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# Optimizing hydration and performance of phosphogypsum based cementitious system through multiphase composites

Shouwei Jian<sup>a</sup>, Xinxin He<sup>a</sup>, Bo Peng<sup>a</sup>, Xin Gao<sup>a</sup>, Jianxiang Huang<sup>a</sup>, Fei Dai<sup>a</sup>, Jiaxuan Chen<sup>a</sup>, Baodong Li<sup>a,b,\*</sup><sup>o</sup>

<sup>a</sup> School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

<sup>b</sup> Department of Architecture and Civil Engineering, Chalmers University of Technology, Gothenburg 412 96, Sweden

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## ABSTRACT

Thermal treatment of phosphogypsum (PG) to produce construction-grade gypsum is a promising approach for large-scale utilization. However, the single-phase composition of calcined gypsum necessitates the addition of retarders to control hydration speed, often compromising material performance. To address this, we propose a multiphase gypsum system that leverages synergistic interactions among various gypsum phases to regulate hydration kinetics. This study examines the workability, mechanical properties, water resistance, hydration heat, and microstructure of multiphasic PG. We systematically analyze the interaction mechanisms between different gypsum phases, including II-anhydrite (AII), III-anhydrite (AIII), β-hemihydrate (HH), and dihydrate (DH), within the multiphasic PG system. Results indicate that incorporating optimal amounts of AIII and AII effectively adjusts PG hydration process, enhancing workability and water resistance. Specifically, a composite of 30 % AIII and 20 % AII yields significant improvements in mechanical strength and water resistance (with a softening coefficient reaching 0.81), extends setting time, and reduces water demand. Interactions among AII, AIII, HH, and DH effectively regulate hydration rates in phosphorus-based gypsum cementitious materials. Early-stage hydration of AIII releases substantial heat, promoting the hydration of HH and AII. In turn, AII modulates HH's hydration rate, providing a retarding effect that enhances early strength. At later stages, hydration of AIII and HH increases the exothermic rate of AII's hydration, while DH serves as a nucleation site for AII crystallization, producing a dense structure. Additionally, unhydrated AII absorbs infiltrated water molecules, further improving water resistance and enhancing long-term strength.

# 1. Introduction

Phosphogypsum (PG) is an industrial by-product generated from the wet-process production of phosphoric acid, with approximately 4.5–5.5 tons of PG produced per ton of phosphoric acid output [1]. Global PG emissions have exceeded 6 billion tons, with new annual emissions estimated at 200–400 million tons. In China alone, cumulative PG stockpiles have reached around 870 million tons, increasing annually by about 80 million tons, yet utilization remains below 10 % [2–5]. Currently, most PG disposal involves dumping or stockpiling, leading to significant environmental pollution. Consequently, the safe and resourceful utilization of PG has garnered attention [6,7]. However, the hydration and hardening mechanisms of PG-based multiphase composites are expected to differ from those of natural or flue gas desulfurization gypsum-based systems, which are with high purity and

minimal impurities [8]. The presence of impurities in PG influences hydration kinetics, phase transformation, and microstructural development. Therefore, understanding the self-regulation mechanism of different PG phases during hydration is crucial for optimizing its performance in MPPG cementitious materials.

Common PG valorization strategies include its use in road construction, as a cement retarder, in gypsum board production, and particularly in construction gypsum, which is considered a promising direction for large-scale, value-added utilization [9–11]. For instance,  $\beta$ -hemihydrate gypsum (HH) products, despite advantages like abrasion resistance, adhesion, good slurry fluidity, and low expansion [12]. However, single-phase gypsum materials produced by heat treatment face limitations in engineering applications, like fast setting times and limited water resistance [13,14]. Current research efforts primarily focus on modifying construction gypsum properties using additives, but

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<sup>\*</sup> Corresponding author at: School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China. *E-mail address:* baodong.li@chalmers.se (B. Li).

such approaches often yield limited strength improvements. For example, while additives like carboxylic cellulose and citric acid may extend setting times and improve flow, they frequently compromise mechanical strength [15,16].

When heat-treated between 100 and 1800 °C, PG can transform into various phases, including  $\beta$ -HH, dihydrate gypsum (DH), and multiple forms of anhydrite (AIII, AII, and AI) [17–19]. Each phase exhibits distinct solubility, hydration rates, and crystal formation behaviors, influencing the mechanical and hydration characteristics of the resulting material. For example,  $\beta$ -HH, commonly obtained by low-temperature calcination of PG in the range of 120–180 °C, is mainly transformed from the DH phase through dehydration. AIII, generated at a temperature range of 200–450 °C, the DH phase of PG first undergoes dehydration to transform into HH, and then HH continues to dehydrate and transforms into AIII is highly reactive and hydrates rapidly. AII is obtained by calcining PG in the temperature range of 450–800 °C, where the DH phase is completely dehydrated. It is nearly insoluble and has minimal hydration reactivity [20–22].

Research indicates that interactions between these phases can influence overall performance even without additive-based regulation. Pan [23] reported that mixing  $\beta$ -HH and AII results in HH promoting the hydration of AII. Similarly, Yang [24] found that in HH-AII composites, the rapid hydration of HH contributes to early strength, while AII hydration is essential for late-stage strength development. These studies suggest that a composite of multiple gypsum phases could achieve self-regulation of hydration; however, existing research often considers limited phase combinations, which restricts comprehensive hydration control.

To systematically investigate the self-regulation mechanisms among various phases in MPPG, we synthesized dihydrate gypsum with controlled phase compositions by calcining PG at different temperatures. MPPG cementitious materials with varied phase assemblies were prepared and evaluated their standard consistency, water demand, setting time, compressive strength, and hydration activity via calorimetry. Phase interactions were further explored using X-ray diffraction (XRD) and scanning electron microscopy (SEM) analyses. This study aims to elucidate the hydration dynamics of different gypsum phases, paving the way for advanced composite PG materials and offering theoretical insights to enhance PG utilization in construction applications.

#### 2. Materials and test methods

#### 2.1. Raw material

The raw materials for this experiment were obtained from Yuntianhua Company in Yunnan Province. The purified and treated PG appeared as a gray powder, with the primary chemical composition detailed in Table 1, with a calculated CaSO<sub>4</sub> content of 64.88 %. The raw PG was initially dried at 40 °C, and its characterization results, including XRD, SEM, and thermogravimetric-differential scanning calorimetry (TG-DSC) analyses, are presented in Fig. 1(a) shows that the main mineral phases of raw PG are calcium sulfate dihydrate (CaSO<sub>4</sub>·2H<sub>2</sub>O) and quartz (SiO<sub>2</sub>), with minimal presence of other substances such as phosphates and metal oxides. Fig. 1(a) also displays the microscopic morphology of the untreated PG, revealing a large, plate-like crystal structure with flat surfaces and irregular shapes. Fig. 1(b) presents the mass loss profile as PG is heated from room temperature to 1000 °C at 10 °C/min. The rate of mass loss accelerates after 120 °C, with a pronounced endothermic peak observed between 120 and 180 °C at 151.9  $^{\circ}$ C, indicating a dehydrated mass loss of approximately 15.52 %, mainly due to the gradual release of crystallization water as calcium sulfate dihydrate converts to HH [25].

