Study on the Waterproofing Performance of FGD Gypsum Building Products from Inorganic-Organic Composite Additives

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Abstract In this article, poly methyl triethoxy silane was compounded with an inorganic waterproof admixture at a certain ratio to improve the performance of gypsum products; a new type of high-efficiency compound water-proofing additive was also investigated. Furthermore, the waterproof mechanism and the various properties on the hardened gypsum plaster were investigated in detail by XRD and SEM. The results show that the intenerate coefficient of gypsum plaster increased to more than 0.9; the water absorbing rate decreased to less than 10%. Both the bending strength and the compressive strength of gypsum plaster increased by various degrees. The intenerate coefficient reached a maximum value of 0.73 and the strength of the samples showed almost no change when 5% cement alone was added. In this new type of the high-efficiency compound with waterproof additive, the optimal technological parameters for formulas were obtained to be: 5% cement, 18% mineral powder, and 0.8% poly methyl triethoxy silane, to compound gypsum plaster. Meanwhile, the production of high performance gypsum as a building material has become possible.

Key words gypsum, water-proofing additive, intenerate coefficient, waterproof mechanism.

1. Introduction

The FGD gypsum products, which is harmless to the human body and can be recycled for something else, is promoting the development of the international green cementing materials because of the good volume stability.¹² Due to its low strength, poor water-proofing property(interate coefficient: 0.3~0.5) and high water absorption(water absorbing rate: 30% above), generally it cannot meet the needs of architectural construction,³⁵ so the reasonable waterproofing performance of gypsum should be improved by using water-proofing additive.

The traditional building gypsum water-proofing additives (eg.wax emulsion and styrene-acrylic emulsion), which improved the waterproofing performance of gypsum plaster, have negative impact on the strength of plaster.⁶⁻⁷ While the silicone building water-proofing additive have low impact on the strength of it. There is a biggest advantage that the organic silicon monomer molecules formed a layer of silicon resin network by the condensation of hydroxide radicals and attached to the substrate surface by the combination of residual hydroxyls, as a result, the gypsum plaster had hydrophobic effect because of the hydrophobic groups oriented consistently outwards.⁸⁻⁹ The silicone networks do not jam the narrow-pores of building gypsum and result in a better water repellency and a higher breathability.¹⁰ But the interate coefficient of gypsum plaster still cannot reach more than 0.8 when the silicone building water-proofing additive added alone, meaning the results that the gypsum products can't get a wide range of applications in the building construction.

Cement and mineral powder, the excellent waterproof materials, not only can greatly improve the water resistance performance of gypsum product but also can increase the strength of it when a certain proportion of cement and mineral powder added in the gypsum plaster. It would significantly overcome the disadvantage of low strength, worse waterproof performance and poor moisture-

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proof shortcomings when they were compounded with the silicone building waterproofing additive.

2. Materials and Characterization

2.1 Raw materials

The poly methyl triethoxy silane used in this work is the commercial industrial product. P32.5 cement is from Wuhu Conch Cement Plant (in China). The modal composition: C3S 50.23%, C2S 24.58%, C3A 9.32%, C4AF 10.32%, and physical properties: initial setting time 83 min and final setting time 115 min, and compressive strength: 26.6 MPa (3 day), 42.5 MPa (28 day). Mineral powder is from Ma On Shan Mineral Powder Plant (in China). The specific surface area is 0.421 m²/g. Table 1 shows the chemical component of the above two materials. The particle size distribution of mineral powder is shown in Table 2 to observe the effect of the particle size on the properties of gypsum products. Fig. 1 shows the corresponding thermograms (DSC/TG) of FGD gypsum, in which an endothermic peak and weight loss at 137 °C, characteristic of dihydrate gypsum moisture release, can be seen for this material. There is an exothermic process at 482 °C, which might be assigned to the hemihydrate gypsum decomposition. The FGD gypsum content 71.4% dihydrate gypsum and 14.7% semi-hydrated gypsum, which was calculated from the thermograms (DSC/TG). The specific surface area is 0.267 m²/g, and particle size distribution of hemihydrate is shown in Table 3.

