Review

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Review

Application and Development Prospects of Phosphogypsum in Different Phases: A Review

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Abstract: The phosphogypsum (PG) pile of solid waste is of immense proportions and poses a grave threat to the ecological environment, with its reserves steadily increasing year after year. The urgent need for large-scale consumption and high-quality utilization of PG in industrial production has become apparent. The present study provides a comprehensive analysis of the correlation between the macroscopic mechanical properties and microstructure of PG, elucidating the crystal morphology characteristics in different phases and outlining the crystallization preparation process. By integrating the physical and chemical properties of diverse PG phases with the intricacies associated with its preparation process, it is imperative to explore avenues for its high-value utilization, investigate possibilities for industrial-scale production, and analyze and predict the application trends and developmental directions in comprehensive PG utilization. These endeavors hold immense significance in guiding the realization of resource utilization potential inherent in PG.

Keywords: solid waste; phosphogypsum phases; crystal morphology; mechanical properties; comprehensive utilization

1. Introduction

The phosphate fertilizer industry plays a pivotal role in both the chemical sector and the national economy, with phosphoric acid serving as a vital raw material in its production[1]. However, the production of 1 ton of phosphoric acid results in the emission of 5 tons of phosphogypsum (PG)[2],. The PG contains soluble phosphorus, fluorine, organic matter, and other impurities[3], Low strength, acidic, pH around 3[4]. These defects restrict the utilization of PG to storage in warehouses, hindering its full potential. The global cumulative stockpile of PG has surpassed 6 billion tons[5] and continues to grow at a rate of 280 million tons per year[6]. However, the accumulation of a substantial amount of PG not only occupies a significant land area that could have been utilized for agricultural activities but also leads to the migration of impurities into water and soil through leachate, thereby continuously deteriorating the environmental quality in the surrounding areas. For instance, The PG generated in the Spanish city of Huelva over a span of 40 years was directly discharged into the estuary of the Huelva River, resulting in persistent water pollution that will endure for approximately three decades[7,8]. The effects of PG dumps on surface water systems in southern Brazil were investigated by Barros de Oliveira et al., revealing significantly elevated levels of Barium, Zirconium, and Thorium in water sediments compared to the local background level[9]. The North Florida region currently stores approximately 100 million tons of PG[10], which contains radium concentrations ranging from 3 to 26 pCi/g. Consequently, the United States Environmental Protection Agency strictly prohibits the utilization of PG exceeding a radium concentration threshold of 10 pCi/g [11]. The Poland's Vitowski chemical plant has accumulated more than 5 million tons of PG containing rare earth elements, which is classified as a key raw material in the European Union (EU) [12]. Russia has accumulated over 500 million tons of PG.[13]. Due to the environmental and human health risks associated with PG the dumping of this substance into the sea or its storage in controlled warehouses is prohibited by EU environmental legislation. [14]. Therefore, the realization of harmless treatment and resource utilization of PG is crucial in preventing environmental pollution, alleviating government pressure, and meeting material market demands. However, current utilization methods still face several challenges:

1. Technical or cost difficulties exist in the current utilization process for PG, and the comprehensive utilization rate remains low at less than 25%[15].
2. The large stock of PG piles necessitates a corresponding market for its extensive consumption.
3. Downstream products derived from PG have low added value and suffer from serious homogenization.

To enable large-scale consumption of PG, it is imperative to enhance the value of its products and expand the market for them. And the material's mechanical properties are inherently linked to its crystal structure. The PG ($CaSO_4{\cdot}2H_2O$)[16] can undergo phase transformations into six distinct crystal phases: dihydrate gypsum ($CaSO_4{\cdot}2H_2O$), hemihydrate gypsum (α-$CaSO_4{\cdot}0.5H_2O$ and β-$CaSO_4{\cdot}0.5H_2O$), and anhydrate gypsum (I-$CaSO_4$, II -$CaSO_4$, III-$CaSO_4$)[17]. The scanning electron microscopy (SEM) diagram in Figure 1 illustrates the diverse phases of gypsum, revealing an irregular and sheet-like microscopic morphology of PG crystals with a significant presence of fine particles. Consequently, this characteristic contributes to diminished strength and negligible improvements in the mechanical properties of PG products[18,19]. The presence of hemihydrate gypsum and anhydrous gypsum crystal surface fine particles leads to a significant reduction, thereby enhancing the mechanical properties. Notably, β-hemihydrate gypsum and anhydrous gypsum crystals exhibit a plate or sheet-like structure similar to PG, facilitating their preparation[20,21]. The α-hemihydrate gypsum exhibits a hexagonal prism shape that is more regular, resulting in superior mechanical properties[22]. The mechanical properties and hydration characteristics of PG vary across different phase states, thereby offering a broader scope for the comprehensive utilization of this material. Figure 2 illustrates the process route for preparing PG into various phase states, aiming to explore the potential of high-value resource products derived from PG by analyzing its preparation process and physical and chemical properties in different phases. This study aims to enhance the reference and guidance for optimizing the utilization process.

