Development of porosity of cement paste blended with supplementary cementitious materials after carbonation

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ABSTRACT

Supplementary cementitious materials (SCMs) like fly ash (FA) and blast furnace slag (BFS) are normally used to replace parts of Ordinary Portland cement (OPC) to reduce the cost and CO_2 emission. During the carbonation, a relatively high amount of C-S-H with low Ca/Si ratio will be carbonated in cement paste blended with SCMs. Therefore, it's very important to figure out the influences of the carbonation of C-S-H on the pore structure of SCMs blended cement paste.

In this paper, Mercury Intrusion Porosimetry (MIP) are used to determine the pore volume and size distribution of capillary pores. Results reveal that carbonation of most of the species of C-S-H results in increased porosity of cement paste. Total and effective capillary porosity of pastes blended with high amount of BFS increase after carbonation. This will bring adverse effects on the durability of blended cement concrete exposed to the carbonation.

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1. Introduction

Carbonation of calcium-bearing phases inside the concrete is the main deterioration process of infrastructure in open area with high average annual relative humidity. The consequence of this ageing phenomenon is the reduction of alkalinity, which makes the reinforcement prone to corrosion. In general, calcium-bearing phases involved in carbonation could be hydration products like portlandite (CH), calcium silicate hydrate (C-S-H), as well as unhydrated cement clinkers like tricalcium silicate (C_3S), dicalcium silicate(C_2S). Normally, the reactions between unhydrated cement and CO_2 can be ignored because their weak competition for CO_2 in front of CH and C-S-H [1]. From thermodynamic point of view, the carbonation of CH has a priority comparing with C-S-H [2]. However in experiments the initial rate of carbonation is quite similar [3]. Therefore, the main carbonation reactions in concrete are as follows:

$$CH + \overline{C} \rightarrow C\overline{C} + H \tag{1}$$

$$C_xSH_y + x\overline{C} \rightarrow xC\overline{C} + SH_t + (y-t)H \tag{2}$$
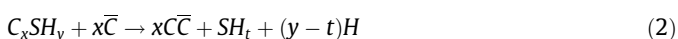
In cement chemist's short hand notations, $C = CaO$, $H = H_2O$, $S = SiO_2$, $A = Al_2O_3$, and $\overline{C} = CO_2$. x, y and t are the molecular numbers. As the number of S is normally set as one when describing the formula of C-S-H, x and y also equal to the Ca/Si and H_2O/Si ratio.

It is universally acknowledged that the carbonation of CH leads to a reduction in porosity which is ascribed to the positive difference of molar volume between CH and the formed $CaCO_3$ [4–9]. But if considering the carbonation of C-S-H, the effect of the carbonation on the porosity and microstructure of cement paste is still controversial. Carbonation of C-S-H has been studied by many authors [3,10–12]. It is agreed that a complex decalcification-polymerization process of the C-S-H occurs and amorphous silica gel is formed, see Eq. (2). The molar volume change due to the carbonation of C-S-H depends on the properties of C-S-H (like Ca/Si ratio, water content) and the water remaining in silica gel.

Based on the Eqs. (1) and (2) describing the carbonations of CH and C-S-H, the solid volume changes due to the carbonation can be expressed as following Eq. (3) [13].

$$\Delta\phi = \Delta\phi_{CH} + \Delta\phi_{CSH}$$
$$= n_{C\overline{C}}^{CH}\left(V_{C\overline{C}}^{CH} - V_{CH}\right) + n_{C\overline{C}}^{CSH}\left[V_{C\overline{C}}^{CSH} + \frac{V_{CSH}(t) - V_{CSH}(t_0)}{C/S(t_0) - C/S(t)}\right] \tag{3}$$

In which, $V_{C\overline{C}}^{CH} = V_{C\overline{C}}^{CSH} = 36.93\ cm^3/mol$ and $V_{CH} = 3.07\ cm^3/mol$, are the molar volume of $C\overline{C}$ and CH respectively. $n_{C\overline{C}}^{CH}$ and $n_{C\overline{C}}^{CSH}$ are the molar number of $C\overline{C}$ contributed by the carbonation of CH

and CSH. $C/S(t_0)$ and $C/S(t)$ are the Ca/Si ratio of C-S-H before and after carbonation. $C/S(t_0)$ varies from 0.75 to 2.0 and $C/S(t)$ equals to zero. $V_{CSH}(t)$ is the molar volume of C-S-H before carbonation; $V_{CSH}(t_0) = V_{SH_t(gel)}$ is the molar volume of carbonation product $SH_t(gel)$, which is in the range of 12–34 cm^3/mol [14].

By applying the above-mentioned parameters, the volume change per 1 mol of $C\bar{C}$ contributed by the carbonation of C-S-H can be calculated by Eq. (4).

$$\Delta\phi^0_{CSH}(cm^3/mol) = 36.93 - \frac{V_{CSH}(t_0) - V_{SH_t(gel)}}{C/S(t_0)} \qquad (4)$$

The total volume changes due to the carbonation of CH and C-S-H can be calculated by Eq. (5).

$$\Delta\phi = \Delta\phi_{CH} + \Delta\phi_{CSH}$$
$$= 3.85 \times n^{CH}_{C\bar{C}} - \left[36.93 - \frac{V_{CSH}(t_0) - V_{SH_t(gel)}}{C/S(t_0)}\right] \times n^{CSH}_{C\bar{C}} \qquad (5)$$

Making an assumption that $\Delta\phi^0_{CSH} = 0$, then

$$V_{CSH}(t_0) = 36.93 \times C/S(t_0) + V_{SH_t(gel)} \qquad (6)$$

The linear relationships between $V_{CSH}(t_0)$ and $C/S(t_0)$ are drawn in Fig. 1. The value of $V_{SH_t(gel)}$ is chosen as 12, 20 and 25 cm^3/mol, respectively. The data points in the same figure are the relevant parameters of C-S-H used in the Refs. [15–21].