Between 180 and 450 °C, the rate of mass loss slows, corresponding to the continued dehydration process, transforming the dihydrate to semi-anhydrous and subsequently to AIII. At around 450 °C, a minor endothermic peak indicates the onset of AII formation [26]. A third endothermic peak appears at approximately 900 °C, with a slight mass loss on the TG curve, likely due to further transformations within anhydrous gypsum and the decomposition of residual impurities [21]. The result of internal (I<sub>Ra</sub>) and external exposure index (I<sub>γ</sub>) met the requirement of Chinese standard (GB 6566–2010), as shown in Table 2). The heavy metals contents measured by ICP were lower required values of Chinese standard GB 18582-2008 (Table 3). The Pb, Cd, Cr and Hg contents of the raw material used in this study is far below the limits of standards. Therefore, it can be thought that the building materials product valorized from this PG will not cause environmental damage.

# 2.2. Sample preparation

#### 2.2.1. Sample processing

The raw PG was initially dried in a standard constant temperature and humidity curing chamber at 40 °C for 48 h to remove surface moisture. After drying, agglomerates in the untreated PG were crushed and ground using a horizontal ball mill in preparation for calcination. To minimize the impact of particle size on the performance of multiphase gypsum, a sieving pretreatment to PG was applied, which ensured a consistent particle size distribution across all temperatures, with most particles ranging from 10 to 100 µm. The treated PG was then heated in a muffle furnace from 50 °C at a controlled rate of 5 °C/min until reaching specific temperatures, followed by a holding period to obtain PG samples with different phase compositions [27]. To stop AIII from absorbing moisture from the air and turning into hemihydrate gypsum, we need to use the PG right after it's calcined at 300°C. Thus, the contacting time between gypsum and air can be reduce, which lessens the chance of it soaking up water. It helps to keep the amount of AIII stable. Detailed PG calcination parameters are provided in Table 4. Experimental testing was conducted to determine phase contents at various temperatures, leading to the selection of three optimal calcination temperatures: 160 °C, 300 °C, and 600 °C. According to the Chinese national standard GB/T 36141-2018, the calculated content of HH and AIII phase accounts for approximately 36.25 wt% and 35.86 wt% of the total PG content (including other non-gypsum phase impurities), respectively. The proportion of each gypsum phase in the PG calcined at the three temperature ranges in Fig. 2(a), the other components include quartz, phosphates, and metal oxides. XRD patterns for PG calcined at these temperatures are presented in Fig. 2(b), which guided the design of MPPG compositions.

#### 2.2.2. Proportioning of MPPG

The phase proportioning design for each experimental group is presented in Table 5. Based on the proportions of each gypsum phase in the total PG content (including other non-gypsum phase impurities) measured in Fig. 2(a). When preparing the MPPG samples, the proportions of each gypsum phase in the total PG were converted to their respective proportions in the total gypsum phases, as shown in Table 5. Conversion formula as shown in Eq. (1).

$$\omega_0 = \frac{\omega_a}{\omega_p} \tag{1}$$

Table 1		
Chemical composition of raw	PG	(wt%).

Component	SO <sub>3</sub>	CaO	SiO <sub>2</sub>	$P_2O_5$	$Al_2O_3$	K <sub>2</sub> O	Fe <sub>2</sub> O <sub>3</sub>	MgO	LOI
Values	38.196	25.414	12.257	1.110	0.585	0.207	0.144	0.092	21.123



Fig. 1. Characterization results of raw PG, (a) XRD pattern and SEM image, (b) TG-DSC pattern.

Table 5

## Table 2

The limits of radionuclides in raw PG and the test results.

	<sup>40</sup> K (Bq/ Kg)	<sup>226</sup> Ra (Bq/Kg)	<sup>232</sup> Th (Bq/Kg)	Limits of standards	Test results
Radionuclide	72.04	58.61	13.89	$\substack{I_{Ra} \leq 1.0 \\ I\gamma \leq 1.0}$	$\substack{I_{Ra} \leq 0.29 \\ I\gamma \leq 0.27}$

 $\omega_0$  represents the mass fractions of each gypsum phases in the total gypsum phases ,  $\omega_a$  represents the mass fractions of each gypsum phase in the total PG ,  $\omega_p$  represents the mass fraction of the total gypsum phases.

The blank group represents HH calcined at 160°C, with its fundamental physical properties detailed in Table 6 and assessed according to

## Table 3

The limits of heavy metals in raw PG and the test results.

	Heavy metals (mg/Kg)			
	Pb	Cd	Cr	Hg
Limits of standards Test results	90 15.92	90 2.20	90 35.18	90 1.20

# Table 4

The calcination system of PG.

Gypsum	Target	Heating	Heating	Soaking
phase	temperature	rate	time	time
DH	40 °C	0	48 h	-
HH	160 °C	5 °C/min	22 min	3 h
HH/AIII	300 °C	5 °C/min	50 min	3 h
AII	600 °C	5 °C/min	110 min	3 h

Group number	Number	Different gypsum phase content ratio ( $\omega_0$ )					
		AIII (%)	AII (%)	HH (%)	DH (%)		
	Blank	0	0	90	10		
	III-15 %	15	0	75	10		
	III-20 %	20	0	70	10		
A	III-25 %	25	0	65	10		
	III-30 %	30	0	60	10		
	III-45 %	45	0	45	10		
	II-15 %	0	15	75	10		
	II-30 %	0	30	60	10		
В	II-45 %	0	45	45	10		
	II-60 %	0	60	30	10		
	II-75 %	0	75	15	10		
	II-100 %	0	100	0	0		
	III30 %-II0 %	30	0	60	10		
	III30 %-II5 %	30	5	55	10		
	III30 %-II10 %	30	10	50	10		
A-B	III30 %-II15 %	30	15	45	10		
	III30 %-II20 %	30	20	40	10		
	II-100 %	0	100	0	0		



Fig. 2. Phase assemblage of calcined PG, (a) phases content, (b) XRD pattern.

GB/T 9776–2008 standards. Based on the results of the three-phase gypsum test and Eq. (1). Group A investigates varying proportions of AIII (15 %, 20 %, 25 %, 30 %, and 45 %) with a constant 10 % DH and a balance of HH. In Group B, phase proportions of AII, DH, and HH are adjusted by combining HH calcined at  $160^{\circ}$ C with AII calcined at  $600^{\circ}$ C, setting AII content at increments of 0 %, 15 %, 30 %, 45 %, 60 %, 75 %, and 100 %, while maintaining HH at 10 %, except for the 100 % AII sample. Groups A-B illustrate the MPPG preparation, where four gypsum phases are combined, with AII content adjusted from 5 % to 20 % and AIII held at 30 %. The control group includes a fixed 30 % AIII content.

## 2.3. Test method

## 2.3.1. Test methods of Gypsum phase composition

According to GB/T 36141-2018, the determination of the content of AIII, HH, and DH phases involves the following basic principles and operating procedures.

Determination of AIII and bound water: Based on that soluble AIII can hydrate into HH in 95 % anhydrous ethanol, while under the same conditions HH cannot hydrate into DH, the content of AIII is calculated by measuring the increase in weight as it hydrates in 95 % anhydrous ethanol. The mass fraction of the soluble AIII phase is determined using the HH hydration reaction formula shown in Eq. (2).

$$CaSO_4 + 0.5H_2O = CaSO_4 \cdot 0.5H_2O$$
<sup>(2)</sup>

If there is no soluble AIII present in the sample, the mass of the sample before drying will be greater than the mass after reaching a constant weight upon drying. This allows for the calculation of the mass fraction of bound water.

