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Preparation of α -calcium sulfate hemihydrate from industrial by-product gypsum: a review

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Abstract: In recent years, the massive accumulation of industrial by-product gypsum, especially flue gas desulfurization (FGD) gypsum and phosphogypsum (PG), not only encroaches on lands but also causes serious environmental pollution. The preparation of α -calcium sulfate hemihydrate (α -HH) from industrial by-product gypsum is an important way to solve the massive accumulation. α -HH possessing larger, dense and well-grown crystals with fewer cracks and pores has high added value and a wide range of application. Hitherto the preparation methods of α -HH from industrial by-product gypsum mainly include the autoclave process, salt/acid solution process, or alcohol-water solution process. Thereinto, the autoclave process is the only method to realize industrialization. In order to solve the high energy consumption and unfavorable continuous operation of the autoclave process, researchers suggested alternative approaches, such as salt/acid solution process and alcohol-water solution process. However, these methods are basically in the laboratory stage or pilot scale test at present. Compared with FGD gypsum, the utilization rate of PG with a larger emission is very low owing to the high impurity content. And combining the preparation of α -HH with the recovery of valuable impurities from PG seems a promising way to solve the bulk deposition of PG.

Keywords: α -calcium sulfate hemihydrate, industrial by-product gypsum, FGD gypsum, phosphogypsum, preparation method

1. Introduction

1.1. α -calcium sulfate hemihydrate

Calcium sulfate hemihydrate generally exists in two forms, i.e., α - and β -forms. As an important building material, the industrial production and application of β -form began more than 100 years ago. In Recent years, due to superior workability, better biocompatibility, and more excellent performance, α -form possessing larger, dense and well-developed crystals with fewer cracks and pores has a wide range of applications. For instance, α -HH particles with a low aspect ratio or spherical shape possess better injectability and higher mechanical strength, and are preferable for using in ceramic molds, precision casting and dental materials. And α -HH whiskers with high aspect ratio has extremely high tensile strength and elastic modulus, and can be used as material reinforcing components, friction materials and other materials. (Luo et al., 2010; Thomas and Puleo, 2009; Jung et al., 2010; Peng et al., 2008).

So far, the crystal structure of α -calcium sulfate hemihydrate (α -HH) has not been completely determined, and even the crystal water content is controversial (Note: the term "hemihydrate" is not

strictly limited to $n=0.5$ in $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$). Some researchers believe that α - and β -HH have the same crystal structure, and the observed differences between the two should result from other properties such as lattice imperfections, particle size and grain orientation (Bensted and Prakash, 1968; Goto et al., 1966). However, no one heretofore has given a persuasive explanation for the distinguished different behaviors upon heating between the two forms (Dantas et al., 2007). Recent studies tend to support a viewpoint that the two structures are different. From the research results we can basically confirm that the α -HH crystal structure is monoclinic, space group C2 (I2, I121) (No. 5) (Christensen et al., 2010; Prince and Wilson, 2004), even if various scholars got slightly different research results for the specific unit cell parameters (Table 1). In the crystal structure the Ca^{2+} - SO_4^{2-} -chains directed along the c axis forms channels that accommodate the water molecules, as shown in Fig. 1.

Table 1. Literature overview of recent published α -HH structures

Formula	a/Å	b/Å	c/Å	$\beta/^\circ$	Crystal system, Space group	Ref.
$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	17.5180(8)	6.9291(1)	12.0344(2)	133.655(1)	Monoclinic, C2	H. Schmidt et al. (Schmidt et al., 2011)
$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	17.559(3)	6.9619(7)	12.071(2)	133.56(1)	Monoclinic, C2	H. Weiss et al. (Weiss and Braeu, 2009)
$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	12.027(1)	6.918(1)	12.613(1)	90.29(1)	Monoclinic, I121	A.N.Christensen et al. (Christensen et al., 2008)
$\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$	12.0317(4)	6.9269(2)	12.6712(3)	90.27(1)	Monoclinic, I121	C. Bezou et al. (Bezou et al., 1995)
$\text{CaSO}_4 \cdot 0.53\text{H}_2\text{O}$	12.028	6.931	12.692	90.18	Monoclinic, I2	H. J. Kuzel et al. (Kuzel and Hauner, 1987)
$\text{CaSO}_4 \cdot 0.67\text{H}_2\text{O}$	12.028	6.927	12.674	90.21	Monoclinic, I2	N.N. Bushuev et al. (Bushuev, 1982)

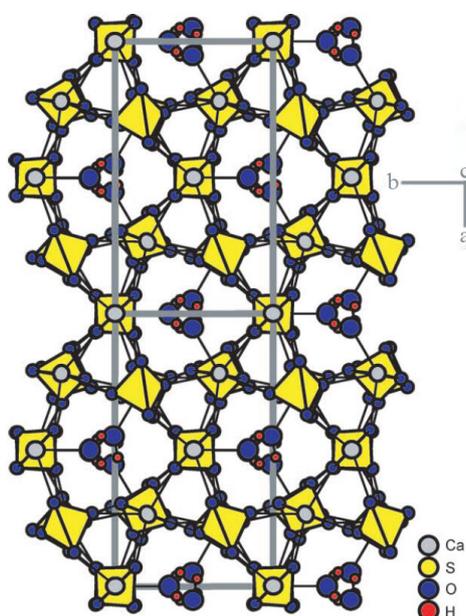


Fig. 1 Part of the α -HH crystal structure(Weiss and Braeu, 2009)

