Mechanism of Degradation of the Properties of Recycled Plaster Mixed Aluminate Cement

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1. Introduction

At present, commercial gypsum is one of the most commonly used materials in ceramic mold [1, 2] and general construction work [3, 4] because of its characteristics of light weight, stable volume, heat insulation, sound insulation, good fire resistance, and humidity adjustment [5]. Lots of waste gypsum is therefore usually produced after use. According to Suárez et al., the amount of waste gypsum produced each year is as high as 80 million tons, of which about 15 million tons are landfilled [6]. It not only takes up a large amount of arable land and pollutes the environment, but also produces hydrogen sulfide gas when it is mixed with organic matter, which is harmful to humans [7, 8]. Therefore, reutilization of waste gypsum is necessary to protect the environment. However, the current use of waste gypsum is mainly in cement as a retarder [9], as a roadbed material [10, 11], and as a ceramic additive [12]; this utilization of waste gypsum is rare.

It is well known that hydration of hemihydrate gypsum can produce dihydrate gypsum, and the dihydrate gypsum can be calcined to form hemihydrate gypsum, which is the basis of gypsum recycling [13]. Thus, gypsum recycling turns into feasible by only calcining the waste gypsum to produce a fresh hemihydrate gypsum. Based on this, recycled plaster can be produced by a reversible transformation of dihydrate gypsum into hemihydrate gypsum in an electric furnace at the temperature of 180°C [14]. Ren [15] presented the water/plaster ratio, hydration, and strength of pure recycled plaster without any impurities, and the initial setting time and final setting time were 29 min and 40 min, respectively. The flexural strength and compressive strength were 1.66 MPa and 2.94 MPa, respectively, and the extended hydration and degraded strength of pure recycled plaster could be found in relative to commercial plaster. Zhu et al. [16] analyzed the degradation mechanisms of pure recycled plaster mechanical performance and attributed it to the increased porosity and larger pore size of recycled plaster.

In addition, some scholars have reported the properties of recycled plaster calcined by the waste of hydrated commercial plaster from construction works. Bardella and Camarini [17] described the physical properties and mechanical properties of recycled plaster. Camarini et al. [18] showed the thermal analysis results of recycled plaster. Pinheiro and Camarini [19] reported the chemical results of recycled plaster in different number of recycles. Geraldo
et al. [20] showed that the main phases of recycled plaster did not change with the recycling process. The results showed that the physical, mechanical, thermal, and chemical properties and phases were similar to those achieved from commercial plaster. Indeed, other materials, such as cement, dolomite, quicklime, are always added to commercial plaster to improve their performances. Most of the setting time, water/plaster ratio and strength of recycled plaster may depend on their existence. Therefore, mastering the properties of recycled plaster mixed with other materials is very important and urgent for its use. Ren, Bardella, Camarini, Pinheiro, and Geraldo did not analyze the effect of other existing materials on the properties of recycled plaster.

Camarini et al. investigated the influence of retarder on the workability, setting time, and strength of recycled plaster [21] and found that the citric acid decreased the water/plaster ratio, prolonged the setting time, and reduced the compressive strength of recycled plaster. Heloísa et al. [22] studied the effect of impurities, like dolomite, on the properties of recycled plaster, and concluded that apparent bulk density and bulk density were both decreased, while the setting time, water content to normal consistency, and compressive strength of recycled plaster were all increased. Li et al. [23, 24] studied the degradation of the properties of recycled plaster mixed ordinary Portland cement and quicklime. They attributed the fast hydration to the quick recycling of AFt and increasing of Ca$^{2+}$ in the saturated solution in regard to the Ca$^{2+}$ and SO$_2^−$ ions, respectively. However, little research has been done on the degradation of the properties and action mechanism of recycled plaster mixed aluminate cement (RAP), which severely hampers the use of waste gypsum.