Determination of HH: By utilizing the complete hydration of HH and AIII into DH, the hydration increment of the gypsum in pure water is measured. This is done by determining the total amount of DH formed from HH and AIII, and then subtracting the content of AIII previously measured. This gives the content of HH, which is calculated according to the hydration reaction formulas in Eq. (3) and Eq. (4).

$$CaSO_4 \cdot 0.5H_2O + 1.5 H_2O = CaSO_4 \cdot 2H_2O$$
 (3)

$$CaSO_4 + 2H_2O = CaSO_4 \cdot 2H_2O \tag{4}$$

Determination of DH: By heating construction gypsum to 200  $^{\circ}$ C or higher, the DH undergoes dehydration to transform into AIII. The total dehydration amount is calculated by subtracting the combined dehydration loss of HH and bound water from the sum of the dehydration losses of DH, HH, and bound water. This calculation yields the content of the residual DH. The dehydration reactions upon heating are represented by Eq. (5) and Eq. (6).

$$CaSO_4 \cdot 2H_2O \triangleq CaSO_4 + 2H_2O$$
(5)

$$CaSO_4 \cdot 0.5H_2O \triangleq CaSO_4 + 0.5H_2O \tag{6}$$

# 2.3.2. Water consumption and setting time

According to GB/T 17669.4-1999, the PG obtained from calcination at different temperatures is weighed, prepared, and thoroughly mixed. Then, 300 g of MPPG powder is poured into the estimated amount of water within 5 s and stirred for 30 s to obtain a uniform multiphase

Table 6

The physical properties of HH.

Water- gypsum ratio (%)	Setting time (min)		24 h compressive strength (MPa)	24 h flexural strength	Initial fluidity
	Initial	Final		(MPa)	(mm)
62	3.25	5.40	3.54	0.86	148

gypsum paste. The paste is then quickly poured into the consistometer cylinder. The paste's spreading diameter on a glass plate is measured 50 s after the PG comes into contact with water. The water volume used when the paste's spread reaches ( $180 \pm 5$ ) mm is the standard consistency water requirement for the MPPG building plaster. Additionally, the initial and final setting times of 200 g of MPPG prepared into a uniform paste are recorded.

## 2.3.3. Mechanical strength

The mechanical properties are determined according to the standard GB/T 17669-1999. The MPPG was prepared according to the proportions outlined in Table 5. Following the uniform mixing of the prepared powder with mixing water, the resultant mixture was poured into 40 mm  $\times$  40 mm  $\times$  160 mm test molds. Demolding occurred within 24 h. Each group comprised 12 test blocks, evaluated at three curing ages: 1d, 7d, and 28 d. In order to study the strength changes and water resistance of different groups of composite gypsum blocks in humid (90 % RH and 20  $\pm$  5 °C) and dry (50 % RH and 20  $\pm$  5 °C) environments, the gypsum blocks were placed in these two different curing environments. The development of strength at 1 day, 7 days, and 28 days for the blocks was monitored, and their water resistance after 28 days was ultimately evaluated. After being cured under two conditions until the required age, both sets of test blocks are dried to a constant weight. Their dry compressive strength is used to compare mechanical strength, which can maximumly avoid moisture affecting the material's structure and performance. The compressive strength test for the paste test blocks employed a loading rate of 0.5 kN/s, while the flexural strength test utilized a rate of 0.1kN/s.

#### 2.3.4. Water resistance

The water resistance of each group of MPPG was characterized using the softening coefficient and water absorption metrics. For each sample group, two sets of test blocks were prepared and cured for 28d. One set was dried to a constant weight in the oven and then undergoes dry strength testing, while the other was soaked in water at  $20 \pm 5$  °C for 24 h for the wet strength test. The average values from every three samples were used as reference values. The softening coefficient ( $K_r$ ) is defined as the ratio of the wet compressive strength ( $f_1$ ) to the dry compressive strength ( $f_0$ ) of the test block, as expressed in Eq. (7). Water absorption (P) is calculated as the percentage change in mass of the test block immersed in water for 24 h at 20 ± 5 °C as shown in Eq. (8).

$$K_r = f_1 / f_0 \tag{7}$$

 $K_r$  Represents the softening coefficient,  $f_1$  represents the wet strength (MPa),  $f_0$  represents the dry strength (MPa).

$$P = 100\% \times (m_1 - m_0)/m_0 \tag{8}$$

P represents the water absorption rate ,  $m_1$  represents the mass of the specimen after absorbing water after 24 h (g) ,  $m_0$  represents the mass of test piece after drying (g).

## 2.3.5. Hydration heat

To assess the hydration heat of each MPPG group, the amount of material was calculated based on a reference of 3 g of water. The powder raw materials were rapidly mixed with water and placed into a C80 micro calorimeter (SETARAM, C80 Micro Calorimeter) for testing the kinetic parameters of hydration heat release, including total heat release and heat release rate.

# 2.3.6. Microscopic characterization

The crystal phase composition of samples with varying hydration ratios and ages was analyzed using XRD (Empyrean, Netherlands). Test specimens, once they reached the desired hydration level, were crushed and soaked in anhydrous ethanol to halt further hydration. The XRD analysis parameters included a scanning angle range of  $5^{\circ}$  to  $80^{\circ}$  and a

scanning speed of 5 °/min, with a step length of  $0.02^{\circ}$ . To examine the microscopic morphology of hydration products at different stages, test blocks were broken into particles measuring 3–6 mm in size, with a volume of less than 1 cm<sup>3</sup>, and dried to constant weight. The microscopic morphology was analyzed using SEM (JSM-7500F, Japan), with a magnification range of 5–3000 times. The elemental distribution of the microscale area were analyzed by Energy-Dispersive Spectroscopy (EDS).

# 3. Results and discussion

# 3.1. Water consumption and setting time

As illustrated in Fig. 3, the standardized consistency water consumption of MPPG varies with different phase compositions. In Group A, an increase in the content of AIII phase within the three-phase composite correlates with a gradual rise in the water consumption required for achieving standard consistency. Specifically, the water consumption increased from 62 % in the control group (comprising solely HH) to 68 % when the AIII content reached 45 %. This trend aligns with previous findings, which demonstrated a continuous increase in water absorption rates from HH (solubility of 8.15 g/L at 20 °C) to AIII (solubility of 6.3 g/L at 20 °C) [18]. Consequently, the addition of AIII consistently augmented the water consumption necessary for standard consistency. In Fig. 3(b), Group B shows that at 100 % AII phase content, the water requirement for standard consistency is 55 %. This is due to AII phase's low solubility (2.7 g/L at 20°C), leading to limited water reactivity and low absorption. High-temperature calcination of anhydrite reduces large plate-like crystals and increases small ones, which decreases particle size, raises specific surface area, and leads to denser packing, all of which reduce water consumption [18,28]. Moreover, as the content of AIII increases, a discernible pattern emerges in water consumption, showing an initial rise followed by a decline, peaking at 65 % when the AIII content is 45 %. Fig. 3(c) presents the findings from Group A-B, where a four-phase composite was created with a fixed AIII phase content of 30 %, while the content of AII varied between 5 % and 20 %. The water consumption for standard consistency in this group ranges from 67 % to 71 %, which is notably higher than that observed in Groups A and B. The overall trend in this composite indicates an initial increase followed by a subsequent decrease in water consumption. When the AII content is set at 5 %, a slight increase in standard water consumption is observed, suggesting that AII may promote the hydration of both AIII and HH phases. However, as the AII content increases, the hydration effect of MPPG appears to diminish, leading to a gradual decrease in water consumption.

