



Effect of protogenetic anhydrite on the hydration of cement under different curing temperature



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HIGHLIGHTS

- We investigated using protogenetic anhydrite instead of added gypsum to make cement.
- The optimum content of protogenetic anhydrite in cement increased with increasing temperature.
- Curing temperature made the concentration of sulfate ion in pore solution changed.
- Higher temperature increased the risk of delayed ettringite formation in cement paste.

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ABSTRACT

Compared with the added gypsum, protogenetic anhydrite is the anhydrite in clinker and cement admixture. And using protogenetic anhydrite as the setting retarder instead of added gypsum to make cement could be an effective way to make full use of clinker and wastes with high sulphur content. However, the high temperature sensitivity of solubility property of protogenetic anhydrite may result in unhydrated anhydrite exist in cement paste under high curing temperature at early age, and that may make a bad influence on the properties of cement. This work investigated the effects of protogenetic anhydrite on the long-term strength, volume stability and hydration products of cement paste under different curing temperature. It is shown that higher curing temperature caused the greater value of optimum content of protogenetic anhydrite in cement, and protogenetic anhydrite could not make the bigger volume expansion and worse strength of cement than gypsum when the high curing temperature being used. But curing temperature caused the dissolution of protogenetic anhydrite change and influenced the concentration of sulfate ion in the pore solution of hardened cement paste. The results of XRD patterns showed that the risk of delayed ettringite formation in hardened cement paste cured at high temperature had been increased. The results will be helpful to understand the role of protogenetic anhydrite in cement, and further promote the use of clinker and wastes with high sulfate.

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1. Introduction

In the process of cement production a certain amount of gypsum is added in order to adjust setting time of cement, contribute for strength acceleration in early stage and reduce drying shrinkage of hardened cement paste [1–3]. In Portland cement, usually the added gypsum is natural dihydrate gypsum, but mixed gypsum and chemical gypsum are also used in cement [4,5]. In fact, in addition to the kinds of gypsum mentioned above in cement, some gypsum from clinker and admixture, which always have been subjected to high temperature process and exists in anhydrous

gypsum. Compared with the added gypsum, those anhydrous gypsums (anhydrite) in clinker and cement admixture are not intentionally added to cement. In this study, the anhydrous gypsum from clinker and admixture can be classified as protogenetic anhydrite, which is different from added gypsum including natural anhydrite.

Generally, the types of sulphates in cement clinker is mainly alkaline sulfate and the content of protogenetic anhydrite is usually low, even some researchers think that there was no anhydrite in cement clinker produced in cement plant [6]. In contrast, the type of sulphates in admixtures (as fly ash, CFBC ash and so on) is mainly anhydrite. With desulfurization technology developing, the content of anhydrite in fly ash and CFBC ash has been an upward trend [7]. In order to use industrial wastes with high

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content of anhydrite in cement, many researchers try to make cement with no or less added gypsum and use anhydrite in wastes as cement setting retarder instead of added gypsum. Our previous works [8,9] showed that protogenetic anhydrite from CFBC ash could retard setting time and enhance the strength of the cement paste, and did not have an adverse impact on the volume stability of cement when the SO_3 content of cement was no more than 4.0%. Some researchers also found that the calcined anhydrite which was similar with the protogenetic anhydrite in industrial wastes could further improve the performance of cement [10,11].

Generally, the main research directions about protogenetic anhydrite used in cement is focused on the setting retarding and strength of cement. However, besides the solubility property of protogenetic anhydrite is different from gypsum added at room temperature, the sensitivity of solubility property of two kinds of gypsum has a big difference. The solubility of protogenetic anhydrite would be quickly decreased with the temperature rising, instead the temperature had a little influence on the solubility of gypsum [12]. Due to the particularity of the solubility property of protogenetic anhydrite, if the cement including protogenetic anhydrite was used for the concrete with high curing temperature at early age or the mass concrete, that would result in the solubility property of protogenetic anhydrite so lower because of temperature rising that there would be unhydrated anhydrite in cement paste. If the unhydrated anhydrite continues to hydrate in the later hydration period, the DEF and gypsum would be produced that may make a bad influence on the strength and the volume stability of cement [13].