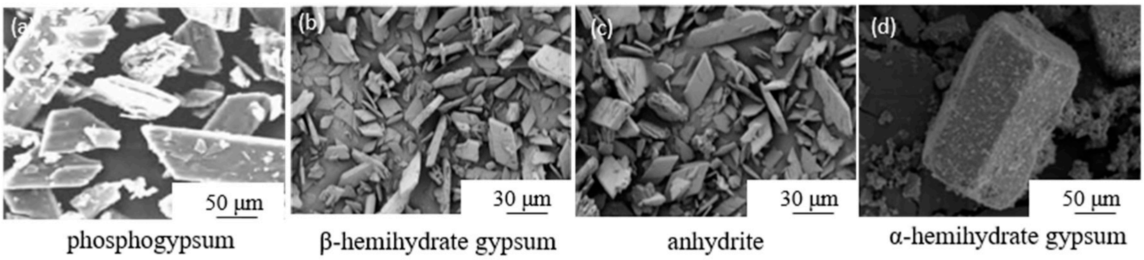


Figure 1. The SEM images depict various phases of gypsum. [18,23]. (a) PG: 50μm; (b) β-hemihydrate gypsum: 30μm; (c) anhydrite: 30μm; (d) α-hemihydrate gypsum: 50μm.

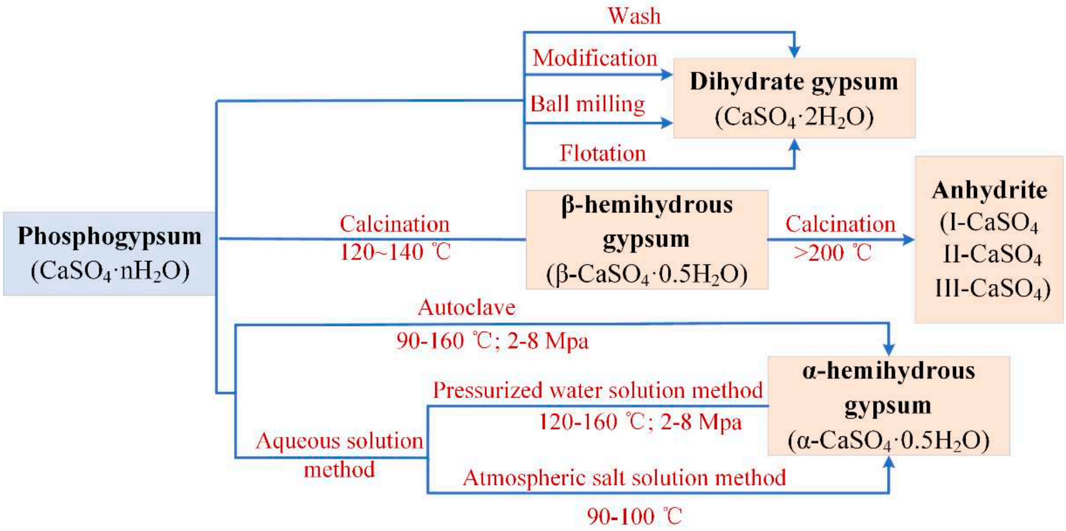
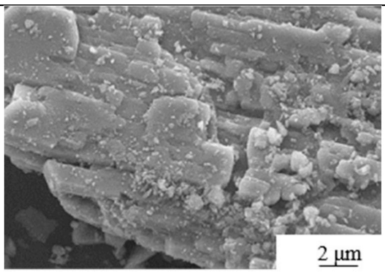
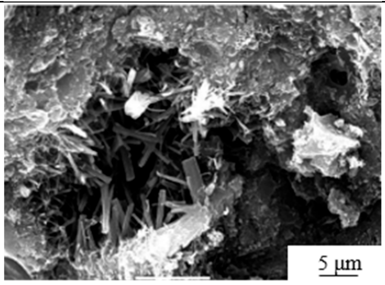
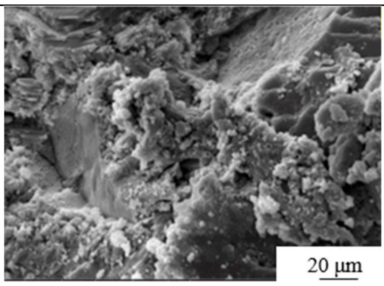
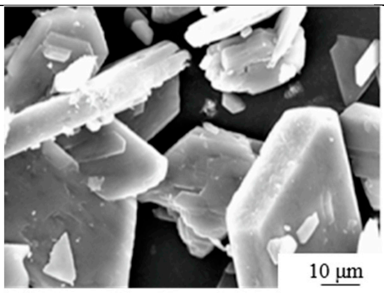


