 d. At the end of curing, the strength test was conducted using the Shimadzu AGX-250 electronic universal testing machine.

After the grouting material was injected into the crack of the bottom plate, as the mining depth increases gradually, it was necessary for the crack filling to have high enough density so that the sealed cracks can resist the hydrostatic pressure.
during the pre-inrush and reduce the permeability coefficient of floor crack. This is the first requirement the grouting material needs to meet. On the basis of meeting the applicability of the project, the foaming agent is used to replace part of the cement, and the amounts of clay and fly ash are increased. The results of strength tests under different amounts of clay, fly ash, and foaming agent are shown in Figs. 2, 4, 5 and Table 10.

From Fig. 3, the compressive strength of the consolidation of new material changes with the addition of clay and fly ash. As the contents of clay and fly ash increased, the strength of the grouting consolidation first increased and then decreased. When the amount of cement was constant, the strength of the grouting consolidation did not have obvious changes initially with the increase in the amount of clay. As the amount of fly ash increased, the strength of grouting consolidation gradually increased, which indicated that the internal structure of the low-activity contents, SiO₂ and Al₂O₃, in the fly ash was broken. The activity of fly ash was excited, and SiO₂ and Al₂O₃ in the fly ash after excitation can chemically react with the hydration product of cement, Ca(OH)₂, to form a cementitious

<table>
<thead>
<tr>
<th>number</th>
<th>The compressive strength/MPa</th>
<th>Number</th>
<th>The compressive strength/MPa</th>
<th>Number</th>
<th>The compressive strength /MPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>A-0</td>
<td>10.7</td>
<td>E-0</td>
<td>15.3</td>
<td>I-0</td>
<td>13.7</td>
</tr>
<tr>
<td>A-1</td>
<td>9.9</td>
<td>E-1</td>
<td>17.7</td>
<td>I-1</td>
<td>13.1</td>
</tr>
<tr>
<td>A-2</td>
<td>9.6</td>
<td>E-2</td>
<td>14.7</td>
<td>I-2</td>
<td>12.6</td>
</tr>
<tr>
<td>B-0</td>
<td>12.7</td>
<td>F-0</td>
<td>15.4</td>
<td>J-0</td>
<td>10.5</td>
</tr>
<tr>
<td>B-1</td>
<td>11.7</td>
<td>F-1</td>
<td>13.4</td>
<td>J-1</td>
<td>9.6</td>
</tr>
<tr>
<td>B-2</td>
<td>11.1</td>
<td>F-2</td>
<td>12.5</td>
<td>J-2</td>
<td>9.1</td>
</tr>
<tr>
<td>C-0</td>
<td>11.2</td>
<td>G-0</td>
<td>13.3</td>
<td>K-0</td>
<td>11.6</td>
</tr>
<tr>
<td>C-1</td>
<td>10.7</td>
<td>G-1</td>
<td>11.6</td>
<td>K-1</td>
<td>10.9</td>
</tr>
<tr>
<td>C-2</td>
<td>10.2</td>
<td>G-2</td>
<td>11.1</td>
<td>K-2</td>
<td>10.1</td>
</tr>
<tr>
<td>D-0</td>
<td>12.6</td>
<td>H-0</td>
<td>13.1</td>
<td>L-0</td>
<td>13.5</td>
</tr>
<tr>
<td>D-1</td>
<td>12.1</td>
<td>H-1</td>
<td>11.4</td>
<td>L-1</td>
<td>12.9</td>
</tr>
<tr>
<td>D-2</td>
<td>11.6</td>
<td>H-2</td>
<td>10.8</td>
<td>L-2</td>
<td>11.6</td>
</tr>
</tbody>
</table>

Fig. 1 – The experimental process.
material such as hydrated calcium silicate, hydrated calcium aluminate and hydrated calcium aluminosilicate. The cementitious material can fill the microporous structure in the pore partition of the hardened grout, improve the compactness of the hardened grout, and thereby improve the strength of the cement-clay-based material. When the content of fly ash was 30%, the presence of the fly ash can improve not only the workability of the grouting material but also the strength of the pore partition of the grouting consolidation. When the content of fly ash was higher than 30%, the strength of the grouting consolidation had a decreasing trend.