Fig. 4 illustrates the setting time of MPPG with different gypsum phase compositions. In Fig. 4(a) for Group A, the blank group (HH) exhibited a rapid setting and hardening speed, with an initial setting time of 3 min and a final setting time of 5 min. As the content of AIII

phase, known for its strong hydration activity, increased, the setting time gradually shortened, displaying an overall trend of first increasing and then decreasing. When the AIII phase content is 15 %, the initial setting time is 4 min, and the final setting time is 7 min, which reflects a delay compared to the blank group. Subsequently, the setting time accelerates with increasing AIII content, reaching an initial setting time of 2 min and a final setting time of 5 min at 45 % AIII phase content. In Fig. 4(b), Group B shows that as the AII phase content increases, the initial setting time extends from 3 min to 5 min, and the final setting time increases from 5 min to 10 min. Notably, at 100 % AII composition, the initial and final setting times were measured at 22 h and 45 h, respectively. This indicates that the introduction of AII leads to interactions between HH and AII within this MPPG group. Specifically, AII exhibits a retarding effect on HH, while HH accelerates the setting and solidifying process of AII. In Fig. 4(c), when AIII and AII are mixed simultaneously, based on a 30 % AIII mixture, the setting time gradually increases with rising AII content. The final setting time extends from 6 min to 9 min in the control group comprising 30 % AIII and 20 % AII. This represents the initial and final setting times of the AIII 30 %-AII 20 % group, with the initial setting time increasing from 3 min to 4 min. The results indicate that when comparing the setting times of the threephase composite in Groups A and B, the combination of AIII, AII, HH, and DH exhibits a retarding effect.

## 3.2. Mechanical strength

Fig. 5 illustrates the flexural and compressive strengths of MPPG sample specimens from Groups A, B, and A-B at different curing ages under moist curing conditions. In Fig. 5(a) and (b), the mechanical properties of Group A are presented. The flexural strengths of the blank group (HH) were measured at 0.86 MPa, 1.06 MPa, and 1.15 MPa for curing ages of 1d, 7d, and 28d, respectively. Correspondingly, the compressive strengths were 3.54 MPa, 5.05 MPa, and 3.21 MPa. As the content of the AIII phase increased from 0 % to 45 %, both flexural and compressive strengths increased up to a maximum at 30 % AIII, reaching 1.31 MPa and 6.06 MPa, respectively. However, the compressive strength decreased from 6.06 MPa at 1d to 2.61 MPa at 28d, indicating a 50 % reduction due to the dissolution of PG and its dehydrated products in water, leading to strength loss [29,30]. The humid environment minimally affects early strength but significantly weakens the bonding between MPPG crystals over time.

Fig. 5(c) and (d) show the strength changes for Group B. The flexural and compressive strengths decreased with increasing AII content, attributed to the low hydration activity of AII. Initially, the 1d strengths were lower than those of the blank group. At the age of 1 day, after HH is completely hydrated into DH crystals, the strength of each group decreases with the increase of AII content due to its low hydration activity and slow dissolution rate. However, at 7d, the compressive strength increased to 5.45 MPa with 15 % AII, a 54 % improvement over 1d. As



Fig. 3. Standard consistency water consumption of, (a) Group A, (b) Group B, (c) Group A-B.



Fig. 4. Setting time of, (a) Group A, (b) Group B, (c) Group A-B.

the age develops to 7 days, AII continues to slowly hydrate and form DH crystals. These newly formed crystals fill in the skeleton of the DH crystals that were created earlier by the HH hydration, acting as a filler and significantly increasing the 7-day strength of the mixed-phase gypsum in the group. When hydrated to 28 days, the hydration reaction continues due to the presence of AII, but the moist environment causes the growth and alignment of the newly formed crystals to become disordered. The original regular crystal structure becomes loose, and this loose structure cannot provide enough cohesion, leading to a decrease in the overall flexural and compressive strength of the test blocks [31–35]. Strength decreased under humid conditions, suggesting that AII's presence influences later strength development due to the hydration dynamics with HH [36].

Fig. 5(e)-(f) shows the strength change of the MPPG sample test block when AIII and AII are mixed. The strengths of the MPPG sample blocks with mixed AIII and AII phases are analyzed. With 30 % AIII as a control, the flexural strengths at 1d, 7d, and 28d were 1.58 MPa, 1.13 MPa, and 0.95 MPa, while compressive strengths were 5.22 MPa, 3.91 MPa, and 2.61 MPa, respectively. Early strength significantly improved compared to the AII-only group, while late strength decreased by about 20 % in humid conditions, notably less than the 50 % reduction in Group A. The combination of the four phases optimally enhanced early strength through AIII and HH, while AII contributed positively to later strength development.

Fig. 6 shows the development and change of the strength of composite gypsum under two curing conditions: moist (at a temperature of  $20 \pm 5^{\circ}$ C and a relative humidity of 50 %RH) and conventional dry ( $20 \pm 5^{\circ}$ C and a relative humidity of 90 %RH). To study the effect of different curing regimes on the later strength of different groups of composite gypsum, the groups with better strength performance (AIII30 %, 15 %, AIII30 %-AII20 %) as shown in Fig. 5 were selected for curing. Compares the compressive strength at 7d and 28d between conventional wet and dry curing environments for selected groups demonstrating optimal mechanical properties. Group A consisted of 30 % AIII, Group B contained 15 % AII, and Group A-B combined 30 % AIII with 20 % AII, with each group cured in both conditions.

In Fig. 6(a), under wet curing, the 7d strength of the blank group was 5.1 MPa, dropping significantly to 3.2 MPa at 28d, a 36 % reduction. The compressive strength of the AIII30 % group under dry curing reached 8.3 MPa at 7d, indicating that the inclusion of AIII enhances early strength, However, under wet curing, the compressive strength fell to 4.9 MPa due to water erosion. By 28d, the strength of the MPPG test block continued to decline. This indicates that while incorporating AIII improves early strength, prolonged exposure to high humidity conditions negatively affects volume stability [37]. Conversely, in Fig. 6(b), the compressive strength of the blank group (HH) reached 6.5 MPa at 7d in a dry environment, decreasing to 5.5 MPa at 28d, representing an 11 % decline. Under dry curing conditions, the mechanical strength of test blocks from each group also showed varying degrees of reduction at

the 28-day curing period. This is mainly because when cured at 50 % relative humidity, the gypsum test blocks can still absorb trace amounts of moisture from the air. This moisture interacts with the ions in the crystal structure within the gypsum test blocks, causing interference with the already formed crystal structure, which in turn affects the overall stability of the test blocks [38,39].

Comparing the strength of the specimens under both wet and dry curing conditions. The gypsum specimens with a four-phase composite of AIII, AII, HH, and DH showed less strength reduction compared to other groups, indicating a significant improvement in water resistance.

#### 3.3. Water resistance

To further investigate the reduced strength deterioration of MPPG in humid environments with the combination of four phases, the test blocks that were cured in a moist environment for 28 days were evaluated, and the softening coefficient and water absorption rate of MPPG after 28 days of hydration were measured. As shown in Fig. 7(a) and (b), the blank group (HH) has a water absorption rate of 31 % and a softening coefficient of 0.62. When the content of AIII is 30 % and AII is 15 %, the improvement in water resistance of these two MPPG groups is not significant compared to the blank group. For the MPPG specimens cured in a humid environment, when AIII, HH, and DH are combined, the early hydration of AIII and HH forms a dense structure. However, as the age increases, the humid environment causes the early-formed dihydrate gypsum columnar crystals to dissolve, and the intrusion of water leads to sample expansion and structural deformation [40], thereby reducing water resistance. When AII, HH, and DH are combined, the presence of AII allows the hydration reaction to continue, but the humid environment causes the newly formed crystals to grow and align in a disorderly manner, making the original regular crystal structure loose [34]. This loose structure cannot provide sufficient cohesion, resulting in a decrease in the overall flexural and compressive strength of the specimens and their water resistance [35]. However, the MPPG group containing 30 % AIII and 20 % AII demonstrates a water absorption rate of 35 % and a softening coefficient of 0.81, which is a 23 % increase over the control group. This enhancement is attributed to the synergistic effect of AIII, AII, HH, and DH, where the rapid hydration of AIII and HH gypsum densifies the MPPG structure. Additionally, a small amount of AII absorbs moisture from the building gypsum, continuing hydration and forming a denser crystalline structure, thereby enhancing the MPPG's resistance to moisture and water [41,42]. The microstructure of the crystals can be further observed in subsequent SEM analysis.