2.2 Experimental methods

Contradistinctive methods were employed to analyze the influences of the gypsum water-proofing additive on gypsum strength, intergrate coefficient, water absorbing rate and crystal formation.

2.3 Samples shaping

First, weigh 2 kg FGD gypsum, and add the poly methyl triethoxy silane in different percentage (0, 0.4%, 0.8%, 1.2%, 1.6%) into JSA-195 stirrer with 1.3 L water separately, and stir evenly; then pour the gypsum powder quickly and stir for 2 min; finally pour the plaster into two 4 × 4 × 16 cm triplicate model to shape by vibration. After 1 h, unmold the samples and cure in a standard conservatory for 7 days.

Repeat above-mentioned process, and replace part of FGD gypsum by using a certain amount of cement and mineral powder (cement: 0, 2%, 5%, 10%, 15%; mineral powder: 0, 6%, 12%, 18%, 24%). Compare the performance of these samples, and mix the inorganic admixtures according the best ratio, then add the poly methyl triethoxy silane in different percentage (0, 0.4%, 0.8%, 1.2%, 1.6%) separately, finally repeat above-mentioned process.

All the above-mentioned pastes were prepared in JSA-195 stirrer with the water/solid weight ratio assumed the values, w/s = 0.65.

Table 1. Chemical component of main materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>CaO</th>
<th>MgO</th>
<th>SO₃</th>
<th>R₂O</th>
<th>Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>P32.5 cement</td>
<td>21.71</td>
<td>5.75</td>
<td>3.38</td>
<td>64.98</td>
<td>1.97</td>
<td>0.96</td>
<td>--</td>
<td>0.12</td>
</tr>
<tr>
<td>Mineral powder</td>
<td>38.56</td>
<td>20.36</td>
<td>0.84</td>
<td>34.33</td>
<td>9.56</td>
<td>0.04</td>
<td>0.80</td>
<td>0.40</td>
</tr>
</tbody>
</table>

Table 2. Particle size distribution curve of mineral powder.

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>45</th>
<th>75</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
<td>0.74</td>
<td>3.62</td>
<td>8.42</td>
<td>22.42</td>
<td>39.77</td>
<td>65.47</td>
<td>91.77</td>
<td>98.19</td>
<td>99.67</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table 3. Particle size distribution curve of β-hemihydrate gypsum.

<table>
<thead>
<tr>
<th>Particle size (μm)</th>
<th>0.5</th>
<th>1</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>45</th>
<th>75</th>
<th>100</th>
<th>200</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition (%)</td>
<td>1.71</td>
<td>2.98</td>
<td>4.27</td>
<td>5.98</td>
<td>8.80</td>
<td>19.69</td>
<td>69.37</td>
<td>95.21</td>
<td>99.39</td>
<td>100.00</td>
</tr>
</tbody>
</table>
2.4 Experimental methods

2.4.1 Building gypsum performance testing

Three samples from one triplicate model were used to obtain the bending and compressive strength of dry samples, the rests were used to obtain the bending and compressive strength of waterish samples after soaking for 24 hours according to GB9776-88 in China.

2.4.2 Intenerate coefficient and water absorbing rate testing

The intenerate coefficient was calculated from the ratio of the bending strength of waterish samples and that of dry samples. The qualities of samples were weighted by the electronic scale, and the results of waterish samples were recorded as $G_2$ and the results of dry samples were recorded as $G_1$. The water absorbing rate would be worked out by the calculation mode of $(G_2 - G_1)/G_1 \times 100 \%$.

2.4.3 XRD analysis and SEM examination

The samples were characterised in terms of mineralogical composition by D8-ADVANCE X-ray diffraction. After the curing period the samples were examined by HITACHI S-3000H SEM at \( \times 2000 \) magnification to observe micro-structural details and evaluate the effect of the waterproof additive on the cured plaster.