Figure 2. Process for preparing PG based powder materials[24–28].

2. Dihydrate Gypsum

The PG can undergo various pretreatment processes, such as washing, ball milling, modification, and flotation, to effectively eliminate the majority of impurities without inducing any phase change. As a result, the primary constituent of PG with pretreatment remains gypsum dihydrate. Shun Chen[29] et al. enhanced the conventional washing process and successfully achieved efficient water-saving purification of PG by integrating mechanical activation method with chemical solubility method. By disrupting the chemical bonds within PG crystals through grinding and enhancing the chemical microenvironment, they accomplished grain refinement of PG, resulting in a successful increase in whiteness from -9.84 to 63.37. Moreover, the soluble phosphorus content decreased from 0.366 ppm to 0.043 ppm, as observed in SEM images depicting thin and rod-like morphology of treated PG. Xiangguo Li [30] prepared the cementing material of PG-lime-fly ash system, and used mechanical grinding to improve the particle size distribution. The 28 days compressive strength of the prepared specimen reached 27.76 MPa. The microstructure of the specimen is shown in Figure 5. It can be observed that the sample structure is very dense, and the hydrated products formed fill between the skeleton. Xingli Bei[31] et al. employed calcium carbide slag and circulating fluidized bed fly ash, along with other solid wastes, for comprehensive modification of PG required in the production of cement retarder. Experimental findings demonstrated that incorporating 6wt% calcium carbide slag and 4wt% CFB fly ash into PGyielded optimal results by significantly enhancing its strength after a 7-day aging period, rendering it suitable as a cement retarder. The modified PG exhibited the highest flexural strength (6.6 MPa) and compressive strength (34.4 MPa). SEM images revealed that the cement prepared using modified PG displayed enhanced hydration levels, characterized by abundant formation of C-S-H gels and an overall denser structure. Fang Ji[32] et al. employed the "reverse direct flotation" technique, which resulted in a PG concentrate with enhanced whiteness of 63.42 and a $CaSO4·2H_2O$ concentration of 96.70% after closed-circuit flotation. The SiO_2 content decreased significantly from 11.11% to merely 0.07%, while achieving an impressive gypsum recovery rate of up to 85%. SEM images demonstrated the successful elimination of fine particles and quartz particles, leaving behind clean and smooth surfaces on the PG particles. To further elucidate the intricate relationship among process preparation, experimental conditions, and crystal morphology, Table 1 presents a comprehensive comparison of crystal morphologies across different process routes.

Table 1. Comparison of preparation process conditions and product morphology of Dihydrate Gypsum.