# 3.4. Hydration heat

Fig. 8(a) and (b) present the hydration heat release rate and total hydration heat release curve for group A. The addition of AIII initiates a vigorous hydration reaction, marked by a distinct sharp peak in the heat



Fig. 5. Mechanical strength, (a) and (b) Group A, (c) and (d) Group B, (e) and (f) Group A-B.

release profile. It is known that the hydration reaction between HH and water begins immediately, resulting in dissolution. After a few minutes, the reaction accelerates, leading to an increase in heat release and a pronounced peak [22]. As hydration progresses, a slower exothermic process develops [43]. In Fig. 8(a), the hydration heat release rate of the control group peaks at 0.056 W/g at 5.74 min, marking the end of the induction period for HH. As the content of AIII increases, the HH and AIII rapidly undergo hydration reactions with water within the initial 10 min, releasing a significant amount of heat. The peak of the hydration exotherm gradually decreases and forms more slowly with the increasing content of AIII. For the AIII45 % sample, the initial hydration

exotherm curve shows a downward trend followed by an upward trend, with a high level of cumulative heat release, thus shortening the setting time. Due to the rapid hydration and substantial heat release, this can lead to an imperfect crystal structure, resulting in a relative decrease in strength compared to the AIII 30 % group [44].

Fig. 8(c) and (d) depict the hydration exothermic rate and total hydration exothermic amount for group B. The blank group (HH) shows a rapid release of substantial heat, while the AII100 % group exhibits no detectable exothermic peak, indicating a slow hydration process. The primary hydration exothermic peaks for the other groups are delayed and concentrated between 5.74 and 15 min. The induction period for



Fig. 6. Compressive strength of MPPG (a) wet curing (b) dry curing.



Fig. 7. Water resistance results, (a) softening coefficient, (b) water absorption.

these groups is similarly compressed with increasing AII content, suggesting that AII slows the hydration of HH while stimulating its own hydration [28]. The blank group reaches a peak total exothermic value of approximately 42.6 J/g at around 120 min. Subsequently, as AII content increases in other groups, the total exothermic output decreases.

Fig. 8(e) and (f) illustrate the exothermic rate and total exothermic curves for MPPG samples in the four-phase composites of groups A-B, AIII, AII, HH, and DH. The MPPG group exhibits lower exothermic peaks than the HH blank, with both groups showing two distinct exothermic peaks. The initial exothermic peak, observed due to AII, indicates a delay in the early hydration of AIII and HH. As AII content increases, the initial peak rises, reaching 0.043 W/g at AIII30 %-AII20 %. Meanwhile, the intensity of the second peak decreases, and the timing of the peak shows a slight delay with higher AII content. Studies suggest that PG uses quartz and hard gypsum as crystallization centers, accelerating gypsum precipitation during hydration [43]. The hydration of AIII and HH promotes the hydration of AII, while AII delays early hydration of the former two, enhancing early strength. Conversely, AIII and HH improve the reactivity of II-anhydrous gypsum, fostering late strength. In this four-phase composite, these interactions secure both early and late strength development for MPPG [45]. The total exothermic curve in Fig. 8(f) shows stabilization around 80 min for the control (III30 %-II0 %). The sample AIII30 %-AII20 % reaches the highest exothermic amount as AII content increases. The hydration of AIII occurs in two stages: a rapid transformation to HH upon contact with water (0-2 min), followed by the hydration of HH to DH (after 10 min). Compared to the hydration of regular HH to DH (2-15 min), the first

stage of AIII hydration precedes and the second stage follows it. The rapid hydration of AIII has two effects: 1) it accelerates the hydration of HH to DH, and 2) it releases impurities from PG, slowing down the hydration of HH. With a small amount of AIII, the slowing effect on HH is more pronounced, while a larger amount of AIII promotes the hydration of HH. Overall, the hydration behavior is governed by the interplay between the different phases, where AIII enhances rapid early hydration, while AII modulates the reaction kinetics, ensuring both early and late strength development in the composite materials [46,47].

#### 3.5. XRD analysis

Fig. 9 shows the XRD patterns of three groups of MPPG at 1 day, 7 days, and 28 days under conventional dry curing conditions. The main minerals in MPPG are calcium sulfate dihydrate (CaSO<sub>4</sub>·2 H<sub>2</sub>O) and quartz (SiO<sub>2</sub>). According to Fig. 9(a), in Group A, AIII and HH fully hydrate within the first day, and by the 28th day, there is little change in the characteristic peaks of DH, indicating that all AIII and HH have been fully hydrated and turned into DH. Fig. 9(b) shows that for the multiphase plaster composed of AII, HH, and DH phases, as the age increases from 1 day to 28 days, the hydration process to form dihydrate calcium sulfate is slow due to the low dissolution rate of anhydrous calcium sulfate gradually weakens with the development of age, while the diffraction peak of dihydrate calcium sulfate gradually intensifies [48,49]. Fig. 9(c) shows that as hydration progresses, the characteristic peaks of DH gradually increase, while the peak values of



Fig. 8. Hydration rate and total heat release, (a) and (c) Group A, (b) and (d) Group A, (e) and (f) Group A-B.

AII gradually decrease. This suggests that hydration reactions or secondary crystallization are still ongoing by the 28th day, which gradually reinforces the material's structure as it cures [50]. It also shows that HH and AIII can continuously activate AII, speeding up its hydration and hardening rate.

The observed crystallographic evolution indicates that the long-term stability and strength of MPPG are closely associated with the progressive formation of the DH phase [51]. The increased peak intensity at later ages suggests a denser, well-crystallized microstructure, which likely contributes to enhanced compressive strength, reduced solubility, and improved resistance to degradation [52].

# 3.6. SEM analysis

SEM analysis was conducted on the blank and three modified MPPG samples (blank group, AIII30 %, AII15 %, AIII30 %-AII20 %) cured in a humid environment. At 1 day, as seen in Fig. 10 (a), the hydration products in the blank group are mainly flocculent substances that aggregate into small dihydrate gypsum crystals with some impurities from HH hydration. In contrast, the crystal structures in the modified groups exhibit significant changes. In Fig. 10 (d), the gypsum crystals are predominantly short, columnar, and interlocking, with numerous contact points between crystals, forming a dense structure of floccules and plate-like crystals, indicating early strength development. In Fig. 10 (g), the addition of AII introduces unhydrated sheet-like AII crystals and needle-like formations from HH hydration. In Fig. 10 (j), with both AII



Fig. 9. XRD patterns of MPPG, (a) Group A, (b) Group B and (c) Group A-B.