4.1.1. Stress-strain relationship of grouting consolidation
The strength test results of a set of test pieces with the content of foaming agent of 1% are shown in Figs. 3 and 4. The change of the strength can basically be divided into three stages. The first stage was a fully compaction stage. The surface of the grouting consolidation was relatively uneven, while the internal pores are uniformly distributed. Thus at the initial contact between the surface of the test block and the pad, the stress on the contact surface gradually had a uniform distribution with the increase of loading. The second stage was the elastic deformation stage. At this stage, the test block mainly underwent elastic deformation, that is, the indenter was in close contact with the test block, and the stress-strain curve was positively rising. The slope of the curve was the elastic modulus of the test block. This stage is the main ascending segment of the stress-strain curve. The third stage was the yield stage. After the elastic stage, the large through cracks gradually appeared in the test block, and the axial stress started to decrease after the peak value. At this stage, the material was deformed rapidly, resulting in a decrease in stress. It can be seen from the stress-strain curves of the test blocks that the strength of the three sets of the grouting material was about the same at 11.6 MPa, but the strains corresponding to the peak strength were different, which were 0.8%, 1.0%, and 1.7%, respectively.

![Fig. 2 – Uniaxial compressive strength changes of fly ash content of 28 d at 20%, 30% and 40%.](image)

![Fig. 4 – Stress-strain relationship curve.](image)

![Fig. 3 – Test results of compressive strength of each group.](image)
Therefore, there was a divergence on the mechanical property of the foam grouting materials.

4.1.2. Effect of foaming agent amount on the strength of test block

The stress-strain relationship of the grouting consolidation corresponding to different amounts of the foaming agent is shown in Fig. 5. From Fig. 5, when the content of the foaming agent is 0%, the strength of the grouting consolidation is biggest and the maximum value is about 14.5 MPa. When the content of the foaming agent is 1%, the maximum strength of the grouting consolidation is about 13.6 MPa. When the content of the foaming agent is 2%, the maximum strength of the grouting consolidation is about 12.5 MPa. Therefore, as the amount of foaming agent increased, the strength of the grouting consolidation gradually decreased. When the amount of the foaming agent was 0%, 1%, 2%, respectively, the corresponding deformation increased with the increase of the amount of the foaming agent. This phenomenon was because when the amount of the foaming agent was increased, the pores had more uniform distribution and a larger volume, thus the deformation of the grouting consolidation corresponding to the peak stress was increased.

4.2. Rheological properties of new grouting materials

The rheological properties of the fluid need to be expressed by the shear stress as a function of shear rate [35]. For Newtonian fluid, the viscosity does not change with shear rate. However, the new foam grout is a non-Newtonian fluid whose viscosity changes as the shear rate changes. Thus the viscosity is usually expressed by the apparent viscosity at a point, and the rheological properties need to be analyzed using the rheological curve [36].

Currently, the rheological property of the new grouting materials is mostly analyzed using the Bingham rheological model or the H-B fluid model. The equations for the two fluid models [37] are as follows:

1) Equation of Bingham model

\[ \tau = \tau_0 + \eta_{pl}\gamma \]

where \( \tau \) is the shear stress (Pa), \( \tau_0 \) is the yield stress (Pa), \( \eta_{pl} \) is the plastic viscosity (Pa-s), and \( \gamma \) is the shear rate (s\(^{-1}\)).

2) Equation of Herschel-Bulkley model

\[ \tau = \tau_0 + K\gamma^n \]

where \( \tau \) is the shear stress (Pa), \( \tau_0 \) is the yield stress (Pa), \( K \) is the viscosity coefficient (Pa·sⁿ), and \( n \) is the rheological coefficient. When the rheological coefficient \( n \) is less than 1, the shearing of the grout is getting thinner; when the rheological coefficient is greater than 1, the shearing of the grout is becoming thicker.

The yield stress in the above equation is generated by the friction between the various components in the grout, which is the maximum stress to prevent plastic deformation of the grout. The viscosity of the grout indicates the impedance property of the internal structure to prevent the grout from flowing. The viscosity has a significant impact on the flow loss of the grouting material during the grouting process. In this study, the grouting material with the foaming agent was a pseudoplastic material, thus the viscosity decreased as the gradient of the flow velocity increased. The studies in both China and other countries have shown that foaming fluids are non-Newtonian fluids with initial yield stress and are suitable for the H-B rheological models. Compared with the Newton model, the H-B rheological model has the initial yield stress (i.e., the molecular cohesion of the fluid at rest), which can fully reflect the rheological properties of the fluid.

The rheological properties of the new grouting materials included viscosity, initial yield stress, and rheological index. The rheological properties of the new grouting material were tested using the NXS-IIA rotary viscometer. The experimental results and analysis are as follows.

