КРАТКИЕ СООБЩЕНИЯ / SHORT MESSAGES

УДК 548.5:666.9

DOI: 10.19110/geov.2020.9.6

CRYSTALLIZATION FEATURES OF CALCIUM SULFATE IN THE PROCESS OF “ARTIFICIAL AGING”

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Gypsum binders are widely used in construction, mining and the oil and gas industry. The use of these binders is conditioned by stability of their technical characteristics, which is achieved by using a technological operation “artificial aging”.

The features of artificial aging are: 1) hydration of calcium sulphate hemihydrate in liquid phase deficiency; 2) the resulting dihydrate gypsum crystallizes in a limited volume of micropores of the original binder.

From the standpoint of the quaternary concept, the features of the crystallization of gypsum dihydrate in the micropores of the original gypsum binder are considered. The effect of artificial aging conditions and the degree of supersaturation on the growth mechanism and the morphology of gypsum dihydrate crystals was determined.

The use of artificial “aging” results in healing of defects in the structure of the original binder, decreasing water demand and increasing strength.

Keywords: crystallization of quaternary, calcium sulfate, artificial aging, gypsum binder.

ОСОБЕННОСТИ КРИСТАЛЛИЗАЦИИ СУЛЬФАТА КАЛЬЦИЯ ПРИ «ИСКУССТВЕННОМ СТАРЕНИИ»

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Гипсовые вяжущие широко применяются в строительстве, горном деле, в нефтегазовой отрасли. Их использование обусловлено стабильностью технических характеристик, которая достигается применением технологической операции «искусственного старения».

Особенностями искусственного старения являются: 1) гидратация полугидрата сульфата кальция при дефиците жидкой фазы; 2) образующийся двухводный гипс кристаллизуется в ограниченном объеме микропор исходного вяжущего.

С позиций кватеронной концепции рассмотрены особенности кристаллизации двухводного гипса в микропорах исходного гипсового вяжущего. Установлено влияние условий искусственного старения и степени пересыщения на механизм роста и морфологию кристаллов двухводного гипса.

Применение искусственного старения приводит к залечиванию дефектов в структуре исходного вяжущего, снижению его водопотребности и повышению прочности.

Ключевые слова: кристаллизация кватерон, сульфат кальция, искусственное старение, гипсовое вяжущее.

Introduction

Gypsum binders have been used for many years in not only construction industry, but also in mining industry to prepare hardening backfill mixtures, building of explosion-proof bridges, as well as in the oil and gas industry in drilling and grout mixes [3, 7, 11]. Regardless of the field of application of the gypsum binders, it is necessary to ensure the stability of their technical characteristics.

To improve the construction and technical properties of the gypsum binder, a technological operation of artificial “aging” is used. The essence of this process lies in keeping the gypsum binder in the environment with different relative humidity. In this case, the hydration of the gypsum binder occurs with the formation of dihydrate gypsum, which is accompanied by “self-healing” of defects. The ar-

tificial “aging” results in decreasing water demand of the gypsum binder and increasing its strength.

Materials and research methods

This study included an analysis of features of the crystallization of gypsum dihydrate during artificial aging of the gypsum binder. As an object of experimental research, we used β -modification gypsum binder of G4AII brand of the Chelyabinsk gypsum plant, taken from a gypsum boiler after the end of the heat treatment process. When firing gypsum, a soluble anhydrite is formed, as well as internal and external structural defects (Fig. 1) [12]. The “aging” of the gypsum binder was carried out during storage in desiccators at a temperature of 20 °C

Fig 1. Microdefects of gypsum particles

Рис 1. Микродефекты частиц строительного гипса

and relative humidity of 60 %, 80 % and 100 % ($\varphi = 0.6$; 0.8; 1.0) for 14 days.

Results and discussion

The artificial aging process has two features:

- hydration of calcium sulfate hemihydrate occurs with a deficiency of the liquid phase;
- the resulting dihydrate gypsum crystallizes in a limited volume of micropores of the original binder.

The process of “aging” of calcium sulfate hemihydrate is conditioned by its hydration with the participation of water adsorbed on the active centers of the surface and on defects of its particles, and also by condensation of water vapor in ultrafine pores (fractures). Depending on the relative humidity of the air, liquid films of various thicknesses and structures are formed on the solid surfaces, which predetermines the possibility of changing mechanism and kinetics of hydration.