Additionally, it must be made clear that α - and β -HH have been originally defined thermodynamically according to the difference in thermodynamic properties (Mcadie, 1964) or according to the preparation method (Bensted and Verma, 1972), not from a standpoint of crystallography or mineralogy. α -HH is formed by hydrothermal dehydration of dihydrate, whereas β -HH can be obtained by calcination of gypsum (Christensen et al., 2010; Schmidt et al., 2011).

1.2. Industrial by-product gypsum

Industrial by-product gypsum is the chemical end product of industrial processing plants, consisting primarily of calcium sulfate dihydrate, $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Pressler, 1984). Among industrial by-product gypsum, flue gas desulfurization (FGD) gypsum and phosphogypsum (PG) have the largest output.

FGD gypsum originates from the flue gas desulfurization installations by sorption of SO_2 in power stations. For example, in the wet-lime desulfurization method, the sorption reaction occurs via the reaction formulas (1, 2) (Roszczynialski et al., 1996a). Due to the relatively pure chemical composition, the utilization rate of FGD gypsum is high. For example, the average utilization rate of FGD gypsum was 58% in USA from 2002 to 2018 (data from ACAA), and in Europe (EU 15), it reached 75% in 2016 (data from ECOBA). However, the gypsum stockpile is still large because of the huge output. In USA, 140 million tons of FGD gypsum is deposited as wastes from 2002 to 2018 (Fig. 2). Additionally, the reuse of FGD gypsum is mainly concentrated in low value-added areas, as shown in Fig. 3 and Fig. 4.

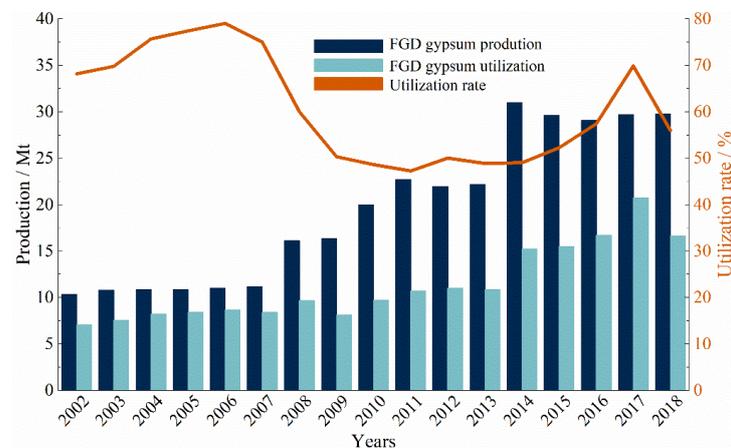
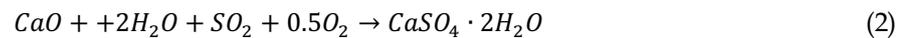
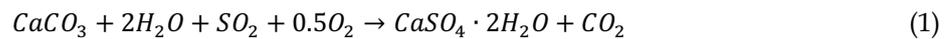


Fig. 2. FGD gypsum production and utilization in USA from 2002 to 2018, source-ACAA

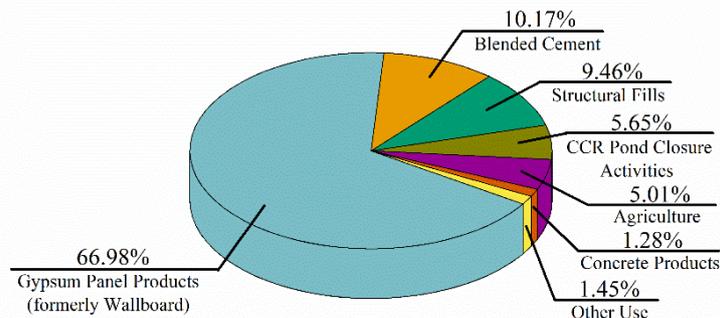


Fig. 3 Proportion of various utilization ways of FGD gypsum produced in USA in 2018, source-ACAA

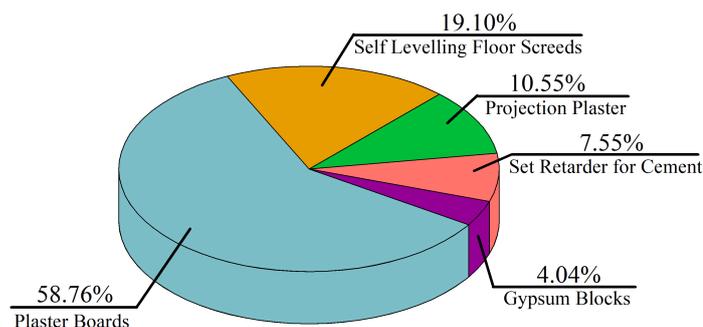
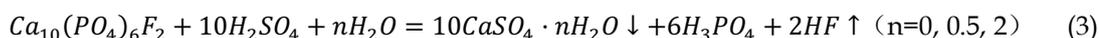


