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Influence of Neutralization on Hydration of Hemihydrate Phosphogypsum Plaster

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Abstract. Effect of lime on hydration of hemihydrate phosphogypsum (HPG) plaster were investigated aiming at neutralizing HPG since it was obtained by calcining phosphogypsum without any purification. Results showed that neutralization would lead to retardation and strength degradation, particularly with small amounts of lime (0.1%-0.4%). As a result, the role of lime in HPG plaster can be described as 1) reacting with impurities in HPG and the reactant would affect the dissolution of HPG, gypsum nucleation and growth; 2) increasing ion concentration and supersaturation by excessive lime which can promote the hydration again. The gypsum crystal changed from needle-like to tiny crystal with little interlocking and then long prismatic crystal with comparable strength due to the mechanism of lime. Therefore, sufficient lime is needed for neutralization which is economic and beneficial for the application of HPG.

1. Introduction

Over 70 million tons of industrial wastes are produced annually in China from the phosphoric acid process for manufacturing fertilizers. Out of this, over 40 million tons of phosphogypsum (PG) is stacking directly without any treatment. At present, the surface stockpile of PG in China is estimated to be above 300 million tons [1-5]. PG contains impurities such as water-soluble phosphate (P_2O_5), water-soluble fluoride (F), insoluble P_2O_5 substituted in the gypsum crystal lattice, residual acid and organic matters which cause environmental concern [6-8]. The commercial importance of gypsum is due to its ability to form hemihydrate plaster, thus hemihydrate PG (HPG) is obtained by thermal dehydration from PG directly which complies with the requirements in Chinese standard calcined gypsum (GB/T 9776-2008) including radioactivity. HPG is generally used in preparation of gypsum block and plaster board [9]. Due to the fact that the cleanup PG often lead to increasing costs of production, the commercial HPG in China are still acidic, set fast and contain impurities which deteriorate the performance of HPG and thus restrict its further use in building materials.

In order to broaden the application scope of HPG and improve its performance, neutralization is necessary. As reported, lime water washing is a good way to reduce, eliminate and remove impurities from PG [10]. Meanwhile, lime is a common traditional material which is also one of the hydration products of cement. How about adding lime to HPG plaster directly? Would it affect the properties of HPG plaster? The influence of lime is helpful to guide the development of HPG based composite cement. Investigations were, therefore, undertaken regarding the hydration process of HPG plaster after neutralization. It was interesting to find that a small amount of lime has adverse effect on the hydration of HPG plaster while beyond a certain lime content, HPG plaster can set and harden well.



2. Experimental Methods

2.1. Materials and Mix Proportions

HPG was from longmang Co., Ltd., in Deyang Sichuan province China and it was obtained by thermal dehydration from PG after three time's water washing. Retarder (Retardan-200P) was added to acquire a desired operation time at the rate of 0.06% by mass of HPG powder and the water to powder was 0.64 which was the water requirement of HPG for normal consistency. Lime powder ($\text{Ca}(\text{OH})_2$) was also added by mass percent and the ratio of materials HPG:retarder:water:lime was 100:0.06:64:x (varies from 0.1 to 4.4).

2.2. Setting Time and Compressive Strength

The setting time of HPG plaster were examined by Vicat apparatus specified in GB/T 17669.4-1999. Prismatic specimens of size $40 \times 40 \times 160 \text{ mm}^3$ were prepared according to above mix proportion and cured at $20.0 \pm 1^\circ\text{C}$, $60 \pm 5\%$ relative humidity. After curing for seven days, specimens were dried at 40°C until the weight was constant and then compressive strength was tested by reference to GB/T 17669.3-1999 in China.

2.3. pH and Hydration Degree Testing

The powder with above mix proportion (before hydration) or by grinding hydrated samples at 7 days after drying at 40°C (after hydration) were mixed with water (the ratio is 1:10). After stirring for 5 min and waiting for 25 min, upper supernatant were used for pH testing by a Digital pH Meter Model PHS-25 (Leici, Shanghai). The hydration degree was calculated through chemically combined water which was tested according to Chinese standard GB/T 5484-2012.

2.4. Hydration Heat and SEM Analysis

An eight channel TAM Air Isothermal Calorimeter was used to analyze the hydrate heat of HPG plaster by the direct method in accordance with GB/T 12959-2008. The fragments from samples after compressive strength were analyzed by SEM.

3. Results and Discussion

3.1. Setting Time and Compressive Strength

HPG is acidic arousing concern in application which would corrode the equipment and get mildewed. Addition of lime to neutralization comes to our mind firstly with respect to solve this problem. Since natural gypsum is neutral and being alkaline is beneficial to make the best use of admixture, a small amount of lime (0.1 to 0.4 by wt.% of gypsum plaster) were added to adjust the pH of HPG plaster in alkaline range (pH 7.19-11.08). As shown in Figure 1, it was clearly that once the lime was added, the setting time increased from 72 min to above 1000 min while the strength dropped from 10 MPa to 3 MPa. However, with the further increase of lime regardless of pH, the setting time of HPG plaster decreased greatly and presented little variation when the contents of lime were 2.4%-4.4%. In addition, the strength of HPG plaster increased with enhancement in lime content indicating that the role of lime in HPG plaster was not just neutralization. Through the pH before and after hydration in Figure 2(b), it was clear that lime had reacted with impurities and thus affected the hydration of hemihydrate to gypsum resulting in abnormal setting and hardening of HPG plaster while the excessive lime had eliminated the influence of reactants contributing to the decrease in setting time and increase in strength.