Process	Experiment Condition	Crystal Morphology
Modified water washing[29]	Mechanical activation + Water phase grinding Micellar agent: CH_3COOH，Al_2O_3	
Mechanical grinding[30]	PG: fly ash: lime mass ratio of 50:30:20 mixed Grinding time: 15min Sample preparation additives: 5% cement, 3% AC reinforcer and 0.5% polycarboxylic acid water reducer	
Modification[31]	Modifier: 6wt% calcium carbide slag and 4wt%CFB fly ash	
Reverse direct flotation[32]	Collector: Kerosene Foaming agent: industrial grade pine oil	

Due to its similar composition to natural gypsum and even higher calcium sulfate dihydrate content [33], PG can serve as a substitute for natural gypsum as a cement retarder or cementing material. In the microstructure of many cement applications utilizing PG, the hardened paste structure exhibits greater density and increased cement strength[34]. As reported in Japan, PG has been successfully utilized as a cement retarder in place of natural gypsum, accounting for 1/3 to 1/4 of total PG utilization [35]. However, due to immature technology, fluctuating product quality and lack of price advantage, widespread promotion of PG-based cement retarders is currently limited.

3. Hemihydrate Gypsum

As one type of hemihydrate gypsum, the α- hemihydrate gypsum is formed by dissolving and recrystallization of dihydrate gypsum in saturated water vapor medium or aqueous solution. The α-hemihydrate gypsum is slightly soluble in water, soluble in strong acid and alkali, and belongs to air-hard gelling material [36]. The β-hemihydrate gypsum, the other type of hemihydrate gypsum, is obtained through the high-temperature calcination of dihydrate gypsum, resulting in the loss of 1.5 crystal water molecules. Due to the direct removal of water during the calcination process, numerous voids are formed, leading to a collapse in the crystal structure of β- hemihydrate gypsum. This results in an irregular morphology with abundant surface pores and low strength, consequently reducing its economic utilization value [37]. The Figure 3 illustrates the cellular structures of two types of hemihydrate gypsum crystals.

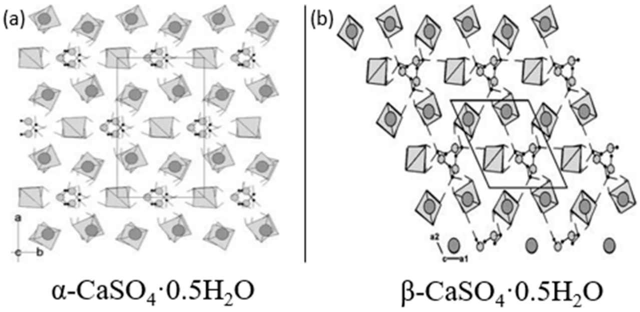


Figure 3. Cell structure diagram of gypsum crystal [38]. (a) α-$CaSO_4 \cdot 0.5H_2O$; (b) β-$CaSO_4 \cdot 0.5H_2O$.

3.1α-. Hemihydrate Gypsum

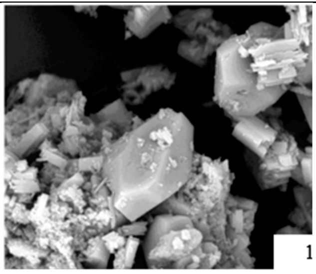
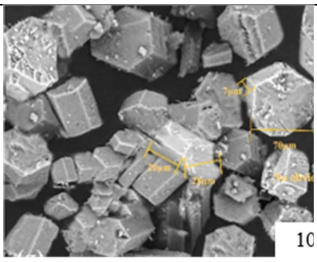
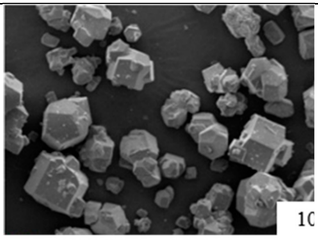
The preparation methods of α- hemihydrate gypsum can be divided into two categories according to the dehydration method: autoclave method and aqueous solution method, and aqueous solution method can be divided into pressurized aqueous solution method and atmospheric pressure salt solution method according to different pressures[39], as shown in Table 2.

