



Materials and Product Engineering

Enhancing the hydration reactivity of hemi-hydrate phosphogypsum through a morphology-controlled preparation technology☆

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ARTICLE INFO

Article history:

Received 2 December 2015

Received in revised form 25 February 2016

Accepted 3 March 2016

Available online 13 April 2016

Keywords:

Hydration reactivity

Morphology-controlled

Water channel

Hemi-hydrated phosphogypsum

ABSTRACT

The distribution of water channels in the crystal morphology of type- α hemi-hydrated gypsum (α -HH) was theoretically detected to investigate the effect of water channels on the hydration reactivity of hemi-hydrate phosphogypsum (HPG). Results showed that water channels were mainly distributed in the cylinders of α -HH crystal, whereas no water channel existed in the conical surfaces parallel to the z -axis. Increasing the number of water channels was critical to enhance the hydration activity of HPG compared with the hydration reactivity of industrial HPG and type- α high-strength gypsum. Controlling the technological parameters of crystallization by concentration of liquid-phase SO_4^{2-} made it possible to obtain HPG which had the stumpy crystals of α -HH and high hydration reactivity.

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1. Introduction

Wet-process phosphoric acid is an intermediate for producing phosphorus-containing fertilizers. When producing 1 ton of ortho-phosphoric acid in wet-process phosphoric acid, approximately 5 tons of by-products are formed, including $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$, and CaSO_4 phosphogypsum [1]. With the rapid development of the phosphate fertilizer industry, the output of phosphogypsum has exhibited a trend toward rapid growth. Over 22 million tons of phosphogypsum are produced annually across China. In 2010, the total generated phosphogypsum in China reached over 100 million tons [2]. At present, only 15% of worldwide phosphogypsum production has been used to manufacture building materials, agricultural fertilizers, soil stabilization amendments, Portland cement retarder, and sulfate acid [3–8]. Most phosphogypsum piled up and occupied considerable land resources, which eventually led to serious environmental contamination.

Hemi-hydrate phosphogypsum (HPG) is obtained during the hemi-hydrate process of wet-process phosphoric acid [9,10]. The main mineral composition of HPG is type- α hemi-hydrated gypsum (α -HH) that corresponds to the gypsum binding material. Thus, HPG can be used to produce building materials and gypsum products. However, the low hydration reactivity of HPG leads to poor gelling strength, which causes production enterprises to discard HPG. Consequently, the surrounding environment is polluted by this substance [11]. Therefore, a research that aimed to

enhance the hydration reactivity of HPG could provide considerable practical values to realize resource utilization of HPG. The hydration reaction of HPG is characterized by a phase transition from α -HH to dihydrate gypsum. The description of water channel occupation and space group in the crystal structure of α -HH has been reported in the literature [12,13]. According to several studies, α -HH has a honeycomb-shaped channel structure. These honeycomb-shaped channels are partly occupied by $x \text{H}_2\text{O}$ ($0 < x < 0.8$) [14,15]; hence, channels with a diameter of approximately 0.03 (i.e., water channels) are formed in the honeycomb-shaped channels, through which water molecules from the outside can enter α -HH crystal inside and then hydrate into dihydrate gypsum. In this manner, α -HH can completely hydrate within a short period [16].

Many influencing factors, such as specific surface area and residual phosphorus acid content, play a role in the hydration reactivity of HPG. According to dissolution–crystallization theory, the hydration reactivity of HPG simultaneously increases with specific surface area and decreases with residual phosphorus acid content [17]. However, in the hemi-hydrate process of wet-process phosphoric acid, the crystal size of HPG should be generally big, and residual phosphorus acid content should be reduced to improve the filtration strength and recovery rate of phosphoric acid [18,19]. Accordingly, a critical method that enhanced the hydration reactivity of HPG by increasing the number of water channels without considering the increase in its specific surface area was proposed. The distribution of water channels was eventually reflected on the crystal morphology; hence, a study on the crystal morphology of α -HH was meaningful to test its influence on hydration reactivity.

In the present study, we theoretically analyzed the distribution of water channels in the crystal morphology of α -HH, compared the

☆ Supported by the Guizhou Province Fund Project (2014)7618.

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difference in hydration reactivity between industrial HPG and type- α high-strength gypsum, and prepared different crystal morphologies of HPG in the experiment. Through the contrast between the crystal morphology and hydration apparent activation energy of HPG, we could investigate the role of water channels in hydration and provide a theoretical basis for the type of HPG morphology that should be controlled in the hemi-hydrate process of wet-process phosphoric acid to enhance hydration reactivity.

2. Experimental

2.1. Materials

Industrial HPG was obtained from a phosphoric acid plant in Guizhou Province. The chemical composition (calculated for the dry product) was (wt%): CaO 34.16, SO₃ 49.81, Fe₂O₃ 0.05, Al₂O₃ 0.35, MgO 0.59, SiO₂ 4.75, total F 0.70, water-soluble F 0.25, total P₂O₅ 1.18, water-soluble P₂O₅ 0.40, and crystal water 7.75. The specific surface area determined using the Blaine method was 330 m²·kg⁻¹.

Type- α high-strength gypsum was obtained from Hubei Province. The chemical composition (calculated for the dry product) was (wt%): CaO 37.12, SO₃ 51.34, SiO₂ 1.75, MgO 1.09, and crystal water 6.51. The specific surface area determined using the Blaine method was 342 m²·kg⁻¹.