3. Results and Discussion

3.1 Effects of poly methyl triethoxy silane

Poly methyl triethoxy silane had significant improvement on the waterproofing performance of gypsum as shown in Fig. 2 (curve a). The intenerate coefficient reached 0.71, up to its maximum, when the 0.8% poly methyl triethoxy silane added, and basically no longer increased when further increasing the content of waterproofing additive. The water absorbing rate of gypsum also declined with the increase of waterproofing additive, as shown in Fig. 3, and declined from $33.3\%$ to $31.7\%$, when the 0.8% poly methyl triethoxy silane added. The strength of gypsum appeared a slight downward trend. It was shown in Fig. 4 that the bending strength of the dry samples decreased by nearly $17\%$ and the compressive strength of it decreased by nearly $14\%$ when the 0.8% poly methyl triethoxy silane added.

![Fig. 2. Influence on intenerate coefficient of samples with the different proportion of waterproofing additive (curve a, FGD gypsum without inorganic admixtures; curve b, FGD gypsum with 5% cement and 18% mineral powder).](image)

![Fig. 3. Influence on water absorbing rate of samples with the different proportion of waterproofing additive (curve a, FGD gypsum without inorganic admixtures; curve b, FGD gypsum with 5% cement and 18% mineral powder).](image)

![Fig. 4. Influence on the strength of samples with the different proportion of waterproofing additive.](image)
3.2 Effects of inorganic water-resistant admixtures

Cement and mineral powder, the water-resistant admixtures, not only increased the strength of gypsum products but also improved the water-resistant performance. It was shown in Fig. 5 that the strength of samples changed a little bit when the only 2~5% of cement added; then increased significantly when more than 10% of cement added. The intenerate coefficient (Fig. 6) also increased significantly when the 2~10% of cement added; and reach up to the maximum value of 0.73 when the 5% of cement added. Fig. 7 and 8 showed the effect of the mineral powder on the behavior of FGD gypsum samples. The strength of samples, especially the strength of waterish samples increased significantly, but the intenerate coefficient changed a little bit. Both the cement and the mineral powder almost did little impact on the water absorbing rate of gypsum.

Fig. 9 compared the double mixing test of FGD gypsum samples, which added the cement and mineral powder together (Cement: 2%, 5%, 10%, Mineral powder: 12%, 18%, 24%), and showed a best results that the intenerate coefficient could be increased to more than 0.8 when 2~5% cement and 18% mineral powder added. Fig. 10 showed the effect of cement on the strength of gypsum samples after adding 18% mineral powder. The strength of samples increased gradually with the increase of cement. The bending and compressive strength of dry samples increased by nearly 13% and 14% respectively when 5% cement and 18% mineral powder added. However, the bending and compressive strength of waterish
samples increased by nearly 69% and 167% respectively when the same proportions of materials added.

3.3 Effects of inorganic-organic composite additives

In this test, 5% cement and 18% mineral powder were compounded with the gypsum plaster, then the poly methyl triethoxy silane in different percentage was added into plaster to improve the intermolecular coefficient of gypsum products. As a result, the intermolecular coefficient reached up to the maximum value of 0.92 and the water absorbing rate was also expected to slow sharply, from 35.5% to 9.7%, when 0.8% poly methyl triethoxy silane added, as was shown in Fig. 2(curve b) and Fig. 3(curve b). The poly methyl triethoxy silane had low impact on the strength of samples, as was shown in Fig. 11. The bending and compressive strength of waterish samples increased by nearly 60% and 160% respectively, compared the samples without any additives added.

For the above situations, a new type of the high-efficiency inorganic-organic compound waterproofing additive was invented, and the optimal technological parameters for formulas were obtained to be: 5% cement and 18% mineral powder, plus 0.8% poly methyl triethoxy silane to compound gypsum plaster respectively.

3.4 X-ray diffraction(XRD)

As shown in Fig. 12, the phase compositions of samples that added the high-efficiency inorganic-organic...
compound waterproofing additive were obtained by using X-ray diffraction (XRD). Fig. 12(b) compared the X-ray diffractogram of the blank samples and showed that, besides the expected presence of dihydrate gypsum crystals, other phases such as quartz and CaCO$_3$ were also found, probably as a result of the hydration of cement and the introduction of mineral powder. It can be seen from the diffraction patterns that both of them contain the major phases of dihydrate gypsum, but the diffraction intensity of cave b decreased obviously, compared the two X-ray diffractograms, probably as a result of the structured intact crystallization decreasing and the crystalline of dihydrate gypsum deteriorating.