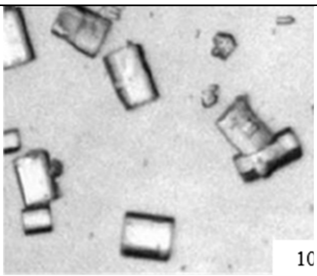
Table 2. Preparation technology and advantages and disadvantages of α- hemihydrate gypsum

Process		Principle	Advantage	Disadvantage
Autoclave		Process of heating and pressurization in saturated water vapor removing of 1.5 molecules of water	1) Simple process 2) High yield 3) Easily control of process [40]	1) High temperature 2) High pressure 3) High energy consumption 4) High cost [18]
Aqueous solution method	Pressurized water solution method	Crystallization reaction of PG and water solution under pressure	High product quality	1) Complicated process 2) Subsequent dehydration increasing the cost 3) High energy consumption [41]
	Atmospheric salt solution method	Crystallization reaction between PG and salt solution at atmospheric pressure	1) Mild reaction conditions 2) Not requiring special equipment 3) Easily control of conversion process and product quality [42]	1) Low yield 2) Corrosion of sodium, magnesium, and calcium plasma to the equipment [18]

To further elucidate the intricate relationship among process preparation, experimental conditions, crystal morphology, and material strength, Table 3 presents a comprehensive comparison of crystal morphologies across different process routes. The [G was initially pretreated using the ball milling method by Hongbin Tan et al.[43] Subsequently, a mixture of gypsum and tap water in a mass ratio of 1:5 was introduced into an autoclave, followed by the addition of maleic acid to adjust the solution's pH value to 5. After stirring for 30 minutes and aging at 140℃ for 2 hours, the product flexural strength /compressive strengths of 8.2 MPa/25.4 MPa. The SEM image revealed a smooth crystal surface with a short columnar morphology. α-hemihydrate gypsum was prepared by flotation + autoclaving method under the guidance of Mingxia Du et al[44]. The optimal mechanical properties, with a compressive strength of 40.96 MPa and a flexural strength of 6.09 MPa, were achieved when the reaction temperature was set at 140℃ for 120 minutes, with aluminum sulfate and Maleic acid contents of 2.0wt% and 0.13wt%, respectively. The resulting product exhibited diamond-shaped crystal morphology with a plate structure, minimal presence of fine particles, a length-diameter ratio (L/D ratio) of 0.7, and small pore size. Wenda Lu[45] et al. employed the atmospheric pressure salt solution method to synthesize α-hemihydrate gypsum in a circulating $CaCl_2$ solution. The highest flexural and compressive strength of the product, achieved through alcohol-washing and drying at 97±1℃ for 120 minutes, reached 4.7 MPa and 37.6 MPa respectively. In the SEM images of the product, the crystals exhibited a short prism-like shape with regular morphology and a length-to-diameter ratio close to unity. The pressurized aqueous solution method was employed by Jinshui Shen et al. [46] to synthesize short columnar crystals with a L/D ratio of 1.5 at a reaction temperature of 130℃, an EDTA content of 0.40%, and pH=7 for a duration of 4 hours.

Table 3. Comparison of preparation process conditions and product morphology and properties of α-hemihydrate gypsum

Process	**Experiment Condition**	**Crystal Morphology**	**Flexural Strength**	**Compressive Strength**	**L/D ratio**
Ball milling + Autoclave [43]	pH: 5 Temperature: 140℃ Autoclave time: 2 hours Crystal modifier: Maleic acid		8.2	25.4	—
Flotation + Autoclave [44]	Temperature: 140℃ Autoclave time: 2 hours Crystal modifier: 0.13wt% Maleic acid 2.0wt% Aluminum sulfate		6.09	40.96	0.7: 1
Atmospheric salt solution [45]	Temperature: 97±1℃ Time: 2 hours Crystal modifier: maleic acid		4.7	37.6	1.0: 1

Pressurized aqueous solution [46]	Temperature: 130℃ pH: 7.0 Autoclave time: 4 hours Crystal modifier: EDTA		—	—	1.5: 1