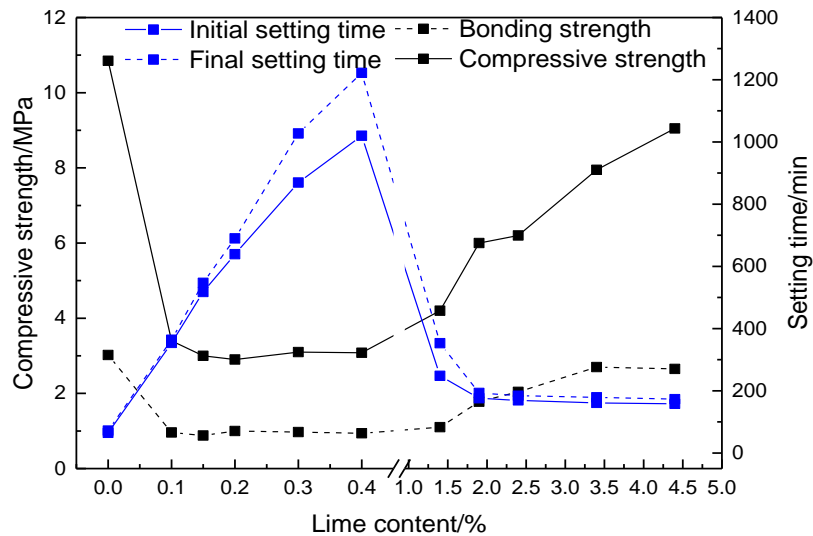


Figure 1. The setting time and strength of HPG plaster with different lime content.

3.2. Hydration Kinetics Analysis

The influences of the lime content on the hydration heat evolution rate, hydration degree and pH before and after hydration of HPG plaster were presented in Figure 2a and b. Figure 2a shown that a sharp and transient exothermic peak was formed probably owe to the fast dissolution of HPG after contacting with water. Then the heat emission rate decreased dramatically. The plaster was in a dihydrate gypsum nucleation and the supersaturation process of Ca^{2+} and SO_4^{2-} . The induction period was prolonged greatly with the increased dosage of lime within 0.4% and subsequently, shortened with further increase in lime content. Accordingly, the maximum heat evolution rate and the hydration degree were decreased at first and then increased with enhancement in lime content which was good in line with the results in Figure 1. It can be deduced that the reactants from lime and impurities have effect on the the dissolution of HPG and gypsum nucleation as well as the growth of gypsum, therefore the induction period got longer and the hydration heat evolution rate peaks came smaller while the excessive lime increased the ion concentration and supersaturation which promoted the hydration again. In addition, the pH after hydration of HPG plaster within 0.4% lime only increased a little confirming the reaction of lime and impurities. The hydration degree of HPG plaster whose lime content was beyond 2.4% was equal to that of reference, but its setting time was a little longer and strength was a bit lower. That was why the peaks of heat evolution rate were on the right side of the reference indicating the retardation of reactant. Besides, their peaks width were much longer proving that the hydration was gently promoted by crystal nucleus and higher ion concentration from excessive lime. Furthermore, the intensive heat evolution was avoided which would reduce the risk of temperature deformation and was better for the application of HPG plaster.

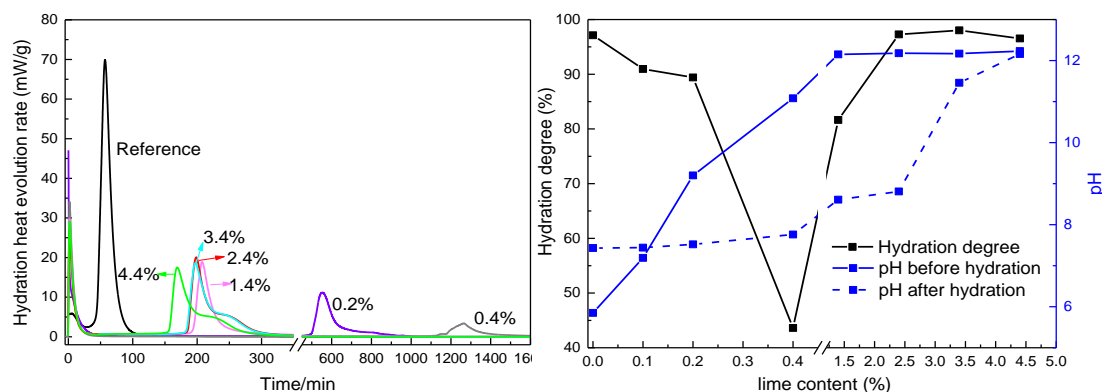


Figure 2. Effect of lime content on (a) heat flow; (b) hydration degree and pH.