In this paper, the water/plaster ratio, setting time, and strength of recycled plaster mixed aluminate cement (RAP) have been investigated, and its degradation mechanism is also analyzed by using scanning electron microscope (SEM) and Differential Scanning Calorimeter/Thermogravimetric analysis (DSC/TG). The authors hope that this research will help the disposal of waste gypsum.

2. Materials and Methods

2.1. Materials. The original gypsum (OG) comes from Yuhuan gypsum factory in Yingcheng, Hubei, China. The aluminate cement is produced by Guizhou Xifeng Rendu Building Materials Co., Ltd., CA-50. Their chemical compositions were measured by X-ray fluorescence (XRF). The chemical composition analysis of OG is displayed in Table 1, and its main chemical components are SO$_3$ and CaO. Its main mineralogical composition is dihydrate (CaSO$_4\cdot$2H$_2$O). The specific surface area and chemical composition analysis are displayed in Table 2. The content of CaO and Al$_2$O$_3$ are 34% and 53.85%, respectively, and the main mineralogical composition is CaO$\cdot$Al$_2$O$_3$ and CaO$\cdot$2Al$_2$O$_3$.

2.2. Recycling Process. The recycling process is shown in Figure 1, and it contains the processes of crushing, calcination, and hydration. First, OG was crushed with a jaw crusher, and grounded with a laboratory steel ball mill for 2 minutes. Second, the powdered OG was calcined at the temperature of 180°C for 3 hours in an electric oven. Commercial plaster (CP) was obtained and added into aluminate cement of 10%. Third, the mixture was mixed with water to obtain the hardened commercial plaster-mixed aluminate cement (CAP), and the water to plaster ratio was 0.60. Finally, the hardened CAP was dried till mass stabilization at 45°C, and the recycled plaster-mixed aluminate cement (RAP) and hardened RAP were achieved as the same process above. Specially, the water to plaster ratio of RAP was 0.86 when the same fluidity was reached. When the aluminate cement was not added in the CP, recycled plaster (RP), hardened CP, and hardened RP were obtained following the same steps as before, and the water to plaster ratio of CP and RP were 0.63 and 0.85, respectively. The properties tests were conducted based on the Chinese standard GB 9776-2008 [25]. The test methods for w/p (consistency), setting time, and strength have been described in our previous research [24]. The sample dimensions for mechanical properties determination was 40 mm × 40 mm × 160 mm. And the compressive strength and flexural strength were measured after curing for 14 days. For flexural strength, 3 independent samples were determined and the average value was calculated. While for the compressive strength values, the average of six independent samples were taken.

2.3. Experimental Methods. Partial replacement of commercial plaster by aluminate cement was adopted to investigate degradation law and analyze action mechanism of recycled plaster-mixed aluminate cement, and the dosage of aluminate cement was 10 wt.%. The experiment was carried out by adding aluminate cement to commercial plaster and then crushing after hydration and calcining into recycled plaster mixed aluminate cement.

A program was created during the test to help understand the progress of the processes, which is shown in Figure 2. In brief, the water to plaster ratio of powdered CP, CAP, RP, and RAP were tested first, and then the setting time of CP, CAP, RP, and RAP were measured based on their water to plaster ratios. Afterwards, the flexural strength of

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**Table 1: Chemical composition analysis of original gypsum.**

<table>
<thead>
<tr>
<th>Component</th>
<th>Original gypsum (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SO$_3$</td>
<td>47.57</td>
</tr>
<tr>
<td>CaO</td>
<td>38.73</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1.15</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>0.42</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.13</td>
</tr>
<tr>
<td>K$_2$O</td>
<td>0.07</td>
</tr>
<tr>
<td>SrO</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Table 2: Specific surface area and chemical composition analysis of aluminate cement.**

<table>
<thead>
<tr>
<th>Specific surface area (m$^2$/kg)</th>
<th>Loss CaO Al$_2$O$_3$ SiO$_2$ MgO SO$_3$ Fe$_2$O$_3$ TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CA-50</td>
<td>335.06  34.00  53.85  5.06  0.53  0.06  1.89  2.75</td>
</tr>
</tbody>
</table>
2.4. Materials Characterization. The compositions of hardened CP, hardened CAP, hardened RP, and hardened RAP were determined by simultaneous DSC-TG device (SMP/PF7548/MET/400 W) and X-ray diffraction analysis (XRD), and the DSC-TG was from room temperature up to 600°C, using a heat rate of 10°C/min. The morphological investigations of hardened CP, hardened CAP, hardened RP, and hardened RAP were made by SEM (TESCAN VEGA III LMH).