and AIII present, the structure shows a higher concentration of needlelike crystals compared to Fig. 10 (d), enhancing strength. By 7d, the blank group's microstructure transitions from a flocculent structure to rod-like crystals, correlating with a noticeable strength increase. For the AIII30 % sample in Fig. 10 (e), the structure shifts from short columnar crystals to a loosely interlaced, flocculent structure, indicating strength loss due to humidity-induced loosening. In Fig. 10 (h), the AII15 % sample evolves into a dense cluster of interconnecting needle-like crystals, which form a robust network with improved mechanical properties. This is due to the newly formed dihydrate gypsum crystals gradually filling in the skeleton of dihydrate gypsum crystals formed by the hydration of early hemihydrate gypsum, playing a filling role and significantly improving the 7-day strength of this composite gypsum group. The AIII30 %-AII20 % sample in Fig. 10 (k) shows rod-like crystals becoming amorphous and loose in a humid environment, suggesting that AII in MPPG promotes needle-like crystal structures that support mechanical strength. By 28d in a wet environment, crystal morphologies in all samples show varying degrees of water-induced degradation. Fig. 10 (c) shows the blank group's long rod-like structures breaking down into granular crystals. The AIII30 % sample (Fig. 10 (f)) exhibits a loose, flocculent structure as moisture distorts and dissolves contact points, leading to recrystallization and strength reduction. In Fig. 10 (i), the AII15 % sample transitions from a dense to a loose needle-rod structure, at 28 days of hydration, under moist conditions, the hydration reaction of AII continues. During this process, the growth and alignment of the dihydrate gypsum crystals become disordered, and the originally well-structured crystals become loose. This loose structure, along with the newly formed dihydrate gypsum crystals, cannot provide sufficient cohesion and strength, resulting in a decrease in the overall flexural and compressive strength of the hardened material. Meanwhile, the AIII30 %-AII20 % sample (Fig. 10 (l)) retains some stability, maintaining needle-like structures advantageous for structural

integrity, even in a humid environment.

Fig. 11 presents SEM images of MPPG samples from four groups cured for 28 days under dry conditions. In Fig. 11 (a), the blank group (HH) displays overlapping needle-like crystals, which differ from the short rod-like and flocculent structures seen under humid conditions in Fig. 10 (c), highlighting the pronounced impact of humidity on HH. When AII content reaches 15%, as shown in Fig. 11 (b), the crystal structure remains similar to that seen in Fig. 10 (i) under humid conditions, though it exhibits higher density under dry curing. This indicates that humidity has a minimal effect on AII stability. For the AIII 30 %-AII 20 % group, substantial differences in crystal morphology emerge between humid (Fig. 10 (l)) and dry conditions (Fig. 11 (d)). Under humidity, the crystals are mainly needle-like and flocculent, while under dry conditions, they shift to long, slab-like formations, emphasizing the structural response to curing environments. Fig. 9(c) shows that in Group A-B, with 30 % AIII and 20 % AII anhydrous calcium sulfate, the peak values gradually decrease while the characteristic peaks of dihydrate calcium sulfate gradually increase. This indicates that by the 28th day of hydration, hydration reactions or secondary crystallization are still slowly proceeding, and new dihydrate gypsum crystals continue to form.

#### 3.7. SEM-EDS analysis

To better understand the distribution of phases such as DH and AIII, as well as impurities in the multiphase plaster, we conducted SEM-EDS point scanning analysis on the HH and AIII30 %-AII20 % samples after 28 days of hydration, as shown in Fig. 12. Through point elemental analysis using EDS spectra, we can determine the phase composition of the samples based on the elemental ratios. It can be observed that for the HH sample, points 1, 2, and 3 all show high O/Ca ratios, indicating the presence of DH [53,54]. In the AIII30 %-AII20 % sample, points 1 and 2



Fig. 10. SEM images of samples at 1d, 7d and 28d ages under wet curing condition, (a) - (c) blank group, (d) - (f) AIII 30 %, (g) - (i) AII 15 %, (j) - (l) AIII 30 % - AII 20 %.



Fig. 11. SEM spectra of samples at 28 d age under dry curing condition, (a) blank group, (b) AIII 30 %, (c) AII 15 %, (d) AIII 30 %-AII 20 %.

show low O/Ca ratios, which, according to the XRD results, suggest the presence of unhydrated AII. Point 3, however, has a high O/Ca ratio, indicating DH. Additionally, the phosphorus impurities on the surface of the multiphase plaster crystals are found to be less compared to those on the surface of the hemihydrate plaster crystals.

# 3.8. Hydration and hardening mechanism discussion

The hydration mechanism of MPPG is fundamentally governed by the synergistic interactions among its constituent phases (AIII, AII, HH, and DH). As illustrated in Fig. 13, the hydration and hardening processes can be divided into distinct stages, with each phase contributing uniquely to the material's mechanical and durability properties.

In the early stage of hydration, AIII undergoes a rapid reaction upon contact with water, producing a sharp exothermic effect that significantly enhances the early strength of the material. This reaction results in the formation of a dense crystal network, which serves as the initial structural framework. Simultaneously, HH hydrates to form needle-like dihydrate gypsum crystals, which interlock with the AIII matrix, further reinforcing the composite and contributing to the rapid development of mechanical properties [48,55].

As hydration progresses, the role of AII becomes more prominent. AII, acting both as a retarder and a water-absorbing agent, moderates the hydration of HH during the intermediate stage [56,57]. While it initially slows down the hydration process, its delayed reaction promotes the formation of a denser crystalline structure over time [53]. This mechanism enhances the material's later strength by filling voids and improving the densification of the microstructure. Additionally, the delayed hydration of AII stabilizes the moisture resistance of the composite, ensuring its long-term durability.

The interplay between these phases highlights the importance of their relative proportions and hydration kinetics. For instance, When AIII, HH, and DH are combined, upon contact with water, AIII and HH rapidly undergo hydration reactions. The DH crystals formed by these reactions interlock in a dense structure in the form of short prisms. The hydration process releases a large amount of heat, which macroscopically manifests as an increase in early strength. However, the later strength is unstable. When AII, HH, and DH are combined, HH begins to hydrate. However, the presence of AII delays the hydration of HH, while the hydration of HH in turn stimulates the early hydration of AII. The DH crystals formed exist as short prisms and needle-like clusters. The peak



Fig. 12. SEM-EDS spectra of samples at 28 d age under dry curing condition, (a) blank group (HH), (b) (AIII 30 %-AII 20 %).



Fig. 13. Mechanism diagram.

heat release is delayed, and the overall heat release during hydration is reduced. Both early and later strengths are not satisfactory while the integration of AII, HH, and DH phases delays hydration but leads to enhanced microstructural densification and moisture resistance at later stages [58]. When all four phases (AIII, HH, AII, and DH) are combined, AIII and HH quickly hydrate and release a large amount of heat. HH starts to hydrate slightly later than AIII to form DH. AII is stimulated by the combined action of AIII and HH to hydrate early and continuously at a slow rate. In the early stages of hydration, the crystal structure of the hardened body mainly consists of short prisms and unhydrated AII plate-like crystals. As the hydration reaction continues, the DH crystals mainly exist in the form of columnar structures. Macroscopically, this combination results in an increase in early strength and stable development of later strength.

# 3.9. Cost evaluation of PG calcination

The calcination cost of PG and the cost of preparing composite gypsum after calcination are shown in Fig. 14. When calcining PG at 160  $^{\circ}$ C, 300  $^{\circ}$ C and 600  $^{\circ}$ C, the cost increases with the increase of calcination temperature, especially at 600  $^{\circ}$ C. Different composite gypsum was



Fig. 14. The cost of per ton of PG.

obtained by compounding the calcined PG, and the cost of different composite gypsum was estimated. The cost of three groups of composite gypsum was significantly lower than that of high temperature calcined PG. In order to obtain composite gypsum, the demand for gypsum content calcined at different temperatures is different. By reasonably distributing the amount of gypsum calcined at different temperatures, the overall cost can be effectively controlled. The main purpose of this paper is to prepare composite gypsum containing different phases by rationally designing the proportion of gypsum phase distribution, to study the self-regulation mechanism of different phases relative to hydration process under different proportions, and to promote the idea of phase regulation to practical industry.

