Preparation of Organic-inorganic Mixture Material Based on Cementitious Material Base of the Aluminous Rock by Impregnation

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Abstract. Polymerized cementitious materials were prepared by using Al₂O₃ less than 50% aluminous rocks, then the impregnation method is used. The methyl methacrylate (MMA) monomer with containing the curing agent was immersed into the cementitious polymer material. The polymerization reaction was triggered again. An organic – inorganic mixture material was prepared by in-situ polymerization of MMA in inorganic cementitious materials. The pore structure was characterized by N₂ adsorption-desorption. After immersive curing, the pore volume, specific surface area and the average pore diameter of the aluminosilicate polymer all decreased significantly. The most probable pore size was reduced from about 50 nm to about 20 nm, which proved that the organics were loaded into the nano-pores of the inorganic cementitious polymeric materials, the organic phase and the inorganic phase were compounded at the nanometer scale and finally formed the organic-inorganic composites. The mechanical property tests showed that the organic-inorganic composites have better strength and toughness than the aluminosilicate polymers.

Introduction

In this paper, low-grade aluminous rock of Xiuwen County of Guizhou province in China was used as inorganic phase mineral polymer-gel based feedstock, to combine with organic matter to produce organic-inorganic composites. With the expectation of preparing structural materials with good mechanical properties, the paper aims to promote the utilization of low-grade aluminous rock resources. To prepare aluminous rock polymer-based organic-inorganic composites by impregnation method, the main preparation method is as follows: the porous inorganic mineral polymer material with three-dimensional network structure was prepared from aluminum rock, and then the composite was formed by organic impregnation method and organic compound. Compared with the matrix-reinforced composite material, the interpenetrating polymer network composites can combine with the superior properties of the composites better and improve its comprehensive performance [1~8].

Composition of Low Grade Aluminous Rock

The mineral phase compositions and chemical compositions of low grade aluminous rock were analyzed. The results are as following Table 1 and figure 1. Main mineral composition of the sample are tested, the analysis results of Fig.1 are shown mineral composition by XRD pattern. The mineral composition is clay minerals (Kaolinite), Diaspore and a small amount of Anatase, Boehmite.

The results of Table 2 show that the main Chemical composition of the sample including aluminum, silicon, a small amount of iron and titanium elements.
Table 1. XRD analysis results of aluminous rock (%).

<table>
<thead>
<tr>
<th>Composition</th>
<th>Calcite</th>
<th>Anatase</th>
<th>Boehmite</th>
<th>Diaspore</th>
<th>Kaolinite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, %</td>
<td>0</td>
<td>4</td>
<td>3</td>
<td>40</td>
<td>52</td>
</tr>
</tbody>
</table>

Test done by: Institute of Mining in Guizhou University.

![XRD analysis map of sample](image)

Figure 1. XRD analysis map of sample

Table 2. Constant chemical component analysis of aluminous rock.

<table>
<thead>
<tr>
<th>Composition</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>TiO₂</th>
<th>CaO</th>
<th>MgO</th>
<th>K₂O</th>
<th>Na₂O</th>
<th>MnO₂</th>
<th>P₂O₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>Content, %</td>
<td>25.7</td>
<td>53.27</td>
<td>2.12</td>
<td>1.98</td>
<td>0.13</td>
<td>1.35</td>
<td>1.08</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>0.097</td>
</tr>
</tbody>
</table>

Test done by: The real analysis test center of Aoshi, Guangzhou

**Principle and Experiment**

**Principle**

Organic-inorganic composites were prepared by two phase of organic-inorganic interpenetrating method. The preparation process is mainly divided into two parts. First, the inorganic three-dimensional network structure of the polymer matrix of the aluminite mineral is formed, then the organic matter is filled in the pores of the three-dimensional network of the base material by impregnation[9~10].

**Experiment**

Material of organic-inorganic composites preparation process was the matrix preparation, dehydration, drying, impregnation and curing, the order shown in Fig.2:

![Process of the preparation of material](image)

Figure 2. Process of the preparation of material.

**Matrix Material Preparation**

The matrix material was a cementitious material which was shaped according to a cement paste preparation process. The process flow was shown in Fig.3. In the experiment, NaOH was first added into the water glass to dissolve and the modulus was adjusted to about 1.2. Then, the calcined low-grade aluminous rock powder was mixed with the adjusted water glass, adding appropriate amount of water to make the slurry has a certain degree of mobility to facilitate mixing. To put the slurry into a cement agitator has in a slow and automatic stirring. After the slurry was stirred evenly, it was poured into a 40mm × 40mm × 160mm triple mold, vibrated for 3-5min on a vibrator, cured in a standard curing box until the mold release happened, and finally putting in a certain condition conservation for a while before testing and analysis.
After curing for 7 days, the substrate was further treated and analyzed under the condition of curing temperature 60°C. In order to prevent the matrix from cracking because of water loss, it was necessary to replenish moisture to keep the surface wet.