The objective of this work is to study the effects of protogenetic anhydrite on the performance of cement under different curing temperature. And the long-term strength, volume stability and hydration products of cement paste cured by high temperature at early ages were the key subjects of investigation. The aims of this research are to determine whether protogenetic anhydrite is used as the cement set retarder safely.

2. Experiment

2.1. Materials

Portland cements used in this study were obtained by inter-grinding Portland cement clinker and protogenetic anhydrite or gypsum with a certain proportion in the laboratory ball mill. A natural gypsum with 95.0% $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was used, and protogenetic anhydrite was obtained from the natural gypsum by calcining at 850 °C in order to simulate the temperature that the sulphates in CFBC fly ash withstood. The chemical compositions of the clinker are given in Table 1, and the cement with 2.0% SO_3 content were shown in Table 2.

2.2. Test methods

2.2.1. Curing temperature and curing process

Three representative curing temperatures as 20 °C, 65 °C and 90 °C were selected in the test. All test specimens were cured as follows: after mixing, all specimens with moulds were covered with plastic film and placed in the moist room at 20.0 ± 3.0 °C for 3 h, and then the specimens needing high curing temperature should be moved into curing box and underwent three stages of

Table 2
Physical properties of cement.

Properties	Cement
Specific surface, m^2/kg	375
Specific gravity, g/cm^3	3.04
Water requirement of standard consistency, %	28.2
Initial setting time, min	110
Final setting time, min	190
7 days compressive strength, MPa	–
28 days compressive strength, MPa	43.1

temperature elevating, holding and dropping. The rate of temperature elevating and dropping stages were about 10 °C/h, and duration of temperature holding stage was 6 h. After about 24 h from mixing, the moulds were removed and all specimens were placed in lime-saturated water at 20 °C for different ages.

2.2.2. Samples preparing and test procedures

The mortar specimens were used for strength and volume stability measurement. Mortar strengths were measured on 40 mm × 40 mm × 160 mm prism specimens and volume stability was characterized by linear wet-expansion and was determined by measuring length changes of 25 mm × 25 mm × 280 mm prisms. All mortars were cast at a sand-to-cement ratio of 2.5 by mass, and water-to-cement ratio was determined to bring the mortars to a flow of 180–190 mm. The flexural and compressive strengths were measured at ages of 3, 28, 56 and 90 days. The linear wet-expansion was recorded by measuring variation of the length of specimens with the vertical contraction instrument.

The procedure to test the dissolution rate of protogenetic anhydrite in water under different temperature conditions was as follows. 1 g protogenetic anhydrite was mixed with 100 ml of distilled water at the temperatures of 20, 65 and 90 °C. The mixture was then respectively kept at constant temperature for different ages. After that, the solution was filtrated and the content of protogenetic anhydrite in the filtrate was determined by precipitation with barium chloride.

Cement pastes for studies of hydration products and pore solution were prepared with water requirement for normal consistency. At the set time, the hardened paste specimens were crushed into small pieces and soaked in acetone to stop further hydration. Then the samples were dried in a vacuum desiccator and ground to pass through a 0.08 mm sieve prior to analysis. The pore solution of hardened cement was acquired by using solid-liquid extraction technique [14]. 5 g samples with hydration samples were mixed with 50 ml of distilled water for 5 min, and then the solution was filtrated. The content of sulfate ion in the pore solution was determined by precipitation with barium chloride. X-ray diffraction (XRD) was used to determine phase compositions for the hydrated cements at 10 h and 7, 28 days.

3. Results

3.1. Strength

Fig. 1 gives the strength of cement mortar with different SO_3 content under different initial curing temperatures. The SO_3 content of cement were adjusted by adding protogenetic anhydrite.

Table 1
Chemical composition of clinker (%).

CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	LOI
56.78	20.32	7.21	4.69	2.31	1.25	1.23

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