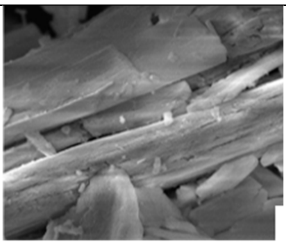
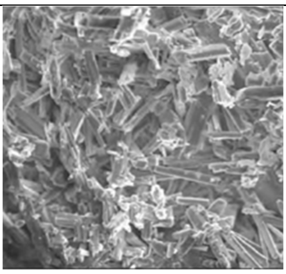
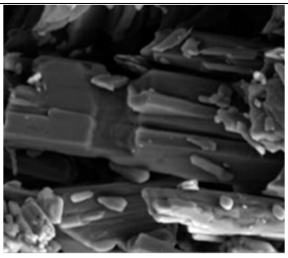
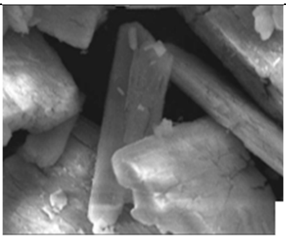
The studies have demonstrated that the mechanical properties of crystals are enhanced when their shape exhibits a L/D ratio ranging from 2:1 to 4:1, leading to flexural/compressive strengths exceeding 6/35 MPa [47]. The α-hemihydrate gypsum exhibits high strength and excellent water resistance, rendering it suitable for the production of novel wall materials, self-leveling compounds, fireproof door core panels, and other decorative and construction materials [48]. However, due to the complex process and high production cost of PG preparation of α-hemihydrate gypsum, large-scale industrial application is difficult, and the laboratory and semi-works scale are still the main scale.

3.2. β-Hemihydrate Gypsum

Currently, the primary method for preparing β-hemihydrate gypsum in China is through a calcination process. Table 4 provides a comparison of preparation conditions and crystal morphology across various processing routes. The calcination process was adopted by Rodrigo H. Geraldo et al.[49], and the experimental results demonstrated that a temperature of 150℃ and a residence time of 2 hours were optimal parameters for achieving significant β-hemihydrate gypsum content with low energy consumption, resulting in a compressive strength of 6 MPa. SEM characterization revealed elongated and prismatic crystals with uniform distribution and size, indicating excellent crystal interlacing. The β-hemihydrate gypsum was prepared by Guang Yang et al. [50] using a concentration of 0.5% polycarboxylic acid superplasticizer (PS-L). This resulted in the reduction of thick plate crystal type and improved the bonding between crystals, thereby enhancing the mechanical properties and achieving compressive/flexural strength values of 14.8/3.8 MPa. β-hemihydrate gypsum was prepared by Meng Liu et al. [51] through a washing + calcination process, where the gypsum was calcined for 1 hour at 130℃. SEM characterization revealed that the hydration products of the washed samples exhibited predominantly rod-shaped crystals with enhanced bonding strength, thereby improving the mechanical properties of the gypsum products, and the 2 hours compressive/flexural strength of the products was 5.7/3.0 MPa. Longjian Zhang et al.[52] discovered that, under the experimental conditions of calcination at 180℃ for 4 hours, PG underwent complete transformation into β-hemihydrate gypsum. At this stage, the product exhibited a compressive strength of 9.2 MPa after 28 days. Furthermore, SEM characterization revealed the presence of numerous interlocked columnar crystals in the microstructure, which significantly enhanced the mechanical properties of the material.

The β-hemihydrate gypsum exhibits a scale-like morphology with fine particles, rendering it easily manageable and controllable [50]. However, due to its relatively lower strength compared to α-hemihydrate gypsum, its performance slightly lags behind. Consequently, it finds frequent application in decorative materials such as gypsum boards and putties that demand lower strength requirements. Currently, the industrial-scale production of β-hemihydrate gypsum from PG has surpassed that of α-hemihydrate gypsum [53], representing a significant pathway for large-scale utilization of PG in China [54]. Nevertheless, the prevailing process still faces technical challenges including suboptimal heat transfer efficiency, excessive energy consumption, inconsistent product quality, and limited production capacity that necessitate further resolution [28].

Table 4. Comparison of preparation process conditions and product morphology and properties of β-hemihydrate gypsum

Process	Experiment Condition	Crystal Morphology	Flexural Strength	Compressive Strength
Pre-grinding + calcination[55]	Temperature: 150℃ Calcination time: 2 hours		—	6.0
Calcination[50]	Temperature: 130℃ Autoclave time: 3 hours Polycarboxylate superplasticizer: 0.5 %		3.8	14.8
Washing + calcination[51]	Temperature: 130℃ Calcination time: 1 hours		3.0	5.7
Calcination[56]	Temperature: 180℃ Calcination time: 4 hours		—	9.2