Fig. 4 Proportion of various utilization ways of FGD gypsum produced in Europe (EU 15) in 2016, source-ECOBA

PG is generated from the processing of phosphate rock by the “wet acid method” in plants producing phosphoric acid and phosphate fertilizers. During the process, phosphate ore is digested with sulfuric acid, as shown in the reaction (3) (Kovler, 2012; Jamialahmadi and Müller-Steinhagen, 2000). About 4~5 tons of PG are generated for every ton (P_2O_5) of product acid produced. Depending on the production process, the precipitate may be anhydrite ($n=0$), hemihydrate ($n=0.5$) or dihydrate ($n=2$) of calcium sulfate. And the classical dihydrate technique is the main process to produce phosphoric acid in fertilizer industries. Additionally, anhydrite and hemihydrate gypsum are unstable, with the extension of the accumulation time, they slowly hydrate into dihydrate gypsum. Therefore, the main component of PG is calcium sulfate dihydrate ($CaSO_4 \cdot 2H_2O$).



World PG production is variously estimated to be around 100-280 Mt per year (Parreira et al., 2003; Yang et al., 2009; Reijnders, 2007; Walawalkar et al., 2016).

However, only 15% of world PG production is recycled as building materials, agricultural fertilizers or soil stabilization amendments and as set controller in the manufacture of Portland cement, while the remaining 85% is disposed of without any treatment (Tayibi et al., 2009). In Florida the gypsum has accumulated more than 1 billion tons (Kovler, 2012), and in China the PG stockpiles approximates 500 million tons produced from 2010 to 2018 (Fig. 5). Additionally, a huge amount of PG has also stacked up in Europe, in Canada, Morocco, Togo, India, Korea, Russia, and other parts of the world (Degirmenci, 2008; Mun et al., 2007; Kovler, 2012).

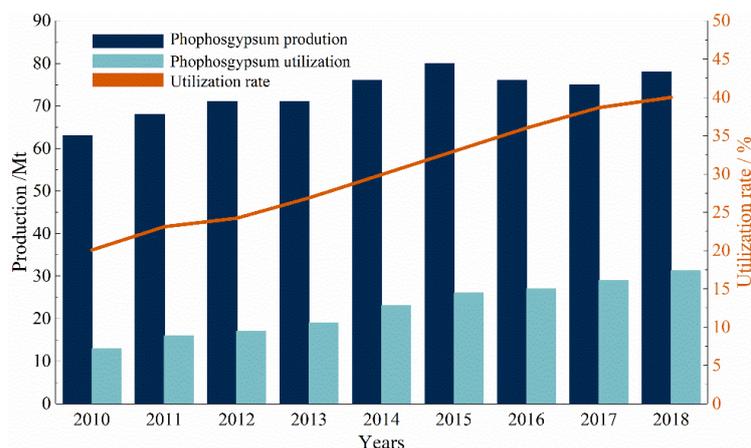


Fig. 5 Phosphogypsum production and utilization in China from 2010 to 2018 (Yang, 2018)

The bulk deposition of the industrial by-product gypsum causes severe environmental pollution and the increasing cost of land. How to reuse the huge amounts of by-product gypsum has become an urgent problem for the government. Since the last century, the preparation of α -HH with high-value added, due to the wide use range and large transportation radius, has become a research focus in the field of by-product gypsum recycling (Li et al., 2018; Tang et al., 2015; Guan et al., 2008; Ma et al., 2013a).

According to the reaction vessel or reaction medium, the common methods for producing α -HH from industrial by-product gypsum (mainly calcium sulfate dihydrate) can be classified as: commercialized autoclave process, salt/acid solution process, and alcohol-water solution process (Guan et al., 2019b; Guan et al., 2019a). The autoclave technology that involves heating dihydrate at elevated temperature (above 100 °C) and pressures, is energy-intensive (Ling and Demopoulos, 2005). In order to prepare α -HH from dihydrate under mild conditions, the mixed boiling or near-boiling solutions of inorganic acids or their salts have been used as the crystallization medium (Alfred et al., 1991; Guan et al., 2011a). Recently, another autoclave-free approach to producing α -HH in aqueous solutions of alcohols has also been suggested (Guan et al., 2011b; Guan et al., 2011c). However, so far, the autoclave-free processes have failed to achieve commercial production, which may be attributed to the technical challenges and cost coverage.

In this review, an overview of research on preparing α -HH from industrial by-product gypsum (mainly FGD gypsum and PG) is given. And recommendations to realize the comprehensive utilization

of by-product gypsum (especially PG) during the α -HH preparation are proposed.

