International Journal of Mineral Processing 125 (2013) 5–9

Contents lists available at ScienceDirect

International Journal of Mineral Processing

journal homepage: www.elsevier.com/locate/ijminpro

Effect of carboxymethylcellulose on gypsum re-hydration process

Leila Magalhães Baltar [a,*], Carlos Adolpho Magalhães Baltar [a], Mohand Benachour [b]

[a] Department of Mining Engineering, Federal University of Pernambuco (UFPE), Recife, 50740-530, Brazil
[b] Department of Chemical Engineering, Federal University of Pernambuco (UFPE), Recife, 50740-530, Brazil

ARTICLE INFO

Article history:
Received 6 May 2013
Received in revised form 20 August 2013
Accepted 31 August 2013
Available online 8 September 2013

Keywords:
Alpha gypsum
Additives
Polysaccharides
Setting time

ABSTRACT

When in contact with water, calcined gypsum rehydrates through dissolution, nucleation and crystallization steps. Additives may be used to improve the paste workability and the mechanical properties of the hardened piece. This study investigated the effect of addition of polysaccharides on the setting time, hydration heat, consistency and compressive strength. The changes in the gypsum microstructure were observed by scanning electron microscopy (SEM). The results showed that dextrin, starch and cellulose did not affect the gypsum properties. However, the addition of only 0.025% of carboxymethylcellulose (CMC) results in an increase in the initial and final setting time of 12 and 52%, respectively, without significantly affecting the mechanical strength of the hardened piece. The effect of CMC is attributed to the formation of calcium carboxylate, which reduces the availability of calcium in the crystallization step, slowing down the setting time.

1. Introduction

Gypsum is a calcium sulfate dihydrate mineral that occurs in several regions around the world with a wide variety of industrial applications. It can be used in its natural or dehydrated form. Depending on the calcination process, alpha or beta hemihydrate types can be obtained (Baltar et al., 2006). These hemihydrates differ from each other by their crystal structure and reactivity, allowing the production of plasters that can be applied in many different products.

Dihydrated calcium sulfate shows the peculiar facility to lose and recover water due to crystallization. During the calcination process, it loses 3/4 of water due to crystallization, and changes into calcium sulfate hemihydrate ($CaSO_4 \cdot 1/2\ H_2O$), as shown in reaction (R-01).

$$\underset{\text{(gypsum)}}{CaSO_4 \cdot 2H_2O} \quad \underset{125-180\,^{\circ}C}{\rightarrow} \quad \underset{\text{(hemihydrate)}}{CaSO_4 \cdot ½H_2O} \quad + \quad \underset{\text{(steam)}}{3/2\ H_2O} \qquad (R-01)$$

When in contact with water, however, the hemihydrate rehydrates back to the dihydrate form as shown in reaction (R-02).

$$2\ CaSO_4 \cdot ½\ H_2O + 3\ H_2O \rightarrow 2\ CaSO_4 \cdot 2H_2O + \text{heat} \qquad (R-02)$$

Antunes (1999) Karni and Karni (1995) reviewed the first studies on plaster hydration that have been published by Lavoisier in 1798, and Le Châtelier in 1887. Le Châtelier explained the hydration mechanism through the crystallization theory in three steps: 1) chemical dissolution phenomenon — when the crystals hemihydrate ($CaSO_4 \cdot 1/2\ H_2O$), mix with water, dissolve and originate a saturated solution of Ca^{2+} and $(SO_4)^{2-}$ ions; 2) physical crystallization phenomenon — when the solution is saturated and the dihydrate crystals ($CaSO_4 \cdot 2H_2O$) precipitate in the form of needles and 3) mechanical hardening phenomenon — when the paste hardening is caused by the increased concentrations of crystals.

Thus, the hemihydrate in contact with the mixing water forms a saturated solution of Ca^{2+} and $(SO4)^{2-}$ ions. During the induction period, the first nucleation points occur (forming the first dihydrate crystals). Due to the fact that dihydrate crystals are less soluble than the hemihydrate, they accumulate in the medium until reaching a critical number of crystals, starting the setting time. With continued formation of crystals, the medium becomes saturated of crystals, hardens and acquires mechanical resistance. The crystallization theory has been cited and used to explain the hydration mechanism of the plaster up to the present time by several authors (Antunes, 1999; Hincapie and Cincotto, 1997; Leinfelder and Lemonf, 1989; Phillips, 1984).

The number of nuclei per solution volume unit influences the microstructure growth rate and crystal size (Antunes, 1999). Thus, by increasing or decreasing the number of nuclei per volume unit it is possible to modify the crystalline structure and, consequently, the mechanical properties of the hardened product. In order to obtain adequate paste fluidity to appropriate manipulation and casting, an amount of water larger than stoichiometric amounts must be used. During the crystallization process, the evaporation of excess water results in the appearance of pores that contribute to reduce the mechanical strength of the hardened piece (Leinfelder and Lemonf, 1989; Phillips, 1984). An illustrative diagram of the steps from dihydrate dehydration up to hemihydrate hydration is shown in Fig. 1.

* Corresponding author.
E-mail addresses: lmb@ufpe.br (L.M. Baltar), camb@ufpe.br (C.A.M. Baltar), mbena@ufpe.br (M. Benachour).