Apatite powders were collected from a phosphoric acid plant in Guizhou Province. The chemical composition (calculated for the dry product) was (wt%): SiO₂ 6.29, Fe₂O₃ 0.31, Al₂O₃ 0.23, CaO 49.63, MgO 1.04, SO₃ 0.67, P₂O₅ 35.05, F 2.57, and acid non-soluble substance 6.05. The specific surface area determined using the Blaine method was 151 m²·kg⁻¹.

Phosphoric acid (wt% P₂O₅ 85) and sulfuric acid (wt% H₂SO₄ 98) were of reagent grade and purchased from Sinopharm Chemical Reagent Co., Ltd.

2.2. Experiment methods

2.2.1. Theoretical calculation of α -HH growth morphology and the distribution of water channels

A single-crystal structure of α -HH was obtained from the American Mineralogist Crystal Structural Database. The molecular mimicry software *Material Studio* [20] was used to build a unit cell structure of α -HH. The attachment energy (AE) method regards the growth rate of crystal surface increases with the attachment energy of crystal surface increase in the crystal growth process; thus, the theoretical growth morphology of the crystal can be calculated [21]. Therefore, we selected the AE morphology module of the molecular mimicry software *Material Studio* to forecast the growth morphology of α -HH crystal. Different force fields such as COMPASS, pcff, and cvff were set as initial force fields of single-crystal structure of α -HH.

To investigate the distribution of water channels in various crystal planes, 3D modeling extended the single-crystal cell structure of α -HH to obtain the super cell structure based on its symmetry ($2\bar{a} \times 2\bar{b} \times 2\bar{c}$), which was then carved to obtain the planes with slices measuring 2.0 nm thick.

2.2.2. Measuring hydration reactivity

Hydration reactivity was characterized by the hydration rate of the hemi-hydrate gypsum. In order to eliminate the effect of water-soluble impurities such as phosphorus and fluorine of industrial HPG on the hydration reactivity, hot water at 90 °C was used to wash the industrial HPG until the solution was tested to be neutral. The residues were then dried and set as industrial HPG samples.

The samples were mixed with double pure water (calculated by mass ratio) and placed into a 250 ml Erlenmeyer flask. Thermostatic water bath oscillator was used to maintain the reaction temperature at 20 °C.

Stirring speed was 100 r·min⁻¹. At a designated time, the samples were removed and filtered; the residues were placed into the vacuum drying oven (temperature 60 °C, vacuity 60 kPa) to keep them dry after they were washed with absolute ethyl alcohol. When the mass of the residues became constant, the preparation of the hydration samples was finished. The hydration rate was calculated using Eq. (1):

$$a = \frac{(w_2 - w_1) \times 100 \times M_{\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}}}{1.5M_{\text{H}_2\text{O}} \times \varepsilon} \times 100\%, \quad (1)$$

where α refers to the hydration rate, w_1 and w_2 represent the crystal water content of the samples before and after hydration, respectively (calculation method refers to GB/T 5484-2000), $M_{\text{H}_2\text{O}}$ refers to the molecular weight of H₂O, $M_{\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}}$ refers to the molecular weight of hemi-hydrate calcium sulfate, and ε indicates the hemi-hydrate gypsum content of industrial HPG or type- α high-strength gypsum samples (calculated in the manner of building gypsum phase distribution GB/T 9776-2008).

2.2.3. Preparing HPG

The following solutions were prepared: Solution (a): 36 wt% P₂O₅ and Solution (b): 98 wt% H₂SO₄. Then, 2055 g of Solution (a), 315 g of apatite powders, and 288 g of Solution (b) were obtained.

A small amount of Solution (b) (calculated by the concentration of liquid-phase SO₄²⁻) was poured into Solution (a). The mixed solution with different concentrations of liquid phase SO₄²⁻ was then placed in a cylindrical reactor (40 cm high, 25 cm inside diameter) and heated to 95 °C using a thermostatically controlled oil bath. Apatite powders were then slowly and evenly added into the cylindrical reactor within 30 min and stirred at a speed of 135 r·min⁻¹. The remaining Solution (b) was poured into the cylindrical reactor using a separating funnel at a dropping speed of 4.5 g·min⁻¹. After 150 min of allowing crystals to grow, the slurry was filtered to obtain the filtrate, which was the finishing phosphoric acid. The residues were repeatedly washed with 90 °C water until the washing solution was tested to be neutral. The residues were then dried in a 60 °C $\pm$ 1 °C oven until their weight was constant. HPG was produced.

2.2.4. Calculating hydration apparent activation energy

Experiment method (Section 2.2.2) was adopted to test the hydration rate of HPG under different temperatures: 20, 30, and 40 °C. The least square method of the Avrami crystallization kinetic equation was used to launch a fitting toward the relation curve between the hydration rate of HPG and the change in hydration time. The Avrami crystallization kinetic equation is shown in Eq. (2):

$$1 - \alpha = \exp(-Zt^n), \quad (2)$$

where t refers to the hydration time, Z refers to the composite crystallization rate constant, α refers to the hydration rate that corresponds to the hydration time, and n refers to the Avrami parameter.

Eq. (2) was transformed into a linear equation, i.e., Eq. (3):

$$\ln[-\ln(1 - \alpha)] = \ln Z + n \ln t, \quad (3)$$

Plotting of $\ln[-\ln(1 - \alpha)]$ against $\ln t$ gives a straight line with slope n and intercept $\ln Z$.

The calculation of the hydration apparent activation energy of HPG was based on the Arrhenius equation, as shown in Eq. (4):

$$\ln Z = \ln A - E_a/RT, \quad (4)$$

where A refers to the pre-exponential factor, E_a refers to the hydration apparent activation energy, R refers to the constant 8.314 J·mol⁻¹·K⁻¹, and T refers to the thermodynamic temperature.