## 4. Conclusion

This study investigates PG as a primary material, analyzing the influence of different gypsum-phase composites on its hydration, hardening, and performance properties. The composites include three-phase systems with AIII, HH, and DH; AII, HH, and DH; and a four-phase composite combining both AIII and AII with HH and DH. Key findings are as follows:

- (i) In three-phase composites, the addition of AIII significantly enhances early strength in construction gypsum, while AII delays hydration, ensuring gradual strength development. However, when AII exceeds 60 %, it reduces early strength. The optimal four-phase composite (30 % AIII and 20 % AII) greatly improves water resistance, achieving a softening coefficient of 0.81—a 23 % improvement over the control—and yielding compressive strengths 20 % higher at 1 d and 14 % higher at 28 d than the control.
- (ii) In four-phase composites, AIII and HH accelerate early hydration, releasing exothermic heat that aids in initial strength gains. A portion of AII hydrates during this process, while the remaining unhydrated AII enhances moisture resistance by absorbing water molecules later, contributing to sustained strength and durability.
- (iii) SEM analysis shows that MPPG with AIII forms a dense, interlocking crystal structure early on, supporting early strength. In four-phase composites, MPPG exhibits dense early-stage crystals that transition into long, columnar structures over time, fostering both initial strength and long-term stability.

This study demonstrates the effectiveness of combining multiple gypsum phases to control hydration dynamics, offering a strategy for designing advanced multiphase PG with improved performance.

## CRediT authorship contribution statement

Dai Fei: Validation, Software, Formal analysis. Chen Jiaxuan: Validation, Formal analysis, Conceptualization. Li Baodong: Writing – review & editing, Supervision, Resources, Methodology. Peng Bo: Software, Investigation, Formal analysis, Data curation. Gao Xin: Visualization, Software, Formal analysis. Huang Jianxiang: Visualization, Validation, Software. Jian Shouwei: Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition, Conceptualization. He Xinxin: Writing – original draft, Visualization, Methodology, Investigation, Data curation.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Data availability

Data will be made available on request.

## References

- Z.H. Jin, C.J. Cui, Z.H. Xu, W.D. Lu, Y. Su, X.Y. He, S. Chen, W.J. Li, B. Wang, Recycling of waste gypsum from αlpha-hemihydrate phosphogypsum: based on the atmospheric hydrothermal process, Constr. Build. Mater. 377 (2023).
- [2] J. Rosales, S.M. Pérez, M. Cabrera, M.J. Gázquez, J.P. Bolivar, J. de Brito, F. Agrela, Treated phosphogypsum as an alternative set regulator and mineral addition in cement production, J. Clean. Prod. 244 (2020).
- [3] H. Tayibi, M. Choura, F.A. Lopez, F.J. Alguacil, A. Lopez-Delgado, Environmental impact and management of phosphogypsum, J. Environ. Manag. 90 (8) (2009) 2377–2386.
- [4] Y. Wang, H. Huo, B. Chen, Q. Cui, Development and optimization of phosphogypsum-based geopolymer cement, Constr. Build. Mater. 369 (2023).
- [5] J. Yang, W. Liu, L. Zhang, B. Xiao, Preparation of load-bearing building materials from autoclaved phosphogypsum, Constr. Build. Mater. 23 (2) (2009) 687–693.
- [6] E.L. Dong, S.Y. Fu, C.Q. Wu, W. Lv, X. Liu, L.Y. Zhang, Y. Feng, Z.H. Shui, R. Yu, Value-added utilization of phosphogypsum industrial by-products in producing green Ultra-High performance concrete: detailed reaction kinetics and microstructure evolution mechanism, Constr. Build. Mater. 389 (2023).
- [7] M. Pliaka, G. Gaidajis, Potential uses of phosphogypsum: a review, J. Environ. Sci. Health A Tox Hazard Subst. Environ. Eng. 57 (9) (2022) 746–763.
- [8] W. Xu, C. Liu, K. Du, Q. Gao, Z. Liu, W. Wang, A brief review on flue gas desulfurization gypsum recovery toward calcium carbonate preparation, Environ. Sci. Adv. 3 (10) (2024) 1351–1363.
- [9] R. Zhao, B. Wang, B.K.G. Theng, P. Wu, F. Liu, X. Lee, M. Chen, J. Sun, Fabrication and environmental applications of metal-containing solid waste/biochar composites: a review, Sci. Total Environ. 799 (2021) 149295.
- [10] C.D. Min, Y. Shi, Z.X. Liu, Properties of cemented phosphogypsum (PG) backfill in case of partially substitution of composite Portland cement by ground granulated blast furnace slag, Constr. Build. Mater. 305 (4) (2021) 124786.
- [11] N. Papon, V. Courdavault, Editorial overview: microbial and plant enzymes in sustainable chemistry and pharmacy, Curr. Opin. Green. Sustain. Chem. 37 (2022).
- [12] J.X. Zhang, K. Cui, J. Chang, L. Wang, Phosphogypsum-based building materials: resource utilization, development, and limitation, J. Build. Eng. 91 (2024).
- [13] K. Elert, R.A. Alaminos, C. Benavides-Reyes, M. Burgos-Ruiz, The effect of lime addition on weathering resistance and mechanical strength of gypsum plasters and renders, Cem. Concr. Compos. 139 (2023).
- [14] Z.H. Jin, B.G. Ma, Y. Su, W.D. Lu, H.H. Qi, P.H. Hu, Effect of calcium sulphoaluminate cement on mechanical strength and waterproof properties of beta-hemihydrate phosphogypsum, Constr. Build. Mater. 242 (2020) 118198.
- [15] L.M. Baltar, C.A.M. Baltar, M. Benachour, Effect of carboxymethylcellulose on gypsum re-hydration process, Int. J. Miner. Process. 125 (2013) 5–9.
- [16] G. Camarini, M.C.C. Pinto, A.G. de Moura, N.R. Manzo, Effect of citric acid on properties of recycled gypsum plaster to building components, Constr. Build. Mater. 124 (2016) 383–390.
- [17] R.H. Geraldo, A.R.D. Costa, J. Kanai, J.S. Silva, J.D. Souza, H.M.C. Andrade, J. P. Gonçalves, P.S.P. Fontanini, G. Camarini, Calcination parameters on phosphogypsum waste recycling, Constr. Build. Mater. 256 (2020).
- [18] S. Liu, J. Ouyang, J. Ren, Mechanism of calcination modification of phosphogypsum and its effect on the hydration properties of phosphogypsumbased supersulfated cement, Constr. Build. Mater. 243 (2020).
- [19] M. Singh, M. Garg, Making of anhydrite cement from waste gypsum, Cem. Concr. Res. 30 (4) (2000) 571–577.
- [20] X.B. Li, Q. Zhang, Dehydration behaviour and impurity change of phosphogypsum during calcination, Constr. Build. Mater. 311 (Dec.13) (2021) 311.
- [21] N.B.S. A, B.M. B, Calcium sulphate hemihydrate hydration leading to gypsum crystallization, Progress in Crystal Growth and Characterization of Materials 53(1) (2007) 57-77.
- [22] ZongshouLin, Cementitious Materials Science, Wuhan University of Technology, Wuhan, 2019, pp. 257–265.
- [23] P. Ling, Study on influencing factors of hydration properties of anhydrous-semiaqueous complex phase phosphogypsum, Guizhou Univ. Eng. Sci. 41 (3) (2023) 7–11.
- [24] Y. Min, Effect of impurities on the properties of phosphogypsum with different forms, Chongqing University (2008).
- [25] W.C. A, W.Y. B, J.L. C, J.P. B, S.Y. A, A facile approach for large-scale recovery of phosphogypsum: An insight from its performance, Construction and Building Materials 309 (2021) 125190.
- [26] X.M. Chen, Y.Z. Liu, Q.H. Wu, Y. Ding, Q.Y. Wang, W.J. Tang, B.Y. Zhu, Study on physical and chemical characteristics of β-hemihydrate phosphogypsum, Case Stud. Constr. Mater. 17 (2022).