2. Preparation of α -HH from industrial by-product gypsum

2.1. Preparation of α -HH from FGD gypsum

FGD gypsum is chemically pure, similar to the natural gypsum of high quality. In Europe, FGD gypsum cannot be considered as a waste but as a secondary raw material or by-product, thus it is not included in the European Waste Catalogue (EWC) nor in the OECD (Organization for Economic Cooperation and Development) Waste List (Hamm, 1994; Wirsching et al., 1994). Consequently, FGD gypsum can replace the natural gypsum as a raw material for preparing α -hemihydrate gypsum to a certain extent. Hitherto the preparation of α -HH from FGD gypsum has been realized by the autoclave process, salt/acid solution process, or alcohol-water solution process.

Table 2. Chemical compositions of FGD gypsum (wt%)

CaO	SO ₃	H ₂ O	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	PbO	K ₂ O	Others
36.21	42.30	19.62	0.65	0.32	0.25	0.10	0.06	0.03	0.46

The FGD gypsum was received from Panzhihua Iron & Steel, Sichuan Province, China

2.1.1. The autoclave process

Lots of researchers have studied the phase transition of three CaSO₄ modifications (namely, dihydrate, α -hemihydrate, and anhydrite) in CaSO₄-H₂O system. The research results show that in pure water the transition temperature from dihydrate to α -hemihydrate is above 100°C (Dahlgren, 1960; Li and Demopoulos, 2006; Charola et al., 2007). Therefore, the autoclave process comes into being.

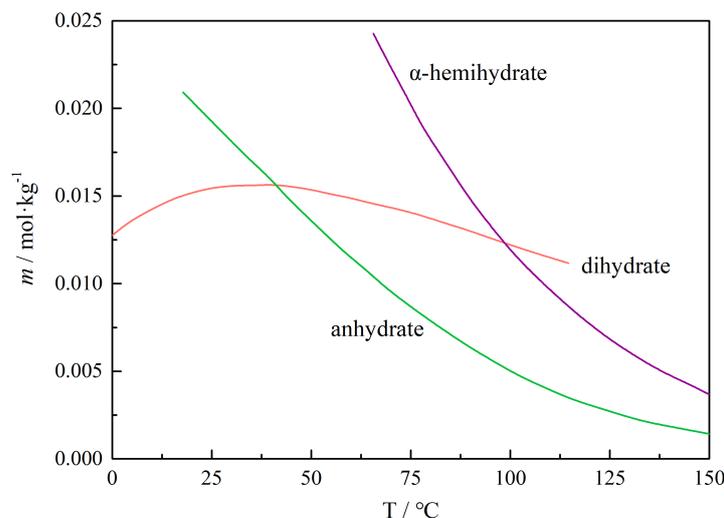


Fig. 6 Solubility curves for gypsum, anhydrite and hemihydrate in the temperature range from 0 to 150°C (Charola et al., 2007)

As early as the 1990s, Germany has industrially produced α -hemihydrate gypsum from FGD gypsum by the autoclave process, which treated the feedstock at around 150°C under pressurized steam (0.14~0.28 Mpa) for 4~6 hours, and operated a plant with annual production capacity 240000 tons (Engert and Koslowski, 1998). The simplified flow chart is shown in Fig. 7.

The autoclave process which involves heating FGD gypsum at elevated pressure and temperature, is energy-intensive. In order to prepare α -HH under mild conditions, the salt/acid solution process and the alcohol-water solution process are developed.

2.1.2. The salt/acid solution process

Because the addition of electrolytes such as salts or inorganic acids can effectively reduce the water acti-

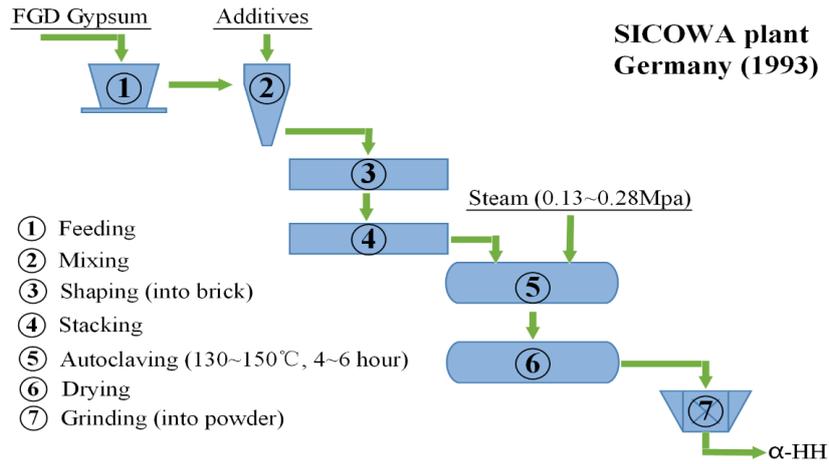


Fig. 7. Simplified flow chart of the autoclaving production process

ity in the aqueous solution and lower the transition temperature of dihydrate to hemihydrate gypsum, the transformation can be completed in salt or inorganic acid solutions under normal pressure. Thereinto, the phase transition process of dihydrate gypsum in H_3PO_4 , H_2SO_4 , HCl , and $CaCl_2$ solutions between 0 and 100°C have been deeply studied, and the phase equilibrium diagrams (as shown in Figs. 8-11) and kinetics models have been established (Ling and Demopoulos, 2005; Li and Demopoulos, 2006; Dahlgren, 1960; Van Der Sluis et al., 1986).