Consequently plotting of $\ln Z$ against $-1/T$ gives a straight line with slope E_a/R and intercept $\ln A$. We could determine E_a , which is the hydration apparent activation energy of HPG.

2.2.5. Characterization

The morphology and particle size of the samples were observed using a scanning electron microscope (SEM, Σ IGMA) and the image analysis software SmartTiff. The crystal structure of the samples was analyzed via X-ray diffraction (XRD, XPert Powder), and the scanning range 2θ was from 10° to 90° .

3. Results and Discussion

3.1. Correlation between α -HH morphology and water channels

XRD patterns of single-crystal structure of α -HH (0019827 [13]), industrial HPG and type- α high-strength gypsum are shown in Fig. 1. It can be seen that the XRD pattern of the single-crystal structure of α -HH matches those of type- α high-strength gypsum and industrial HPG. It indicates that the selected single-crystal model of α -HH is appropriate. The cell parameters of α -HH are as follows: space group I2, $a = 1.20275$ nm, $b = 0.69312$ nm, $c = 1.26919$ nm, $\beta = 90.18^\circ$ and $Z = 12$.

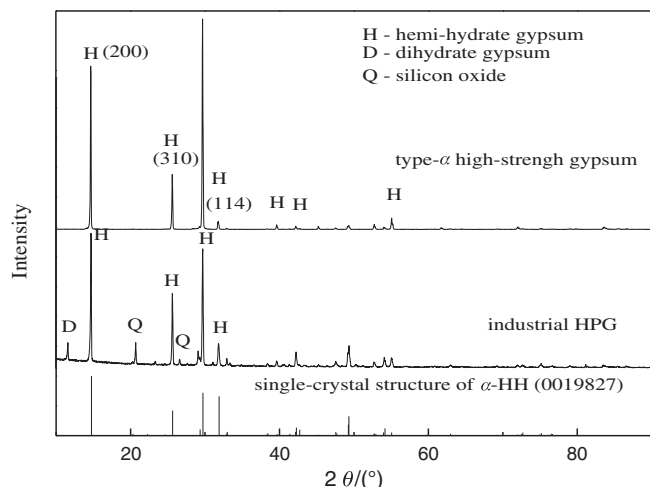


Fig. 1. XRD patterns of single-crystal structure of α -HH, industrial HPG and type- α high-strength gypsum.

The unit cell structure of α -HH is shown in Fig. 2. 12 SO_4^{2-} , 12 Ca^{2+} , and $6 \text{ H}_2\text{O}$ molecules are found in the single-crystal cell. A long chain is constructed by the tetrahedron of SO_4^{2-} and Ca^{2+} along the z -axis. A

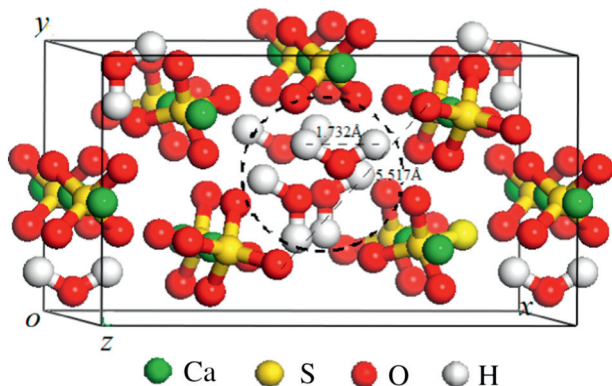


Fig. 2. Unit cell structure of α -HH. The colors indicate: green—Ca, yellow—S, red—O, and white—H. The black dash line indicates water channel. $1 \text{ \AA} = 0.1 \text{ nm}$.

honeycombed tunnel with a diameter of 0.5517 nm is constructed using $6 \text{ SO}_4^{2-}-\text{Ca}^{2+}-\text{SO}_4^{2-}$ long chains, which is filled with H_2O molecules with a length of 0.1732 nm and form a channel with a diameter of 0.3785 nm . This channel allows water molecules from the outside to pass freely; thus, α -HH can easily transform into dihydrate gypsum.

Table 1 summarizes the comparison of the optimized values of α -HH unit cell parameters in different force fields with the experiment values. It shows that there are minimum deviation values of α -HH unit cell parameters using the force field COMPASS as the initial force field. So the force field COMPASS is a suitable force field to forecast the growth morphology of α -HH crystal using AE model.

Fig. 3 shows the prediction of α -HH growth morphology using AE model. It can be seen that the growth morphology of α -HH is a four-faced bipyramid short column constructed with 12 crystal planes. Among which, crystal clusters $\{10\bar{1}\}$, $\{101\}$ form the four cylinders of α -HH crystal, whereas crystal clusters $\{011\}$, $\{0\bar{1}1\}$, $\{110\}$, and $\{1\bar{1}0\}$ form its conical surfaces.

Attachment energy and area of growth surfaces of α -HH crystal are displayed in Table 2. Crystal cluster $\{101\}$ comprises the largest crystal plane area, which accounts for 35.107%. The crystal plane area of $\{10\bar{1}\}$ accounts for 33.133%. The crystal plane area of $\{011\}$ is equal to that of $\{0\bar{1}1\}$, which accounts for 7.467%, whereas the crystal plane area of $\{110\}$ is equal to that of $\{1\bar{1}0\}$, which accounts for 8.413%. It indicates that the growth rates of crystal clusters $\{101\}$ and $\{10\bar{1}\}$ of α -HH are litter than those of other crystal clusters.