4.2.1. Effect of concentration of foaming agent on viscosity of new grouting materials

From Fig. 6, as the shear rate increases, the viscosity of the grouting material gradually decreases, which indicates that the grouting material exhibits the pseudoplastic property of non-Newtonian fluid. With the gradual increase of the shear rate of the rotary viscometer, the bubbles in the foam mortar gradually decreased, the internal structure was destroyed, and the internal cementation of the new grouting material decreased. As a result, the viscosity decreased as the shear rate increased. At each concentration, when the shear rate
reached 100s⁻¹, the viscosity tended to be stable, and the internal structure of the grouting consolidation was also stable. Under the same shear rate, the viscosity of the grouting consolidation decreased with the increase of the concentration. When the shear rate was low, the difference in the viscosity was large among different concentrations. When the shear rate reached 100 s⁻¹, the difference in the viscosity among different concentrations became small. Therefore, when the shear rate increased to infinity, the viscosity tended to be the same at different concentrations.

4.2.2. Relationship between viscosity and shear stress of new grouting materials
With the increase of the shear rate, the shear stress of the new grouting material increased, while the viscosity gradually decreased. As the shear rate increased, there was an inverse relationship between the viscosity and the shear stress. When the viscosity was large, the shear stress was small. On the other hand, when the viscosity was small, the shear stress was large. As the shear rate increased, the resistance between the rotary viscometer rotor and the grout become larger, and the internal structure of the grouting consolidation was destroyed. As a result, an increase in shear stress caused a decrease in viscosity.

4.3. Impermeability of grouting consolidation of new grouting material
The impermeability of the material was characterized by two indexes: permeability coefficient and impermeability pressure. The permeability coefficient was measured by the variable head penetration test [38], and the impermeability pressure was measured by mortar impermeability meter. Variable head permeability coefficient is calculated by the following formula:

\[ K_T = 2.3 \frac{aL}{A(t_2 - t_1)} \log \frac{H_1}{H_2} \]

where \( A \) is the cross-section area of the head pipe (cm²), 2.3 is the conversion factor of ln and log, \( L \) is permeability diameter, i.e., the height of the sample (cm), \( t_1, t_2 \) are the start and end time (s) of the head measurement, respectively, and \( H_1, H_2 \) are the start and end of the water head, respectively.

The permeability coefficient of the grouting material was determined using the variable head penetration test method. The test data are shown in Table 11. From Table 11, the permeability coefficient of the grouting consolidation gradually increases with the increase of the foaming agent. Comparing to the pure cement grout, the permeability coefficient of the grouting material is larger initially, but decreases rapidly with the time of development. Finally, both the grouting material and the pure cement grout have similar permeability coefficient, which is in the grade of \( 1 \times 10⁻¹⁰ \text{ m/s} \) and shows good impermeability. The main reason of this phenomenon is that the utilization of the foaming agent causes the initial expansion of the volume of the grouting consolidation, so that there are relatively uniform bubbles inside and the initial porosity is large. However, with the effect of the foaming agent, the hydration product ettringite is continuously formed from the reaction of the foaming agent with the materials including cement, coal ash, and other materials. Then a network structure is formed inside the grouting consolidation due to the interlacing of the interior, which makes the microstructure more compact.

According to the (Standards for Testing Basic Performance of Building Mortars) [39], the impermeability pressure value of the new grouting consolidation for the floor cracks was measured. In the first step, the grouting material was prepared according to the requirements of the standard test piece for impermeability. After being cured, the test piece was cured according to relevant maintenance standards. After a specified curing duration, the test pieces were taken out and the surface of the test piece was wiped. After the surface was completely dry, it was sealed into the SS-1.5 mortar permeation instrument for impermeability pressure test.

The test results showed that the impermeability of the grouting material for the fractured floor tended to decrease with the increase in the content of the foaming agent. Among the tested pieces, when the foaming agent accounted for 1% of the total volume, the impermeability pressure of the grouting consolidation was 0.7 MPa and the impermeability grade reached 6 grade, which indicated that the grouting material had good impermeability.
Fig. 7 – Electron microscope scanning of grouting consolidation body with fly ash content of 20%.

Fig. 8 – Electron microscope scanning of grouting consolidation body with fly ash content of 30%.

Fig. 9 – Electron microscope scanning of grouting consolidation body with fly ash content of 40%.

Fig. 10 – The foaming agent content was 0%.

Fig. 11 – The foaming agent content was 1%.
4.4. Microscopic analysis on grouting consolidation of new grouting material

The APREO scanning electron microscope produced by FEI Company in the United States was used to test the grouting consolidation sample. In the test, the microscopic morphology and development degree of pores of each component were analyzed [40].

Scanning electron microscopy (SEM) was used to analyze the microscopic morphology of the grouting consolidation samples. The microscopic causes of the final strength of the grouting consolidation were obtained and analyzed. A grouting consolidation specimen with the age of 28 days was analyzed in the microscopic scan test. The following three images show the microstructure of the grouting consolidation sample with the fly ash contents of 20%, 30% and 40%.