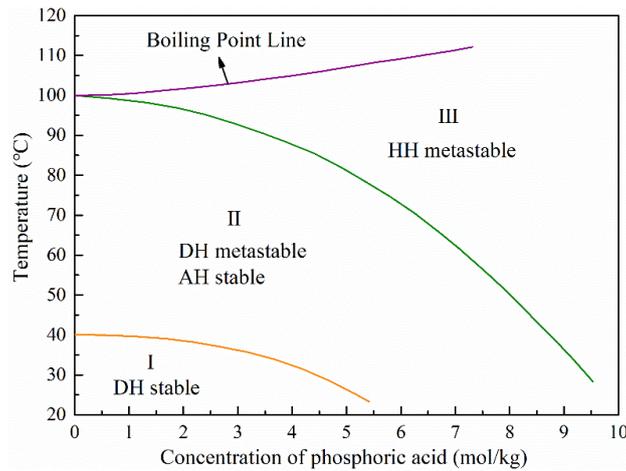


Fig. 8. $CaSO_4$ phase-transition diagram in H_3PO_4 solutions

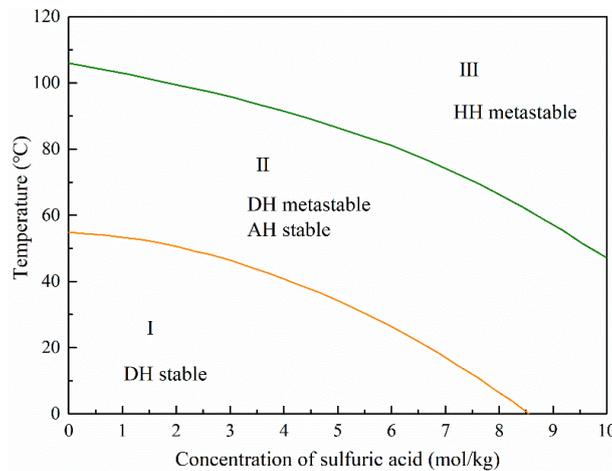


Fig. 9. Calculated diagram for $CaSO_4$ phase-transition in H_2SO_4 solutions

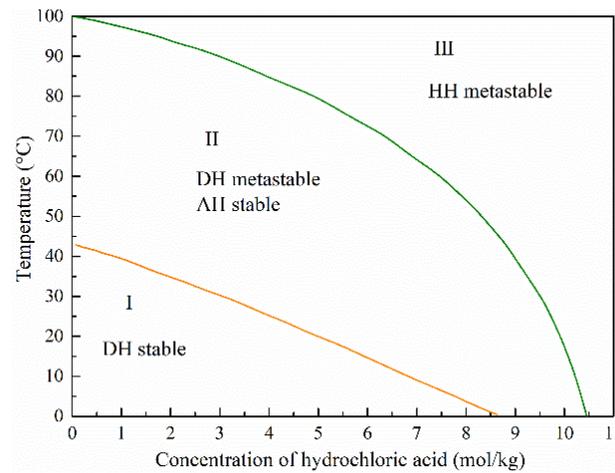


Fig. 10. CaSO_4 phase-transition diagram in HCl solutions

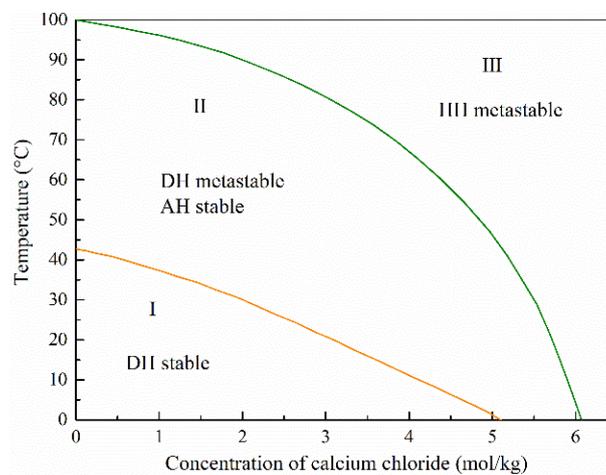


Fig. 11. CaSO_4 phase-transition diagram in CaCl_2 solutions

So far, researchers have successfully prepared α -hemihydrate gypsum in the laboratory from FGD gypsum in H_2SO_4 , NaCl , MgCl_2 , CaCl_2 , NH_4Cl , NH_4NO_3 , $\text{Mg}(\text{NO}_3)_2$, NaNO_3 , MgSO_4 , and some mixed solutions with 15~50wt% electrolyte concentration at 90°C~boiling temperature (Alfred et al., 1991; Guan et al., 2009; Allen, 1975; Schreck, 1978). Generally, the increase of electrolyte concentration and reaction temperature both can promote the transformation reaction. Meanwhile, the addition of some cations can also show a promoting effect on the α -HH precipitation (Guan et al., 2011a; Guan et al., 2010). For example, Guan et al. found that the FGD gypsum dehydration process was enhanced distinctly by the low level of K^+ concentration in a Ca-Mg chloride aqueous medium under mild conditions (Guan et al., 2009). Furthermore, in the mixed salt solutions a pilot scale preparation of α -HH from FGD gypsum was conducted to evaluate the feasibility of the recycling of the salt solution, and the process flow chart is shown in Fig. 11 (Guan et al., 2011d).

Although the crystal modifier, the effects of impurities (such as K^+ , Mg^{2+} , Mn^{2+}) and the nucleation and crystallization process of α -HH have been fully investigated (Guan et al., 2010), and even the pilot scale experiment has proven that the salt solution has the recycling feasibility, the industrialization of the salt solution process for preparing α -HH from FGD gypsum still has a long way to go. There are still many problems to be solved in the industrialization process, such as the treatment of chlorinated wastewater and the equipment corrosion caused by the concentrated salt solution (Guan et al., 2019b). Even worst, salt ions will enter into α -HH crystal lattice and affect the product quality (Ru et al., 2012).