The crystal surface structures of α -HH projected along the $[001]$ direction are shown in Fig. 4. Cylinders $\{101\}$, $\{10\bar{1}\}$ and conical surfaces $\{011\}$, $\{0\bar{1}1\}$ form an angle with the water channels, and approximately three water channels are observed. Because conical surfaces $\{110\}$, $\{1\bar{1}0\}$ are parallel with the water channels, no water channel exists on these surfaces. It indicates that water molecules from the outside can only enter the α -HH crystal inside and then hydrate into dihydrate gypsum along the water channels in the four cylinders and the two conical surfaces $\{011\}$, $\{0\bar{1}1\}$. By contrast, water molecules from the outside cannot enter the crystal inside from the two conical surfaces $\{110\}$, $\{1\bar{1}0\}$. Thus, the exposures of the cylinders of α -HH crystal are positive to hydration reactivity, whereas the exposures of the conical surfaces parallel to the z -axis are negative to hydration reactivity.

3.2. Comparison of hydration reactivity and structure between industrial HPG and type- α high-strength gypsum

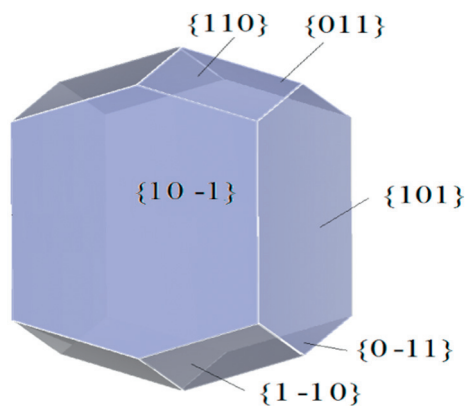
The hydration rates of industrial HPG and type- α high-strength gypsum under different hydration times are shown in Fig. 5. The hydration rate of type- α high-strength gypsum reaches about 74.72% within 15 min, and its complete hydration is achieved within 60 min. However, the hydration rate of industrial HPG is only about 2.76% within 15 min and reaches about 14.36% within 480 min. It can be concluded that the hydration reactivity of type- α high-strength gypsum is considerably higher than that of industrial HPG.

Fig. 6 shows the SEM images of industrial HPG. It can be seen that industrial HPG is made of irregular oriented crystals of schistose shape. As shown in Position *a* in Fig. 6, only two cylinders of industrial HPG are uncovered. Meanwhile, Position *b* in Fig. 6 shows an obvious embossment of the conical surface. SEM image of type- α high-strength gypsum is shown in Fig. 7. It can be seen that type- α high-strength gypsum has stumpy crystals with $20\text{--}40 \mu\text{m}$ long and length-to-diameter ratios of $2\text{--}3:1$. In addition, Fig. 7 shows that cylinders of the crystal clearly appear, whereas the conical surfaces of the crystal are unapparent.

Analyzing the XRD pattern enables us to observe the interior structure of the crystal. As shown in Fig. 1, the main mineral in both industrial HPG and type- α high-strength gypsum is hemi-hydrated gypsum. However, industrial HPG also contains a small amount of dihydrate gypsum and quartz. The rank of the diffraction peak strength of type- α high-strength gypsum is $(400) > (200) > (310) > (114)$, which determines the more complete growth of the cylinders compared with that

Table 1Comparison of the optimized values of α -HH unit cell parameters with the experiment values

Force field	$a/\text{\AA}$	$b/\text{\AA}$	$c/\text{\AA}$	β
Experiment values [13]	12.0275	6.9312	12.6919	90.18°
COMPASS	12.0299 (−0.02%)	6.9339 (0.04%)	12.707 (0.12%)	90.34° (0.22%)
pcff	12.6204 (4.93%)	8.6576 (24.91%)	15.7347 (23.97%)	96.99° (7.55%)
cvff	12.4881 (3.83%)	7.6159 (9.88%)	13.0243 (2.62%)	90.64° (0.51%)

Note: the data in the brackets represents the deviation of α -HH unit cell parameters between the optimized and experiment values. 1 $\text{\AA}$ = 0.1 nm.**Fig. 3.** The prediction of α -HH growth morphology using AE model.

of the conical surfaces. Nevertheless, the decrease in diffraction peak of (400) and (200) in industrial HPG, as well as the increase in diffraction peak of (310) and (114), indicates that the decrease of the crystal cylinders of industrial HPG will allow the conical surfaces to grow better (shown in Fig. 6).

These data above indicate that the increase in exposure degree of the crystal cylinders makes the hydration reactivity of type- α high-strength gypsum considerably above that of industrial HPG. It can also be certificated that water channels are mainly distributed in the crystal cylinders of α -HH. This finding agrees with the theoretical calculations. Therefore, an effective means to enhance the hydration reactivity of industrial HPG is to change its crystal morphology to uncover its crystal cylinders, and thus, increase the number of its water channels.

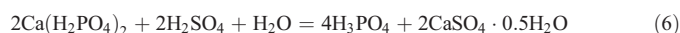
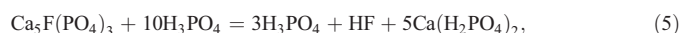
3.3. Morphology control of HPG

HPG1 and HPG2 with different crystal morphologies were prepared by using the following respective concentrations of liquid-phase SO_4^{2-} in the mixed solution: 20 $\text{mg} \cdot \text{ml}^{-1}$ and 40 $\text{mg} \cdot \text{ml}^{-1}$ [22].

The SEM images of HPG1 and HPG2 are shown in Fig. 8. When concentration of liquid-phase SO_4^{2-} is 20 $\text{mg} \cdot \text{ml}^{-1}$, HPG1 has stumpy crystals with 5–15 μm long and length-to-diameter ratios of 3–5:1. When concentration of liquid-phase SO_4^{2-} is increased to 40 $\text{mg} \cdot \text{ml}^{-1}$, HPG2 is made of irregular schistose crystals which appear a small amount of crystal cylinders and become the length-to-diameter ratios less than 1.

