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Microstructural densification and CO_2 uptake promoted by the carbonation curing of belite-rich Portland cement

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ABSTRACT

The present study investigates the effects of the belite content and carbonation curing on the physicochemical properties of cement mortar. The results provide new insight, demonstrating that a higher belite content in cement increases CO_2 uptake during the carbonation curing process and thus promotes microstructural densification. Carbonation-cured cement with a high alite content showed increased pore connectivity, while the cement with a high belite content experienced reduced pore connectivity and more instances of pore closure, resulting in a complex microstructure. The belite phase was mostly consumed by the carbonation reaction during the curing process, resulting in the production of calcite. As a result, the mechanical strength of the carbonation-cured belite-rich Portland cement mortar was significantly improved in comparison with that after normal curing for an identical period. In particular, the reaction of the belite phase influenced by hydration/carbonation interaction at an early age is discussed along with the experimental results.

1. Introduction

Portland cement is a material consisting of the clinker minerals C_3S (referred to as alite), C_2S (mainly β-C_2S; referred to as belite), C_3A (referred to as aluminate) and C_4AF (referred to as ferrite), and a small portion of gypsum (Hereafter, the following cement chemistry nomenclature is used: $C = CaO$, $S = SiO_2$, $A = Al_2O_3$, $F = Fe_2O_3$, $S = SO_3$, $C = CO_2$ and $H = H_2O$). At present, C_3S in the phase composition of ordinary Portland cement accounts for 50–65% of the total proportion and critically influences the development of the concrete strength [1–3]. The hydration reaction of C_3S as expressed in Eq. (1) produces C–S–H and CH, and its rate is more rapid than that of C_2S. Significant heat generation accompanies this reaction [4].

$$C_3S + (3 + m - n)H \rightarrow C_nSH_m + (3 - n)CH. \tag{1}$$

Particular caution is warranted with regard to alite-rich cement in modern days, as it tends to increase the proportion of C_3S and is therefore associated with several issues related to the long-term durability of concrete [1,2,5–10].

On the other hand, the hydration reaction of C_2S, as expressed in Eq. (2) results in the production of CH to a lesser extent given the identical molar mass despite the reaction process being similar to that of C_3S [4].

$$C_2S + (1.5 + n)H \rightarrow C_{1.5+m}SH_{1+m+n} + (0.5 - m)CH \tag{2}$$

It is known that the hydration rate of C_2S is noticeably slower than that of C_3S owing to the different crystalline structure of these two materials [11,12]. Earlier findings regarding the hydration rate of C_2S showed slight differences depending on the study, while a quantitative X-ray powder diffraction analysis with Rietveld refinement recently conducted by Cuberos et al. showed that C_2S is not hydrated during the first three months and that the degree of the hydration reaction after one year is only 14% [13]. Nevertheless, the hydration reaction of C_2S fundamentally produces CH to a lesser extent in comparison with that of C_3S, potentially contributing to the densification and high strength development of concrete [3]. Furthermore, the optimum clinkerization temperature of belite cement is significantly lower than that of ordinary Portland cement and the amount of CO_2 generated is ~0.50 tons of CO_2 per ton of clinker, suggesting that its production demands a lower energy level and is more environmentally friendly [13–15].

Owing to these aspects, numerous studies have attempted to provide a means of overcoming the low reactivity of belite cement (c.f. [35]). These studies include an increase in the specific surface area of belite cement by means of hydrothermal technique [16]; the addition of mineral accelerators such as $CaCl_2$, $Ca(NO_3)_2$, $Ca(CH_3COO)_2$ and K_2CO_3 [12]; enhancement of the reactivity of belite by the utilization of a remelting reaction [17]; activation of the hydraulic reactivity of belite by nano-alumina [18]; the synthesis of belite cement clinkers with high hydraulic reactivity by controlling the cooling rate and with addition of mineralizers such as NaF and Fe_2O_3 [19]; and the activation of belite by doping alkaline oxides [13]. These studies commonly pay particular attention to the hydraulic reactivity of belite. Meanwhile, the carbonation reaction may provide an alternative approach by

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which to induce a belite reaction [20,21]. Ibáñez et al. investigated the hydration and carbonation of monoclinic C_2S and C_3S by means of micro-Raman spectroscopy and found that the carbonation of hydrated C_2S is more rapid than that of hydrated C_3S exposed to an identical condition [21]. The carbonation reaction of belite present in mature cement paste has been, however, revealed to some extent thus far, while the current understanding of the reaction of the belite phase as influenced by the hydration/carbonation interaction at an early age is limited. Moreover, the effects of the carbonation of belite-rich Portland cement on physicochemical properties such as the mechanical strength, microstructure, and the degree of the reaction of hardened paste and mortar are thus far unrevealed.

Studies of CO_2 sequestration and utilization in cementitious materials are recently gaining attention (c.f. [22–25]), and carbonation curing can not only modify hardened belite-rich Portland cement but also sequestrate CO_2 into chemically stable carbonates over a long-term period. The aim of the present study is therefore to investigate the effect of the belite content and carbonation curing on the physicochemical properties of cement mortar. The mechanical strength, microstructure, reaction products and CO_2 uptake capacity are the primary topics of concern here.