2.1.3 The alcohol-water solution process

In recent years, an alternative approach to preparing α -HH from FGD gypsum in alcohol-water solu-

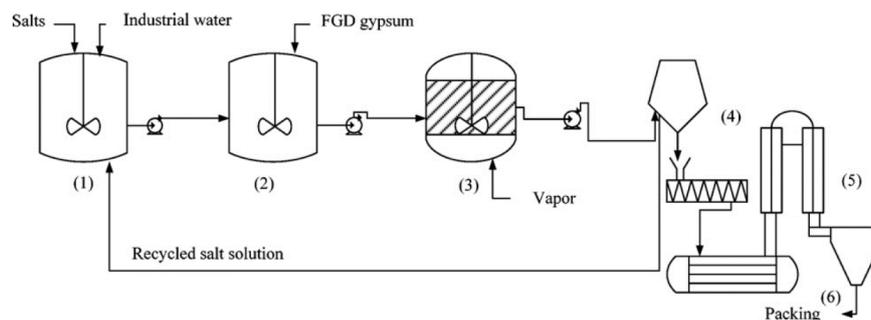


Fig. 12. Schematic diagram of the pilot plant for α -HH preparation from FGD gypsum with salt solution method: (1) salt solution tank; (2) homogenizer; (3) reactor; (4) vacuum belt filter; (5) drier; (6) pneumatic separator.

tions under mild conditions has been suggested. Jiang et al. studied in detail the transition process of α -HH from DH in methanol-water and glycerol-water solutions, and established the phase-transition diagrams by the water activity method (Guan et al., 2011c; Guan et al., 2011b). Although the phase transition kinetics was unfavorable, trace amounts of non-lattice cations (such as Na^+ , K^+ , Cu^{2+} , Zn^{2+} , Mn^{2+} , and Mg^{2+}) as phase transition accelerators could shorten significantly the time of transformation from DH to HH, of which Na^+ has the best performance (Jiang et al., 2013).

Additionally, Guan et al. (2017; 2019b) further studied the role of glycerol during the transition of HH from FGD gypsum in the mixture of glycerol and water, and found that in addition to reducing the water activity it could also control the crystal morphology and particle size of α -HH by surface adsorption and adjusting relative supersaturation.

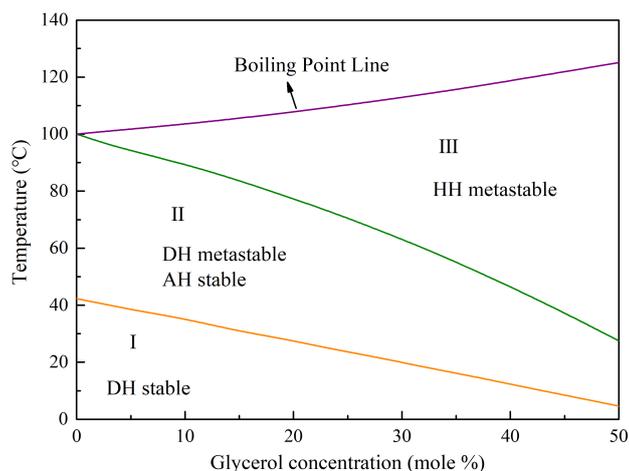


Fig. 13. Phase-transition diagram of CaSO_4 in glycerol-water solution

At present, this method is still in the laboratory exploration stage, and during its industrialization process, researchers still need to solve many problems, such as alcohol recycling and washing water recovery.