The XRD patterns of HPG1 and HPG2 are shown in Fig. 9. The diffraction peak intensities of (200) and (400) in HPG2 are lower than those in HPG1, whereas the diffraction peak intensities of (310) and (114) in HPG2 are higher than that in HPG1. The result indicates that the length of crystal cylinders of HPG is reduced, and conical surfaces are prone to appear with the increase in liquid-phase SO_4^{2-} concentration.

When preparing HPG, apatite powders were poured into the mixed solution of phosphoric acid and sulfuric acid, which caused the reaction system to exhibit the decomposition course of apatite powders and the crystallization process of HPG. The reaction formulas about the reaction of apatite powders with phosphoric acid and sulfuric acid are as follows in Eqs. (5) and (6):



Crystallization of α -HH can be identified two time regions: a period for the crystal nucleus formation and a crystal growth period [23]. Thus when the mixed solution is saturated with respect to Ca^{2+} and SO_4^{2-} ions, this saturated solution becomes supersaturated with respect to α -HH leading to nucleation and crystal growth. After a nucleus has been formed, growth occurs via advancing monolayer steps, predominantly parallel to {1 0 -1} and {101}. The step velocity of {110} and {1 -1 0} steps are higher, relative to {1 0 -1} and {101} steps, which is a result of a stump shape of α -HH crystal (seen in Table 2 and Fig. 3).

During the preparation of HPG, the different concentrations of liquid-phase SO_4^{2-} changed the supersaturation and crystal surfaces growth rate of α -HH; thus crystal morphology of α -HH varied from each other with the change in concentration of liquid-phase SO_4^{2-} . When the concentration of liquid-phase SO_4^{2-} was 20 $\text{mg} \cdot \text{ml}^{-1}$ in initial reaction system, SO_4^{2-} ions reacted with Ca^{2+} ions to produce a small quantity of α -HH, which caused supersaturation of α -HH to decline. A small number of growth units SO_4^{2-} and Ca^{2+} ions were superimposed on the crystal clusters of α -HH, which caused the crystal grains of α -HH to become small. After the rest of the sulfuric acid was poured into the mixed solution, the supersaturation and crystal surfaces growth rate of α -HH increased with the concentration of liquid-phase SO_4^{2-} increase. Many growth units SO_4^{2-} and Ca^{2+} ions constantly were superimposed on the crystal clusters of α -HH, which provided a good opportunity for the crystals to extend along crystal plane clusters {1 0 -1} and {101}. Thus the crystal cylinders of α -HH appear and then the crystal growth morphology eventually present a stumpy shape (seen in Fig. 8 (a)).

Table 2Attachment energy and area of growth surfaces of α -HH crystal

{hkl}	$E_{\text{att}}(\text{total})/\text{kJ} \cdot \text{mol}^{-1}$	$E_{\text{att}}(\text{vdW})/\text{kJ} \cdot \text{mol}^{-1}$	$E_{\text{att}}(\text{electrostatic})/\text{kJ} \cdot \text{mol}^{-1}$	Crystal surface area/%
{1 0 -1}	−28.838	−22.913	−5.925	33.133
{101}	−27.176	−25.372	−1.804	35.107
{011}	−44.459	−38.452	−6.007	7.467
{0 -1 1}	−44.459	−38.452	−6.007	7.467
{110}	−43.580	−39.148	−4.432	8.413
{1 -1 0}	−43.580	−39.148	−4.432	8.413

