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Early hydration and microstructure of gypsum plaster revealed by environment scanning electron microscope

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ABSTRACT

Early hydration and microstructure of gypsum plaster (G) paste in different compositions and hydration time were studied by environment scanning electron microscope (ESEM) coupled with liquid nitrogen cooling. It was observed that small hemihydrate particles rapidly dissolved and hydrated, forming dihydrate crystals network around large hemihydrate particles, which makes an increasingly dense microstructure and promotes the setting of G paste. Besides, different chemical admixtures such as polycarboxylate (PC), hydroxy propyl methyl cellulose (HPMC) and starch ether (SE) would promote the flocculating or deflocculating between particles and therefore modify the fluidity of the paste. This work paves the way to the understanding the setting and rheology of hydraulic materials in the perspective of microstructure evolution.

1. Introduction

It is widely accepted that the setting time and fluidity are two major elements of the workability of hydraulic materials e.g. cement and gypsum plaster and closely related to the early (the period before final setting) hydration and microstructure [1–6]. Therefore, the imaging of hydraulic materials paste in the scanning electron microscopy (SEM) has been the goal of researchers for many years. However, it is difficult to observe the microstructure by using the conventional SEM, because the evaporation of water in high vacuum would cause considerable microstructural rearrangement of the paste. For this reason, most of the microstructure studies of hydraulic materials focus on the period after final setting, when the paste is rigid enough to withstand such microstructural changes. In order to solve this problem, the cryo-SEM technique is developed to transfer the water into a vitreous state by which the microstructure integrity of the paste is maintained [7]. However, this vitreous state is thermodynamically unstable so the observation must be performed at a controlled humidity (above 95%) and temperature (below 123 K) to prevent the evaporation and temperature-induced phase changes. More recently, based on the cryo-SEM technique researchers [8] obtained the high-resolution microstructure images of clay minerals slurries by further sublimating the vitrified water. It seems that the water molecules, no matter in the ice or vitreous state, had better been removed out from the paste since they would hinder the local details of solid particles.

Inspired by previous studies, considering that the water in vitrified state is not easily obtained and need not to be maintained during the observation, the basic idea of this present work is firstly to transfer the water into ice instead of a vitreous state by liquid nitrogen cooling and subsequently to sublimate the ice by controlling the temperature and pressure in the ESEM chamber. It is worth noting that the changes in microstructure caused by volume expansion from water to ice are not considered in the present research. As an illustration, the microstructure of G paste in different compositions and hydration time was studied.

2. Materials and methods

The raw material (Jiangsu Stone Sun Science and Technology Co., Ltd.) is a commercial gypsum plaster with an α-calcium sulfate hemihydrate content of about 98 wt%. The characteristic particle sizes of the plaster are: d_{10} = 7.01 μm, d_{50} = 37.56 μm and d_{90} = 82.92 μm, respectively. Besides, chemical admixtures including PC (Jiangsu Sobute New Materials Co. Ltd.), HPMC (Qingdao Usolf Chemical Technology Co. Ltd.) and SE (AVEBE Co. Ltd.) are all powdered commercial products.

The sample was prepared by pre-mixing chemical admixture with plaster manually for 40 s, then the mixture was blended with

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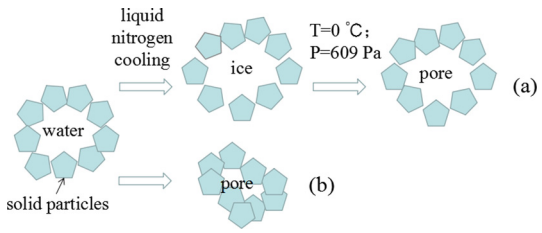

Fig. 1. Diagram of the liquid nitrogen cooling for gypsum plaster paste, (a) with liquid nitrogen cooling; (b) without liquid nitrogen cooling.

32% (by the weight of plaster, similarly hereinafter) water for another 40 s until a homogenous paste was obtained. The paste containing 0.10% PC, 0.20% HPMC and 0.50% SE was named as GPC, GHPMC and GSE, respectively.