3.3. SEM Analysis

The strength of gypsum is closely related with the crystal interlocking except of the influence of hydration degree. As shown in Figure 3(a), the gypsum crystal in reference was mainly needle-like which interlaced with each other tightly contributing to a dense microstructure and higher strength in return. According to the function of lime, the amount of crystal nucleus were reduced after adding lime and gypsum crystal grew slowly, thus bulky and granular gypsum crystal were observed in Figure 3(b) which were well crystallized but there is no interlocking between each other. This is why its strength was not higher than samples in Figure 3(c) in spite of its hydration degree were much higher. Fluffy and floccus substances were filled in Figure 3(c) which were composed of incompletely dissolved hemihydrate and crystallized dihydrate gypsum, since the formation of crystal nucleus and growth of gypsum crystal were strongly inhibited. Compared with Figure 3(c), gypsum crystal in Figure 3(d) grew continuously and interlaced with each other to some extent, but a few undissolved hemihydrate were still visible. Meanwhile, there was no big difference in gypsum appearance in Figure 3(e) and (f) but undissolved hemihydrate disappeared highlighting that the further increase in lime content can really promote gypsum dissolution. However, it would not have influence on hydration degree and gypsum morphology when beyond a certain content. In fact, the higher lime content would lead to higher water requirement. Therefore, the optimal addition of lime for neutralization was in the ranges of 3%-4%. Comparing with the reference sample, the gypsum crystal after adding enough lime in Figure 3(e) and (f) were thick and prismatic resulting in decrease of interlocking and increase of porosity. This was the main reason responsible for lower strength of samples after adding enough lime.

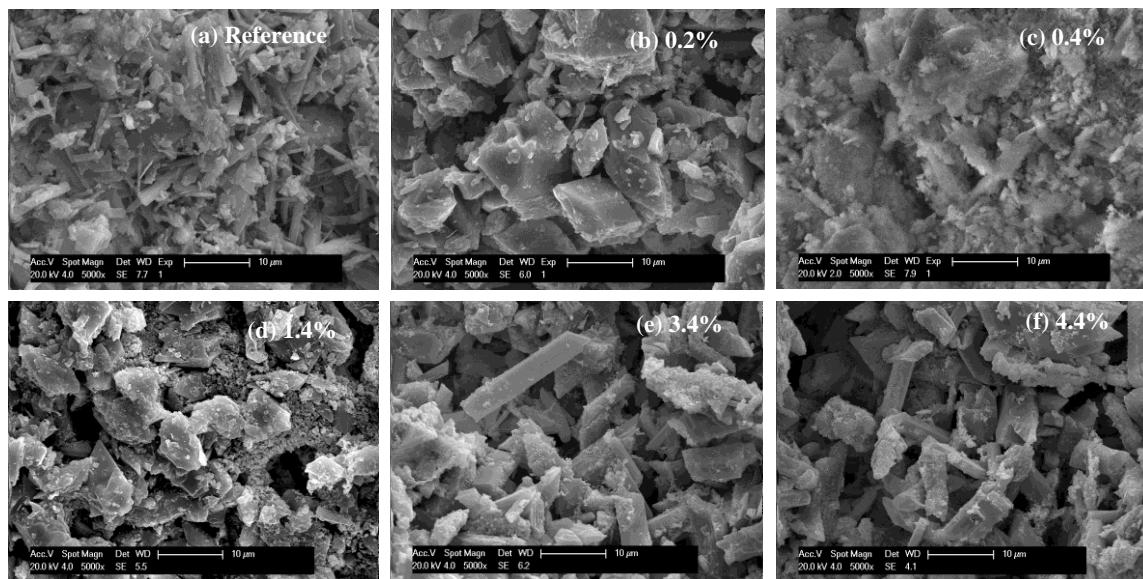


Figure 3. SEM images of HPG plaster with different lime content.

Based on above results, it can be concluded that the impurities in PG would consume a small amount of lime and the reactants would inhibit the dissolution of hemihydrate and growth of gypsum crystal inducing retardation and strength degradation. The hydration can be promoted due to the increase in calcium concentration and supersaturation after further increasing lime content. However, retardation cannot be avoided after neutralization even with high content of lime, thus the amount of crystal nucleus reduced leading to the thick crystal and a little lower strength when compared with the reference samples.

4. Conclusions

Minor amounts of lime (0.1%-0.4%) can change the pH of HPG plaster from 5.85 to 11.08, but it has deleterious effect on hydration leading to abnormal setting and strength degradation. Interestingly, further increase in lime content would promote the rehydration and the development of strength. Therefore, addition of enough lime (3%-5%) is needed to neutralize HPG plaster instead of controlling the pH.

5. Acknowledgments

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