4. Anhydrite

The distribution of Ca^{2+} and SO_4^{2-} leads to the formation of three distinct phase states in anhydrous gypsum crystals: Type III anhydrous gypsum (III-$CaSO_4$), type II anhydrous gypsum (II-$CaSO_4$), and type I anhydrous gypsum (I- $CaSO_4$) [57]. Figure 3 illustrates the conversion conditions for these three types of anhydrous gypsum. When the temperature of PG calcination exceeds 200°C, type III anhydrous gypsum is initially formed, which contains a small amount of crystal water and exhibits strong hydrophilicity, facilitating its conversion into semi-hydrous gypsum in humid environments. At calcination temperatures above 350°C, type III anhydrous gypsum transforms into type II anhydrous gypsum or natural anhydrite characterized by dense and stable crystalline phase with potential hydration properties; however, the hydration rate is relatively slow. Upon reaching a calcination temperature exceeding 1100°C, type I anhydrous gypsum is produced, which is soluble in water but has no hydration activity [58–60]. Among them, type II anhydrous gypsum possesses significant application value due to its inherent stability in nature and distinctive hydration characteristics. The subsequent sections will meticulously analyze and compare the preparation technology as well as morphology characteristics of type II anhydrous gypsum. Table 5 provides a comprehensive summary of the preparation conditions and crystal morphology comparison across different process routes.

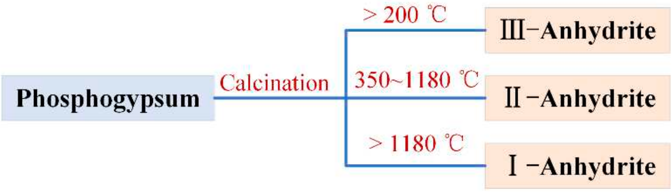
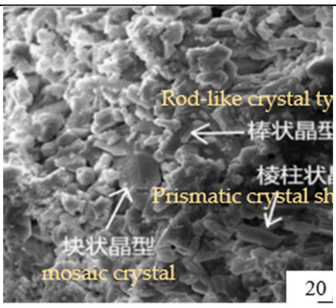
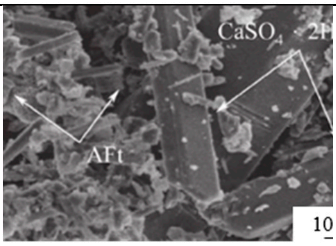
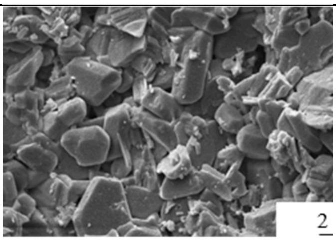
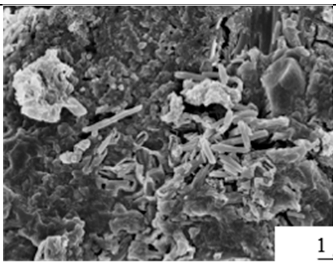


Figure 3. Calcination temperature conditions for preparation of anhydrite from PG

Table 5. Comparison of preparation process conditions and product morphology and properties of II- anhydrite

Process	Experiment Condition	Crystal Morphology	Flexural Strength	Compressive Strength
Calcination + grinding[61]	Temperature: 800℃ Calcination time: 1.6 hours Potassium alum + LA-1		＞6.5	36.5
Calcination[62]	Complexing agent (β-hemihydrate gypsum 6%、Modified steel slag 3%、K_2SO_4 2%、Calcium aluminate cement 0.5%)		＞5	15.4
Calcination [63]	Temperature: 800℃ Calcination time: 1 hours Addition: Ca (H_2PO_4) ·H_2O and NaF		＞6	＞20
Calcination[64]	Temperature: 600℃ Calcination time: 1.5 hours		7-12	25-100