2.2. Preparation of α -HH from PG

Unlike FGD, PG contains large amounts of impurities, such as phosphorus- and fluor-containing compounds, organic matters, as well as some trace metal elements, and even radionuclides (Labrincha et al., 2017; Singh et al., 1996; Reijnders, 2007; El-Didamony et al., 2013). The impurities have a negative impact on the quality of PG products. Therefore, before preparing α -HH, PG tends to be pretreated by lime neutralization (Duan et al., 2017; Li et al., 2018; Li et al., 2019), water washing (He et al., 2014), wet sieving (Singh et al., 1996) or even flotation (Roszczynialski et al., 1996b) in order to solidify or remove the impurities, especially the organics, soluble phosphorus and fluorine. So far, α -HH can be produced by pretreated PG dehydration under elevated temperature and pressure in an autoclave or under atmosphere pressure in salt solutions.

Table 3. Chemical compositions of phosphogypsum (wt%)

CaO	SO ₃	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	MgO	Na ₂ O	K ₂ O	P ₂ O ₅	SrO	Loss
31.52	41.05	3.65	0.20	0.47	0.79	0.20	0.09	1.49	0.064	20.23

The phosphogypsum was obtained from Hubei Yihua Fertilizer Co., Ltd, Yichang city, Hubei Province, China

2.2.1. The autoclave process

Generally, α -HH can be prepared from pretreated PG at a pressure of 0.12~0.70Mpa, a temperature of 105~150°C, and for 2~16h in an autoclave (Singh and Rai, 1988; Yang et al., 2009; He et al., 2014; Duan et al., 2017; Mi et al., 2017).

The well-known commercial process for α -HH production from PG by the autoclave process is the Giulini method (Hignett, 1980; Roszczynialski et al., 1996b). In the method, the PG is first slurried in water, then the suspension is subjected to washing or flotation or both depending on the impurity level of the incoming PG, and subsequently pumped to a buffer tank. From the buffer tank, the suspension is transported to the autoclave for CaSO₄·2H₂O dehydration. Thereafter, the slurry containing α -HH formed in autoclave is centrifuged at 90-100°C to remove the excess liquid phase. Finally, the hemihydrate is washed with hot water and dried at 90°C.

Imperial Chemical Industries Ltd. also develops a continuous process (the ICI process) on a small-scale for the conversion of PG to the α -hemihydrate gypsum. However, it uses a double autoclave system, in which a slurry of gypsum, containing crystal habit modifiers, is heated by direct steam injection to 150°C at a pressure of 0.689 MPa. And the α -hemihydrate product is separated from the liquid phase by centrifuging (Schreck, 1978; Allen, 1975).

Meanwhile, in order to further reduce energy consumption and avoid secondary pollution, researchers proposed the semi-dry process (Duan et al., 2017) and the semi-liquid process (Mi et al., 2017), which adopted an autoclave-drying integrated process without washing steps to simplify the hydrothermal autoclave method.

2.2.2. The salt solution process

Up to now, researchers have investigated the transformation process from PG to α -HH in CaCl₂ (Li et al., 2019; Lu et al., 2019; Ma et al., 2012; Ma et al., 2018), NaCl (Ru et al., 2012), Na₂SO₄ (Li et al., 2018), and Ca-Na-Cl mixed solutions (Ma et al., 2013b) under atmosphere pressure. Ma and Li et al. studied in deep the phase transition from PG to α -HH in CaCl₂ solutions, and found that the reaction time was significantly shortened by higher reaction temperature and CaCl₂ content. And the suitable temperature and CaCl₂ addition of the mixed solutions were ~95°C and ~24 wt.%, respectively. Although increasing the salt solution concentration would accelerate the dehydration of PG, it seems difficult to obtain pure α -HH phase from high concentration of salt solutions. For example, a high concentration of NaCl solution would promote the formation of omongwaite (Na₂Ca₅(SO₄)₆·3H₂O), which adversely affected the product quality. Additionally, chloride-free Na₂SO₄ solution was suggested to prepare α -HH from PG by Li et al. for eliminating the influence of chloride ions.

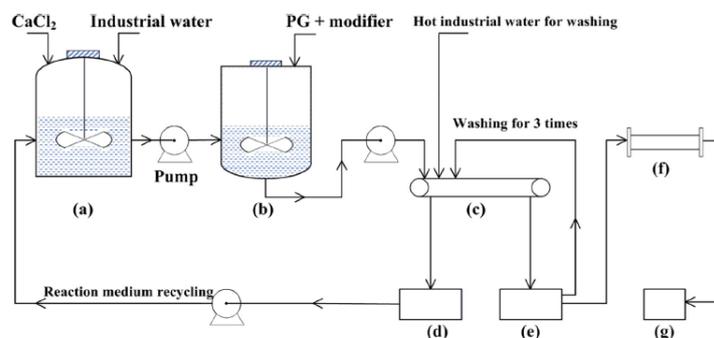


Fig. 14. Schematic diagram of pilot scale test from PG to α -HH with the hydrothermal method: (a) salt solution container; (b) main reactor; (c) belt press filter; (d) liquid container; (e) solid container; (f) roller drier; (g) packing machine