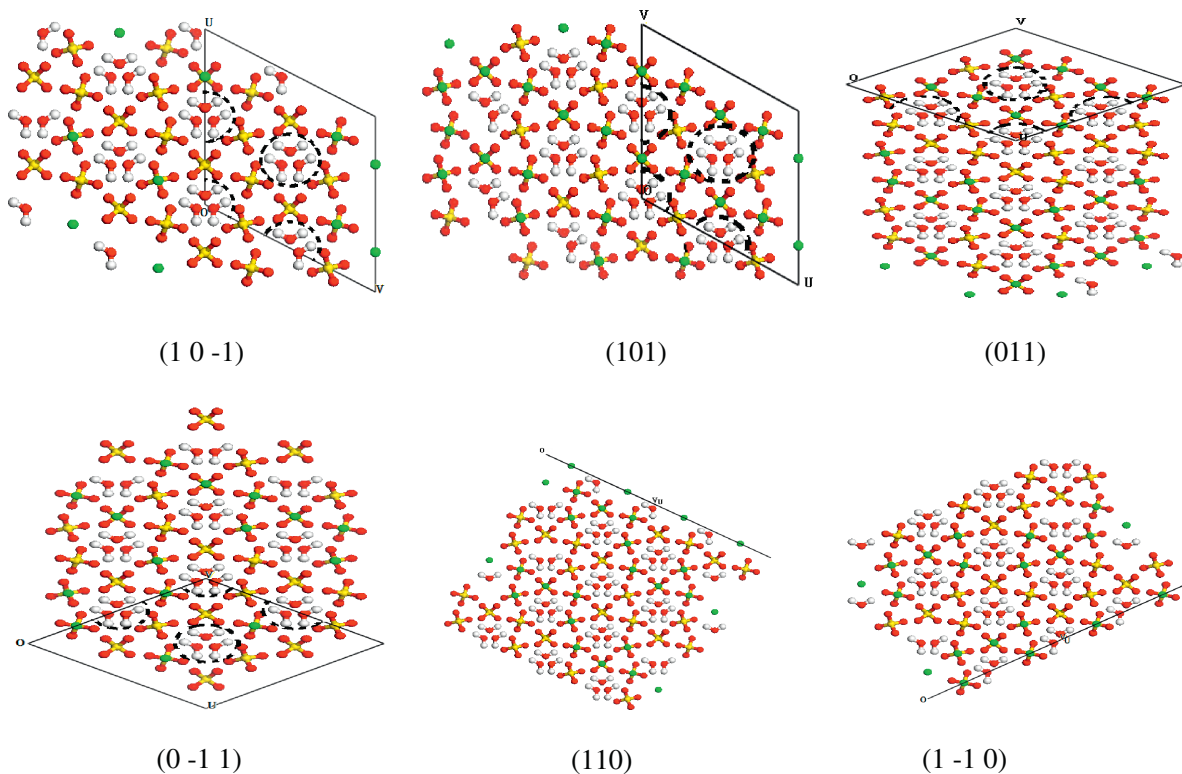


Fig. 4. Crystal surface structures of α -HH projected along the [001] direction. The colors indicate: green—Ca, yellow—S, red—O, and white—H. The black dash line indicates water channel.

However, when the concentration of liquid-phase SO_4^{2-} was increased to $40 \text{ mg} \cdot \text{ml}^{-1}$, the supersaturation of α -HH was higher than that of α -HH in initial reaction system with the concentration of liquid-phase SO_4^{2-} at $20 \text{ mg} \cdot \text{ml}^{-1}$. Thus the crystal particles of α -HH became larger and more easily deposited on the surfaces of apatite particles. The decomposition reaction rate of apatite particles was retarded by α -HH crystals, which caused the concentration of liquid-phase Ca^{2+} to decrease. Simultaneously, the remaining amount of sulfuric acid was reduced. The supersaturation and crystal surfaces growth rate of α -HH decreased; hence, a small number of growth units SO_4^{2-} and Ca^{2+} ions were superimposed on the crystal clusters {1 0 -1} and {101} of α -HH,

which caused difficulty for the crystal cylinders to appear. Therefore, schistose crystals of α -HH are presented (seen in Fig. 8 (b)). Based on the aforementioned experimental results, a schematic illustration of HPG morphological evolution under different concentrations of liquid-phase SO_4^{2-} is presented in Fig. 10.

3.4. Influence of crystal morphology on hydration apparent activation energy

The hydration rates of HPG1 and HPG2 at different hydration temperatures are shown in Fig. 11. When hydration temperature is 20°C , the hydration rate of HPG1 reaches about 67.63% within 15 min and about 86.77% after 480 min of hydration. However, the hydration rate

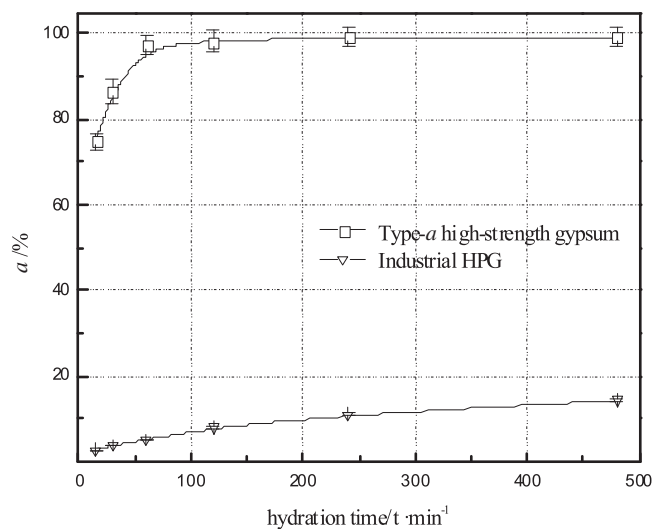


Fig. 5. The hydration rates of industrial HPG and type- α high-strength gypsum at hydration temperature 20°C .

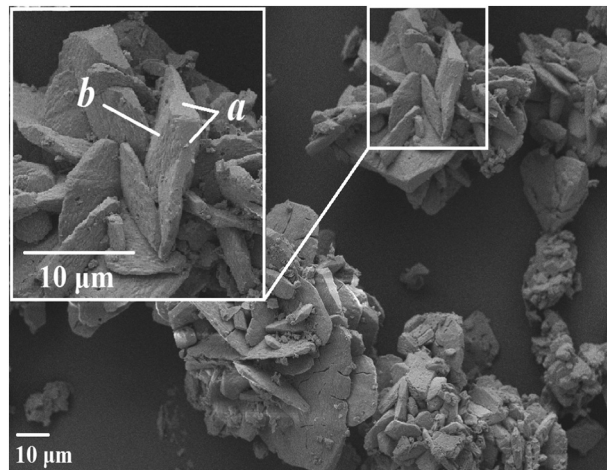


Fig. 6. SEM images of industrial HPG.

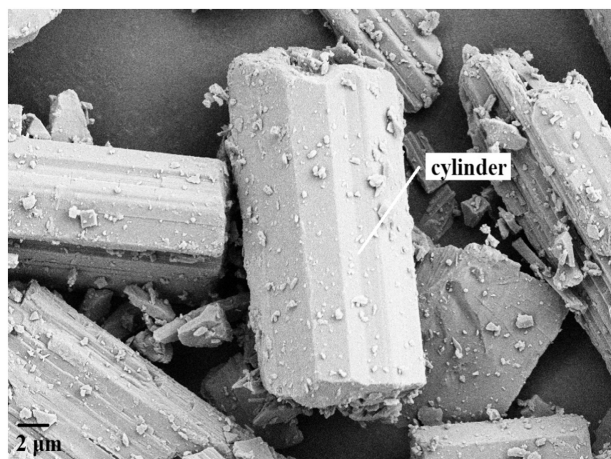


Fig. 7. SEM image of type-α high-strength gypsum.

