

Influence of crystal modifier on the preparation of α -hemihydrate gypsum from phosphogypsum



Zhengyang Duan, Jianxi Li ^{*}, Tianguo Li, Shurui Zheng, Weiming Han, Qingyu Geng, Huibin Guo

Faculty of Environmental Science and Engineering, Kunming University of Science and Technology, Kunming, Yunnan 650500, PR China

HIGHLIGHTS

- Original phosphogypsum was utilized for the preparation of α -CaSO₄·0.5H₂O.
- Semi-dry method process was adopted for the preparation of α -CaSO₄·0.5H₂O.
- Low cost, high value-added and met the requirements of Chinese standard of α -CaSO₄·0.5H₂O were prepared.

ARTICLE INFO

Article history:

Received 3 February 2016

Received in revised form 20 September 2016

Accepted 16 December 2016

Keywords:

Crystal modifier

α -Hemihydrate gypsum

Phosphogypsum

Semi-dry method

ABSTRACT

Crystal modifier is an important factor in preparation of α -hemihydrate gypsum (α -CaSO₄·0.5H₂O) from phosphogypsum (PG). Here, α -CaSO₄·0.5H₂O was prepared from PG using a semi-dry method. SEM, XRD, XPS were used to explore the effects of one or more crystal modifiers on crystal growth and mechanical properties after hydration and hardening of α -CaSO₄·0.5H₂O. The results showed that addition of RCOO[−] can delay the hydration process of α -CaSO₄·0.5H₂O and improve productivity. Al³⁺ can be adsorbed selectively on the gypsum crystal surface, inhibiting the crystal growth along axis c, which could alter the speed in all directions and turn the crystal into a short hexahedron pole. But when RCOO[−] and Al³⁺ were composited, a superposition effect occurred, resulting in production of a crystal with a smaller length to diameter ratio and more perfect crystal form. When RCOO[−] and Al³⁺ were both added in 0.06% level, the flexural and compressive strength of the hardened α -CaSO₄·0.5H₂O could reach to 6.7 and 25.65 MPa, respectively.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

α -CaSO₄·0.5H₂O, being well known as a high-strength gypsum, is formed from CaSO₄·2H₂O dehydration in a high temperature and humid environment by autoclaving or hydrothermal methods [1,2]. This material is different from ordinary building gypsum (β -CaSO₄·0.5H₂O), and α -CaSO₄·0.5H₂O exhibits high strength, light weight, without pollution and other dangers. At present, the α -CaSO₄·0.5H₂O is all most made from the natural or desulfurization gypsum [3]. Desulfurization gypsum is a harmful industrial by-product gypsum that is produced by desulfurization and purification of flue gas when fuel that contains sulfur (mostly coal) is burned. The physical and chemical properties of gypsum produced by desulfurization are basically the same as natural gypsum, but without radioactivity and with fewer harmful impurities, thus this material can be used to replace natural gypsum as raw materials for the building materials industry [4,5]. PG is an industrial waste

by-product that forms from production of phosphoric acid and phosphate fertilizer, produced in factories that are mainly distributed in Sichuan, Yunnan, Guizhou and Hubei of China. The amount of PG yearly emission is about 120 million tons in the world, of which 70 million tons are produced each year in China, where more than 250 million tons are stored [6,7]. Unlike natural gypsum, PG is not utilized, but instead must be stored indefinitely due to the weak radioactivity of this material. The increasing production of PG increase, is requires additional land resources for disposal, and also presents serious environment pollution and health hazards. Therefore, studies of PG are of high interest, both at home and abroad. One important research direction is to try to modify PG to produce high strength α -CaSO₄·0.5H₂O for use as building materials. This approach would have broad market potential and vital environmental benefits because it would reduce the use of land for the disposal of a waste residue, and convert this by-product to a usable material, conserving natural gypsum.

Currently, the autoclaving and salt solution method have been used to produce α -CaSO₄·0.5H₂O. However, these methods have many disadvantages need optimization, including process com-

^{*} Corresponding author.

E-mail address: jianxili2015@sina.com (J. Li).

plexity, higher cost, which confine the applications in the building materials. In order to reduce energy consumption and costs, we proposed a new semi-dry process [8]. This approach differs from traditional methods that separate the processes of autoclaving and drying, semi-dry process adopted an autoclaved-drying integrated process without washing steps. Because the crystal morphology influences the mechanical properties of α -CaSO₄·0.5H₂O significantly. Crystal modifier application remains a key approach to regulate and control crystal formation of high strength α -CaSO₄·0.5H₂O using the semi-dry process [9–13]. The role of crystal modifier for the preparation of α -CaSO₄·0.5H₂O with PG has been widely studied in recent years [14,15]. For a dynamic hydrothermal method, a compound of organic acids (or salt) and inorganic salt can be used to obtain a large and uniform α -CaSO₄·0.5H₂O crystal [16]. The application of inorganic-organic salt can obtain a high mechanical strength α -CaSO₄·0.5H₂O powder in the autoclaving method [17]. In pure water medium, crystals of α -CaSO₄·0.5H₂O can grow into a needle crystals, but this growth habit was slowed and the crystal was coarsened in organic acid salt medium [18]. In the α -CaSO₄·0.5H₂O crystal formation process, the impact of a crystal modifier (succinic acid or succinic acid salt) on gypsum produced by desulfurization was greater than the effect on natural gypsum [19].