The type II anhydrous gypsum was prepared by Qiang Bi et al. [61] through the combination of potassium alum with home-made lignin-based surface activity (LA-1) at a calcination temperature of 800°C, holding time of 1.5 hours, and subsequent grinding until the specific surface area reached 463 m^2/kg. Under these conditions, prismatic crystals were formed, interlacing with each other to create dense structures. Additionally, numerous slender rod-like crystal structures were present, effectively filling the pores and enhancing structural integrity. The resulting sample exhibited a measured compressive strength of 36.5 MPa and flexural strength exceeding 6.5 MPa. The composite agents developed by Yu Zhang et al. [62] consisted of β-hemihydrate gypsum (6%), modified steel slag (3%), K_2SO_4 (2%), and calcium aluminate cement (0.5%) to address the issues of low hydration activity, slow setting, and hardening in type II anhydrous PG. Through microstructural analysis, it was observed that pin and rod-like ettringite crystals were generated and closely bonded with amorphous cementing substances. This resulted in the formation of a network of crystalline structure composed of gypsum dihydrate, leading to improved mechanical properties of the material. The compressive strength of the prepared cementitious material was measured to be 15.4 MPa, while the flexural strength exceeded 5 MPa. Wenxiang Cao et al.[63] mixed PG with $Ca(H_2PO_4)\cdot H_2O$ and NaF solution evenly, and calcined at 800℃ for 1 hour after aging at room temperature for 1 day. The anhydrate gypsum prepared for 28 days had a compressive strength of more than 20MPa and a flexural strength of more than 6MPa. After observation of the product microstructure, it was found that the crystals were short columnar or emulsion, with good overlap and stacking. It has a dense microstructure. Shuhua Liu et al.[64] found through experiments that PG calcined at 600℃ and 800℃ was almost completely dehydrated into anhydrite, and II-U anhydrite and II-E anhydrite were obtained. Moreover, the anhydrite obtained at 600℃ for 1.5 hours had the highest compressive strength, up to 54.6MPa. It can be seen from the observation of sample microstructure that the crystal structure is compact. A small amount of limulus and ettringite, a large amount of calcite and a small amount of vaterite were observed on the surface of the fractures.

Compared with PG, type II anhydrous gypsum eliminates the adverse effects of harmful impurities. Furthermore, it exhibits significantly enhanced water resistance compared to α-hemihydrate gypsum. In addition, it possesses superior physical and chemical properties in comparison to β-hemihydrate gypsum [65], thereby meeting more stringent requirements for building materials such as road construction and mine filling [66]. However, the preparation of high-quality type II anhydrous gypsum from PG requires a slow burning process, and the conditions for complete removal of crystal water and impurities are stringent. Currently, there is no calcination production line in China capable of producing single-phase anhydrous type II gypsum. And β-hemihydrate gypsum and II- anhydrite complex phase gypsum can only be produced by some enterprises [28].

5. Conclusions

Due to the distinct crystal morphology of PG in different phases, its physical and chemical properties vary, leading to diverse preparation processes. In order to achieve large-scale consumption and storage of PG, alleviate environmental pressure, optimize product quality along the utilization path, enhance product added value, and Improve the comprehensive utilization rate of PG, this study conducts the following analysis:

1. the harmless treatment of PG for producing dihydrate gypsum can serve as a cement retarder. The process is straightforward and supported by well-developed technologies. However, due to its non-competitive price, the cement industry heavily relies on natural gypsum, resulting in saturated market demand. Therefore, national and local policies are needed to promote the application's development.
2. The use of hemihydrate gypsum is predominantly observed in the construction industry. In comparison to β-hemihydrate gypsum, α-hemihydrate gypsum exhibits superior physical and mechanical properties. In comparison to anhydrous gypsum, α-hemihydrate gypsum consumes less energy and facilitates scaling, thereby promoting the high-quality development of PG building materials. Consequently, the production of α-hemihydrate gypsum from PG is expected to become the dominant trend in the comprehensive utilization of PG for building materials in the future.
3. type II anhydrous gypsum exhibits high strength, excellent water resistance, chemical corrosion resistance, and toughness. Moreover, its production capacity is significantly higher than that of β-semi-water gypsum. It can be utilized not only in road construction and mine filling materials to achieve significant consumption of PG, but also in the preparation of gypsum whiskers for applications such as paper fillers, rubber compounds, paints, and other advanced processing of novel materials. However, the production of type II anhydrous gypsum is constrained by the

high calcination temperature involved in the preparation process. Moreover, type II anhydrous gypsum exhibits limited hydration activity and slow setting and hardening characteristics, necessitating careful consideration of modification treatments during its application.

Conducting comprehensive theoretical research and practical exploration on the resource utilization of phosphogypsum, enhancing the quality of phosphogypsum products, and ensuring the technological feasibility for industrial production can foster a global recognition that regards phosphogypsum as a secondary resource. This will effectively facilitate the realization of a new paradigm in which phosphogypsum is comprehensively utilized across various domains.

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