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#### Construction and Building Materials 472 (2025) 140848

- [27] W. Cao, W. Yi, J. Peng, S. Yin, Upcycling of phosphogypsum as anhydrite plaster: The positive effect of soluble phosphorus impurities, Constr. Build. Mater. 372 (2023) 130824.
- [28] Y. Hua, J. Qian, Z. Li, Y. Liu, F. Dai, L. Yuan, X. Jia, Preparation and properties of II-anhydrite calcined from phosphogypsum, Constr. Build. Mater. 412 (2024) 134742.
- [29] I.V. Fornés, D. Vaiiukynien, D. Nizeviien, V. Doroevas, The improvement of the water-resistance of the phosphogypsum by adding waste metallurgical sludge, J. Build. Eng. (Suppl. C) (2021) 102861.
- [30] M.V.S A., L.R.D.R A., M.M.d.A.M a, R.B.D.O B., Phosphogypsum, tropical soil and cement mixtures for asphalt pavements under wet and dry environmental conditions, Resources, Conservation and Recycling 144 (2019) 123-136.
- [31] B. Zhang, C. Xu, Q. Wu, X. Qin, J. Wei, Z. Lu, Experimental study on the mechanical properties of modified phosphogypsum at different loading rates, Sci. Rep. 14 (1) (2024).
- [32] C. Ding, T. Sun, Z. Shui, Y. Xie, Z. Ye, Physical properties, strength, and impurities stability of phosphogypsum-based cold-bonded aggregates, Constr. Build. Mater. 331 (2022).
- [33] S. Zheng, M. Chen, T. Liu, G. Yang, G. Jiang, H. Gu, Research on compressive strength and thermal conductivity of lightweight phosphogypsum-based composite cementitious materials, Constr. Build. Mater. 436 (2024).
- [34] S. Ghignone, Gypsum: from the equilibrium to the growth shapes—theory and experiments, Minerals 14 (2024).
- [35] B. Madeja, J. Avaro, D.A.E.S. Van, M. Ruckel, E. Wagner, H. Colfen, M. Kellermeier, Tuning the growth morphology of gypsum crystals by polymers, Cem. Concr. Res. (2023).
- [36] Y. Chengjun, Y. Min, C. Jianxin, Study on hydration and hardening of duplex gypsum binder of hemihydrite phosphogypsum and anhydrite phosphogypsum, Non-Met. Mines 37 (6) (2014) 4.
- [37] Y. Tian, Z. Li, S. Wang, Y. Zhou, D. Li, L. Fu, Application of MICP in water stability and hydraulic erosion control of phosphogypsum material in slope, Appl. Sci. 12 (4) (2022) 1783.
- [38] F. Beaugnon, J.G.D. Preturlan, F. Fusseis, E. Gouillart, S. Quiligotti, G. Wallez, From atom level to macroscopic scale: structural mechanism of gypsum dehydration, Solid State Sci. 126 (2022) 106845.
- [39] Y. Tang, J. Gao, C. Liu, X. Chen, Y. Zhao, Dehydration pathways of gypsum and the rehydration mechanism of soluble anhydrite γ-CaSO 4, Acs Omega 4 (4) (2019) 7636–7642.
- [40] L. Feng, K. Jin, H. Wang, Research on the thermal conductivity and water resistance of foamed phosphogypsum, Coatings 11 (7) (2021).
- [41] I. Lebron, J. Herrero, D.A. Robinson, Determination of gypsum content in dryland soils exploiting the gypsum-bassanite phase change, Soil Sci. Soc. Am. J. 73 (2) (2009) 403–411.
- [42] J. Karni, E.Y. Karni, Gypsum in construction: origin and properties, MaterialsStructures 28 (2) (1995) 92–100.

- [43] X. Chen, Q. Wang, Q. Wu, X. Xie, S. Tang, G. Yang, L. Luo, H. Yuan, Hydration reaction and microstructural characteristics of hemihydrate phosphogypsum with variable pH, Constr. Build. Mater. 316 (2022) 125891.
- [44] D. Xu, Y. Huang, W. Liu, T. Sun, M. Zhang, Preparation of composite microencapsulated phase change material based on phosphogypsum for passive building applications, Constr. Build. Mater. 378 (2023).
- [45] L. Tao, F. Deng, K. Xu, X. Dong, D. Xu, Y. Liao, S. Tang, Effect of calcium sulfoaluminate cement on the hydration process and water resistance of phosphogypsum slag cement, J. Mater. Res. Technol. 33 (2024) 5375–5383.
- [46] Y. Liao, J. Yao, F. Deng, H. Li, K. Wang, S. Tang, Hydration behavior and strength development of supersulfated cement prepared by calcined phosphogypsum and slaked lime, J. Build. Eng. 80 (2023) 108075.
- [47] Y. Wang, L. Xu, X. He, Y. Su, W. Miao, B. Strnadel, X. Huang, Hydration and rheology of activated ultra-fine ground granulated blast furnace slag with carbide slag and anhydrous phosphogypsum, Cem. Concr. Compos. 133 (2022) 104727.
- [48] Q.L. Yu, H.J.H. Brouwers, A.C.J.D. Korte, Gypsum hydration: a theoretical and experimental study (2009).
- [49] G.T. 36141-2018, Methods for phase composition analysis of calcined gypsum, State Administration of Market Supervision and Administration China National Standardization Administration (2012).
- [50] M. Singh, M. Garg, S.S. Rehsi, Durability of phosphogypsum based water-resistant anhydrite binder, Cem. Concr. Res. 20 (2) (1990) 271–276.
- [51] C. Kothari, N. Garg, Quantitative phase analysis of anhydrous Portland cement via combined X-ray diffraction and Raman imaging: synergy and impact of analysis parameters, Cem. Concr. Res. 186 (2024) 107662.
- [52] R. Fu, Y. Lu, L. Wang, H. An, S. Chen, D. Kong, The effects of admixtures on the durability properties of phosphogypsum-based cementitious materials, Constr. Build. Mater. 411 (2024) 134379.
- [53] Z. Wang, W. Lan, Z. Jia, M. Lin, D. Li, Research on the mechanical properties of composite grouting materials based on ordinary portland–sulphoaluminate cement, Buildings 14 (11) (2024).
- [54] Y.W. Wang, Y.Y. Kim, H.K. Christenson, F.C. Meldrum, A new precipitation pathway for calcium sulfate dihydrate (gypsum) via amorphous and hemihydrate intermediates, Chem. Commun. 48 (2011).
- [55] A.J. Lewry, J. Williamson, The setting of gypsum plaster, J. Mater. Sci. 29 (20) (1994) 5279–5284.
- [56] X. Zhou, Y. Zhao, H. Zhu, Q. Zhou, Performance activation and strength evolution mechanism of carbide slag on anhydrous phosphogypsum backfill material, Constr. Build. Mater. 419 (2024) 135503.
- [57] Y. Zhao, X. Zhou, Q. Zhou, H. Zhu, F. Cheng, H. Chen, Optimization design of anhydrous phosphogypsum-based backfill materials incorporating carbide slag and blast furnace slag by response surface method, Miner. Eng. 215 (2024) 108820.
- [58] L. Zeng, W. Wang, S. Xiong, S. Wang, J. Zhang, Dehydration behaviors and properties of anhydrite II prepared by phosphogypsum with low-temperature calcination, Constr. Build. Mater. 438 (2024) 136936.