3.5 SEM examination

The effect of additives on the microscopic structure of gypsum samples was shown in Fig. 13. Fig. 13(a) showed a typical gypsum crystal morphology of acicular or needle-shape crystals with a high degree of interlocking, as expected. Fig. 13(b) showed the crystal morphology of sample with 0.8% poly methyl triethoxy silane added, the crystal morphology changes little, compared with Fig. 13(a). This proved the reason that the strength of sample decreased a little bit or remained intact. The crystal morphology of sample after adding 5% cement changed little, except the expected appearance of the C-S-H gels and the micro-crystal hydrated calcium aluminate produced from the hydration reaction of cement, as was shown in Fig. 13(c). Fig. 13(d) showed the morphology of acicular or needle-shape crystals with a high degree of interlocking increased and a large number of small particles filled into the gaps between dihydrate gypsum crystals, as a result of the addition of 18% mineral powder. This lead to the improvement in the strength and

Fig. 13. SEM examination of samples.
water resistant performance of gypsum products because of its insoluble features. Where it was stated that the needle crystal plates and crystals that could produce effective overlapping points were very important to the high-strength gypsum, especially to the high-flexural strength gypsum.11 As may be seen from the Fig. 13(e), the C-S-H gels and the micro-crystal hydrated calcium aluminate are also produced from the hydration reaction when 5% cement and 18 % mineral powder added. The morphology shown in Fig. 13(f) almost had no change, compared with Fig. 13(e), and this discovery had once again proven that the poly methyl triethoxy silane almost did not affect the strength of samples.

4. Waterproof Mechanism

The waterproof mechanism of this high-efficiency inorganic-organic compound waterproofing additive should be divided into two aspects, as shown in Fig. 14. In one aspect, the organic silicon monomer molecules formed a layer of silicon resin network by the condensation of hydroxide radicals and attached to the substrate surface by the combination of residual hydroxyls, as a result, the gypsum plaster had hydrophobic effect because of the hydrophobic groups oriented consistently outwards.12-14 The silicone networks did not jam the narrow-pores of building gypsum and resulted in a better water repellency and a higher breathability. In another aspect, the active materials in the cement and mineral powder could improve the intenerate coefficient and the strength of gypsum. A large number of small particles of cement and powder mineral jammed the narrow-pores of building gypsum to prevent moisture migrating to the insides of gypsum products. In particular, the C-S-H gels and micro-crystal hydrated calcium aluminate produced from the hydration reaction of cement and mineral powder was filled into the gaps between dihydrate gypsum crystals, as a result, the water resistant performance was greatly enhanced and the strength of gypsum products was obviously improved because of its insoluble features.

5. Conclusions

1) The poly methyl triethoxy silane was a effective water-proof additive and almost did not affect the strength of samples. The intenerate coefficient reached up to the maximum value of 0.71 and the water absorbing rate reduced by 33.3 % to 31.7 % with the optimal dosage of 0.8 %.

2) Cement and mineral powder, the water-resistant admixtures, not only increased the strength of gypsum products but also improved the water resistant performance of them. The intenerate coefficient reached up to the maximum value of 0.73 and the strength of samples almost had no change when the 5 % cement added alone. In contrast, the intenerate coefficient changed a little bit, and the strength of samples, especially the strength of waterish samples increased significantly when a certain amount of mineral powder added.

3) When 2% – 5% cement and 18 % mineral powder added in the gypsum products, the intenerate coefficient could be increased to more than 0.8, meanwhile, the bending and the compressive strength of waterish samples increased to more than 69 % and 167 % respectively.

4) A new type of the high-efficiency compound waterproof additive was invented, and the optimal technological parameters for formulas were obtained to be: 5 % cement and 18 % mineral powder, plus 0.8 % poly methyl triethoxy silane to compound gypsum plaster respectively, meanwhile, the production of high performance gypsum building products(high intenerate coefficient: more than 0.9, low water absorbing rate: less than 10 %, and the high strength, compared the samples without any additives added) had become possible.

Acknowledgments

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References