Calculation of volume changes based on the values of the point above the linear curve will give a negative value of $\Delta\phi^0_{CSH}(<0)$; otherwise a positive value. The negative value of $\Delta\phi^0_{CSH}$ means the carbonation of these types of C-S-H will cause a negative increase of the solid volume and the increase of the pore space volume or porosity of the cement paste matrix.

From Fig. 1, carbonation of most of the species of C-S-H will result in the increase of the porosity of cement paste. It should be noticed that the effects of the carbonation on the porosity evolution will be different for some types of C-S-H, if the value of $V_{SH_t(gel)}$ is chosen as a different value.

In Portland cement paste, the Ca/Si ratio (C/S) in C-S-H is about 1.5–1.9. The addition of supplementary cementitious materials (SCMs) like fly ash results in the formation of a C-S-H with lower C/S, which is generally agreed to have a tobermorite-like structure $C_{0.83}S_2H_{1.5}$ but with many defects, mainly in bridging tetrahedron [22–24]. The formation of C-S-H with a low C/S leads to an increased uptake of aluminium in the C-S-H, called C-A-S-H [25]. Therefore, in cement paste blended with SCMs like fly ash, there are at least two types of C-S-H: C-S-H with high C/S from the hydration of C_3S and C_2S (high Ca C-S-H), C-S-H with low C/S from the pozzolanic reaction (low Ca C-(A-) S-H). The proportions of them are determined by the replacement level of SCMs, which is confirmed by the thermodynamic modelling from B. Lothenbach et al. [26]. Moreover, the decalcification of C-S-H may cause the shrinkage of cement paste, especially for the C-S-H with Ca/Si lower than 1.2 [27].

In cement paste blended with SCMs, the amount of CH is quite lower than that in the Portland cement paste. More proportion of C-S-H with high or low Ca/Si ratio is carbonated. The changes of microstructure due to carbonation is mainly caused by the carbonation of C-S-H, or the complex mixture which consists of different types of C-S-H. Therefore, concerning the influence of carbonation on the microstructure of SCMs blended cement paste, the limited data which were published in the scientific literature do not show a real consensus.

The aim of this work is to provide further evidence and improved understanding of the effects of carbonation on the microstructure (porosity and pore size distribution) of cement paste blended with different SCMs, on the basis of Mercury Intrusion Porosimetry and nitrogen adsorption isotherm. Especially, the influence of carbonation of C-S-H is investigated.

2. Experimental

2.1. Raw materials

Ordinary Portland cement (PC) used was type CEM I 425 N, from ENCI in the Netherlands. Fly ash (FA) and blast furnace slag (BFS) were used to replace part of PC in cement paste blended with SCMs. FA is Class F fly ash, according to ASTM C 618. BFS is produced by ECOCEM in the Netherlands. Main chemical compositions of raw materials are determined by X-ray fluorescence spectrometry (XRF). The results are compared in Table 1.

Major crystalline phases of above raw materials were tested by X-ray diffraction (XRD). The X-ray source used is Cu K radiation (λ = 0.154056 nm). The scan step size was 0.03°, from 5° to 70° (2θ). X-ray test results are shown in Fig. 2.
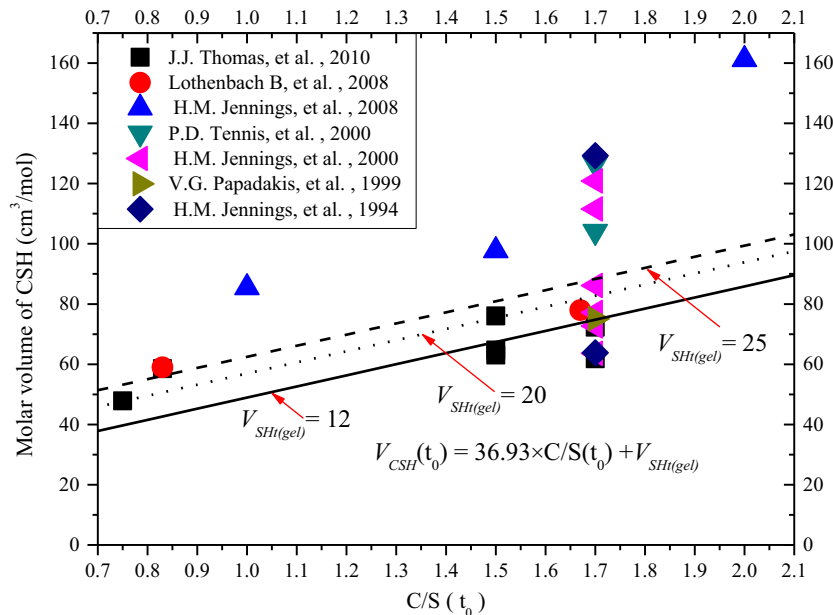

Fig. 1. Relations between molar volume and Ca/Si ratio of the C-S-H.