Under a high relative humidity ($\varphi = 1$), liquid films about 90 μm thick are formed. Water is in a droplet-liquid state (bulk water) in such a film. At the same time, at $\varphi = 0.8$, the film thickness is within 5.6 ... 8.1 μm , and at $\varphi = 0.6$ the liquid film has a thickness of less than 3 μm . According to [4], water films that form on the surface of gypsum particles at $\varphi \leq 0.8$ have anomalous properties, in particular, they have a high viscosity and a low dissolving power. As a result, the through-solution mechanism of hydration of hemihydrate calcium sulfate becomes impossible [8]; a non-traditional explanation of the hydration process is needed. This process with the participation of “anomalous” water can be considered within the quataron concept [1,2]. Its key position is the existence of specific clusters of nanometer sizes in nonequilibrium conditions — quatarons.

When liquid water is formed through quatarons, there are several ways of condensation with their merging or aggregating. The condensation of quatarons of different structure and size results in formation of different condensed phases of water. At low degrees of supersaturation ($\varphi \leq 1$) the condensation of quatarons occurs with the formation of structured water, which differs from the bulk liquid by properties [2]. Since quatarons have an increased reactivity, the participation of this water in

the hydration of hemihydrate calcium sulfate is carried out according to the topochemical mechanism with the formation of crystal hydrates of variable chemical composition [8]. According to I. V. Melikhov [6] at the solid-phase gypsum hydration, lamellar crystal hydrates of $\text{CaSO}_4 \cdot n\text{H}_2\text{O}$ composition are formed at $n = 1.86 \pm 0.05$. Such variable chemical composition of hydration products predetermines their morphological heterogeneity and multistage crystallization process, which also corresponds to the quataronic concept [1].

The size of micropores in the initial gypsum binders does not exceed 1 ... 1.5 μm , therefore, even under conditions of low supersaturation, quatarons of dihydrate gypsum appear in them, which then turn into contact nuclei. Since these quatarons are topologically and chemically close to the structure of the substrate (its role is played by the crystals of the initial binder), they are adsorbed on its surface and become sources of growth of gypsum dihydrate crystals.

In the course of growth, as noted above, the composition and structure of the crystals change. Each growing crystal captures a non-equilibrium amount of quatarons, and growth structural defects are formed in its volume, which can be active centers for the formation of intergrowths that bind crystals into an agglomerate (crystallization bridges) at any supersaturation of the medium. Resulted from the deposition of matter on the walls of micropores and cracks, a concentration gradient develops there, and the concentration is maximum at their entrance, where the intergrowths are formed, the adhesion of which results in a crystallization bridge [6].

With decreasing degree of supersaturation, the growth of gypsum dihydrate crystals through the attachment of 2D nuclei becomes energetically unfavorable. In this case, crystal growth develops according to the dislocation mechanism [5, 9]. At the dislocation mechanism of growth, when particles of a crystallizing substance are embedded in the lattice of a growing crystal, several crystals are formed from one crystallization center. This phenomenon is known as crystal splitting [5]. It is connected with the fact that secondary nuclei appear on the surface of the primary nucleus of dihydrate gypsum, which formed on the walls of the microcrack, i. e. there is 2D nucleation on its own substrate. The primary

nucleus of calcium sulfate crystals faces the solution with (–111) facet, because it is this facet that grows according to 2D nucleation mechanism [10]. The formation of secondary gypsum nuclei and their growth on the surface of the primary nucleus continues until they completely cover the entire surface of the microfracture and fill its volume (Fig. 2).

Fig. 2. Dihydrate gypsum crystals in the microfractures of the gypsum binder particles

Рис. 2. Кристаллы двухводного гипса в микротрещинах частиц гипсового вяжущего

Such self-healing of particle microdefects is accompanied by decreasing specific surface area of the original gypsum binder by 33 % and decreasing water demand by 14 %.

Conclusion

The conducted studies of the crystallization process of dihydrate gypsum in the micropores of a gypsum binder in the process of its artificial “aging” do not contradict the quaternary mechanism of microcrystal growth. The obtained results indicate the potential and need to use this technological conversion in the production of binders based on calcium sulfate.

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Поступила в редакцию / Received 19.08.2020