0301-7516/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.minpro.2013.08.005

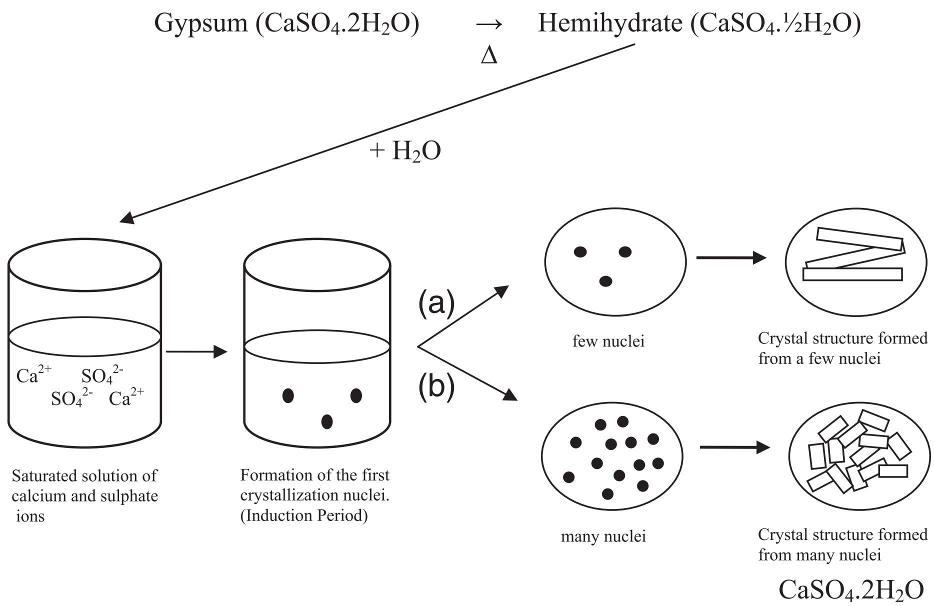

Fig. 1. Representation of the gypsum dehydration process; dissolution crystallization and hardening of the hemihydrate.

The crystal growth conditions directly affect the physical and mechanical properties of the products in the fresh and hardened states, which allowed both to adjust the paste workability to the time required for handling and to adjust the mechanical strength of the product in the hardened state to meet the market standard requirements. The amount of water, impurities and use of additives in the paste may interfere in the crystal growth and modify the mechanical properties of products. The paste workability increases by increasing the water/gypsum ratio that, in turn, results in reduced mechanical strength. Thus, a great challenge to the gypsum technology is to obtain paste with the following antagonistic characteristics: easy handling (adequate consistency), adequate setting time and good mechanical strength of the hardened piece.

In the production of more elaborated commercial plasters, different reagents are added to reach consumers' requirements for each particular application. The reagents used to delay or to accelerate the setting time change the crystal morphology (Jorgensen and Posner, 1959), modifying the mechanical strength of the hardened piece (Henao and Cincotto, 1997; Singh and Garg, 1997).

Various additives have been used to modify the setting time (Baltar et al., 2005; Domínguez and Santos, 2001; Peres et al., 2008): Potassium sulfate and calcium are cited as accelerators (Leinfelder and Lemonf, 1989), while citric acid and its sodium salt, acetates and borax, among others, are known as retardants (Henao and Cincotto, 1997; Hincapie and Cincotto, 1997; Lòpez, 1997; Peres et al., 2008). The present research aimed to observe the effect of different polysaccharides on the gypsum properties and to determine the action mechanism of these reagents. The influence of polysaccharides was evaluated in terms of paste consistency, setting time, hydration heat and mechanical strength. Scanning electron microscopy (SEM) was used to support the evaluation of the gypsum characteristics.

2. Materials and methods

2.1. Materials

2.1.1. Sample

A commercial alpha gypsum sample produced and provided by Minera San Jorge (MSJ) — Pernambuco/Brazil, with average particle size of 14.3 μm (Fig. 2) was used in experiments.

2.1.2. Equipment

Mechanical stirrer, IKA Eurostar, microcontroled.
Vicat apparatus, manufactured by SOLOTEST.
Manual Hydraulic Press, with capacity of 20 tons and digital display of force sensitive to 1 kg Pseudo-adiabatic system with thermocouple.
Table by shock compaction, with controller digital, manufactured by SOLOTEST. Elektro Therm Oven.
Scanning Electron Microscope (SEM), model 200F, FEI QUANTA.
Particle Size Analyzer, laser, model Mastersizer 2000, Malvern.

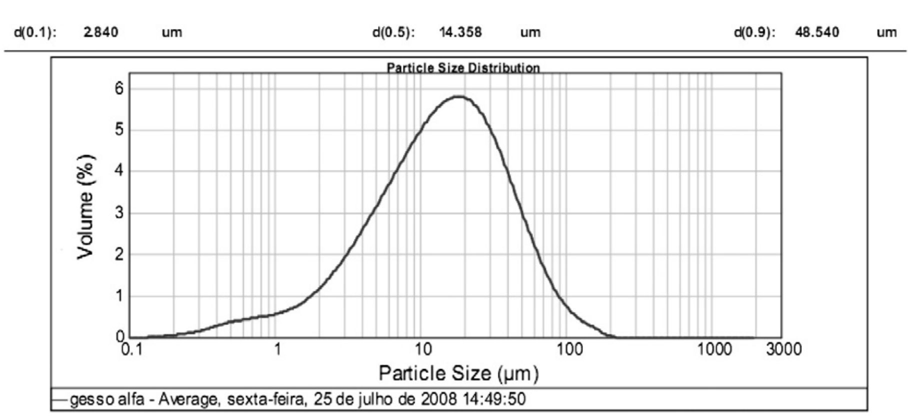

Fig. 2. Particle size distribution of gypsum samples used in experiments.