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Carbonation of low heat portland cement paste precured in water for different time

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Abstract: The carbonation technique was applied to accelerate the hydration of low heat portland cement (LHC). Before carbonation, the demoulded pastes were precured in water for 0, 2, 7, and 21 d, respectively. The results show that precuring time in water strongly influences the carbonation process. The phenolphthalein test indicates that the paste precured in water for a shorter time is more quickly carbonated than that for a longer time. The content of calcium hydroxide increases with increasing the precuring time in water, whereas, the amount of absorbed carbon dioxide changes contrarily. Scanning electron microscope (SEM) observation shows that portlandite always fills up big air bubbles in the paste during precuring in water, and the mercury intrusion porosimetry (MIP) results show that there are less large capillary pores in the paste precured in water for a longer time. It is found that the paste without precuring in water has more carbon dioxide absorption during curing in carbon dioxide atmosphere, and its total pore volume decreases remarkably with an increase in the carbonation time than that precured in water. X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) surface area analyses indicate that the carbonate products are vaterite and calcite; C_xSH_y formed from carbonation has low BET surface area in comparison with that of C–S–H formed from curing in water.

Key words: carbonation; carbon dioxide absorption; vaterite; BET surface area; pore size distribution

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1. Introduction

Low heat portland cement (LHC) is attracting a great deal of interest worldwide for its lower energy consumptions and CO_2 emissions on manufacture than ordinary portland cement. But its application is comparatively restricted because of the slow hydration and low early strength. These disadvantages can be improved by using a number of techniques, such as, activating of belite or introducing reactive additives [1-2]. It was reported [3-4] that LHC could accelerate hydration under a CO_2 curing condition accompanied by highly developed strength. In this process, a significant proportion of CO_2 was fixed by the carbonation reaction, which could provide an effective way of sequestering CO_2 as important solid phases to produce construction materials [5]. However, the precuring condition that is most suitable for the carbonation reaction of LHC, and the details of the carbonation process with different precuring time in water are not clear. K. Koibuchi *et al.* [4] said short precuring time in water is in favor of absorbing carbon dioxide; E. Sakai *et al.* [3] investigated the carbonation reaction of hardened low heat cement under 2 d precuring in water. In this article, the effect of precuring time in water on the carbonation process of LHC was studied.

2. Experimental

2.1. Materials

The LHC was from Taiheiyo Cement Co., Japan. Its composition (wt%) was: SiO_2, 26.12; Fe_2O_3, 2.29; Al_2O_3, 2.87; CaO, 63.94; MgO, 0.75; SO_3, 2.26; TiO_2, 0.12; LOI, 0.87. Its mineral composition (wt%) by Bogue is: f-CaO, 0.10; C_3S, 32.30; C_2S, 50.60; C_3A, 3.74; C_4AF, 6.96; $CaSO_4$, 3.84, with a density of 3.22 g/cm^3 and a Blaine surface area of 3280 cm^2/g. Moreover, an antifoamer and two compositions of the viscosity improver (viscoA and viscoB) were used to reduce air bubble formation when mixing, to prevent the slurry from segregation.

2.2. Preparation

The mix proportions were: water-to-cement mass ratio 0.4, antifoamer to water 5×10^{-4}, and viscoA and viscoB to water 0.04 respectively. Initially, viscoA, antifoamer, and distilled water were mixed together, and

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Corresponding author: Deping Chen, **E-mail:** chendeping@ces.ustb.edu.cn then poured into the LHC, and stirred for 2.5 min. Next, viscoB was added and again stirred for 2.5 min. The slurry turned to viscous paste.

The fresh paste was cast into a mould of 20 mm×20 mm×80 mm. The paste with mould, after vibrating for 1 min, was put into a closed plastic box for 24 h at 20°C. The demoulded samples were first immersed in distilled water for 0, 2, 7, and 21 d (it was called 'precuring in water' below), and then placed in the carbonation apparatus (SH-221 from ESPEC Corp.) for 0, 3, 7, 21, 42, and 70 d (curing in CO_2). Throughout the curing temperature is 20°C; the carbonation condition is relative humid, 60%, with 5vol% CO_2.