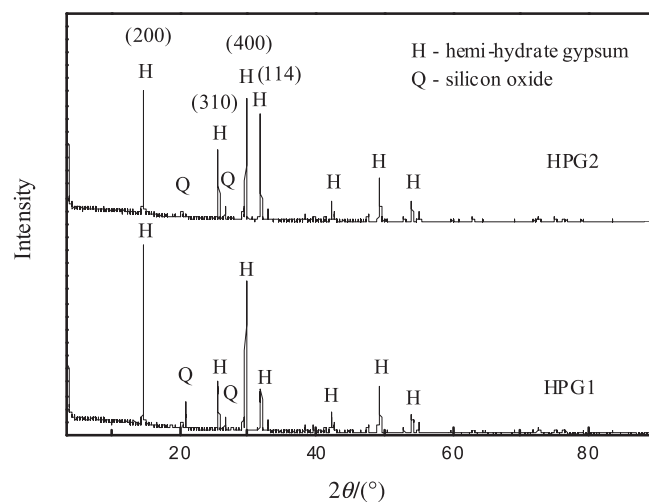


Fig. 9. XRD patterns of HPG1 and HPG2.

of HPG2 is low, i.e., only about 19.86% after 480 min of hydration in 20 °C water. The results indicate the hydration reactivity of HPG1 is considerably higher than that of HPG2. Fig. 11 also shows that the hydration rates of HPG1 and HPG2 decrease with the rise of hydration temperature, which exhibits a “negative temperature effect”. This is because the hydration of α-HH is an exothermic reaction. Meanwhile, the supersaturation of the α-HH solution subsides when temperature increases [23,24].

Hydration kinetics parameters and hydration apparent activation energies of HPG1 and HPG2 are displayed respectively in Tables 3 and 4. The strength rank of the hydration apparent activation energies of HPG is as follows: $|E_{a(\text{HPG2})}| > |E_{a(\text{HPG1})}|$. Based on the activation energy criteria of chemical reaction and diffusion control [25], $E_{\text{diffusion}} < 25.12 \text{ kJ} \cdot \text{mol}^{-1} < E_{\text{chemical}}$; hence, we can determine whether the hydration of HPG is controlled by chemical reaction or diffusion. The hydration of HPG1 is controlled by diffusion, whereas the hydration of HPG2 is controlled by chemical reaction. This is because the number of water channels increases with the exposure degree of the crystal cylinders increase. Thus when the length-to-diameter ratio of α-HH crystals is more than 1, the number of water channels in the crystal increases. Water molecules from the outside enter the crystal inside of α-HH rapidly and hydrate into dihydrate gypsum; thus the velocity for hydration reactivity of HPG1 is higher than that for hydration products dihydrate gypsum diffusion. However, when the length-to-diameter ratio of α-HH crystals is less than 1, the number of water channels in the crystal decreases. The velocity for hydration reactivity of HPG2 is lower than that for hydration products dihydrate gypsum diffusion.

4. Conclusions

Analysis of growth morphology of α-HH has shown that water channels are mainly distributed in the crystal cylinders, whereas no water channel exists in the conical surfaces parallel to the z-axis.

The investigation of micro-morphology and hydration reactivity has proved that the exposure degree of the crystal cylinders of α-HH directly affects the hydration reactivity of both industrial HPG and type-α high-strength gypsum. The exposures of the crystal cylinders of α-HH are positive to hydration reactivity, whereas the exposures of the conical surfaces are negative to hydration reactivity. By adjusting the concentration of liquid-phase SO_4^{2-} makes possible to control the growth rate of the crystal cylinders of α-HH and to obtain HPG having the stumpy crystals of α-HH and high hydration reactivity. The appropriate concentration of liquid-phase SO_4^{2-} is $20 \text{ mg} \cdot \text{ml}^{-1}$ for the crystallization process of HPG.

Nomenclature

A	pre-exponential factor, h^{-1}
E_a	hydration apparent activation energy, $\text{kJ} \cdot \text{mol}^{-1}$
E_{att}	attachment energy, $\text{kJ} \cdot \text{mol}^{-1}$
$M_{\text{H}_2\text{O}}$	molecular weight of H_2O
$M_{\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}}$	molecular weight of hemi-hydrate calcium sulfate
n	Avrami parameter
R	constant, $\text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$
T	thermodynamic temperature, K
t	hydration time, hour

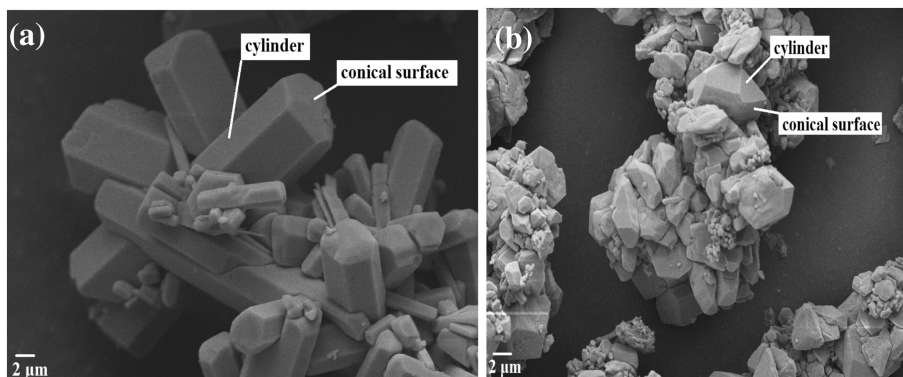


Fig. 8. SEM images of HPG with different crystal morphologies (a) HPG1, (b) HPG2.