3. Results and Discussions

3.1. Water/Plaster Ratio and Setting Time of the Powdered CP, CAP, RP, and RAP. Figure 3 shows the water to plaster ratios of the composites. As can be seen, the water to plaster ratio of CAP does not reach the pure CP and is 5% lower than that of CP. This result is expected due to the low water requirement of aluminosilicate cement. This is consistent with the research of Zhao et al. [26]. On the contrary, the water-plaster ratio of RAP and pure RP is 35% and 43% higher with respect to that of CP and CAP, and the water to plaster ratio of RAP exceeds the pure RP.

The setting time of plaster and plaster mixed aluminosilicate cement is presented in Figure 4. As can be seen, the initial setting time of RP is 33 minutes and its final setting time is 13 minutes longer than the initial setting time, a result that agrees with the findings of Ren [15]. However, aluminosilicate cement significantly shortens the setting time of RAP. The initial and final setting time are reduced to 5.5 minutes and 10.5 minutes, respectively, which are 83% and 77% lower than that for the initial setting time and final setting time of RP. This is due to the rapid recycling of ettringite (AFT) (Figure 5). Unlike the recycled products, the initial setting time of CAP is increased from 8.5 minutes to 13.5 minutes in comparison to CP and is 59% longer than that of CP, and the final setting time is raised from 13.5 minutes to 17.5 minutes, which is 30% longer than that of CP. The opposite trend in setting time can be found between RAP and CAP.
3.2. Strength of Hardened CP, Hardened CAP, Hardened RP, and Hardened RAP. Figure 6 presents the strength of hardened CP, hardened CAP, hardened RP, and hardened RAP, from which we can see that hardened RP and hardened RAP exhibit low strength, while hardened CP and hardened CAP display steadily high strength. The addition of aluminate cement increases the flexural strength (FS) of the hardened CAP from 5.29 MPa to 5.89 MPa, and the compressive strength (CS) increases from 10.08 MPa to 13.54 MPa. The rate of increase in strength can be seen in Figure 7(a). In contrast, the flexural strength and compressive strength of the hardened RAP are reduced from 2.70 MPa to 2.40 MPa and from 4.80 MPa to 4.59 MPa, respectively. The rate of increase in strength can be seen in Figure 7(a). In contrast, the flexural strength and compressive strength of the hardened RAP are reduced from 2.70 MPa to 2.40 MPa and from 4.80 MPa to 4.59 MPa, respectively. The strength reduction rate of hardened RP is about 50% with respect to the pure hardened CP, the number rises swiftly in the presence of aluminate cement (Figure 8), as the strength decrease rate of hardened RAP is as high as 65%. Therefore, it can be concluded that the opposite strength development trend can be seen between hardened RP, hardened RAP and hardened CP, hardened CAP. Moreover, the rate of strength reduction of hardened RAP is much higher than that of hardened RP without aluminate cement.

3.3. SEM Images. Figure 9 shows that aluminate cement significantly changes the microstructure of hardened plaster. The hardened CP has a needle-like crystal structure. After the addition of aluminate cement, the crystals of the hardened CAP have changed, and a large number of gelatinous crystals have appeared. The hydrated products of
Figure 6: Results of strength.

Figure 7: The strength changing rate of commercial plaster and recycled plaster aluminate cement mixes. (a) The increasing rate of CAP. (b) The decreasing rate of RAP.

Figure 8: The strength decreasing rate of recycled plaster before and after adding aluminate cement.
Aluminate cement, AFt, and AH3, are dispersed in the crystals, reducing the voids of the hardened CAP and enhancing its stability. Therefore, the strength of the hardened CAP is improved.