**Impregnation Process.** Using atmospheric pressure impregnation method, the Benzoyl peroxide (BPO) was mixed at a rate of 0.3% by mass with the Methyl Methacrylate (MMA) of liquid in a ventilated cooker until completely dissolved to prepare an impregnation solution. After dehydration treatment, the base material was immersed in the impregnation solution to stay stationary. In order to get a better impregnated effect and to allow more organic matter to be immersed in the substrate, a method of prolonging the impregnation time was selected. The effects of immersion time on the immersion of organic matter were shown in Fig.4:

![Figure 4. Effect of dip time on mass of organics immerged into the body material.](image)

It was found that the immersion amount of organic matter was nearly saturated during 4 days immersion under normal pressure. The immersion time after 4 days did not significantly promote the immersion of organic matter. Therefore, the impregnation was carried out under normal pressure, and the optimum immersion time was 4 days.

**Curing Process Violent Polymerization.** The organic matter was solidified with a polymerization reaction after heating. In the solidification. In order to prevent the volatilization of the organic matter at the edge of the matrix and the phenomenon of the over-polymerization with organic matter at the time of polymerization reacting process, the curing process was as follows: the impregnated substrate was first irradiated under UV light until the surface organics were cured, then the material was pre-polymerized at 80°C for 2h before quick and intensive chilling to room temperature, and finally the material was allowed to stand at 100°C for 2h to complete the reaction following the polymerization at 50°C for 24h.

**Experiment Results**

The mineral was made into aluminosilicate polymer matrix material after activation and alkali motivating. During dehydration drying, impregnation and curing process, the organic monomer was immersed in the matrix material successfully, at the same time enabled it to in-situ polymerize in
the inorganic matrix, to form a macroscopically homogeneous organic-inorganic composite material.

**Materials Mainly Performance Characterization Analysis**

On macro uniform of organic and inorganic composite aperture and mechanical performance analysis, it is concluded that the material of the main performance characteristics.

**Analysis of Pore Size Distribution of the Material**

Table 3 and Fig. 5 show the pore parameters of the two materials and the pore size distribution respectively. There are some discoveries made by comparing the matrix material's pore structure with the composites'. The pore size of the composites decreased during immersing, crosslinking and curing with the organic materials. Meantime the pore volume decreased with the pore size distribution, which indicates that the immersion of the organic polymer monomer to the nanopores of the matrix material, and generated organic polymer with polymerization reaction, so the two phases were compounded on the microscopic scale.

<table>
<thead>
<tr>
<th>materials</th>
<th>Specific surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Average pore size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix Material</td>
<td>5.4421</td>
<td>0.050157</td>
<td>33.0675</td>
</tr>
<tr>
<td>Composites</td>
<td>0.2199</td>
<td>0.001856</td>
<td>22.8086</td>
</tr>
</tbody>
</table>

Figure 5. Comparison of pore size distribution between two materials.

**The Mechanics Properties of the Composites Characterization**

Table 4 is a comparison of mechanical properties of the two materials, the table has shown that the compressive strength of composites is nearly twice as strong as the matrix material, the flexural strength is 8 times more than the latter, and the mechanical strength is also greatly improved. The ratio of compressive strength to flexural strength was often used to characterize the flexibility of a material, which means the lower the ratio of compressive strength to flexural strength, the better the flexibility of the material. Compared with the matrix material, the ratio of compressive strength to flexural strength of the composites was significantly reduced, and its flexibility was better.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Compressive strength (MPa)</th>
<th>Flexural Strength (MPa)</th>
<th>Compressive- Flexural ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Matrix Material</td>
<td>58.7</td>
<td>3.8</td>
<td>15.44</td>
</tr>
<tr>
<td>Composites</td>
<td>116.1</td>
<td>31.5</td>
<td>3.68</td>
</tr>
</tbody>
</table>
Conclusion

In this paper, the following main conclusions are drawn from the experiments and analyses.

1) The main constituents of the low-grade aluminous rock in Xiwen area of Guizhou Province were aluminum and siliceous, and the mineral compositions were kaolinite and diaspore. The content of kaolinite was 52%.

2) The best preparation method of the material was the step-by-step method. Preparing the inorganic network structure and then introducing the organic substance to generated the organic network structure to form the interpenetrating network structure.

3) In the process of atmospheric pressure impregnation experiments the immersion amount of organic matter increased gradually with the immersion time, when the immersion time reached 4d, the immersion amount of organic was nearly saturated, reaching 15%.

4) The results shown that the compressive strength of the composites increased from 58.7 MPa to 116.1 MPa, and the flexural strength increased from 3.8 MPa to 31.5 MPa, and the mechanical properties of the composites were improved obviously compared with the matrix materials.

5) The composites were characterized by XRD and N2 adsorption and desorption, a comparison with the pore structure of the matrix material indicated that the organic material was loaded into the nanopore of the matrix material. It is presumed that the microstructure of organic-inorganic hybrid network, and the interpenetrating network structure on slightly larger scale may be formed in the composite, so that the mechanical properties of the composites can be improved greatly.

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Author: Zhang Jie, (1955-), born in Fei County of Shandong Province, Professor, engaged in the studies of mineral materials and the application of mineralogy.

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