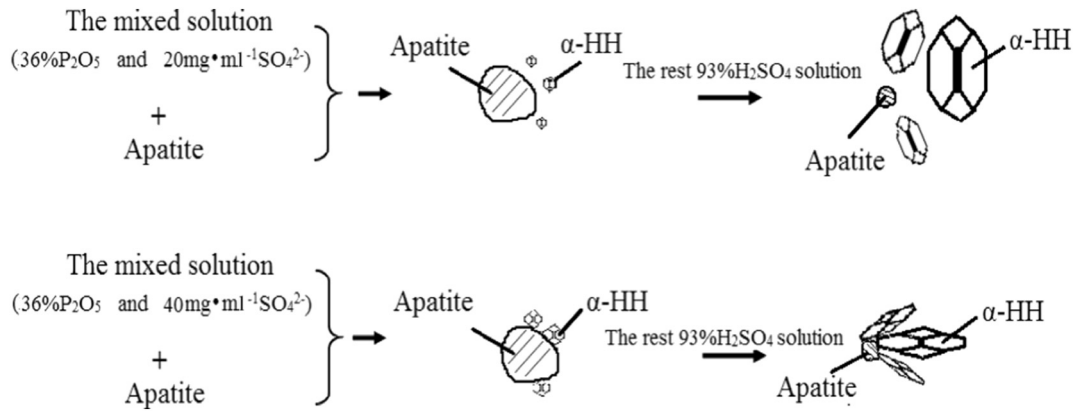


Fig. 10. Schematic illustration of the HPG morphological evolution under different concentrations of liquid-phase SO₄²⁻.

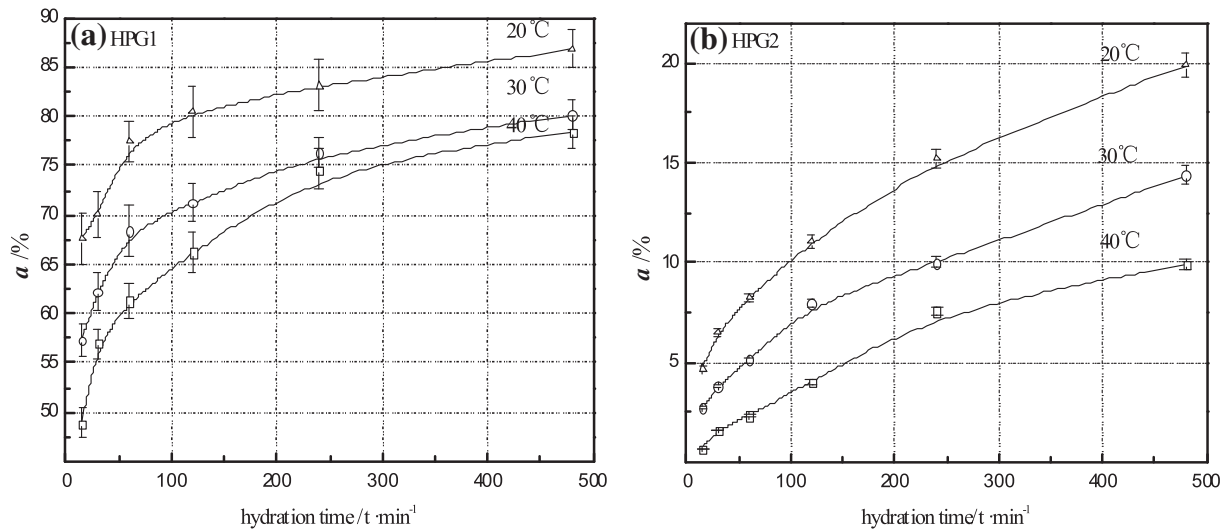


Fig. 11. The hydration rates of HPG at different hydration temperatures (a) HPG1, (b) HPG2.

w	crystal water content, %
Z	composite crystallization rate constant
α	the hydration rate, %
ε	hemi-hydrate gypsum content, %

Subscripts

α-HH	type-α hemi-hydrated gypsum
HPG	hemi-hydrate phosphogypsum

Table 3
Hydration kinetics parameters of HPG1 and HPG2

Sample	T/K	n	lnZ	Linear regression coefficient
HPG1	293	0.1723 ± 0.0040	0.3528 ± 0.0737	0.9903 ± 0.0003
	303	0.1836 ± 0.0016	0.1066 ± 0.0533	0.9972 ± 0.0034
	313	0.2357 ± 0.0035	-0.0476 ± 0.0472	0.9948 ± 0.0004
HPG2	293	0.4382 ± 0.0014	-2.4255 ± 0.0306	0.9993 ± 0.0006
	303	0.4949 ± 0.0040	-2.9000 ± 0.0297	0.9980 ± 0.0003
	313	0.7669 ± 0.0013	-3.7284 ± 0.0297	0.9929 ± 0.0004

Table 4
Hydration apparent activation energies of HPG1 and HPG2

Sample	Morphology characteristics	E _a /kJ·mol ⁻¹	A/h ⁻¹	Linear regression coefficient
HPG1	length-diameter ratio of 3–5:1	-15.30 ± 0.72	2.68 ± 0.13 × 10 ⁻³	0.9936 ± 0.0014
HPG2	length-diameter ratio less than 1	-49.34 ± 0.20	1.62 ± 0.21 × 10 ⁻¹⁰	0.9848 ± 0.0011

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