The setting time and fluidity of the gypsum plaster paste was evaluated according to GB/T 17669.4 (China national standard for gypsum plaster). Liquid nitrogen cooling method was applied to remove water without changing the microstructure of the paste. Specifically at certain hydration time, the prepared paste was immediately transferred into the minor groove of a stainless steel sample holder and rapidly cooled in liquid nitrogen. Afterwards, the frozen paste together with sample holder was placed in the cooling stage of an ESEM (Sirion from FEI) for the observation. The ESEM examinations were carried out at a voltage of 20 kV. The temperature and pressure of the observation chamber were controlled at 0 °C and 609 Pa respectively. This condition being a little below that of the three-phase point of water (T = 0.0076 °C; P = 610.75 Pa) is to guarantee that the ice can slowly sublimate and leave the in-situ pore (seen in Fig. 1(a)). Otherwise, the network structure of particles would collapse if the water was directly removed from the paste as described in Fig. 1(b).

3. Results and discussion

Fig. 2 displays the ESEM images of G paste at different hydration time. It shows that at the early hydration of 2 min small hemihydrate particles are easily forming the flocculation structure, which wraps water inside and acts as the bridge of large particles. As a result, a flocculation structure network is formed in G paste. Along with the hydration, hemihydrate particles keep dissolved and at 5 min some needlelike dihydrate crystals start to precipitate on the surface of large hemihydrate particles. These dihydrate crystals grow fast with time and at 8 min form a much stronger flocculation structure network around large hemihydrate particles. At the same time, because a lot of water is consumed in the hydration process, the paste gradually loses its fluidity and presents the initial setting. At 12 min, all of the small hemihydrate particles seem to be dissolved. Moreover, a compact dihydrate crystals network with high degree of interlocking is formed around large hemihydrate particles. At this time, the paste has certain structural strength and presents the final setting.

Fig. 3 shows the ESEM images of G paste with different chemical admixtures. As it reveals the flocculation structure in GPC paste is obviously broken up, whereas in GHPMC and GSE paste the flocculation structure is strengthened when compared with that in G paste. According to the previous study [9], the more the

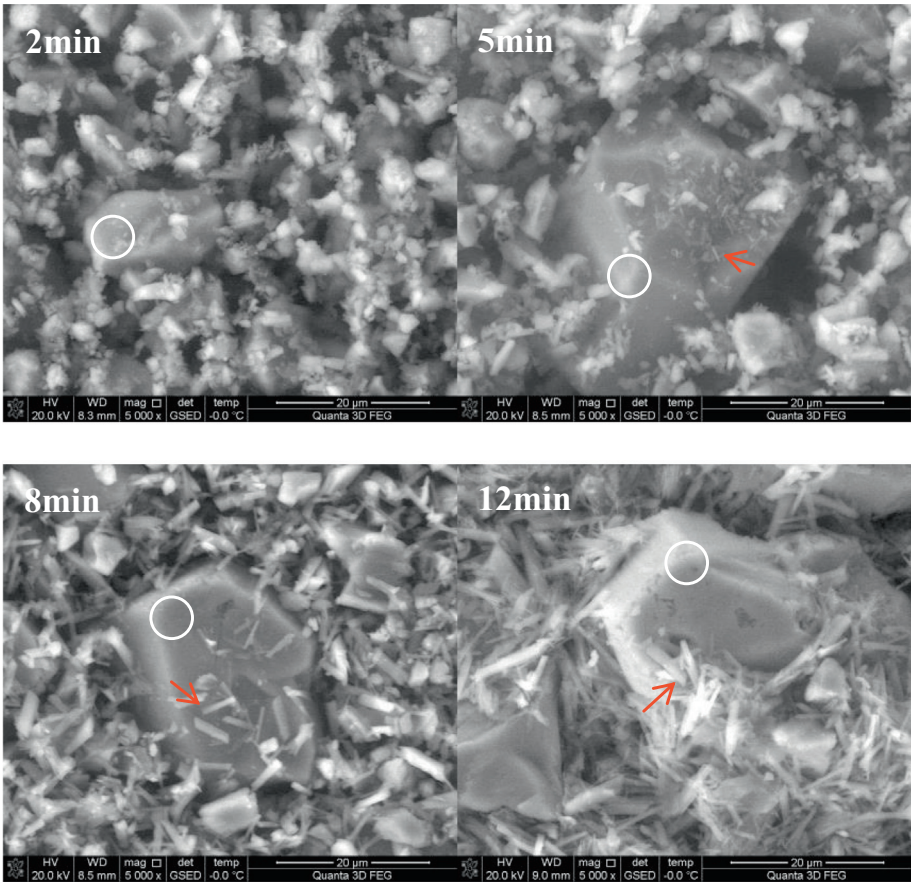

Fig. 2. ESEM images of pure gypsum plaster paste at different hydration time. White circles and red arrows in figures indicate the hemihydrate particles and dihydrate crystals, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)