In order to avoid the secondary pollution caused by the used electrolyte solution containing complicated impurities, Lu et al. (Lu et al., 2019) explored the feasibility of recycling electrolyte solution in α -HH preparation from PG in laboratory and pilot scale tests. And the tests demonstrated that CaCl_2 solution could be recycled for 6 times without affecting the α -HH quality. The schematic diagram of pilot scale is shown in Fig. 14. Furthermore, on the basis of investigating in detail the recycling of pretreated wastewater and salt solutions, and the impact of impurities, Ru (Ru, 2013) conducted preliminary industrial tests and produced thick and well-growth α -HH crystals, and the flow chart is depicted in Fig. 15.

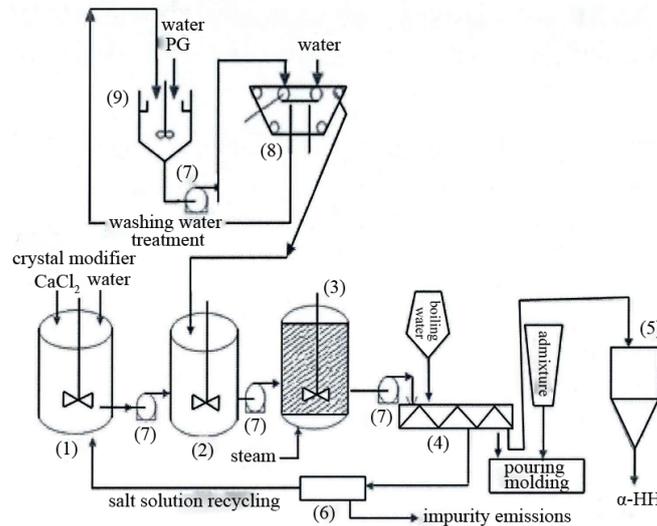


Fig. 15. Schematic diagram of industrial scale test for α -HH preparation from PG with salt solution method: (1) activity agent solution tank; (2) slurry mixing tank; (3) hydrothermal reaction tank; (4) vacuum washing filter; (5) drier; (6) leachate treatment tank; (7) slurry pump; (8) filter; (9) raw material processing tank

3. Conclusions and recommendations

Research on preparation of α -HH with high value-added from industrial by-product gypsum (mainly $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) is essential for solving the increasingly serious accumulation of solid waste gypsum, especially phosphogypsum (PG).

So far, the phase transition from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to α -HH can be completed in the autoclave under high temperature and pressure, or in salt/acid/alcohol solutions under atmosphere pressure. Thereinto, the autoclave process is the earliest method to achieve industrialization. However, due to the high energy consumption and unfavorable continuous operation of the autoclave process, the alternative approaches, such as salt/acid solution process and alcohol-water solution process, have become the research hotspot for the past few years. Nevertheless, these methods are basically in the laboratory stage or pilot scale test at present, and there are still many problems to be solved during the industrialization process.

Among all the industrial by-product gypsum, flue gas desulfurization (FGD) gypsum and phosphogypsum (PG) have the largest emissions. Owing to the low impurity content, FGD gypsum can almost completely replace natural gypsum, and its reuse rate is high. On the contrary, for PG with a larger emission, its utilization rate is very low because of the high impurity content. PG tends to be pretreated to remove the impurities before utilization, which is bound to increase the reuse cost and reduce its utilization. Therefore, how to improve the reuse rate of PG is the key to solving the large accumulation of industrial by-product gypsum.

Preparation of α -HH from PG is maybe great potential feasible when combined with the recovery of impurities (especially high-value metal elements, such as rare earth elements) from PG. For example, sulfuric acid is often used for the leaching of rare earth elements (REEs) in PG (Walawalkar et al., 2016; Rychkov et al., 2018), but the leaching efficiency is not high, because REEs are mainly presented in the form of isomorphous substitution (Lokshin et al., 2010; Samonov, 2011), and it is difficult to extract them without destroying the lattice structure of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (Habashi, 2010); on the other hand, in sulfuric

acid solution the phase transition from $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ to α -HH can be realized through a dissolution-recrystallization process (the so-called through-solution reaction mechanism) under atmosphere pressure (Freyer and Voigt, 2003). During the dissolution process, REEs presented in the lattice of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ can be completely released, and during the recrystallization process, the α -HH crystal morphology and particle size can be controlled by adding crystal modifiers to reduce the adsorption of released REEs on the newly formed crystal surfaces (Alfred et al., 1991; Wang et al., 2008), thereby greatly improving the leaching rate of REEs. This will not only obtain high-quality α -HH, but also efficiently recover high-value REEs.

Therefore, combining the preparation of high value-added products with the recovery of valuable impurities from industrial by-product gypsum seems a promising method to solve the bulk deposition of industrial by-product gypsum, especially PG.

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