2.3. Testing methods

(1) Measuring the depth of carbonation.

The carbonation depth was measured in a traditional way, by spraying phenolphthalein alcohol solution onto the surface of a split prism of the carbonated LHC paste. The neutralization area of transect was then calculated. The ratio of the neutralization area to the whole area of transect was defined as the carbonation area ratio.

(2) XRD analyses.

The paste samples were crushed and manually grounded with an alumina mortar and pestle. Their phase compositions were examined by X-ray diffraction (XRD) with a Toshiba powder diffractometer using Cu K_α radiation.

(3) Thermogravimetric/differential thermal (TG/DTA) analysis.

The powder samples were submitted to thermal analysis using the TG-DTA 2000S equipment (Mac Science Co.), which permits performing TG and DTA analysis simultaneously. In testing, approximately 33 mg of powder samples were heated from room temperature to 1000°C at a heating rate of 10°C/min in flowing N_2 (150 mL/min). After testing, TG and DTA curves were obtained.

With the help of TG/DTA curves, the $Ca(OH)_2$ content in the paste was determined from the following equation:

$$\mathrm{CH(wt\%)} = \mathrm{WL_{CH}(wt\%)} \times \frac{\mathrm{MW_{CH}}}{\mathrm{MW_H}} \qquad (1)$$

where CH(wt%) is the content of $Ca(OH)_2$, WL_{CH}(wt%) is the weight loss of $Ca(OH)_2$ that occurred during the dehydration of portlandite, MW_{CH} and MW_H are the molecular weights of $Ca(OH)_2$ and water, respectively.

(4) CO_2 absorption tests.

The inorganic carbon content C(wt%) of the powder samples was tested at 200°C with 5% H_3PO_4 on alumina carrier boats using TOC-5050A Total Organic Carbon Analyzer equipped with SSM-5000A Solid Sample Module (Shimadzu Corporation, Japan). The amount of CO_2 absorption by LHC was calculated by using the following equation:

$$\mathrm{CO_2(wt\%)} = \frac{\mathrm{C(wt\%)} \times \mathrm{MW_{CO_2}}}{(1-\mathrm{LOI\%}) \times \mathrm{MW_C}} \qquad (2)$$

where CO_2(wt%) is the amount of absorbed CO_2 by LHC, C(wt%) is the content of inorganic carbon, LOI% is the mass loss by heating at 1000°C for 30 min, MW_{CO2} and MW_C are the molecular weights of CO_2 and carbon, respectively.

(5) Brunauer-Emmett-Teller (BET) specific surface area analyses.

The specific surface area of the powder samples was analyzed by using the HORIBA SA-6200 serials BET surface area analyzer (Horiba Ltd., Japan). All the samples were placed in an Aspirator for 7 d to dry, and stored in sealed plastic vials before testing.

(6) Pore size distribution and total pore volume tests.

A piece of 5-10 mm sized sample was submitted to pore size distribution and total pore volume testing with mercury intrusion porosimetry (MIP) using the Pascal 140 and Pascal 240 porosimeter (CE Instruments, Italy). The samples were under 1 d of D-drying before testing.

(7) SEM observations.

SEM observations for the characterization of carbonated LHC pastes were carried out using JSM-5310 scanning electron microscope (JEOL Ltd., Japan). To obtain a conductive surface for analysis, a thin gold layer was deposited over it.

3. Results and discussion

3.1. Carbonation area ratio

The carbonation area ratio of LHC pastes with carbonation time was shown in Fig. 1. The neutralization rate of LHC paste without precuring in water is higher than that with precuring in water. The paste without precuring in water was soon fully carbonated at the carbonation time of 21 d, whereas, the others needed more time for it. As the phenolphthalein test is based on the color change at which the pH is about 9, it denotes the presence of $Ca(OH)_2$ [6]. The content of $Ca(OH)_2$ in the paste, obtained by TG/DTA analysis, with the carbonation time is shown in Fig. 2. The $Ca(OH)_2$ contents of the paste without precuring and with 21 d precuring in water before carbonation are 5.92wt% and 12.22wt%, respectively. After 21 d carbonation, the