The SEM images of hardened RP and RAP are exhibited in Figure 10. It is evident that the morphology and habits of the crystals have changed. The crystals of the hardened RP are obviously coarsened and arranged into parallel beams; but it is still interconnected with each other. As for the hardened RAP, the crystals contain not only cluster crystals similar to those of hardened RP, but also a large number of fine crystals, which are dispersed and not filled into the plaster voids, thereby weakening their overlapping. Furthermore, the presence of AH3 of noncementing reduces the strength of hardened RAP as well. Thus, the strength of the hardened RAP is decreased.

3.4. DSC/TG. Figure 11 shows the DSC/TG curves for hardened CP and hardened CAP. Figure 11(a) obviously reveals that endotherms at 139°C and 152°C occur as a result of the dehydration of dihydrate gypsum to hemihydrate gypsum and hemihydrate gypsum to anhydrite III, and the endotherms near 340°C and 450°C are due to the transformation of anhydrite III to anhydrite II and lattice rearrangement, illustrating the existence of dihydrate gypsum, which agrees well with Tong [27] and Zhao et al. [28]. And it is also confirmed by XRD (Figure 11(c)). However, other peaks are emerged in the hardened CAP (Figure 11(b)) as well. For example, the occurrence of an endothermic peak at 80°C is due to the decomposition of AFt into monosulfate (AFm). The small endothermic peak at 248°C is caused by the endothermic peak of AH3, which is consistent with Zhao et al. [26]. Moreover, the endotherms at 139°C and 152°C are reduced relative to the hardened CP. The above indicates that AFt and AH3 are present and the quantity of gypsum is low in the hardened CAP. It is fully described that the strength of the hardened CAP is obtained through the hydration products of AFt and AH3, which agrees with the previous finding [26].

In Figure 5(a), there are two consecutive endothermic peaks near 136°C and 145°C due to the dehydration of dihydrate gypsum to hemihydrate gypsum and hemihydrate gypsum to anhydrite III, and the endotherms around 330°C and 440°C are due to the transformation of anhydrite III to anhydrite II and lattice rearrangement, which is similar to the endothermic peaks of hardened CP, consistent with Tong [27] and Zhao et al. [28], and the endotherm near 330°C is
also confirmed by Geraldo et al. [20]. To our surprise, the DSC/TG curves of the hardened RAP have changed significantly, and the endothermic peaks of the hardened RAP at 136°C and 145°C are reduced due to the addition of aluminate cement (Figure 5(b)). This is owing to the low quantity of gypsum and presence of undecomposed AH₃ and recycled AFt, which is identical to Li et al. [23]. It manifests that the hydration products of aluminate cement are resided in the hardened CAP and hardened RAP, but the roles of AH₃ played in the hardened CAP and hardened RAP are different, and their formation process are not exactly the same. As a result, it can be concluded that the compressive and flexural strengths of hardened RAP are decreased by the presence of noncemented AH₃ and low-strength recycled AFt, while a high-strength hardened CAP is obtained by its hydration products of AFt and AH₃.

4. Conclusions

In this paper, properties and degradation mechanism of recycled plaster mixed aluminate cement are studied. Obviously, the setting time of RAP is shortened by the rapid recycling of AFt, while the hydration of CAP becomes slow for the low hydration rate of aluminate cement. Surprisingly, the strength of RAP is reduced, which is not aligned with the routine situation of aluminate cement for increasing the strength of commercial plaster. The decreased strength of RAP is caused by the noncemented AH₃ and low-strength recycled AFt and the fine crystals of the hardened RAP, which was confirmed by SEM and DSC/TG analysis. In principle, this research on recycled plaster mixed aluminate cement will lay a theoretical foundation for the use of recycled plaster.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

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Figure 11: DSC/TG curves of hardened CP (a) and hardened CAP (b) and XRD patterns of hardened CP (c).
References