2. Experimental procedure

2.1. Materials and sample preparation

Four types of Portland cement with different chemical compositions, produced from batch plants of Ssangyong Cement Industrial Co., Ltd. of South Korea, were used in this study. The chemical and physical properties of the cements are provided in Table 1. It should be noted that all cements satisfy the Portland cement specifications of Types III, I, II and IV in ASTM C150 [26]. Hence, the Blaine fineness of B16, which is classified as Type III cement with high-early strength, is different from that of the other cements. In this paper, B48 is occasionally referred to as "belite-rich Portland cement" for convenience.

Mortar specimens were fabricated with a constant mass ratio (water:cement:sand) of 1:2:3. Standard graded quartz sand was used as a fine aggregate. A cement paste specimen was fabricated with an identical w/c ratio of 0.5 to exclude the influence of the fine aggregate on the chemical analysis. Mixing was conducted for 5 min to ensure the homogeneity of the mixture. Mortar specimens were cast in a mold with dimensions of 40 × 40 × 160 mm and paste specimens were cast in a mold with dimensions of 10 × 10 × 150 mm. All specimens were sealed with plastic wrap to prevent the moisture from evaporating. They were pre-cured at 20 °C for 24 h before demolding. After demolding, the specimens were immediately placed in carbonation curing chamber.

2.2. Curing conditions and test methods

The specimen code, curing condition, and test series are summarized in Table 2. The carbonation curing was conducted in a carbonation chamber at 20 °C, RH 60% and with an atmospheric CO_2 concentration of 5%. Normally cured control specimens were provided with a condition free from carbonation in which mortar specimens for a strength test were cured at 20 °C and RH 60% and paste specimens were sealed and cured at 20 °C considering that the influence of natural carbonation on specimens of this size may be more severe.

Table 2
Summary of the test plan.

Specimen code	Curing condition	Test series[a]
B16-N	Normal curing	Series II
B23-N	(20 °C, 60 R.H.% (mortar) or sealed (paste))	Series I & II
B35-N		Series II
B48-N		Series I & II
B16-C	Carbonation curing	Series II
B23-C	(20 °C, 60 R.H.%, 5% CO_2)	Series I & II
B35-C		Series II
B48-C		Series I & II

[a] Series I involves tests of compressive strength, flexural strength and carbonation degree (using phenolphthalein indicator) using mortar specimen; and Series II involves tests of MIP, XRD and TG/DTA using paste specimen.

The experiment was systematically designed to explore the influence of carbonation curing on the carbonation degree and mechanical properties of belite-rich Portland cement mortar, along with changes in the physicochemical properties induced by carbonation curing. Series I in Table 2 is related to the former objective, and Series II is linked to the latter objective. Mortar specimens were used for Series I and paste specimens were used for Series II. The carbonation degree was measured by a phenolphthalein indicator which was sprayed onto a portion of prisms broken under a flexural strength test. Calculations were done using the ratio of the area where no color change occurred to the total cross-sectional area of the specimen. Two prism mortar specimens were tested for their flexural strength in accordance with ASTM C348. Three specimens, the portions of the prisms broken under flexure, with a cross-sectional area of 40 × 40 mm were tested for their compressive strength in accordance with ASTM C349. A universal testing machine with a loading capacity of 3000 kN was used for both tests.

Three analytical techniques were used to investigate the influence of the belite content on the changes of the physicochemical properties induced by carbonation curing. The microstructural characteristics of the normally cured and the carbonation-cured samples were evaluated by means of mercury intrusion porosimetry (MIP) on an Autopore VI 9520 machine by Micromeritics Corp. The pressure range in the MIP test was as high as 414 MPa (60,000 psi). Fractured samples at 28 days were used in the test. The hydration and carbonation products were quantified by means of thermogravimetry and differential thermal analysis (TG/DTA) using samples at 28 days. EA 1108 CHNS-O/FISONS Instruments were used; the temperature in the test was varied from 30 °C to 1000 °C with a heating rate of 30 °C/min. The clinker minerals, hydrates, and carbonation products were measured by means of X-ray diffractometry (XRD) using samples at 28 days. A SmartLab device manufactured by Rigaku was used for the XRD analysis. XRD was conducted with CuKα radiation at 40 kV and 30 mA. The scan range was 5° to 90° and the scan speed was 0.2°/min. Samples used for TG/DTA and XRD analyses were dried using desiccator and ground to pass a 100 μm sieve.

Table 1
Chemical and physical properties of the cements used in this study.

Cement	Chemical composition (wt%)						Mineral composition (wt%)[1]				Density (g/cm^3)	Blaine (cm^2/g)
	CaO	SiO_2	Al_2O_3	Fe_2O_3	SO_3	R_2O	C_3S	C_2S	C_3A	C_4AF		
B16	62.1	19.7	5.9	3.0	4.2	0.6	59	16	12	8	3.12	4400
B23	62.5	21.0	5.9	3.2	2.1	0.8	49	23	10	9	3.15	3300
B35	63.4	23.3	3.9	3.6	1.9	0.6	42	35	5	12	3.17	3350
B48	62.5	25.3	3.1	3.6	2.0	0.5	31	48	3	11	3.20	3400

[1] The mineral composition is calculated from the Bouge's equations.