From Figs. 7, 8 and 9, when the amount of fly ash is continuously increased, the pores inside the grouting consolidation are gradually enlarged, and the arrangement of the bubbles is relatively uniform. After special treatment, it can be seen that when the amount of fly ash was 30%, the internal pores of the grouting consolidation are evenly distributed. The volcanic ash in the fly ash reacted with the calcium hydroxide to form the reaction products such as hydrated calcium silicate, hydrated calcium aluminate, and hydrated calcium sulfoaluminate, which can densely fill the internal pores of the grouting consolidation. Thus both the impermeability and the durability of the grouting consolidation were improved. Based on the comparison of the three sets of images, it is found that the addition of fly ash significantly improves the density of the grouting consolidation, which indicates that the fly ash can be used to fill the pores inside the grouting material.

Figs. 10, 11 and 12 show the microstructure of the grouting consolidation with the contents of the foaming agent of 0%, 1.0%, and 2.0%, respectively. From the figures, as the amount of foaming agent increases, the internal pores of the grouting consolidation are more uniformly distributed and more regular shape. From the pictures, in the grouting consolidation with the foaming agent of 2%, the pores have the largest area and are relatively loose. The apparent density of the grouting consolidation with the foaming agent content of 2.0% was obviously reduced and the strength was also greatly reduced. Therefore, the content of foaming agent of 1.0% was recommended from the application in engineering practice.

In summary, the new grouting material for the reinforcement of the fractured floor in coal mines was developed with the solid waste product, fly ash, from the coal burning at the power plants together the supplementary materials of clay and cement. The physicochemical properties and microstructure of the new grouting material were good and the compressive strength of the grouting consolidation was 17.7 MPa. The optimal ratio for the new grouting material (including 1% foaming agent) was as follows: 40% cement, 30% clay, and 30% fly ash. The grouting material can meet the requirements on the grouting reinforcement strength and the impermeability of the sealed cracks in the floor. In addition, the grouting material should have high applicability and economic benefits. The specific application performance of the new grouting material needs to be further determined after being applied in the field.

5. Conclusions

In this paper, a new type of inorganic grouting material was developed based on the full utilization of solid waste from industrial and mining enterprises. The conventional foaming agent was used to mix the solid waste products, and then the grouting material was tested using the component screening test, the mechanical property test, the rheological property test, the impermeability test, and the microscopic analysis. The following conclusions can be obtained:

1) The new grouting material for reinforcement of the fractured mine floor was obtained using the burning coal solid waste product, fly ash, together with the supplementary materials of clay and cement. The physicochemical properties and microstructure of the grouting material were good, and the compressive strength of the grouting consolidation was suitable. The optimal ratio of the grouting material (containing 1% foaming agent) is as follows: 40% cement, 30% clay, and 30% fly ash. The new grouting material can meet the requirements of grouting reinforcement strength and high impermeability of the sealed cracks in the mine floor.

2) The optimal content of fly ash in the new grouting material is 30%. At this ratio, the potential activity inside the fly ash is excited, and the strength of the grouting consolidation is significantly improved, which not only improves the workability of the grouting material, but also facilitates the strength development of the pore partition in the grouting consolidation.

Fig. 12 – The foaming agent content was 2%.
3) The optimal content of foaming agent in the new grouting material is 1%. At this ratio, the internal pores in the grouting consolidation have a uniform and intensive distribution, which can effectively improve the filling density and late-stage stability of the new grouting material in the cracks of the mine floor.

4) The new grouting material can be simulated using the H-B rheological model. As the flow rate increases, the friction force of the grouting material decreases during transportation, the viscosity gradually decreases, the flow loss decreases, and the grouting cost is reduced.

5) Through the variable water head penetration test, the impermeability of the grouting consolidation was analyzed. Based on the results, the impermeability pressure of the grouting material reached 0.7 MPa and the impermeability reached Level P6, which indicated that the grouting material has a good impermeability.

6) The new inorganic grouting material developed in this paper has been tested in the laboratory. The ratio of different components and the performance parameters of the new grouting material have been obtained. It is necessary to investigate the practical application of the grouting material at the mine site to further determine the performance in the reinforcement of the fractured floor and improve the ratio of different components.

**Conflicts of interest**

The authors declare no conflicts of interest.

**Acknowledgements**

This article is grateful to the National Natural Science Foundation of China (5177040049) and the Natural Science Foundation of Shandong Province for the support of major basic research projects (ZR2018BC0740). Thanks to the xinzhaizhuang Coal Mine of Shandong Energy and Fertilizer Group and Shandong New Dragon Energy Co. Ltd. Supported by the raw materials and geological data provided by qiuji Coal Mine of Lin Mining Group.

**REFERENCES**