However, the effect of different crystal modifiers on crystal morphology using the new semi-dry method have not been studied for the process of PG dewatering into α -CaSO₄·0.5H₂O. Therefore, the goals of this study were to determine the influence of crystal morphology, mechanical properties, and the mechanism of a crystal modifier in the semi-dry method. The purpose of this work is also to explore a simple, high value-added and limit cost α -CaSO₄·0.5H₂O technology.

2. Materials and experimental methods

2.1. Materials

Sodium citrate (Na₃C₆H₅O₇·2H₂O) and aluminum sulfate (Al₂(SO₄)₃·18H₂O) were used as crystal modifier, analytically pure, purchased from Tianjin chemical reagent research institute. PG was provided by phosphate fertilizer plant (Yunnan, China). CaO holds 29.82%, SO₃ holds 40.86% and other impurities. The impurities in PG can greatly influence the preparation process for α -CaSO₄·0.5H₂O, so the PG must be pretreated. To do this, a certain mass of CaO must be added to the PG to neutralize the acid in PG and to solidify the soluble phosphorus and soluble fluorine in PG by precipitation. The chemical composition of PG before and after pretreatment of samples is shown in Table 1.

Table 1 shows that the PG after CaO pretreatment, the impurity content was decrease and the soluble phosphorus disappeared, but the total phosphorus content was basically unchanged. This indicates that the pretreatment causes the soluble phosphorus to solidify, and the phosphorus deposit was formed inside the PG.

2.2. Preparation of α -CaSO₄·0.5H₂O powder

First, we weighed PG 2000 g and added 1% of the pretreatment agent CaO. Separately, the crystal modifier was dissolved in deionized water, and then was added to the PG samples according to the

experimental parameters and stir evenly. Next, the sample was made 5 cm in size by artificial and placing it in an autoclave kettle, and autoclaving at a pressure of 0.17 MPa, temperature of 120 °C, and for 4 h time. When the autoclaving process was completed, the sample remained in the autoclave and the temperature was kept constant and the sample was allowed to dry for 4 h under normal pressure. After this drying step, the α -CaSO₄·0.5H₂O powder was produced by grinding.

2.3. Determination ratio of water to α -CaSO₄·0.5H₂O

The water consumption of normal consistency for plaster was tested according to GB/T 17669.4-1999 (China national standard for gypsum plasters) and the water requirement for normal consistency of α -CaSO₄·0.5H₂O was 0.45 (weight ratio).

2.4. Samples shaping

The preparation of paste was carried out at the water requirement for normal consistency of α -CaSO₄·0.5H₂O. Briefly, α -CaSO₄·0.5H₂O powder (1300 g) was slowly transferred into a mixing bowl containing with water, and stir evenly for 30 s. Then the paste was cast into three iron molds (40 mm × 40 mm × 160 mm). Each iron mold was compacted by jolting three times to remove air. The excess paste was removed with a spatula. After 1 h, unmold the samples and cure for 24 h under natural conditions. The plasters were dried to a constant weight at 60 ± 5 °C, and ready for mechanical properties test. Contradistinctive methods were employed to analyze the influences of the crystal modifier additive on α -CaSO₄·0.5H₂O crystal formation and mechanical properties.

2.5. Experimental methods

2.5.1. α -CaSO₄·0.5H₂O mechanical properties test

Test the mechanical properties of α -CaSO₄·0.5H₂O according to GB9776-88 in China. (Electric cement bending test machine, KZJ-

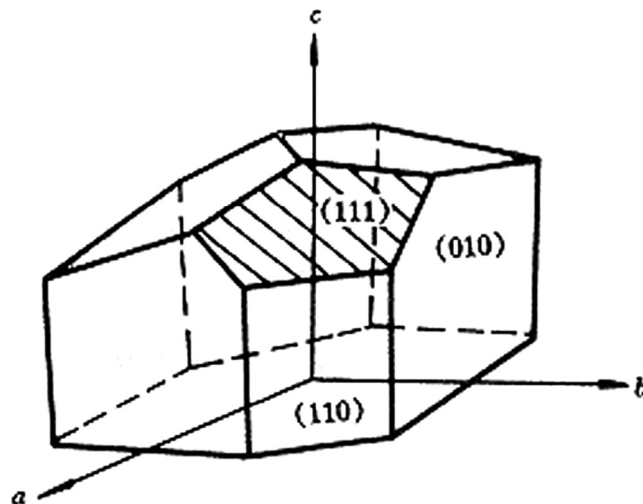


Fig. 1. Crystal shape of α -CaSO₄·0.5H₂O.

Table 1
The chemical composition of PG before and after pretreatment (%).

Components	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	MgO	SO ₃	t-P ₂ O ₅	w-P ₂ O ₅	F	Na ₂ O + K ₂ O
PG	29.82	0.137	0.236	9.43	0.055	40.86	1.17	0.87	0.52	0.13
PG + pretreatment	32.52	0.05	0.05	8.82	–	40.48	1.18	–	0.27	–

Download English Version:

<https://daneshyari.com/en/article/4913778>

Download Persian Version:

<https://daneshyari.com/article/4913778>

[Daneshyari.com](https://daneshyari.com)